A SELECTED-ION FLOW TUBE STUDY
OF SOME GAS-PHASE ION-MOLECULE REACTIONS
OF POTENTIAL RELEVANCE TO THE CHEMISTRY
OF DENSE INTERSTELLAR CLOUDS.

A thesis
presented for the Degree
of
Doctor of Philosophy in Chemistry
in the
University of Canterbury

by
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University of Canterbury
1991
To C., D., E., H., and S.

(They know who they are.)
Results are reported for the studies of several systems of ion-molecule reactions of potential relevance to the chemistry of interstellar clouds. Measurements were obtained using a selected-ion flow tube operated at room temperature (300 ± 5 K) and using helium buffer gas at a pressure of 0.30 ± 0.01 Torr.

The proton affinities of C4H2 and C2N2 were determined by measurement of the rate coefficients for forward and reverse proton transfer reactions involving compounds of similar proton affinity. The results obtained were PA(C2N2) = 674 ± 4 kJ mol⁻¹ and PA(C4H2) = 741 ± 4 kJ mol⁻¹: this latter quantity is significantly below the literature value, based on an earlier measurement obtained from ICR bracketing.

Isomerism of the ions C2N⁺, C3N⁺, CHN⁺ and CH₂N⁺ was investigated, using reactivity with various neutrals to distinguish between isomers. The ions CCN⁺/CNC⁺ and CCCN⁺/c-C3N⁺ were distinguished on the basis of their reactivity with H₂: in both instances, the isomer featuring a terminal N atom reacted rapidly while the other isomer was unreactive. Identification of the isomers HCN⁺/HNC⁺ was complicated by the occurrence of tautomeration of HCN⁺ to the more stable isomer HNC⁺ by the mechanism of 'forth and back' proton transfer which occurred with several neutral reagents: reaction with CF₄ was subsequently used to distinguish between these isomers, since HCN⁺ reacted rapidly with CF₄ while HNC⁺ was unreactive. The reactions of all of these isomeric systems were examined with several neutrals abundant in interstellar clouds. The ions HCNH⁺ and CNH₂⁺ could not be distinguished on the basis of reactivity with the neutrals surveyed: we cannot exclude the possibility that only one of these isomers, HCNH⁺, was formed using the ion producing methods used.

The reactivity of several ions C₃HₙN⁺ (n = 1 → 4) and C₃HₙO⁺ (n = 0 → 3), with various neutrals, was investigated to ascertain the importance of these ions in the interstellar synthesis of acrylonitrile, tricarbon monoxide and propynal. Several ion-molecule reactions of CH₂CHCN were also studied to this end. The results indicate that C₃HₙN⁺ (n > 0) and C₃HₙO⁺ (n > 0) are unreactive with the
most prominent cloud constituents H₂ and CO; thus dissociative recombination of these ions should represent a significant source of the target molecules. Several ion-molecule reactions of the types X⁺ + CH₂CHCN, and C₃HₙN⁺ + X, produce ions which, on dissociative recombination, are expected to yield cyanopolyynes and cyclopropenylidene. Several reactions of the C₃HₙO⁺ ions suggest pathways to higher-order polycarbon monoxides and dioxides.

The reactivity of the molecular ions of C₂N₂, C₄N₂ and C₃O₂ have also been studied, to gauge the likely consequences of reactions of such ions within interstellar clouds.

The thermochemistry of the reaction HCN⁺ + CF₄ → CF₃⁺ + HF + CN is explored with regard to the proposal that this reaction may be 'entropy-driven'.

The interstellar significance of a novel class of neutral-neutral reactions has been considered.

The reactivity of the ions C₄Hₙ⁺ (n = 0 → 4), C₃HₙN⁺ (n = 0 → 4), and C₃HₙO⁺ (n = 0 → 3) with the neutrals H₂, CO, C₂H₂ and HCN is discussed in greater detail. Previous studies have determined that ions featuring linear carbon-chain skeletons are more reactive with H₂ and with CO if they feature 'bare' (non-hydrogenated) terminal carbon atoms: the present study suggests that ions with bare terminal C atoms are also more reactive than ions where the terminal atom is N or O rather than C. This observation may be explained by the degree of carbene character evident in such ions. These results are also discussed with reference to the predominance of very highly unsaturated linear molecules within interstellar clouds.
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### Errata

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ACKNOWLEDGEMENTS:

The following have, in various ways, assisted in the completion of this thesis:

My supervisor, Dr. Murray J. McEwan, and my assistant supervisor, Dr. Peter W. Harland.

My parents, Catherine and Derek Petrie, and my brother, Hamish, and sister, Elizabeth.

Staff members and fellow researchers, Dr. Colin G. Freeman, Paul F. Wilson, Dr. John S. Knight, Pravit Sudkeow, Dr. Sean C. Smith, Dr. Robert G.A.R. McLagan, Professor Leon F. Phillips, Ryan P.A. Bettens, Professor Eldon E. Ferguson, Dr. Michael Meot-Ner, Dr. Vincent G. Anicich, Kathryn M. McGrath, Barry A. Wells, Tania Chirnside, Brett R. Cameron, Roger F. Meads, Mark Morrison, David Marsden, and Katrina Mackle.

Chemistry Department technical staff in the Mechanical, Glassblowing and Electronics workshops, and the Secretarial offices.

The University of Canterbury, for the provision of a University of Canterbury scholarship, and the Chemistry Department, for the provision of a Teaching Assistantship.

The staff of the Physical Sciences and Engineering Libraries.
Friends, associates, and positive influences, Michael T., Tim, Annette & Fitz, Caligula the cat, Linda & Johnnie, Mary, Francisco, Jim, Lind & Andrew, Ian, Geoff & Liz, Brenda, Dave, Donna, Helen, Tony, Mark, Alex, Steve, Clarrie & Rosalie, Julian, Owen & Joy, Michael H., David, Jefferson Airplane, Libby & Richard, Gay, Rudi, Brian & Caitlin, Mark, John, Gabrielle, anyone else whose name I've omitted accidentally, and Nick, David, Grant, Andrew, and Phil.

Last but by no means least, Sandi McGowan.
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PUBLICATIONS:

The following publications are related to the research presented in this thesis:

Knight J.S., Petrie S.A.H., Freeman C.G., McEwan M.J, McLean A.D., DeFrees D.J.
Structural isomers of C$_2$N$^+$: a selected-ion flow tube study.

Petrie S.A.H., Freeman C.G., McEwan M.J., Meot-Ner (Mautner) M.
The proton affinity of cyanogen and ion / molecule reactions of C$_2$N$_2^+$.

Petrie S., Freeman C.G., Meot-Ner M., McEwan M.J.,Ferguson E.E.
An experimental study of HCN$^+$ and HNC$^+$ ion chemistry.

The proton affinity and selected ion-molecule reactions of diacetylene.

Petrie S., Freeman C.G., McEwan M.J., Ferguson E.E.
The ion chemistry of HNC$^+$/HCN$^+$ isomers: astrochemical implications.

Petrie S.
Interstellar reactions of kinetically excited radicals with molecular hydrogen.

Petrie S., Chirnside T.J., Freeman C.G., McEwan M.J.
The ion-molecule chemistry of CH$_2$CHCN.

Petrie S., Freeman C.G., McEwan M.J.
The ion-molecule chemistry of acrylonitrile: astrochemical implications.

Petrie S., Knight K.S., McGrath K.M., McEwan M.J., Freeman C.G.
C$_3$N$^+$ isomerism: a selected-ion flow tube study.

Bettens R.P.A., Petrie S., McEwan M.J., Freeman C.G.
To be written.
A selected-ion flow tube study of the ion-molecule chemistry of C$_3$H$_n$O$^+$ (n = 0-3).
Petrie S., McEwan M.J., Freeman C.G., McGrath K.M.
To be written.
CH$_2$N$^+$ isomerism: a selected-ion flow tube study.
CHAPTER 1.

INTRODUCTION.

Section 1.1: The chemistry of the interstellar medium.

Dense interstellar clouds are among the least visually captivating objects in the night sky, since they appear usually as an absence or a paucity of stars in a particular line of sight. Yet these clouds are (in their own way) fascinating, since they constitute the largest storehouse of chemical substances within our Galaxy.

Conditions throughout most interstellar space (see table 1.1) are not at all conducive to the existence of molecules, even the simplest bimolecular structures: particle densities are phenomenally low, and so collisions are very infrequent, providing very little opportunity for chemistry to occur. In these conditions, ultraviolet and cosmic radiation provide efficient channels for the destruction of molecules: only the simplest species such as CH can be formed in competition with these destruction processes. Within this harsh environment, dense clouds exist as some sort of oasis for the chemist in a desert which is, in general, of interest only to the physicist and astrophysicist.

The density of a dense cloud is not great: a thousand particles per cubic centimetre is a typical cloud density - higher densities, up to $10^{10}$ particles per cm$^3$, are found in particularly dense clumps of large clouds. Clouds can be
described as "dense" only in comparison to most reaches of interstellar space (where, in any given cubic centimetre, you are lucky to find any particles whatsoever). Because of the pressure gradient which decreases outwards from the cloud's centre, clouds (once formed) must be large enough to be gravitationally self-contained or else their lifespan will be short. Most clouds have diameters of a few parsecs and range in mass from several times the mass of the sun to several million solar masses. Most clouds are very cold (typically having a temperature of about 20K); they are also largely opaque to any electromagnetic radiation more energetic than microwave radiation, so ionizing and dissociating radiation cannot usually penetrate to the centre of a cloud (though cosmic rays can: under cloud conditions, cosmic rays act as much for the propagation of molecules as for their destruction). The cloud's opacity derives

<table>
<thead>
<tr>
<th>Object / system</th>
<th>T a,b</th>
<th>n c</th>
<th>P d</th>
<th>Composition e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial atmosphere f</td>
<td>3 x 10^2</td>
<td>3 x 10^{19}</td>
<td>7.6 x 10^2</td>
<td>O_2, N_2, Ar</td>
</tr>
<tr>
<td>Solar core</td>
<td>1.5 x 10^7</td>
<td>~ 10^{26}</td>
<td>~10^{14}</td>
<td>H^+, He^{2+}, e</td>
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<tr>
<td>Solar photosphere</td>
<td>5.8 x 10^3</td>
<td>~ 10^{17}</td>
<td>10^{1} → 10^{2}</td>
<td>H^+, He*, e</td>
</tr>
<tr>
<td>Tenuous IS &amp; space</td>
<td>10^6 → 10^6</td>
<td>~ 10^2</td>
<td>10^{16} → 10^{15}</td>
<td>H^+, H, He^{2+}, e</td>
</tr>
<tr>
<td>Diffuse IS cloud</td>
<td>10^2 → 10^4</td>
<td>10^{-2} → 10^{-2}</td>
<td>10^{-15} → 10^{-13}</td>
<td>H, He, CH</td>
</tr>
<tr>
<td>Dense IS cloud</td>
<td>10^9 → 10^2</td>
<td>10^3 → 10^{10}</td>
<td>10^{-15} → 10^{-8}</td>
<td>H_2, He, CO</td>
</tr>
<tr>
<td>Intergalactic space</td>
<td>&gt; 10^4 ?</td>
<td>&lt; 5 x 10^{-9} ?</td>
<td>?</td>
<td>H^+, He^{2+}, e ?</td>
</tr>
</tbody>
</table>

Notes
a. All values are approximate and intended merely to give an indication of 'typical' conditions. There exists a continuum of physical conditions within, between and beyond the ranges tabulated here.
b. Temperature, in degrees Kelvin.
c. Particle density, in particles cm^{-3}.
d. Pressure, in torr.
e. Only the predominant chemical components are listed.
f. At sea level.
g. IS = Interstellar.
in part from its large size and the large quantity of gas contained within, and also from the small grains of dust which are present and which serve to scatter or absorb any incident radiation.

Virtually all the information concerning cloud constituents has come from radio astronomy: radio-frequency spectra of molecular clouds feature lines which correspond to rotational excitation and de-excitation of particular molecules. The variety of chemicals identified within clouds is slight - to date, less than a hundred molecules, molecular ions and radicals have been observed as cloud components (see table 1.2) - but the existence of many exotic and unusual species within this list indicates that the chemistry occurring within these clouds differs substantially from that seen under normal terrestrial conditions. Common features of cloud constituents are single and triple C-C bonds, triple C-N bonds, a predominance of straight-chain organic species, an absence of branched-chain organics and a lack of inorganic, metal-containing, multifunctionalised and cyclic compounds. The detectability of a species within a cloud does not merely relate to its presence: to be observed, a species must not only be present in reasonable abundance but also (because most species are detected via rotational transitions) its rotational spectrum must be known and must contain lines of sufficient strength to be perceived in astronomical observations. Molecules which have a nonpolar or negligibly polar ground state will not, in general, be observed because their rotational spectra are weak or nonexistent. There are several observed but unidentified features in cloud spectra, and many molecules (e.g. CH₄, C₂H₂) which are very likely cloud components but are by their nature completely undetectable.
Several recent reviews treat the broad topic of interstellar chemistry \(^3,5,8-20\) and related topics such as cloud physics,\(^{21,22}\) observed cloud conditions,\(^{23,24}\) interstellar dust,\(^{25,26}\) interstellar modelling \(^{27,28}\) and organic synthesis.\(^{29,30}\)

Table 1.2: Molecules observed within interstellar clouds. \(^3-7\) This table lists molecules detected in clouds but not those species which have only been identified in circumstellar shells, since ion-molecule chemistry is thought to be less important a process in the chemical evolution of the latter regions. There is also very strong evidence for the presence of polycyclic aromatic hydrocarbons (PAHs) in interstellar clouds, though no individual PAH has yet been identified as a cloud constituent.

<table>
<thead>
<tr>
<th>CH</th>
<th>CH(^+)</th>
<th>CN(^-)</th>
<th>HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNC</td>
<td>HCNH(^+)</td>
<td>CH(_2)NH</td>
<td>CH(_3)NH(_2)</td>
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<tr>
<td>CO</td>
<td>HCO(^-)</td>
<td>HCO(^+)</td>
<td>HOC(^+) (?)</td>
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<td>H(_2)CO</td>
<td>CH(_3)OH</td>
<td>CS</td>
<td>HCS(^+)</td>
</tr>
<tr>
<td>H(_2)CS</td>
<td>CH(_3)SH</td>
<td>NH(_2)CN</td>
<td>OCN(^-) (?)</td>
</tr>
<tr>
<td>HNCO</td>
<td>HCONH(_2)</td>
<td>HNCS</td>
<td>HOCO(^+)</td>
</tr>
<tr>
<td>HCOOH</td>
<td>OCS</td>
<td>C(_2)</td>
<td>C(_2)H</td>
</tr>
<tr>
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<td>CH(_3)NC</td>
</tr>
<tr>
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<td>CH(_3)CHO</td>
<td>HCOOCH(_3)</td>
<td>CH(_3)OCH(_3)</td>
</tr>
<tr>
<td>CH(_3)CH(_2)OH</td>
<td>c-SiC(_2)</td>
<td>C(_2)S</td>
<td>C(_2)H</td>
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<tr>
<td>c-C(_3)H(_2)</td>
<td>CH(_3)C(_2)H</td>
<td>C(_2)CN(^-)</td>
<td>HC(_2)CN</td>
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<td>CH(_2)CHCN</td>
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<td>C(_2)CN</td>
<td>HC(_2)CHO</td>
</tr>
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<td>CH(_2)COCH(_3)</td>
<td>C(_2)CS</td>
<td>C(_2)C(_2)H</td>
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<tr>
<td>C(_2)C(_2)H (^+)</td>
<td>HC(_2)C(_2)CN</td>
<td>CH(_3)C(_2)H</td>
<td>C(_2)C(_2)H</td>
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<td>CH(_2)C(_2)CN</td>
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<td>HC(_2)C(_2)C(_2)C(_2)CN</td>
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<tr>
<td>H(_2)</td>
<td>H(_2) (^+)</td>
<td>NH(_3)</td>
<td>OH</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>H(_2)O(^+)</td>
<td>SiH(_4) (?)</td>
<td>H(_2)S</td>
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<td>NO(^-)</td>
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</tr>
<tr>
<td>PN</td>
<td>NS(^-)</td>
<td>NaOH (?)</td>
<td>SiO</td>
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Section 1.2: Ion-molecule reactions as a basis of interstellar chemistry.

Once astronomy and other broadly physical disciplines have determined the composition and the conditions which prevail within dense interstellar clouds, it becomes a problem in chemistry to explain the species which are present. The very low pressure within a cloud means that the only reactive processes which need be considered are unimolecular and bimolecular processes: three-body collisions (and, of course, those of higher order) are so exceedingly rare as to be totally unimportant. The low cloud temperatures additionally constrain viable reactions to be only those which are exoergic or thermoneutral and which lack activation energy barriers, since the reactive species to be considered in any collision will have negligible internal energy. The main experimental effort in modelling cloud chemistry has thus been in studying exothermic two-body reactions.

The processes which are held to be of some importance include radical-radical reactions, radiatively stabilised bimolecular association reactions, some bimolecular reactions with activation barriers (between neutral species of high abundance) and some processes occurring on interstellar dust grains but the predominant interstellar gas process is the reaction between a positive ion and a neutral, usually stable, molecule. Positive ion-molecule reactions are often very efficient under interstellar conditions, because they usually lack activation barriers (see figure 1.1) - thus when they are exoergic they occur at the collision rate. Support for the importance of ion-molecule reactions in interstellar chemistry comes from the generally good agreement between observed cloud
composition and expected composition (as inferred from model mechanisms comprising many hundreds of ion-molecule reactions) - though there are some aspects of the ion-molecule models which do not mirror well the cloud conditions. Notable shortcomings in the present models of ion-molecule reactions are:

Figure 1.1: Generalised reaction profiles for (a) exothermic and (b) endothermic positive ion-molecule reactions, and for (c) reaction between two neutral species. Ion-molecule reactions lack effective activation energy barriers, because of the long-range attractive electrostatic interaction between $A^+$ and $B$ as they approach: the energy required for rearrangement into products is provided by this attraction, in most cases. The lack of an activation barrier is extremely important at 10K (a typical temperature in a cold interstellar cloud) where the mean internal energy of a thermalised ion or molecule is approximately $0.08 \text{ kJ mol}^{-1}$. The efficiency of ion-molecule reactions explains their predominance in the partially-ionised cloud environment. [Figure adapted from reference 29].
(i) The production of sulphur-bearing species. According to models, production of H₂S and SO in the amounts observed requires some high-temperature processing, but these species are also seen in very cold clouds. It has also been suggested that sulphur chemistry requires grain surface reactions.

(ii) Incorrect abundances obtained for nitrogen species in models suggest that the starting materials may be in a different form from that assumed. Models incorporating neutral-neutral processes are better able to account for the observed abundances of simple nitrogen-containing molecules.

(iii) The formation of CH and CH⁺ is held to require high temperatures and the presence of shock waves resulting from violent events - such as star formation - within the cloud.

(iv) Predicted abundances of some polyatomic ions such as HC₃NH⁺ and CH₃CNH⁺ are at least an order of magnitude above the observational upper limits for these species. Reactions between neutral species may account for this discrepancy.

A notable success of ion-molecule chemistry has been in its modelling of the very large deviations, from terrestrial (and presumably interstellar) abundances, of the H/D ratios observed within interstellar molecules. Very recently, models have been developed which account for the long-term, dynamical development of the cloud or which include accretion processes onto dust grain surfaces: these more sophisticated models claim better agreement with
observation than earlier, pseudo-time-independent ion-molecule models, although such agreement may merely reflect the greater degree to which more complex models can be 'fitted' to observed conditions in the absence of sufficient observational constraints on these conditions.

**Ion production** within cloud interiors is most typically by cosmic-ray bombardment of H₂ or He:⁴⁴,⁴⁸

\[
\text{c.r.} + \text{H}_2 \rightarrow \text{H}_2^+ + e^{-} + \text{c.r.} \quad [0.80] \quad (1.1a)
\]

\[
\text{c.r.} + \text{H}_2 \rightarrow \text{H}^+ + \text{H} + e^{-} + \text{c.r.} \quad [0.04] \quad (1.1b)
\]

\[
\text{c.r.} + \text{He} \rightarrow \text{He}^+ + e^{-} + \text{c.r.} \quad [0.16] \quad (1.1c).
\]

A cosmic ray is most usually a proton, electron or α-particle having a kinetic energy of several MeV. The chief Galactic source of such cosmic rays is held to be Type I supernovae. Calculations have shown that 2 MeV cosmic rays from such events have a range of several hundred parsecs within the diffuse interstellar medium;⁴⁹ each cosmic ray can initiate many ionisations, since only \( \sim 60 \text{ eV} \) is lost per ionisation. Some of this energy is expended in translational excitation of the products, chiefly of the electron (typically \( E_T \sim 30 \text{ eV} \)) which thus may be able to induce further ionisation

\[
\text{H}_2 + e^{-} \rightarrow \text{H}_2^+ + e^{-} + e' \quad (1.2).
\]

An ionisation rate per hydrogen molecule \( \zeta'_{\text{H}_2} \sim 1.1 \times 10^{-15} \text{ s}^{-1} \) has been suggested as the mean Galactic value for cosmic-ray induced ionisation, but this rate will be lower within dense clouds because of the finite permeability of such a dense
Models of dense cloud chemistry usually adopt an ionisation rate of $1 \times 10^{-17}$ s$^{-1}$, reflecting the attenuation of cosmic rays by the gas and dust constituting the cloud.$^{13}$

It is worth noting also that alternative methods of ionisation exist, even in the absence of irradiation. A process of chemi-ionisation has been suggested$^{48}$

$$\text{CH}_2^+ + \text{O} \rightarrow \text{CHO}^+ + e$$ (1.3)

for which a rate coefficient $k_{1.3} = 7 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ has been estimated at 25K.$^{51}$ Such processes involving small, reactive neutrals may be important at relatively low pressures (i.e. on cloud fringes) and during the early stages of a cloud's development, when the abundance of these species is highest; however, cosmic-ray production of H$_2^+$ is considered the dominant primary process.

Subsequent reaction of H$_2^+$ with molecular hydrogen yields H$_3^+$, which is unreactive with H$_2$

$$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}^+$$ (1.4)
$$\text{H}_3^+ + \text{H}_2 \rightarrow \text{no reaction}$$ (1.5)

$k_{1.4} = 2.0 \times 10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$  
k$_{1.5} < 1 \times 10^{-14}$ cm$^3$ molec$^{-1}$ s$^{-1}$

and which thus persists to react with other chemicals present within the cloud - for example,
\[ \text{H}_3^+ + \text{CO} \rightarrow \text{CHO}^+ + \text{H}_2 \]  
\( \text{k}_{1.6} = 1.7 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \) (1.6).

With such reactions, the synthetic chemistry of the cloud is under way. Subsequent reactions between progressively larger reactants (at, in general, progressively lower abundances) can succeed in producing quite large molecules such as the cyanopolyynes \( \text{R(C}_2\text{nCN, n = 0 → 5 observed for R = H, n = 0 → 2 observed for R = CH}_3 \) ). Reaction classes of importance include charge-transfer, proton-transfer, atom abstraction, radiative association and dissociative recombination processes (see figure 1.2). Of these processes, the first three are studied with relative ease in the laboratory, and their implications for interstellar chemistry are well established.

**Radiative association** of ions with molecules, first suggested by Williams,\(^{53}\) is held to be of importance in collisions involving polyatomic reactants.\(^{31}\) Under cloud conditions, termolecular association reactions are precluded by the extremely low pressure (at \( n = 10^3 \) particles cm\(^{-3} \) and \( T = 100 K \), a molecule or ion is likely to undergo a *bimolecular* collision once every few weeks) and so reactions yielding products which require collisional stabilisation cannot occur. Association reactions *can* occur if the initially-formed collision complex can be stabilised by radiative de-excitation within the complex’s lifetime. Typical frequencies for infra-red radiative stabilisation of collision complexes are in the range \( k_r \sim 10^2 \rightarrow 10^3 \text{ s}^{-1} \),\(^{54}\) which is many orders of magnitude below the normal range of vibrational frequencies (vibration being the mode through which fragmentation of the complex is liable to occur). For a long lifetime, the collision complex must possess several internal degrees of freedom wherein the
excess energy of the association may be partitioned (since the complex will easily
dissociate otherwise) and thus, in general, this process is more feasible for more
highly polyatomic products. The low cloud temperatures also favour long
lifetimes: reactants possess essentially no internal energy and so, for dissociation
to occur, essentially all of the internal energy of the collision complex must be
localised in the bond between the initial fragments.

Figure 1.2: Important classes of interstellar ion-molecule reactions.

(a). Charge transfer
\[ A^+ + X \rightarrow X^+ + A \]
Usually fast when exoergic; exoergic if \( IP(A) > IP(X) \)
e.g. \( \text{He}^+ + \text{CO} \rightarrow (\text{CO}^+*) + \text{He} \)
\( \text{HC}_3\text{N}^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{HC}_3\text{N} \)
but \( \text{He}^+ + \text{H}_2 \not\rightarrow (\text{H}_2^+*) + \text{He} \)

(b). Proton transfer
\[ \text{AH}^+ + X \rightarrow \text{XH}^+ + A \]
Fast when exoergic; exoergic if \( PA(X) > PA(A) \)
e.g. \( \text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2 \)
\( \text{HCO}^+ + \text{HCN} \rightarrow \text{HCNH}^+ + \text{CO} \)

(c). Atom abstraction
\[ A^+ + XB \rightarrow AB^+ + X \]
Usually fast when exoergic and \( B = \text{H} \)
e.g. \( \text{CN}^+ + \text{H}_2 \rightarrow \text{HCN}^+ + \text{H} \)
\( \text{HCN}^+ + \text{H}_2 \rightarrow \text{HCNH}^+ + \text{H} \)

(d). Radiative association
\[ A^+ + B \rightarrow AB^+ + \text{hv} \]
Always exoergic; efficient when collision complex \((AB^+)^*\) is long-lived.
e.g. \( \text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{hv} \)
\( \text{CH}_3^+ + \text{HCN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{hv} \)

(e). Dissociative recombination
\[ AB^+ + e \rightarrow A + B \]
Always exoergic for some product channels; almost always exceedingly fast, except for
monatomic ions.
e.g. \( \text{CH}_5^+ + e \rightarrow \text{CH}_3^+ + \text{H}_2 \)
\( \rightarrow \text{CH}_2 + \text{H}_2 + \text{H}^+ \)
\( \not\rightarrow \text{CH}_4 + \text{H}^+ \)
\( \text{H}_2\text{O}^+ + e \rightarrow \text{OH}^+ + \text{H}_2 \)
\( \rightarrow \text{H}_2\text{O} + \text{H}^+ \)

Notes:

a. This product channel has not been identified.
b. This product channel is thought to be inactive.\textsuperscript{52}
The observation of purely radiative association requires very low pressures to ensure that there is no collisional contribution to stabilisation, and so flow tube experiments have more often focussed on termolecular association. Since radiative and termolecular association involve the same collision complex, it is frequently assumed that the strong inverse temperature dependences which are seen for termolecular association are indicative also of similarly strong dependences for radiative association. However, problems can arise with the extrapolation of theoretical studies in the absence of sufficient experimental results. Herbst et al inferring radiative association rate coefficients from observed termolecular association, describe a difference between theoretically calculated and experimentally derived radiative association rate coefficients of a factor of $10^{3.5}$ for the reaction

$$\text{HCNH}^+ + \text{C}_2\text{H}_2 \rightarrow [\text{C}_3\text{H}_4\text{N}]^+$$  \hfill (1.7)

$$k_{1.7e} = 3.3 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad \text{(experimental)}$$

$$k_{1.7c} = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad \text{(calculated)}$$

The values quoted here are two-body rate coefficients giving the effective bimolecular rate for association, with the experimental results indicating that the collision complex is radiatively stabilised in fewer than one collision per $10^6$, in contrast to the theoretical expectations. The discrepancy here is thought to arise from an incorrect structure assigned to the collision complex in the theoretical treatment. The very low rate coefficient in this instance is explained in terms of the predominant production of a cyclic metastable isomer rather than the lowest-energy structure (protonated $\text{C}_2\text{H}_3\text{CN}$). Such a metastable product would have a lower density of available vibrational and rotational states than the lowest-
energy species, and would thus have both a shorter lifetime as a collision complex and a lower probability of collisional stabilisation in laboratory studies.

Some direct experimental observations of radiative association have been made: the reaction

\[ \text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_4^+ + \text{H} \]  

is important in the interstellar synthesis of methane, since

\[ \text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_4^+ + \text{H} \]  

is endoergic. Measurement of \( k_{1.8} = 1 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) at 13K using an ion trap technique\(^5^6\) constitutes the first detection of radiative association at low temperatures and pressures.\(^5^7-5^9\) Bimolecular association has also been observed in several association reactions involving nitriles at room temperature, which are found to be reasonably efficient at low pressures.\(^6^0-6^4\) The only known mechanism for bimolecular association is that of radiative association. Ab initio calculations of the structures of the association complexes in these studies have enabled the association systems to be modelled. There is good agreement between measured and calculated lifetimes of the AB\(^+\) complexes.\(^6^5,6^6\)

**Dissociative recombination** of a positive ion with an electron

\[ \text{AB}^+ + e \rightarrow \text{A} + \text{B} \]
yields two neutral fragments and thus serves as the main terminating step in a chain of ion-molecule reactions initiated by cosmic-ray ionisation. As such, it provides an upper limit to the degree of ionisation within a cloud (typically, about $10^{-8}$). Dissociative recombination reactions are very rapid - for triatomic or larger species, the recombination coefficients observed at room temperature are typically of the order of $10^{-6}$ cm$^3$ molec$^{-1}$ s$^{-1}$, with $\alpha_e(1.10)$ tending to increase with the size of the molecular ion. The reactions also display a strong negative temperature dependence and are thus even more rapid under interstellar conditions - though the variation with temperature diminishes as the size of the molecular ion increases. A notable exception to the general rapidity of these reactions is

$$\text{H}_3^+ + e \rightarrow \text{H}_2 + \text{H} \cdot \quad \quad \quad (1.11a)$$

$$\rightarrow 3\text{H}\cdot \quad \quad \quad (1.11b),$$

which, Smith and Adams claim on the basis of Flowing Afterglow - Langmuir Probe measurements, does not occur to any measurable extent: $\alpha_e(1.11) < 1.0 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Interstellar H$_3^+$ is, as a consequence, given free rein in models to undergo further reactions with trace neutrals. This view has, however, been contested by Amano, who finds a recombination coefficient $\alpha_e(1.11) = 1.8 \times 10^{-7}$ cm$^3$ molec$^{-1}$ s$^{-1}$ in agreement with earlier, stationary-afterglow and merged-beam measurements. In any event, reaction of H$_3^+$ with CO to produce HCO$^+$ is likely to be a more rapid loss mechanism for H$_3^+$ than is dissociative recombination, so the uncertainty regarding this process is not of critical concern in this field.
For triatomic and larger molecular ions, several products are usually possible from a dissociative recombination reaction - unless one bond is notably weaker than the others:

\[ \text{N}_2\text{H}^+ + e \rightarrow \text{N}_2 + \text{H}^- \]  
\[ \alpha_{e(1.12)} = 1.7 \times 10^{-7} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} (\text{at } 300\text{K}) \]

The product distributions of most dissociative recombinations are not well predicted by theory, since it is not intuitively obvious which of the collision complex's bonds will break most rapidly; several theories exist which treat the dissociation process in different ways, and which predict often very different results. Until recently, experimental determination of product channels was not possible. An experiment applying spectroscopic techniques to a FALP apparatus has identified one of the product channels for reaction of ground-state HCO\textsubscript{2}+ with an electron:

\[ \text{HCO}_2^+ + e \rightarrow \text{OH} + \text{CO} \]  
\[ \rightarrow \text{H} + \text{CO}_2 \]  
\[ \rightarrow \text{H} + \text{O} + \text{CO} \]

\[ \alpha_{e(1.13)} = 3.4 \times 10^{-7} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} (\text{at } 300\text{K}) \]

and similar studies have since been performed for H\textsubscript{3}O\textsuperscript{+} and N\textsubscript{2}OH\textsuperscript{+}. A fundamental tenet of astrochemical modelling is that, in accordance with the prevailing temperature, reactants possess negligible internal or translational energy. This is necessarily true (to a very good approximation) for reactions not
involving molecular hydrogen, since preceding collisions with H$_2$ would have thermalised each reactant; but reactions of higher energy species with hydrogen can also be considered relevant.\textsuperscript{86} If a reaction

$$\text{AB}^+ + \text{CD} \rightarrow \text{AC}^+ + \text{BD} \quad (1.14)$$

is exoergic, then the exoergicity of the reaction will be conferred as suprathermal energy of the products. Energy which is channeled into electronic or vibrational modes of a product is likely to be dissipated as electromagnetic radiation before this species can undergo collision with H$_2$, since the time between collisions greatly exceeds the lifetime of most feasible excited states; but translational energy cannot be quenched except by intermolecular collision, and in some cases this energy is sufficient to drive reactions. For example, in nitrogen chemistry, the reaction

$$\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H} \cdot \quad (1.15)$$

is endoergic\textsuperscript{87} for thermalised reactants (\(\Delta H_{1.15} \sim +0.7 \text{kJmol}^{-1}\)). The endoergicity of this reaction can be overcome for N$^+$ produced in some fashions - for example, by collision of He$^+$ (generated by cosmic-ray ionisation) with N$_2$ (which is not observed in interstellar clouds because of its nonpolar nature, but which is probably a species of comparable abundance to CO):

$$\text{He}^+ + \text{N}_2 \rightarrow (\text{N}_2^+)\# + \text{He} \quad (1.16a)$$

$$\text{N}_2^+)\# \rightarrow (\text{N}^+)\# + \text{N} \cdot \quad (1.16b)$$
The N\(^+\) thus produced has an excess translational energy of approximately 1.5 kJ mol\(^{-1}\), which is sufficient to allow NH\(^+\) formation on collision with H\(_2\); nonreactive collisions still dominate, however, leading to thermalisation of the translationally excited N\(^+\) in most cases.

\[
\begin{align*}
(N^+)_\text{fast} + H_2 & \rightarrow NH^+ + H^- \quad (1.17a) \\
& \rightarrow N^+ + (H_2)_\text{fast} \quad (1.17b)
\end{align*}
\]

\[k_{1.17a}(0.038) = 3.7 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ (at KE}_\text{cm} = 38 \text{ meV)}
\]

\[k_{1.17a}(0.26) = 6.2 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ (at KE}_\text{cm} = 260 \text{ meV)}
\]

\[k_c = 1.59 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}
\]

(KE\(_{cm}\) is the centre-of-mass collision energy pertaining to the VT-SIFDT experimental results;\(^8\)\(^6\) \(k_c\) is the collision rate coefficient according to Langevin theory). This notion of 'hot-ion' chemistry in cold clouds has also been treated recently by Brown et al.\(^{41}\)

**Negative ions** may also play a rôle in cloud chemistry\(^8\)\(^8\),\(^8\)\(^9\) - though such a rôle is almost certainly subservient to positive-ion chemistry, because of the necessarily lower total abundances of negative ions. Negative ions may be generated by attachment of low-energy electrons to molecules

\[
\begin{align*}
AB + e & \rightarrow A^- + B \quad (1.18a) \\
& \rightarrow AB^- + hv \quad (1.18b)
\end{align*}
\]

or by UV-induced photoionisation of polar molecules.
\[ \text{AB} + \text{hv} \rightarrow \text{A}^- + \text{B}^+ \] (1.19).

Electron attachment competes with dissociative recombination as a loss mechanism for electrons - collision of an electron with a positive ion rather than a neutral molecule is favoured by the greater electrostatic attraction which is manifested between ions and electrons. Negative-ion production by electron attachment requires that the electrons be of low translational energy. Cosmic-ray ionisation produces high-energy electrons: some of this energy is rapidly expended in further ionisations (reaction 1.2), but a point is soon reached at which a medium-energy electron is incapable of further ionisation. Subsequently, the electron can only be quenched by collision with molecules:

\[ e + \text{H}_2 \rightarrow e' + \text{H}_2 \] (1.20)

Such quenching processes are very inefficient: Cravath\textsuperscript{90} has determined that, for quenching of a highly excited electron by elastic collisions in a neutral gas, only \(~0.00026\) of the electron's kinetic energy is lost per collision with \text{H}_2. Many thousands of collisions will be required to thermalise the electron, and within this time any interaction with a cation is likely to lead to neutralisation. Thus production of negative ions is only feasible if the degree of ionisation is sufficiently low.

Ultraviolet ionisation of molecules (reaction (1.19)), within the more sheltered reaches of a cloud, will occur principally as a byproduct of cosmic-ray ionisation, because of the opacity of clouds to external UV and the lack of other internal UV sources.\textsuperscript{91}
Negative ions, if formed, are very efficiently destroyed by collision with positive ions:

\[
\begin{align*}
AB^+ + CD^- & \rightarrow AB + CD \quad (1.21a) \\
& \rightarrow AC + BD \quad (1.21b).
\end{align*}
\]

The rate coefficients for these processes are faster even than for recombination of positive ions with electrons: values of \(k_{1.21} \sim 10^{-3} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\) have been estimated.\(^72\)

**Shocks** are of importance in driving chemistry in some cloud regions: a shock wave may occur as the result of large-scale upheaval (such as nascent star formation) within a cloud, leading to an increase in local temperature and pressure. Temperatures of several thousand degrees may be attained, permitting a more varied chemistry including endothermic and barrier-inhibited reactions. Chemistry within shocked regions\(^{36,92-98}\) has similarities with the chemistry of circumstellar envelopes,\(^{43,99-101}\) and several molecules not seen in cold interstellar clouds have been seen in such envelopes.

Recent efforts in investigating interstellar chemistry have tended to concentrate on the above areas. In addition, as the interstellar chemistry of carbon, nitrogen and oxygen has become better-understood, much recent work has been done in studying the chemistry of the second-row elements, principally silicon,\(^{102-110}\) phosphorus\(^{111-113}\) and sulphur.\(^{35,97,114-118}\) Evidence is accumulating also for the interstellar presence of polycyclic aromatic hydrocarbons (PAHs),\(^{88,89,94,119-124}\)
which have been implicated as an intermediate stage between smaller molecules and dust grain formation.

Section 1.3: Laboratory study of ion-molecule reactions.

Several types of technique have been developed, mainly within the last twenty-five years, for the study of ion-molecule reactions.\textsuperscript{125}

In ion cyclotron resonance spectroscopy (ICR),\textsuperscript{126} ions are produced in a low-pressure chamber ($P < \sim 10^{-3}$ Torr), constrained by a magnetic field which induces cyclotron motion in the ions. Application of an electric field perpendicular to the magnetic field causes the ions to be propelled along the chamber. Reactions with neutrals can be studied, for example, by the change in ion signal as a function of the variation in pressure of a reactant neutral. The ICR technique, because of the wide pressure range attainable (four orders of magnitude: $\sim 10^{-7} - 10^{-3}$ Torr), is commonly used to study termolecular association processes.\textsuperscript{60,62}

In the CRESU technique\textsuperscript{127} [CRESU = "Cinétique de Réactions en Ecoulement Supersonique Uniforme"], ion-molecule rate coefficients at very low temperatures are studied by supersonic expansion of a partially ionized gas stream through a Laval nozzle into a low-pressure chamber. The gas stream, which is thus internally cooled to very low effective temperatures, contains the ion source gas, the reactant gas and a buffer gas. Detection of the reactant and
product ions is effected by a mass-spectrometer. The CRESU technique is especially useful for studying ion-molecule reactions as a function of temperature, and at the temperatures relevant to dense interstellar cloud conditions. Reaction studies using CRESU have demonstrated\textsuperscript{128} that the reaction

\[
N^+ + H_2 \rightarrow NH^+ + H^-
\]

\[
k_{1.15} = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad [T = 20K]
\]
\[
k_{1.15} = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad [T = 70K]
\]

proceeds much more slowly at 20K than at 70K, due to an apparent slight endothermicity ($\Delta H_{1.15} \sim +0.7 \text{ kJmol}^{-1}$), while the reaction

\[
O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H^-
\]

\[
k_{1.22} = 4.6 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad [T = 20K]
\]
\[
k_{1.22} = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad [T = 70K]
\]

is considerably more rapid at the lower temperature, in accordance with a proposed mechanism involving rearrangement of a weakly-bound, short-lived complex.

A recent refinement of the CRESU technique features mass-selection of the reactant ions,\textsuperscript{129} by a quadrupole mass spectrometer: this adaptation, CRESUS, has been used to measure the temperature dependence of the reaction
Because of the size of the reaction chambers employed, the CRESU techniques consume large flows of carrier gas. An alternative technique developed very recently by M.A. Smith and co-workers uses similar production of a supersonic jet of internally cooled reactants, but produces a pulsed gas flow in a much smaller apparatus: its developers claim a reduction in buffer gas consumption of better than four orders of magnitude over the CRESU technique. Ion detection in this free jet flow reactor is by time-of-flight mass spectrometry, and temperatures as low as 0.5K have been attained for the study of the association process.

\[
\text{Ar}^+ + \text{Ar} + \text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar}
\]  

Effective temperatures attainable by this technique, for reactions involving molecular neutrals, are somewhat higher, since the reactant neutrals are at a higher rotational temperature \( T_{\text{rot}} \sim 10 \text{ K} \); \( T_{\text{rot}} \sim 170 \text{ K} \) for \( \text{H}_2 \).  

Some low-temperature data can also be obtained by ion trap methods using liquid-helium or liquid-nitrogen cooled instruments, but the cooling method used in this instance reduces the chemical versatility of the technique since fewer reagents are volatile at cryogenic temperatures.
Notwithstanding the widespread use of ICR and other techniques, most modelling of interstellar chemical processes has been performed using results produced from one of the many variants of the flow technique originally developed by Ferguson, Fehsenfeld and Schmeltekopf in 1963. The Flowing Afterglow (FA) instrument was constructed after the isolation of a stationary afterglow in helium following electrical discharge ionisation and found early applications in the measurement of reactions relevant to terrestrial upper-atmosphere chemistry. The experimental development and applications of the FA technique to ion-molecule chemistry have been recently reviewed: the central features, and some indications of the versatility, of the technique are outlined below.

In the flowing afterglow apparatus (see figure 1.3), ions are generated within the reaction tube, typically by electron bombardment on the ion-producing gas.
stream of unreactive buffer gas (with which the ion's source gas has been mixed) carries the resulting plasma along the tube towards the aperture at the end of the tube which leads into the mass spectrometer chamber wherein the ions are mass-selected and subsequently detected by a particle multiplier or equivalent device. As the plasma beam traverses the tube axis, it passes several gas inlet ports where a neutral reactant may be added. The reactivity of an ion is judged by the reduction in the initial reactant ion signal with added neutral, and product ions are detected mass-spectrometrically.

Most typically, the buffer gas is helium with a pressure in the range 0.1 to 1.0 Torr: to minimise the effects of radial diffusion (and hence maximise the signal intensity) the gas is rapidly pumped through the tube. The mass-spectrometer chamber, where a much lower pressure must be maintained, is pumped separately from the flow tube. Rate coefficients can be easily obtained from the FA: the comparatively high pressure of the reaction region represents a disadvantage in the modelling of astrochemical processes with respect to "low-pressure" techniques such as ICR (where the pressure is still several orders of magnitude above typical cloud pressures). A compensating advantage of FA is that excited states of the ions are usually rapidly quenched by collisions with the buffer gas.142

The basic refinement of the flowing-afterglow apparatus is the Selected Ion Flow Tube (SIFT), devised by Smith and Adams in the mid-70s.143 The SIFT (see figure 1.4) differs from the FA in having a remote, differentially-pumped ion source chamber: ions are produced by electron impact in the ion source, the ion beam is focussed via a series of electrostatic lenses and is passed through a
quadrupole mass spectrometer so that the desired reactant ion is mass-selected. The ion beam, thus filtered, is then further focussed upon an aperture leading into the flow tube. This aperture is a specially-shaped Venturi inlet designed to minimise the effects of back-streaming of the buffer gas into the (very much lower pressure) ion source chamber.

The greater complexity of the SIFT over the FA technique means that the flight-path for the ion, from inception through possible reaction to eventual detection, is longer and more complex and thus signal losses (through diffusion and processing) are greater. In fact, diffusive loss for ions in a SIFT is substantially lower than the loss of ion signal through ambipolar diffusion in a FA plasma: the major loss in ion signal occurs as a consequence of ion divergence after

Figure 1.4: Schematic diagram of a typical SIFT apparatus. The vertical lines before and after the quadrupole mass spectrometers (QMS) denote the position of electrostatic lenses, used for focussing [Adapted from reference 139].
passage through the upstream quadrupole mass filter, before injection through the Venturi orifice. The disadvantage of lower signals is overridden by the increase in purity of the reactant ion beam, from which other ion masses, neutral contaminants, electrons and negative ions - all likely contaminants in the reaction tube of the FA - have been eliminated as far as possible. This means that product channels (especially) can be more confidently determined using the SIFT in preference to the FA.

Further adaptations of the SIFT technique expand the room-temperature, thermalised ion properties of the FA and the SIFT. These modifications (which had previously been applied to the FA device)\textsuperscript{144,145} include the addition of a drift region\textsuperscript{146} and of a variable-temperature incubating jacket\textsuperscript{141,147} to the tube of the "standard" SIFT. A drift region is essentially an extension to the flow tube along which a voltage gradient can be applied, and is useful in artificially controlling the kinetic energy of the ion within this region: one possible application of such a technique is to determine the binding energy in a cluster ion or adduct - for example, in the study of the reaction

$$^{14}\text{N}_4^+ + ^{15}\text{N}_2 \rightarrow ^{14}\text{N}_2^{15}\text{N}_2^+ + ^{14}\text{N}_2 \quad (1.25),$$

the kinetics of ligand switching were investigated as a function of changing relative kinetic energy in a VT-SIFDT apparatus.\textsuperscript{147}

Adding a variable-temperature jacket permits measurement of reaction rates over a wider range of temperatures (typically 80K to 500K), to study the variation in reaction rate with temperature. Fast ion-molecule reactions, and especially
interactions involving an ion and a polar neutral, are frequently seen to have a negative temperature dependence, since the efficiency of the ion's 'capture' by the neutral's dipole is enhanced at reduced relative velocities.\textsuperscript{148,149} This means that at 10K, in an interstellar cloud, such processes can be very efficient indeed.\textsuperscript{150}

Several other innovations to the FA technique have allowed access to information and to categories of reactions not amenable to study by the above "basic" versions of flow systems. These innovations include incorporation of Langmuir Probe, Laser-Induced Fluorescence, cold finger sampling techniques, and Gas Chromatography / Mass Spectrometry.

The Flowing Afterglow Langmuir Probe (FALP) was developed by Smith and coworkers,\textsuperscript{151,152} and incorporates a probe\textsuperscript{153} to investigate properties of the flow-tube plasma. The FALP has been used to study ion-electron dissociative recombination, electron attachment and positive ion-negative ion mutual neutralisation reactions, all of which are of some relevance to an understanding of the chemistry of interstellar clouds. Smith and Adams have developed a FALP instrument with a variable temperature incubating jacket (the VT-FALP)\textsuperscript{154} which permits investigation of the temperature dependence of plasma processes.\textsuperscript{73}

Analysis of the neutral products of ion-molecule reactions is also possible using special adaptations of the FA technique. Laser-induced fluorescence (LIF) was first coupled with a flowing-afterglow apparatus in 1982\textsuperscript{155} to study the OH vibrational distribution of the reaction
$$O^- + HF \rightarrow OH + F^- \quad \text{(1.26).}$$

More recently, the FALP technique has been combined with LIF by Adams, Herd and Smith$^{84}$ to permit accurate product determinations for astrophysically important dissociative recombination reactions. The investigation of the reaction

$$\text{HCO}_2^+ + e \rightarrow \text{OH} + \text{CO} \quad [0.34] \quad \text{(1.13a)}$$

by this modified FALP technique is worthy of note not only for the experimental innovation involved, and the chemical knowledge gained, but also for the rather lengthy chain of reactions performed in the reactor during the measurement:

$$\text{He} + e \rightarrow \text{He}^+ + 2e \quad \text{(1.27)}$$
$$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He} \quad \text{(1.28)}$$
$$\text{He}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{He} + \text{He} \quad \text{(1.29)}$$
$$\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}_2 \quad \text{(1.30a)}$$
$$\rightarrow \text{H}_2^+ + \text{Ar} \quad \text{(1.30b)}$$
$$\text{ArH}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{Ar} \quad \text{(1.31)}$$
$$\text{H}_3^+ + \text{CO}_2 \rightarrow \text{HCO}_2^+ + \text{H}_2 \quad \text{(1.32).}$$

Addition of argon serves to remove metastable excited helium atoms (He*) from the downstream region of the tube, through the Penning ionisation process

$$\text{He}^* + \text{Ar} \rightarrow \text{Ar}^+ + \text{He} + e \quad \text{(1.33).}$$
The He* species would otherwise continue to ionise reagent gases introduced downstream (thus obscuring the real rate of ion-electron recombination occurring). Addition of H₂ produces a plasma which does not recombine prematurely (as it were), since the reaction

\[
\text{H}_3^+ + e \rightarrow \text{H}_2 + \text{H}^- \quad (1.11a)
\]

\[
\rightarrow 3\text{H}^- \quad (1.11b),
\]

is immeasurably slow. Finally, addition of CO₂ produces the ion of interest, HCO₂⁺, which can then recombine with the free electrons entrained in the buffer gas flow.

Physical isolation of products from reactions in a FA apparatus has proceeded by the trapping of neutral products on a liquid-nitrogen-cooled cold finger, followed by warming and analysis of the sample by GC/MS.¹⁵⁶-¹⁵⁸

It is significant that these innovations have involved FA systems at the expense of SIFT techniques: that this has been the case is understandable in view of the much larger ion signals (and, therefore, much more readily observable neutral products) obtained using the simpler flowing afterglow technique. Further developments may include SIFT analogues of some of the FA devices detailed above. A flow tube with selected-ion injection, variable temperature, drift region, Langmuir probe, and spectroscopic and physical product isolation capabilities would be a formidable instrument indeed ...
Section 1.4: Determination of reaction rates from flow data.

Whatever the nature of the flow technique employed, derivation of the rate coefficient for an observed reaction is essentially the same.

For a bimolecular reaction of the form

$$A^+ + B \rightarrow \text{products}$$

the rate law is given as

$$\text{rate} = \frac{-d[A^+]}{dt} = k [A^+]_t [B]_t$$

where $k$ is the second-order rate coefficient and $[A^+]_t$ and $[B]_t$ are the concentrations of the reactants after a reaction interval of time $t$. In experiments using the SIFT (or other flow) technique, the ion signal $[A^+]$ is not monitored as a function of time but as a function of the neutral reactant concentration $[B]$ and after a fixed reaction distance $z$. The rate law thus needs to be rewritten appropriately. The time elapsed is proportional to the distance travelled by the ion $A^+$, if its velocity $v_{ion}$ is assumed to be independent of its axial and radial position within the tube:

$$\frac{dz}{dt} = v_{ion}$$
so rate \[ \frac{-d[A^+]}{dz} = \frac{k}{v_{ion}} [A^+]_z [B]_z \] \hspace{1cm} (1.iii).

$[A^+]_z$ and $[B]_z$ are the distance-dependent reactant concentrations. In practice, the neutral reactant $B$ is present in large excess and so reaction with the small concentration of the ion $A^+$ leaves it essentially undepleted - thus $[B]$ can be treated as being independent of distance. As a consequence, the rate will exhibit pseudo-first-order behaviour as a function of distance:

\[ \frac{-d[A^+]}{dz} = \frac{k[B]}{v_{ion}} \] \hspace{1cm} (1.iv)

\[ \Rightarrow \quad \frac{-d[A^+]}{[A^+]_z} = \frac{k[B]}{v_{ion}} \, dz \] \hspace{1cm} (1.v)

\[ \Rightarrow \quad \int_0^z \frac{-1}{[A^+]_z} \, d[A^+] = \int_0^z \frac{k[B]}{v_{ion}} \, dz \] \hspace{1cm} (1.vi)

\[ \Rightarrow \quad \ln [A^+]_0 - \ln [A^+]_z = \frac{k[B]z}{v_{ion}} \] \hspace{1cm} (1.vii)

\[ \Rightarrow \quad \ln \left( \frac{[A^+]_z}{[A^+]_0} \right) = \frac{-k[B]z}{v_{ion}} \] \hspace{1cm} (1.viii).

From this expression, it can be seen that if the ion velocity, the reaction distance and the ion signal $[A^+]_o$ at distance zero (that is, before any mixing of the reactants has occurred) are held constant while $[B]$ is systematically varied, then a
plot of ln \([A^+]_z\) versus \([B]\) will yield a line of slope \(-k z/v_{ion}\) and intercept \(ln [A^+]_0\). In this manner, the rate coefficient can be determined

\[
k = \ln\left(\frac{[A^+]_z}{[A^+]_0}\right) \frac{v_{ion}}{[B] z}
\]  

(1.ix),

provided that all the quantities on the right-hand side of this expression (1.ix) are known.

\([A^+]_z\) is measured as the intensity of the signal due to the reactant ion's mass at the particle multiplier (the SIFT's detection device); \([A^+]_0\) cannot be conveniently measured, but it is treated as being equivalent to \([A^+]_{z,0}\) (that is, the ion signal due to \(A^+\) after having passed through the reaction distance \(z\) while \([B] = 0\)) - a correction factor is applied to compensate for effects of radial diffusive loss of the on-axis ion beam (since only those ions which are on-axis are able to be detected). Since the expression involves the ratio of the \(A^+\) ion signals before and after reaction with \(B\), the units of \([A^+]\) are unimportant.

The reaction distance \(z\) can be taken as the distance between the injection portal for the reactant neutral and the exit orifice of the SIFT tube - however, this supposes that mixing of the buffer gas and the reactant neutral is instantaneous. This is physically unreasonable, and in practice the reaction distance is 'end-corrected' to compensate for the axial and radial dependence of the reactant concentration \([B]\). This end correction is made on the basis of repeated measurements of a calibration reaction - for example,
\[
\begin{align*}
C^+ + CH_4 & \rightarrow \text{products} \quad \text{(1.35),} \\
{k_{1.35}} &= 1.4 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}
\end{align*}
\]

for which the value of the rate coefficient is well-established. The end correction can reasonably be assumed to be pressure-dependent, so calibration measurements are necessary at a representative range of pressures.\textsuperscript{159}

The ion velocity \(v_{\text{ion}}\) can be measured by time-of-flight methods, but it is more customary to calculate it from experimental conditions as follows. Adams et al.\textsuperscript{160} have demonstrated that the expression

\[
v_{\text{ion}} = 1.33 v_{\text{buff}} \quad \text{(1.x),}
\]

where \(v_{\text{buff}}\) is the calculated mean velocity of the buffer gas employed, usually gives good agreement with the measured \(v_{\text{ion}}\).\textsuperscript{141} Thus all the quantities required to determine the rate coefficient for a reaction can be determined.

In practice, the analysis of results is a somewhat more complex matter since allowance should be made for radial and axial diffusion of the ions, and for the non-uniform velocity of the carrier gas as a function of position. Analysis of the relevant flow characteristics can provide correction factors for these effects, as has been explained elsewhere.\textsuperscript{160,161} The correction factors applicable to the Canterbury SIFT are detailed in section 2.2.
Section 1.5: Study of isomeric systems by flow techniques.

It is apparent, from a description of the basic aspects of the flow-tube technique, that the SIFT does not directly offer any information on the structure of the reactants or of the product ions which are detected. In fact, the quadrupole mass spectrometers associated with flow-tube ion selection and detection are generally operated at resolutions much too low to discriminate between, for example, CO⁺ and N₂⁺. The use of the SIFT to determine the isomeric content of a reactant ion signal may therefore seem an odd and slightly quaint notion. The SIFT is not capable of delivering any structural information whatever: however, it can discriminate easily between two isomers of an ion if these isomers exhibit differing reactivity with some neutral species.

An ion signal I comprising only one species A⁺ with negligible vibrational and electronic excitation will, as discussed in section (1.4), exhibit a linear decay of the logarithm of the ion signal when plotted against the concentration of the reactant neutral [B] (see figure 1.5). An ion signal comprising both A⁺ and C⁺ (where C⁺ has the same mass-to-charge (m/z) ratio as A⁺, but differs in its reactivity towards B) will not give a linear decay on such a ln(I)/[B] graph. The curved decay resulting (see figure 1.6) in such an instance is the sum of the two decays (each of which would describe a linear decay on a semilogarithmic graph) for A⁺ and for C⁺ reacting with B,

\[
\begin{align*}
A^+ + B & \rightarrow \text{products} & (1.36) \\
C^+ + B & \rightarrow \text{products} & (1.37)
\end{align*}
\]

\[k_{1.36} \neq k_{1.37}\]
and if the ratio of $A^+$ to $C^+$ is known then $k_{1.36}$ and $k_{1.37}$ can be established. If the ratio of $A^+$ to $C^+$ in the initial ion signal is not known, then it becomes an exercise in curve-fitting to separate out the two linear components of the curve: this curve-fitting is usually achieved by applying an iterative computer program to the experimental data.\textsuperscript{162}

A curved decay on a graph does not automatically indicate the existence of two isomers, however. Curved decays can result if the reaction being studied does not occur to completion but sets up an equilibrium in the reaction region; if the detection mass-spectrometer is unable to completely resolve between m/z ($A^+$) and contaminant ions having mass numbers one unit higher or lower; or if the reactant neutral B is added in sufficient concentration to significantly alter the

---

**Figure 1.5**: Semilogarithmic graph of ion signal decay versus reactant neutral partial pressure, in the case where the reactant ion signal contains only one ion form. The example shown is for the reaction of Ar$^+$ (m/z 40) with O$_2$, for which a rate coefficient $k = 4.92 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ was determined from the data depicted here. This is also the type of graph expected in the case where two forms of the reactant ion (two isomers or two forms with different internal energies) are present, but react at the same rate with the neutral - for example, both isomers may react at the collision rate.
Figure 1.6: Semilogarithmic graph of ion signal decay versus reactant neutral partial pressure, in the case where the reactant ion signal comprises two forms of differing reactivity. The observed ion signal is the sum of two logarithmic decays and so does not display a linear relationship when graphed in this manner.

(a) The curved decay in this hypothetical example corresponds to reaction of two forms $A^+$ (which accounts for 76% of the total initial reactant ion signal) and $C^+$ (which accounts for the other 24%, and which reacts 6 times as slowly as $A^+$). The presence of such curvature may indicate isomerism, but can also arise when only one structure is present if a significant population of this form is vibrationally excited.

(b) Experimental decay curve observed for the reaction of $C_3H_3^+$ with $CH_2CHCN$. Two isomers of $C_3H_3^+$ react at distinctly different rates with $CH_2CHCN$: the curve fitted to the experimental data points describes the sum of two exponential terms, yielding $k = 3.97 \times 10^{-6}\ cm^3\molec\ s^{-1}$ for the more reactive $C_3H_3^+$ isomer (29% of the ion signal in this graph) and $k = 1.10 \times 10^{-10}\ cm^3\molec^{-1}s^{-1}$ for the less reactive isomer.
mass flow of the buffer gas. Each of these processes can give a curvature in results which appears suggestive of two ions of identical mass but differing reactivity. Curvature may also be exhibited if a secondary reaction or side reaction occurring in the tube generates a product ion of the same mass as the reactant ion \( A^+ \) being detected; or if the reaction under study has a termolecular mechanism (association reactions, for example):

\[
A^+ + B + M \rightarrow AB^+ + M \tag{1.38}
\]

and occurs more rapidly for \( M = B \) than for \( M = X \), where \( X \) is the buffer gas being used. The nature of the curvature displayed by the last two processes is not so easily mistaken for differing reactivity of isomers.

Even in circumstances where the observed curvature is directly attributable to differing reactivity of two equal-mass ions \( A^+ \) and \( C^+ \), it does not follow that \( A^+ \) and \( C^+ \) are necessarily isomers. They may be ions of totally different general formula: for example, the m/z (29) signal produced from electron impact on 2-methyl propan-2-ol comprises \( C_2H_5^+ \) and \( CHO^+ \). The ions \( A^+ \) and \( C^+ \) may differ only in their vibrational or electronic states: the ionisation process is sufficiently high-energy to permit the population of various excited states in many instances. Nevertheless, vibrational or electronic excitation of reactant ions is usually held to be unimportant for triatomic or larger species (which are, after all, the only species capable of exhibiting isomerism): triatomic species will generally have, at the energy of the excited vibrational state, a sufficiently high density of available vibrational / rotational states to make collisional relaxation by the buffer gas a facile process, and in a flow tube an ion will have several
thousand collisions with the buffer gas before entering the reaction region. Electronic excitation is more problematic, but the physical separation of the ion source from the flow tube means that, in a SIFT, sufficient time for electronic de-excitation has usually elapsed by the time the ion has reached the reaction region. Excitation should definitely be considered as a potential source of curvature in SIFT experiments, and every effort should be made to show whether any curvature exhibited is truly isomeric in origin and does not arise from some other process.

The low temperatures and pressures of interstellar clouds make them an ideal "breeding ground" for otherwise transient species: this is evident by the large number of radicals and molecular ions which have been detected in clouds (see table 1.2). It is logical, therefore, to expect that isomers which would (under terrestrial conditions) isomerise or tautomerise rapidly to more stable forms may exist as long-lived species within clouds. To date, the only vindication of this hypothesis is the widespread occurrence of both HCN and HNC in interstellar clouds. Other low-stability isomers such as H₂CC (vinylidene), HCOH (hydroxycarbene) and HCCNC (isocyanoacetylene) have been proposed as likely interstellar molecules but have not yet been reported. A constant problem with the detection of such exotic compounds is the lack of laboratory measurements of their spectra: for this reason, the search for such isomers requires accurate spectra calculated by ab initio techniques.

Predictions concerning neutral isomers can be made upon the evidence of their ionic precursors, and thus there is some application of ion-molecule reaction measurements in this field. Differences in the reactivity of a pair of isomeric
ions can dictate the prospects for formation of related isomeric molecules. For example, if two ions XYZ$^+$ and XZY$^+$ are likely to be formed within interstellar clouds, and if XYZ$^+$ reacts with H$_2$ while XZY$^+$ is unreactive with H$_2$ and other common cloud constituents

\[
\begin{align*}
XYZ^+ + H_2 & \rightarrow XYZ^+ + H^+ \quad (1.39) \\
XZY^+ + H_2 & \rightarrow \text{no reaction} \quad (1.40)
\end{align*}
\]

then subsequent neutralization of XYZH$^+$ may yield the neutral XYZ while neutralization of XZY$^+$ (which, under cloud conditions, may be expected to occur predominantly by dissociative recombination) will most probably result in the breakage of an X–Z or Z–Y bond. Since with increasing molecular complexity the possibilities for the existence of two or more distinct isomers are enhanced, and since the reactive chemistry of any species is never entirely predictable (this thesis includes examples of unexpected consequences of isomerism for the ions CHN$^+$ and C$_3$N$^+$), experimental measurements are necessary to characterise the differences in reactivity of different isomers.

**Section 1.6: Introduction to the present work.**

The following nine chapters detail the results of experiments performed in the period from February 1987 to December 1990. I have endeavoured to stress the implications, of the present studies, for models of interstellar cloud chemistry.
Chapter Two offers a discussion of the experimental procedures used.

Chapter Three deals with the determination, by examination of proton-transfer kinetics, of the proton affinities (PAs) of C$_2$N$_2$ and C$_4$H$_2$. The study on C$_4$H$_2$ was originally carried out, to a large part, by John Knight$^{166}$ as a part of his Ph.D. research: I have thus dealt here only with measurements which were checked, or first performed, as a part of my own research. Some reactions of C$_2$N$_2^+$ with various neutrals are also reported in this chapter.

Chapter Four deals with investigations of isomerism in the ions C$_2$N$^+$ and C$_3$N$^+$. Most of the kinetic studies on C$_2$N$^+$ reactivity were performed by John Knight$^{166}$ in consequence, I have concentrated here on the efforts which I made to interpret the observed isomeric ratios as a function of the techniques used to generate C$_2$N$^+$ in these experiments. John Knight also performed initial studies on C$_3$N$^+$ reactivity, which showed that two isomers of this ion exist under the conditions in the flow tube. In addition to a detailed examination of C$_3$N$^+$ isomerism, some reaction chemistry of the ion C$_4$N$_2^+$ is also reported.

Chapter Five deals with an investigation of isomerism in the ions CHN$^+$ and CH$_2$N$^+$. The existence of isomerism in these systems has been previously demonstrated by a variety of techniques, but the present work represents the first investigation into differences in isomer reactivity in these systems.

Chapter Six describes the reactivity of C$_3$H$_n$N$^+$ ions (n = 2 to 4), generated from acrylonitrile, with various neutrals. This work was undertaken to investigate
the chemistry of acrylonitrile within interstellar clouds. In addition, some reactions of ions with neutral CH₂CHCN were also performed.

Chapter Seven describes the reactivity of HₙC₃O⁺ (n = 0 to 3) with various neutrals, and the implications of this reactivity for interstellar chemistry. In addition, the reactivity of C₃O₂⁺ generated from carbon suboxide was also explored.

Chapter Eight explores the idea that kinetically-excited products of dissociative recombination reactions may be able to react with H₂ in cold interstellar clouds despite the fact that such reactions are inhibited by activation energy barriers.

Chapter Nine offers a comparison of the reactivities of the ion series C₄Hₙ⁺, C₃HₙN⁺ and C₃HₙO⁺ with the neutrals H₂, CO, HCN and C₂H₂.

Finally, I discuss further work which could be undertaken to investigate some of the aspects left incompletely resolved by the present work.
CHAPTER 2.

EXPERIMENTAL.

Section 2.1: Equipment.

The measurements reported herein were obtained using a Selected-Ion Flow Tube originally constructed in this department during 1982 - 1985. Several modifications were made during the present work, in view of the projected conversion of the original SIFT into an instrument with variable-temperature and drift-region facilities. As a consequence, different versions of the instrument were used for different sets of experiments, as outlined below.

The measurements outlined in Chapters 3 and 4 were obtained principally upon the earliest working version of our SIFT. This instrument has been described previously by Knight\textsuperscript{166} and by Knight et al\textsuperscript{167} and will not be discussed extensively here. This version of the SIFT is illustrated in figure 2.1. A central feature of this version was the colinearity of the ion source chamber and the flow tube: in consequence, photons which were generated in the ionising process were able to traverse the entire axis of the ion source chamber and flow tube, and enter the detection chamber. The particle multiplier (PM), employed as the ion detection device, does not differentiate between ions and photons, and so was deployed in an off-axis configuration to minimise photon noise in the ion signal. Ions were deflected towards the PM by the application of a high positive voltage (+0.6kV) to the 'deflection electrode' situated approximately opposite the PM.
consequence of this configuration was that the instrument was markedly mass-sensitive: ions having a higher mass were deflected less sharply (by the deflection electrode and by the high negative voltage (-2.6kV) applied to the PM) than were ions of comparatively low mass, and so heavier ions were detected less efficiently than ions having m/z <~ 50 amu.

The second working version of the SIFT, shown in figure 2.2, was used to obtain the measurements described in chapters 5, 6 and 7. Qualitative differences between versions are summarised in table 2.1.

Figure 2.1: Schematic diagram of Version 1 of the Canterbury SIFT (not to scale). The particle multiplier (PM) in this version of the SIFT was mounted off-axis to minimise photon noise from the ion source: ions were channeled to the PM by the application of a large positive voltage at the ion deflection electrode (IDE). The reactant gas inlets shown are of the ‘finger’ type: these were subsequently replaced by ring inlets.
Figure 2.2: Schematic diagram of the Canterbury SIFT, Version 2 (not to scale). This version of the SIFT has an off-axis ion source chamber, and substantially modified upstream ion optics, ion source and Venturi orifice components. The position of the additional SIFT chamber, to be constructed, is shown; other projected modifications are the addition of a drift region and the incorporation of a variable-temperature facility.

Table 2.1: A summary of differences between Version 1 and Version 2 of the Canterbury SIFT.

<table>
<thead>
<tr>
<th>Version 1</th>
<th>Version 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-pressure ion source, collinear with the flow tube axis.</td>
<td>High-pressure ion source, displaced off the flow tube axis.</td>
</tr>
<tr>
<td>Electrostatic lenses within ion source chamber configured as shown in reference 166.</td>
<td>Electrostatic lenses within ion source chamber designed using the SIMION program: configured as shown in figures 2.3, 2.4 and 2.6.</td>
</tr>
<tr>
<td>Finger-type reactant neutral inlets.</td>
<td>Ring-type reactant neutral inlets.</td>
</tr>
<tr>
<td>Particle multiplier (PM) displaced off flow tube axis; ion deflection electrode employed to divert ions towards PM.</td>
<td>PM collinear with flow tube axis; no deflection electrode necessary.</td>
</tr>
</tbody>
</table>
The SIMION electrostatic lens analysis program\textsuperscript{168,169} was used to redesign the lens assemblies associated with the upstream quadrupole mass spectrometer. The lens assemblies SIFT1 and SIFT2, shown in figures 2.3 and 2.4, are the results of this analysis. SIFT1 is the design for the lens assembly to train the ions ejected from the ion source into the quadrupole field; SIFT2 focusses the ion beam emerging from the QMS into the Venturi inlet at the entrance of the flow tube. All lenses used in these designs are planar ring lenses, except for L6 for which a cylindrical lens appeared more effective. The lens assemblies actually constructed differed from the configurations shown, since mechanical limitations prevented the incorporation of lens L10 into the SIFT2 assembly. SIFT1 was not fabricated as a single assembly: instead, lenses L1 and L2 were attached to the ion source assembly, while the remaining lenses were mounted on the quadrupole filter anterior endplate. Because of the lack of physical connection between L2 and L3, the spacing between these lenses was variable - in practice, it was found that better ion signals were obtained when this spacing was reduced below the distance specified by SIMION. In addition, the lens L5 was eventually removed from the assembly with no visible impairment to the resulting ion signal.

The trajectory of an ion within the lens assembly is dependent upon the contours of the electric field within the assembly, the ion's initial energy, initial position and initial direction. Trajectory calculations were performed using SIMION, with a 'family' of ions used to approximate the range of trajectories likely to be focussed favourably by the lens configuration. Figure 2.5 illustrates the passage of one such ion family through the lens assembly SIFT2. These calculations were used to determine approximately the optimum voltage settings for the
Figure 2.3: Redesigned ion optics, upstream of UQMS.

(a). Optics designed using SIMION program. The vertical scale of this diagram is twice the horizontal scale. Lens spacings are indicated by figures associated with arrows: lens apertures are indicated by isolated figures (All distances are in mm). (Rep. = repeller; eT = electron trap).

(b). The lens assembly comprising lenses 3, 4 & 5, attached upstream of the ion source quadrupole. The assembly is fastened to the ceramic rod support by bolts (not shown) attached to the quadrupole endplate. Electrical connections to the quadrupole rods and to the lenses are not shown.
Figure 2.4: Redesigned ion optics, downstream of UQMS.

(a) Optics designed using SIMION program. The vertical scale of this diagram is twice the horizontal scale. Lens spacings are indicated by figures associated with arrows; lens apertures are indicated by isolated figures (All distances in mm).

(b) The lens assembly comprising lenses 6, 7, 8 & 9, attached downstream of the ion source quadrupole. Lens 10 could not be incorporated into the assembly due to mechanical limitations. Electrical connections to the quadrupole rods, the exit disc and the lenses are not shown.
Figure 2.5: Voltage contours and ion trajectories for the SIFT2 lens assembly, calculated using the SIMION program, for a repeller voltage of 50V. The red curves in the upper diagram show the voltage contours (10 V spacings), while the blue curves in the lower diagram illustrate the calculated efficiency of ion transmission at this voltage setting.
SIFT1 and SIFT2 assemblies. These calculated optimum settings are shown in table 2.2, in conjunction with the experimental optimum determined for a repeller setting of +10 V. It can be seen that the calculated and experimental optima do not agree closely, but this is not surprising given the differences between the designed assemblies and those constructed - principally, as mentioned previously, the exclusion of lens L10 in the experimental assembly. Table 2.3 presents a more comprehensive display of optimum settings, for repeller voltages from +10 to +65 V, in the absence also of lens L5 (as mentioned above).

Table 2.2: Calculated optimum lens settings for repeller voltages of 10, 20 and 50 V. These settings were determined from trajectory calculations performed using the SIMION ion-optics design program. The experimental optimum found for a repeller setting of 10 V is shown also: differences between the calculated and observed optima may arise from differences in the constructed and designed ion optics assemblies.

<table>
<thead>
<tr>
<th>Repeller voltage</th>
<th>10 V&lt;sup&gt;a&lt;/sup&gt;</th>
<th>10 V&lt;sup&gt;b&lt;/sup&gt;</th>
<th>20 V&lt;sup&gt;a&lt;/sup&gt;</th>
<th>50 V&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron trap</td>
<td>5</td>
<td>7.5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>L1</td>
<td>-50</td>
<td>-72.2</td>
<td>-100</td>
<td>-200</td>
</tr>
<tr>
<td>L2</td>
<td>3</td>
<td>3.0</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>L3</td>
<td>6</td>
<td>1.2</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>L4</td>
<td>-30</td>
<td>-66.7</td>
<td>-90</td>
<td>-50</td>
</tr>
<tr>
<td>L5</td>
<td>2</td>
<td>-13.5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Quad case</td>
<td>-5</td>
<td>0.0</td>
<td>-5</td>
<td>-5</td>
</tr>
<tr>
<td>L6</td>
<td>10</td>
<td>11.4</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>L7</td>
<td>-15</td>
<td>-85.9</td>
<td>-12</td>
<td>-6</td>
</tr>
<tr>
<td>L8</td>
<td>5</td>
<td>0.7</td>
<td>18.8</td>
<td>55</td>
</tr>
<tr>
<td>L9</td>
<td>-40</td>
<td>-171.4</td>
<td>-50</td>
<td>-60</td>
</tr>
<tr>
<td>L10</td>
<td>4</td>
<td>-&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15</td>
<td>42</td>
</tr>
<tr>
<td>Exit lens</td>
<td>0</td>
<td>1.4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Notes
a. Calculated lens voltage settings for this repeller voltage.
b. Observed optimum lens settings at 10 V repeller setting.
c. This lens was not constructed due to mechanical limitations.
In practice, optimum voltages applied to the lenses are larger in magnitude than those determined using SIMION. The observed ion signal is much more sensitive to the voltages on the repulsive lenses (to which positive voltages are applied) than to the settings on the attractive (negative) lenses. For example,

Table 2.3: Variation in optimum lens settings and observed ion currents with repeller voltage. All readings were made at an electron energy setting of 21.4 V, using argon as the ion source gas. The background pressure in the ion source chamber was 2.7 x 10⁻⁶ Torr (in absence of argon); when Ar was added, a pressure of 4.5 x 10⁻⁵ Torr was noted; the total pressure in the ion source chamber was 1.2 x 10⁻⁴ Torr - this includes an effect from the backstreaming of He buffer gas through the Venturi orifice. The ion signals recorded were due to Ar⁺, selected at m/z 40.0 with the upstream QMS resolution set to 2.0 and the downstream QMS resolution at 8.0. In practice, the readings for the flow tube exit disc current and particle multiplier signal were obtained on a separate occasion, since the probe employed upstream resulted in a loss in ion transmission to these sites. The readings for the exit disc current and the PM signal have been adjusted to take into account minor differences in the ion source transmission characteristics on these two occasions; at a low repeller voltage especially, the focussing conditions can change due to oxidation of the lens surfaces.

<table>
<thead>
<tr>
<th>Repeller voltage</th>
<th>10 V</th>
<th>20 V</th>
<th>35 V</th>
<th>50 V</th>
<th>65 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron trap</td>
<td>5.2</td>
<td>10.2</td>
<td>15.0</td>
<td>30.0</td>
<td>45.0</td>
</tr>
<tr>
<td>L1</td>
<td>-80.0</td>
<td>-105.6</td>
<td>-100.6</td>
<td>-135.6</td>
<td>-180.7</td>
</tr>
<tr>
<td>L2</td>
<td>3.6</td>
<td>2.3</td>
<td>2.5</td>
<td>3.9</td>
<td>2.5</td>
</tr>
<tr>
<td>L3</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>L4</td>
<td>-129.6</td>
<td>-94.5</td>
<td>-139.3</td>
<td>-148.4</td>
<td>-204</td>
</tr>
<tr>
<td>L6</td>
<td>0.7</td>
<td>2.2</td>
<td>41.0</td>
<td>59.4</td>
<td>75.4</td>
</tr>
<tr>
<td>L7</td>
<td>-200</td>
<td>-198</td>
<td>-204</td>
<td>-199</td>
<td>-199</td>
</tr>
<tr>
<td>L8</td>
<td>0.4</td>
<td>1.6</td>
<td>11.7</td>
<td>14.9</td>
<td>21.3</td>
</tr>
<tr>
<td>L9</td>
<td>-116.7</td>
<td>-160.7</td>
<td>-132.3</td>
<td>-182.9</td>
<td>-200</td>
</tr>
<tr>
<td>Exit lens</td>
<td>0.4</td>
<td>0.7</td>
<td>0.6</td>
<td>7.9</td>
<td>11.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filament current</td>
<td>2.69 A</td>
</tr>
<tr>
<td>Emission current</td>
<td>237 nA</td>
</tr>
<tr>
<td>Exit lens current</td>
<td>2.1 nA</td>
</tr>
<tr>
<td>Probe current a</td>
<td>26 pA</td>
</tr>
<tr>
<td>Flow tube exit disc current</td>
<td>~ 0.1 pA</td>
</tr>
<tr>
<td>Particle multiplier signal</td>
<td>470 cps</td>
</tr>
</tbody>
</table>

Notes
a. Circular fine wire mesh probe, inserted 80.0 cm upstream of the flow-tube exit disc. A voltage bias of -2.74 V was applied to attract ions onto the probe. The same voltage was subsequently applied to the flow tube exit disc.
a small change (± 2 V) in the voltage on the attractive lens L8 may diminish the signal by a factor of 10, while a large change (± 50 V) on the repulsive lens L7 may have a negligible effect.

Trajectory calculations from SIMION show that the calculated optimum voltages do not result in substantial deceleration of the ions. The initial ion energy is largely determined by the voltage applied to the repeller. The large voltages commonly employed are likely to have an accelerating effect, so that the ions leaving the ion source chamber have high translational energy. Observations which verify this are the common occurrence of lower-mass ion signals due to breakup of the ion selected by the upstream QMS

\[
\begin{align*}
C_2H_5^+ & \rightarrow C_2H_3^+ + H_2 \quad (2.1) \\
C_2H_5OH_2^+ & \rightarrow H_3O^+ + C_2H_4 \quad (2.2a) \\
& \rightarrow C_2H_5^+ + H_2O \quad (2.2b)
\end{align*}
\]

\[\Delta H_{2.1} = +210 \text{ kJ mol}^{-1}\]
\[\Delta H_{2.2a} = +136 \text{ kJ mol}^{-1}\]
\[\Delta H_{2.2b} = +153 \text{ kJ mol}^{-1}\]

and the observation of proton transfer in the reaction

\[
ArH^+ + He \rightarrow HeH^+ + Ar \quad (2.3)
\]

\[\Delta H_{2.3} = +193 \text{ kJ mol}^{-1}.\]

These processes, which usually result in less than 10% depletion of the primary reactant ion signal, are all highly endothermic: they appear due to collision of
translationally (and internally) excited ions with the helium buffer gas, since they are impeded by a reduction in the magnitude of the voltages applied to the electrostatic lenses. Alternatively, the observed breakup could be occurring within the ion source chamber after passage through the QMS. In practice, this phenomenon is usually of minor concern since repeated collision with helium will thermalise all translationally hot ions before these ions can encounter neutral reactants: thus the translational excitation should not affect the observed chemistry beyond the possibility of misinterpreting products from breakup ions as minor products from the reaction of the ion of interest.

**Figure 2.6:** Schematic diagram of the ion source assembly (not to scale). This high-pressure ion source was used in the majority of reaction studies reported in this work, following replacement of the earlier ion source assembly. Pressures attained within the ion source during operation are thought to be of the order of 1 to 10 Torr; the chamber containing the ion source is maintained at approximately $10^{-4}$ Torr during normal operation. L1 and L2 are electrostatic lenses: electrical connections to these lenses are not shown.
The variation in observed ion signal intensity with tube pressure is recorded in table 2.4. These results show that, for the probe situated 80 cm upstream from the flow tube exit disc, the maximum signal intensity is observed at a buffer gas pressure of \( \pm 0.35 \) Torr. This is contrary to expectation: ion loss through diffusion is less at higher tube pressure, so the observed ion signal should increase steadily with pressure. It is likely that, at high tube pressures, laminar flow of the buffer gas has not been reached at this distance: a greater degree of turbulence in the buffer gas from the Venturi nozzle injection would account for the diminished signal with increasing pressure. The suspicion of turbulence at this distance led to a relocation of the upstream reactant neutral inlet (portal 1): this inlet was repositioned at a distance of 66 cm upstream from the flow tube exit disc, to isolate it from the region of suspected turbulence. In practice, all the

<table>
<thead>
<tr>
<th>Pressure ( a,b )</th>
<th>( Q_{He} a,c )</th>
<th>( I_{ex} a,d )</th>
<th>( I_{probe} a,e )</th>
<th>( I_{disc} a,f )</th>
<th>( I_{pm} a,g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.162 ± 0.002</td>
<td>45.6 ± 1%</td>
<td>12.2 ± 0.2</td>
<td>69 ± 2</td>
<td>&lt;0.1 ± 0.2</td>
<td>5 ± ( \sqrt{1} )</td>
</tr>
<tr>
<td>0.183</td>
<td>57.4</td>
<td>12.4</td>
<td>90</td>
<td>&lt;0.1</td>
<td>36</td>
</tr>
<tr>
<td>0.225</td>
<td>80.0</td>
<td>11.2</td>
<td>118</td>
<td>0.2</td>
<td>254</td>
</tr>
<tr>
<td>0.265</td>
<td>99.6</td>
<td>11.0</td>
<td>132</td>
<td>0.6</td>
<td>737</td>
</tr>
<tr>
<td>0.305</td>
<td>122.2</td>
<td>10.1</td>
<td>130</td>
<td>1.0</td>
<td>1274</td>
</tr>
<tr>
<td>0.347</td>
<td>142.3</td>
<td>9.9</td>
<td>153</td>
<td>1.6</td>
<td>2026</td>
</tr>
<tr>
<td>0.389</td>
<td>164.9</td>
<td>8.9</td>
<td>138</td>
<td>2.2</td>
<td>2704</td>
</tr>
<tr>
<td>0.430</td>
<td>186.7</td>
<td>8.7</td>
<td>125</td>
<td>3.0</td>
<td>3239</td>
</tr>
<tr>
<td>0.448</td>
<td>195.4</td>
<td>9.0</td>
<td>114</td>
<td>2.7</td>
<td>3412</td>
</tr>
</tbody>
</table>

Notes
a. Uncertainties for each measurement appear at the top of each column.
b. Tube pressure, in Torr, of He buffer gas.
c. Helium flow in \( \text{cm}^3 \text{s}^{-1} \) at STP.
d. Observed ion current, in nA, on the ion source chamber exit lens.
e. Observed current, in pA, on ion probe inserted 80.0 cm upstream of flow tube exit orifice.
f. Observed current, in pA, on flow tube molybdenum exit disc.
g. Observed ion signal, in counts per second, from the particle multiplier.
rate measurements reported in this work were obtained at a tube pressure of 0.30 Torr, and usually involved addition of the reactant neutral at portal 2 (further removed than portal 1 from the region of suspected turbulence), so the effects of this turbulence are expected to be negligible. The low ion signal recorded at this probe at high tube pressure could also arise through a change in the optimum settings required in the ion source lens assemblies, due to more efficient braking of the ions by helium backstreaming into the ion source chamber from the Venturi orifice. This possibility was excluded since refocussing of the ion source lenses at a higher pressure could not improve the ion signal recorded on the probe. Thus, helium backstreaming has little effect on the ion transmission through the ion source chamber under these conditions. This is corroborated by the similarity seen in settings required for transmission of Ar$^+$ (m/z 40), N$^+$ (m/z 14) and He$^+$ (m/z 4): under low pressure conditions, these ions should all be focussed similarly by the same lens settings. In practice, different optimum settings were determined for these ions, but the differences were slight - all of these ions were focussed well by the optimum settings determined for He$^+$, and refocussing for N$^+$ and for Ar$^+$ resulted in only a small (< 20%) improvement in the ion signal observed for these ions. The signal observed at the flow tube exit disc, and at the particle multiplier, is seen to increase steadily with pressure, as expected: diffusive loss should decrease as the pressure increases.

Another modification to the original version of the SIFT was the replacement of the finger-type reactant neutral inlets with ring-type inlets, since such inlets were found by Upschulte et al.$^{159}$ to have a lower end correction than radial, spiral or finger inlets. The new inlets were constructed as shown in figure 3 in reference
The end corrections for these inlets were determined using the reaction of Ar\(^+\) with O\(_2\)

\[
\text{Ar}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{Ar}
\]

\[k_{2.4} = 4.5 \times 10^{-11} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}\]  

as a calibration reaction. Experiments were performed for a range of tube pressures from 0.22 to 0.38 Torr. Over this pressure range the rate coefficients \(k_{2.4}\) determined for portal 2 \((z_2 = 42.9 \text{ cm})\) were independent of pressure and dictated an end correction of +1.8 cm, yielding an effective reaction distance \(z_2(\text{eff})\) of 44.7 cm. The results for portal 1 were substantially more erratic: rates observed using the true distance \(z_1 = 70.9 \text{ cm}\) were 20% too high, indicating a larger (and negative) end correction for this reaction distance. The observed behaviour for portal 1 most probably arises from turbulence in the region slightly upstream from this inlet: for this reason, portal 1 was not commonly used to determine rate coefficients, although it was routinely used to add various neutrals when it was desirable to effect an additional reaction in the tube prior to the reaction of interest.

No substantial changes were made to the neutral reactant glass handling line. The needle valve associated with portal 1 (in Version 1) was replaced, for greater flow sensitivity, by a variable leak valve of the same type as that used for portal 2. The variable leak valve associated with portal 2 was subsequently reconfigured in a manner illustrated in figure 2.7. This was done because of a phenomenon which was especially apparent when studying a fast reaction involving a 'sticky'
neutral reactant such as H₂O, NH₃ or HCN: for such reactions, a long time delay (often of up to two minutes) was apparent after reduction of the reactant neutral flow, before stabilisation of the reactant ion signal. This time delay could not be effectively reduced by changing the helium flush setting, and it was eventually decided that the delay arose because of the presence of a large 'dead volume' of gas which was not effectively swept out by the helium flush. Rearrangement of the tubing leading to and from the leak valve was performed as shown, and this rearrangement resulted in a reduction of the time delay to a much more acceptable interval of around five seconds.

Figure 2.7: The reconfiguration of the variable leak valve associated with portal 2. The diagram on the left illustrates the configuration used in Version 1 of the Canterbury SIFT: note that, following passage through the sapphire seat valve (in black), the reactant gas is admitted to a large dead volume before it encounters the helium flush. The arrangement shown on the right is that used in Version 2, so as to minimise the size of the dead volume after the sapphire seat valve.
Other features of the instrumentation and equipment of the Canterbury SIFT are as detailed previously\textsuperscript{166,167} and will not be described here.

**Section 2.2: Data acquisition and analysis.**

Data was gathered in a manner similar to that detailed by Knight\textsuperscript{166}. The concentration of neutral reagent molecules within the tube was determined by using a pressure transducer to monitor the change in pressure, as a function of time, in the glass manifold (of known volume) of the gas inlet line. The changing pressure was recorded by an Apple IIe computer using an A/D converter. A program, 'Pressmonitor' (see appendix 1), was used to record the pressure. The reactant and product ion signals were recorded manually.

Following data collection, reaction rates were determined using a suite of programs connected by the menu program 'Options'. A program 'Meanflows' was used to convert the raw flow file from 'Pressmonitor' into a data file containing the averaged flow measurements in Torr s\textsuperscript{-1}, and the signals (in counts per second) recorded at each flow for each of the ions of interest. Analysis of the data file by the program 'Rascal' yielded a calculated reaction rate and a graph illustrating the fit of the calculated rate to the observed experimental data. The rate coefficient was corrected using the expression

\[ k_{\text{corr}} = \frac{k}{C_2(1 - \varepsilon) \gamma} \]

\[ (2.i), \]
in which \( C_2 \) is the radial diffusive correction, \( (1 - \varepsilon) \) is the correction for axial diffusive loss and \( \gamma \) is the correction for non-uniform velocity. These factors may be expressed:\(^{159}\)

\[
C_2 = 1 - \frac{2D^2 j_0^2}{r^2 v_{ion}^2} + \frac{6D^4 j_0^4}{r^4 v_{ion}^4} + \ldots \tag{2.ii}
\]

where \( r \) is the tube radius in cm, \( v_{ion} \) is the ion's velocity in cm s\(^{-1}\), \( j_0 = 2.405 \)\(^{159}\) and \( D \) is the diffusion coefficient

\[
D = 0.02354 K_0 (\frac{760}{P}) (\frac{T}{273.16}) \tag{2.iii}
\]

for pressure, \( P \), in Torr and temperature, \( T \), in degrees K; \( D \) is calculated using

\[
K_0 = 31.11 \sqrt{\mu} \tag{2.iv}
\]

(where \( \mu \) is the reduced mass, in g mol\(^{-1}\), of the ion in the relevant buffer gas) to determine the reduced mobility \( K_0 \).

\[
\varepsilon = \left( \frac{\delta}{\omega r^2} + \frac{\gamma k[B]}{\omega D} \right) \frac{D^2}{v_{gas} v_{ion}} \tag{2.v}
\]

for which \( k \) is the uncorrected rate coefficient for the reaction concerned in cm\(^3\) molec\(^{-1}\) s\(^{-1}\), \([B]\) is the neutral concentration in molec cm\(^{-3}\) and \( \omega \) has the value
\[ \omega = \frac{2}{1 + \frac{552 \lambda}{Pr}} \]  

where \( \lambda \) is the mean free path length (in cm) of the ion in the buffer gas at a background pressure of 1 Torr:

\[ \lambda = 8.59 \eta \sqrt{\frac{T}{m_{He}}} \]  

for helium buffer gas, where \( \eta \) is the viscosity of the buffer gas. The eigenvalues \( \gamma \) and \( \delta \) can be solved as detailed elsewhere; \(^{171,172}\) using the expressions detailed above, for the reaction of \( \text{Ar}^+ + \text{O}_2 \), the correction factors have the values

\[ C_2 = 0.99038 \]
\[ (1 - \epsilon) = 0.9940 \]

and \[ \frac{\omega}{\gamma} = 1.5469. \]

A typical printout from the 'Rascal' program is given in figure 2.8. The 'Rascal' program additionally used, for each experimental run, a format file which listed the values of variables appropriate to the experiment: the date, reactant neutral inlet used, temperature, buffer gas pressure etc. This format file could be modified as required within the 'Rascal' program or created using a file editing program 'Studyfiles', which could also be used to edit the data files to be used by 'Rascal'. A further program, 'Prod rat', was used to produce a graph, from the data file, of the experimental product distribution. For reactions for which isomerism in the reactant ion signal was evident as discussed in section 1.5,
Figure 2.8: A sample printout from the "Rascal" computer program.

---

RATE COEFFICIENT:

---

$m/z = 12$

Run 41 Data file C4H02.13/6/99.R1

T = 297.3 K $P = .298$ Torr of HE ($Tylan$ flow = 256)

Porta 2 Neutral vol = 143.6 cm$^3$

Corrected reaction distance = 42.9 cm

Neutral flow : Ion signal
(torr/s)  

| 0  | 2973 |
| 0.045499999 | 359  |
| 0.0471 | 712  |
| 0.06699 | 1132 |
| 0.0864 | 1252 |
| 0.876E-03 | 2554 |
| 0  | 3499 |

$k$ 

$k (corr) = (1.002 +/- .0296)E-9 cm^3$ molec$^{-1}$ s$^{-1}$

Intercept = $8.064 +/- .0323$ In. counts

$= 3178 +/- 101$ ion counts
multiple exponential decays could be fitted to experimental data using the program 'Mule' which was adapted from the program 'Expon'\textsuperscript{173} to also show a graph illustrating the fit of the calculated decays to the experimental results. Collision rate coefficients, which were calculated according to the ADO method of Su and Chesnavich,\textsuperscript{174} were determined using the program 'Collirat'.

These programs are all listed in Appendix 1.

Section 2.3: Reagents and physical conditions.

Reagents used are as described previously,\textsuperscript{166} with the following exceptions:

C$_4$H$_2$O$_2$Cl$_2$, fumaroyl dichloride (95%), was obtained from Aldrich.

(CH$_2$CHCO$_2$)O, acrylic anhydride (98\% by $^1$H nmr), was provided by Ryan Bettens at Monash University.

HCN, hydrocyanic acid, was produced in vacuo by the addition of KCN (Fluka, 98-99\% cyanide) to 100\% orthophosphoric acid.\textsuperscript{175}

H$_2$S, hydrogen sulphide, was synthesised by the action of orthophosphoric acid upon sodium sulphide (Na$_2$S.xH$_2$O, BDH, 30\% Na$_2$S), according to the method of Melville and Gowenlock.\textsuperscript{175}
C₃O₂, carbon suboxide, was produced by the action of phosphorus pentoxide (Riedel - de Haën, 99+) upon malonic acid (Riedel - de Haën, 99+) upon heating, according to the methods of Miller & Fately and Kim & Roebber. Since C₃O₂ was used only as an ion source gas and not as a neutral reactant, it was not rigorously purified.

CH₃C₃N, methyl cyanoacetylene, was synthesised by the successive action of aqueous ammonia and phosphorus pentoxide upon methyl 2-butynoate (CH₃C≡CCO₂CH₃, Aldrich, 98%), according to the method of Durrant et al.

C₄N₂, dicyanoacetylene, was synthesised by the action of ammonium hydroxide upon dimethyl acetylenedicarboxylate (CH₃O₂CC≡CCO₂CH₃, Aldrich, 99%), followed by heating in calcined sand, according to the method of Khanna et al.

C₂H₂, acetylene, was obtained as instrument grade from NZIG and was further purified by vacuum distillation.

CO₂, carbon dioxide, was obtained from the sublimation of commercially-available dry ice and was further purified by vacuum distillation.

Kr, krypton (>99.9%) was obtained from Airco.

CH₃Cl, chloromethane (Industrial grade), was obtained from Virginia Chemicals.
CH$_2$CHCN, acrylonitrile (99+%), was obtained from Ajax Chemicals. To prevent polymerisation in the absence of air, a trace of the radical scavenger p-methoxy phenol was added.

CCl$_4$, carbon tetrachloride, was obtained from Riedel - de Haën (99+) and from BDH (99.5%).

CF$_4$, carbon tetrafluoride, was obtained from Matheson Gas Products.

SF$_6$, sulphur hexafluoride (Instrument grade), was obtained from Air Products.

CF$_3$Br, bromotrifluoromethane, was obtained from Matheson Gas Products.

CHCl$_3$, chloroform, was obtained as solvent grade and was additionally purified by vacuum distillation.

C$_5$H$_5$NO$_2$, 1-amino-2-methoxy-cyclobutenedione, was prepared by the successive action of aqueous silver nitrate, methyl iodide and aqueous ammonia upon 3,4-dihydroxy-3-cylobutene-1,2-dione (Aldrich, 98%), according to the method of Cohen and Cohen$^{180}$ and was purified by recrystallisation.

NH$_2$CN, cyanamide (99+%), was obtained from Aldrich.

C$_2$Cl$_4$, tetrachloroethylene (AR grade), was obtained from BDH.
C₆H₁₀, cyclohexene (99+%, stabilised with 0.05% hydroquinone), was obtained from Merck.

C₇H₈, toluene, was AR grade.

NO, nitric oxide (CP), was obtained from Matheson and was additionally purified by vacuum distillation.

C₆H₅NH₂, aniline (99%) was obtained from Aldrich.

CH₃CCH, propyne, was prepared according to the method of Brandsma.¹⁸¹

In all instances unless otherwise mentioned, measurements were made using helium (Technical or Instrument grade, stated purity 99.9%, obtained from NZIG) as the buffer gas at a pressure (within the flow tube) of 0.300 ± 0.005 Torr, at a room temperature of 300 ± 5 K. Neutral reactants were typically added at portal 2; ion source gases were added to the ion source at a pressure estimated to exceed 1 Torr in some circumstances. The pressures within the ion source chamber and the ion detection chamber (which were differentially pumped) were monitored by ion gauges and typically did not exceed 10⁻⁴ Torr and 10⁻⁵ Torr respectively. Exceptions to these conditions are identified within the text where appropriate. Other conditions are as described previously.¹⁶⁶ Except where otherwise stated, rate coefficients are quoted from the compilations of Anicich and Huntress¹⁸² and Viggiano et al.;¹⁸³ thermodynamic quantities (ΔH and ΔG, using the "ion convention"¹⁸⁴) at 298K have been obtained from the compilations of Lias and co-workers.¹⁸⁴,¹⁸⁵ Dipole moments have been obtained
from the C.R.C. Handbook of Chemistry and Physics;\textsuperscript{186} polarisabilities have been obtained from Atkins\textsuperscript{187} or Hirschfelder et al,\textsuperscript{188} or calculated using the method given in the latter text.\textsuperscript{188} Rate coefficients determined in this work are considered to have an uncertainty of ± 25%; product distributions are estimated to have an uncertainty of ± 15\%.\textsuperscript{166}
CHAPTER 3.

PROTON AFFINITY OF C₄H₂ AND C₂N₂.

Section 3.1: Determination of proton affinity by equilibrium measurements.

The proton affinity (PA) of a species X is a measure of the stability of the protonated species XH⁺, and is defined as

$$\text{PA} (X) = \Delta H^\circ_f (X) + \Delta H^\circ_f (H^+) - \Delta H^\circ_f (XH^+) \quad \text{(3.1)}.$$  

It can be seen that PA(X) is the enthalpy change in the reaction

$$XH^+ \rightarrow X + H^+ \quad \text{(3.1)}.$$  

Direct experimental study of such a reaction, or its reverse, is not usually feasible: thus for most species it is not possible to determine the absolute proton affinity. The technique normally adopted is to use some indirect method of study (involving comparison of X with a substance of well-characterised PA), yielding a proton affinity value for X relative to the PA of some standard substance. These indirect methods concern the proton-transfer equilibrium.
where $\Delta H^\circ = PA(X) - PA(B)$ [3.ii].

If both the forward and reverse reactions involved can be separately studied, the enthalpy change can be determined from the equilibrium constant:

$$K = e^{\Delta G^\circ / RT}$$ [3.iii]

and $K = k_f / k_b$ [3.iv].

$$\Delta G^\circ = -RT \ln (k_f / k_b)$$ [3.v];

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$ [3.vi]

$$\Delta H^\circ = -RT \ln (k_f / k_b) + T\Delta S^\circ$$ [3.vii].

Some researchers contend that definition of the proton-transfer equilibrium coefficient as $k_f / k_b$ does not give a reliable indication of the free-energy change from left to right. These workers\textsuperscript{189,190} advocate applying a correction factor for equilibria in which the forward and reverse reactions have markedly different collision rates:

$$K = \frac{k_f / k_{(c)f}}{k_b / k_{(c)b}}$$ [3.viii],
where $k_{(c)f}$ and $k_{(c)b}$ are the calculated collision rate coefficients. The equilibrium constant is, in this model, defined as the ratio of the efficiencies of the forward and reverse reactions; this ratio will often be markedly different from $k_f / k_b$, if $X$ is substantially more or less polar or polarisable than $B$.

This modification to $K$ yields

$$
\Delta H^\circ = -RT \ln \left[ \frac{k_f / k_{(c)f}}{k_b / k_{(c)b}} \right] + T\Delta S^\circ
$$

where $\Delta H^\circ = PA(X) - PA(B)$. In this chapter, this model incorporating allowances for variations in collision rate will not be used.

To determine $\Delta H^\circ$, and hence the change in proton affinity, the change in entropy must be known. The usual method employed, in the absence of measurements at different temperatures, is to estimate $\Delta S^\circ$ on the basis of changing rotational symmetry\(^{185}\) from left to right of the equilibrium:

$$
\Delta S^\circ = R \ln \left[ \frac{\sigma_B \sigma_{XH^+}}{\sigma_X \sigma_{BH^+}} \right]
$$

where $\sigma_X$ is the rotational symmetry number of $X$. A problem inherent in this calculation is that it assumes a knowledge of the configuration of the protonated species $XH^+$ and $BH^+$: if the shapes of these ions are not known, but estimated, uncertainty is introduced into this expression for $\Delta S^\circ$. There are other potential sources of inaccuracy in this method of calculation: however, it is a simple
means of estimating the entropy change and so is commonly used in deriving PA values.

In some circumstances, it is not possible to examine equilibrium (3.2) sufficiently closely to obtain an equilibrium constant: if this is the case, then the experimental technique of 'bracketing' may be employed instead. Bracketing involves studying the reaction of a protonated species \( \text{XH}^+ \) with a series of bases \( \text{B}_1 \rightarrow \text{n} \) which have well-established PA values. The extent

\[
\text{XH}^+ + \text{B}_i \rightarrow \text{B}_i\text{H}^+ + \text{X}
\]  

(3.3)

of reaction (3.3) for differing \( \text{B}_i \) allows interpolation of PA(X) at some position within the sequence of PA(\( \text{B}_1 \rightarrow \text{n} \)) values. The disadvantage of the bracketing technique is that it is intrinsically more uncertain than determination of proton affinities from the proton-transfer equilibrium constant: an exothermic proton-transfer reaction may not be observable if other reaction channels are more energetically favourable, and an endothermic proton-transfer process may still occur as a slow reaction. PA values found by bracketing are especially uncertain for compounds which have uncommonly high or uncommonly low PA, since there are relatively few compounds in such ranges to which cross-reference can be made. In this chapter, equilibrium measurements are described which allow the determination of PA(\( \text{C}_2\text{N}_2 \)) and PA(\( \text{C}_4\text{H}_2 \)), these compounds having PA values towards the lower end of the scale.
Section 3.2: The proton affinity of C₂N₂.

Dicyanogen, N≡C–C≡N, is a likely constituent of interstellar clouds, since molecules containing CN functional groups comprise a large minority of the interstellar molecules detected to date. However, NCCN itself will not be easily detectable since it lacks a permanent dipole moment and will not, thus, be visible in the radio window. A less stable isomer, CNCN (isocyanogen) has better prospects for detection since its microwave spectrum has recently been calculated\textsuperscript{191} and since it also possesses a substantial dipole moment (μ = -0.705 debye).\textsuperscript{191,192} Identification of this isomer within clouds would be a very good indication of the probable presence of the more stable NCCN isomer also.

While C₂N₂ has not been detected in the interstellar environment, it has been considered as a precursor to the CN⁻ radical within cometary comae:\textsuperscript{193} it has also been identified within the stratosphere of Titan\textsuperscript{194} at a level of 0.01 → 0.1 ppm. In Titan’s atmosphere, C₂N₂ is thought to arise via the reaction

\[
\text{CN}^- + \text{HCN} \rightarrow \text{C}_2\text{N}_2 + \text{H}^- \quad (3.4)
\]

\[\Delta H_{3.4} = -45 \text{ kJ mol}^{-1}\]

\[k_{3.4} = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} @ 300 \text{ K}.\textsuperscript{195}\]

This reaction has a calculated activation barrier\textsuperscript{196} of \(E_a \sim 17 \text{ kJ mol}^{-1}\) and so will be prohibitively slow in cold interstellar clouds: for this reason, any C₂N₂ formed in the interstellar environment would most probably occur through shock processes or via (as yet unidentified) ion-molecule reactions. The most logical precursor to C₂N₂ in an ion-molecule mechanism is its protonated form,
NCCNH$^+$: this ion has much better prospects for interstellar detection since it possesses a very large dipole moment, $\mu = -6.448 \pm 0.003$ debye.\textsuperscript{191} To accurately assess ion-molecule mechanisms for $\text{C}_2\text{N}_2$ formation within clouds, a knowledge of the relevant thermochemical factors is necessary. One of these factors is the proton affinity, $\text{PA}(\text{C}_2\text{N}_2)$.

The proton affinity of $\text{C}_2\text{N}_2$ was determined by studying the proton-transfer equilibria involving $\text{C}_2\text{N}_2$, $\text{CH}_3\text{Cl}$, and $\text{C}_2\text{H}_4$:

$$\text{C}_2\text{N}_2\text{H}^+ + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5^+ + \text{C}_2\text{N}_2 \quad (3.5)$$

$$\text{C}_2\text{N}_2\text{H}^+ + \text{CH}_3\text{Cl} \rightleftharpoons \text{CH}_3\text{ClH}^+ + \text{C}_2\text{N}_2 \quad (3.6)$$

$$\text{C}_2\text{H}_5^+ + \text{CH}_3\text{Cl} \rightleftharpoons \text{CH}_3\text{ClH}^+ + \text{C}_2\text{H}_4 \quad (3.7)$$

A compilation of thermochemical values relevant to these proton-transfer equilibria, including results from the present work, is shown in Table 3.1.

<p>| Table 3.1: Thermochemical values pertinent to determination of $\text{PA}(\text{C}_2\text{N}_2)$. |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value $^a$</th>
<th>Method of determination</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\circ(\text{C}_2\text{H}_4)$</td>
<td>52.2 ± 1 kJ mol$^{-1}$</td>
<td>-</td>
<td>184</td>
</tr>
<tr>
<td>$\Delta H^\circ(\text{C}_2\text{H}_5^+)$</td>
<td>902 ± 1 kJ mol$^{-1}$</td>
<td>Appearance potential</td>
<td>197,198</td>
</tr>
<tr>
<td>$\text{PA}(\text{C}_2\text{H}_4)$</td>
<td>680 ± 2 kJ mol$^{-1}$</td>
<td>$\text{PA}$ standard value</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>682 ± 7 kJ mol$^{-1}$</td>
<td>SIFT bracketing</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>680 ± 2 kJ mol$^{-1}$</td>
<td>ICR bracketing</td>
<td>200</td>
</tr>
<tr>
<td>$\text{PA}(\text{CH}_3\text{Cl})$</td>
<td>~ 682 kJ mol$^{-1}$</td>
<td>ICR bracketing</td>
<td>184,201,202</td>
</tr>
<tr>
<td></td>
<td>673 ± 4 kJ mol$^{-1}$</td>
<td>SIFT studies</td>
<td>203$^b$</td>
</tr>
<tr>
<td>$\text{PA}(\text{C}_2\text{N}_2)$</td>
<td>674 ± 8 kJ mol$^{-1}$</td>
<td>ICR bracketing</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>681 kJ mol$^{-1}$</td>
<td>MP3/6-31+G** calculation</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>678 ± 8 kJ mol$^{-1}$</td>
<td>SIFT bracketing</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>657 kJ mol$^{-1}$</td>
<td>CEPA-1/SCF calculation</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>674 ± 4 kJ mol$^{-1}$</td>
<td>SIFT studies</td>
<td>203$^b$</td>
</tr>
</tbody>
</table>

Notes

$a.$ in kJ mol$^{-1}$.

$b.$ This work.
Reactant ions were generated by the following techniques:

$\text{C}_2\text{N}_2\text{H}^+$ was produced in the ion source (P $\sim 8 \times 10^{-5}$ Torr) from a 1:40 mixture of $\text{C}_2\text{N}_2$ in $\text{H}_2$:

\[ \text{H}_2^+ + \text{C}_2\text{N}_2 \rightarrow \text{C}_2\text{N}_2\text{H}^+ + \text{H}^- \] (3.8)  
\[ \text{H}_3^+ + \text{C}_2\text{N}_2 \rightarrow \text{C}_2\text{N}_2\text{H}^+ + \text{H}_2 \] (3.9)

and

\[ \text{C}_2\text{N}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{N}_2\text{H}^+ + \text{H}^- \] (3.10)  
\[ \Delta H_{3.8} = -412 \text{ kJ mol}^{-1} \]  
\[ k_{3.9} = 2.2 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]  
\[ k_{3.10} = 9.6 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

Attempts were made to produce $\text{C}_2\text{H}_5^+$ in the ion source, using

\[ \text{H}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}_2 + \text{H}_2 \] [0.7] (3.11a)  
\[ \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \] [0.3] (3.11b)  
\[ \text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \] (3.12)  
\[ k_{3.11} = 2.3 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]  
\[ k_{3.12} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

These techniques were unsatisfactory: upon injection of the m/z 29 ion signal into the flow tube, breakup of the primary ions occurred giving

\[ (\text{C}_2\text{H}_5^+)^* \rightarrow \text{C}_2\text{H}_3^+ + \text{H}_2 \] (3.13)  
\[ \Delta H_{3.13} = +210 \text{ kJ mol}^{-1} \].
The endothermicity of this reaction indicates that under the injection conditions (i.e. the voltage settings on the ion source components and the electrostatic lenses), a significant proportion of the ions being injected have an excitation energy of this magnitude. This excitation is most probably in the form of translational energy as discussed in chapter 2. It was not possible to reduce the injection energy sufficiently to avoid breakup of the primary ions while maintaining an acceptable signal intensity.

To circumvent this problem, chemical ionisation was used to form \( \text{C}_2\text{H}_5^+ \) within the flow tube, via reaction (3.12): \( \text{CH}_3^+ \) (from methane) was injected from the ion source, and \( \text{CH}_4 \) was added at the tube's first inlet port. The \( \text{C}_2\text{H}_5^+ \) signal produced, using gentler conditions and at higher pressure than in the ion source, did not display any tendency to undergo breakup.

\( \text{CH}_3\text{ClH}^+ \) was also generated within the flow tube, since efforts to produce it in the ion source (using a 1:20 mixture of \( \text{CH}_3\text{Cl} \) in \( \text{H}_2 \)) led to breakup analogous to that observed for \( \text{C}_2\text{H}_5^+ \):

\[
(\text{CH}_3\text{ClH}^+) \rightarrow \text{CH}_2\text{Cl}^+ + \text{H}_2
\]

\( \Delta H_{3.14} = +192 \text{ kJmol}^{-1} \).

A 1:10 mixture of \( \text{CO}:\text{H}_2 \) was used to produce a mixture of the ions \( \text{HCO}^+ / \text{COH}^+ \) in the ion source: injection of this isomeric mixture into the flow tube gave \( \text{CH}_3\text{ClH}^+ \) by proton transfer to \( \text{CH}_3\text{Cl} \) (which was added at the tube's first inlet port):
HCO$^+$ + CH$_3$Cl → CH$_3$CHI$^+$ + CO  \hspace{1cm} (3.15)
COH$^+$ + CH$_3$Cl → CH$_3$CHI$^+$ + CO  \hspace{1cm} (3.16)

$\Delta H_{3.15} = -87$ kJ mol$^{-1}$
$\Delta H_{3.16} = -225$ kJ mol$^{-1}$.\textsuperscript{164,206}

The results obtained for the proton-transfer equilibria are shown in table 3.2; the PA values calculated from these measurements are given in table 3.3. The measurements, and the determination of the PA values from the measurements, are discussed below.

Table 3.2: Proton transfer reactions studied to determine PA(C$_2$N$_2$).

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products (^a)</th>
<th>$k_{obs}$(^b)</th>
<th>$k_c$(^c)</th>
</tr>
</thead>
</table>
| C$_2$N$_2$H$^+$ + C$_2$H$_4$ | C$_2$H$_5^+$ + C$_2$N$_2$  
C$_2$H$_5^+$·C$_2$N$_2$ | [0.92] | 0.90 | 1.11 |
| C$_2$H$_5^+$ + C$_2$N$_2$ | C$_2$N$_2$H$^+$ + C$_2$H$_4$  
C$_2$H$_5^+$·C$_2$N$_2$ | [0.40] | 0.21 | 1.12 |
| C$_2$N$_2$H$^+$ + CH$_3$Cl | CH$_3$CHI$^+$ + C$_2$N$_2$ | [1.0] | 0.16 | 2.23 |
| $^{37}$CH$_3$CHI$^+$ + C$_2$N$_2$ | C$_2$N$_2$H$^+$ + CH$_3$Cl | [1.0] | $\geq 0.20$  
0.25\(^d\) | 0.96 |
| C$_2$H$_5^+$ + CH$_3$Cl | CH$_3$CHI$^+$ + C$_2$H$_4$  
C$_2$H$_5^+$·CH$_3$Cl | [0.80] | 0.079 | 2.05 |
| $^{37}$CH$_3$CHI$^+$ + C$_2$H$_4$ | C$_2$H$_5^+$ + CH$_3$Cl | [1.0] | 0.83 | 1.12 |

Notes
a. Product channels reported in brackets, where more than one product was detected.
b. Observed rate coefficient, in units of $10^9$ cm$^3$ molec$^{-1}$ s$^{-1}$.
c. Calculated ADO collision rate coefficient, using the theory of Su and Chesnavich.\textsuperscript{172}
d. Determined by ICR measurement.\textsuperscript{207}
3.2.1. $\text{C}_2\text{N}_2\text{H}^+ + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5^+ + \text{C}_2\text{N}_2$

$\text{C}_2\text{N}_2\text{H}^+ + \text{C}_2\text{H}_4$ : Injection of $\text{C}_2\text{N}_2\text{H}^+$ into the flow tube at high injection energy gave signals at m/z 27 and m/z 53. The signal at m/z 27, which had an intensity of 30% of that of the parent ion (m/z 53) was ascribed to breakup:

\[
\begin{align*}
(C_2N_2H^+)^* & \rightarrow HCN^+ + CN^- \quad (3.17a) \\
& \rightarrow CNH^+ + CN^- \quad (3.17b)
\end{align*}
\]

$\Delta H_{3.17a} = +717 \text{ kJ mol}^{-1}$

$\Delta H_{3.17b} = +643 \text{ kJ mol}^{-1}$.

---

Table 3.3: $\Delta G^\circ$, $\Delta H^\circ$, and PA values calculated from the proton transfer equilibria studied to determine PA(C$_2$N$_2$).

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>$k_f$</th>
<th>$k_r$</th>
<th>$\Delta G^\circ$</th>
<th>$T\Delta S^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{N}_2\text{H}^+ + \text{C}_2\text{H}_4$ $\leftrightarrow \text{C}_2\text{H}_5^+ + \text{C}_2\text{N}_2$</td>
<td>0.83</td>
<td>0.084</td>
<td>-5.7</td>
<td>0</td>
<td>-5.7</td>
<td>674.3 ± 2$^e$</td>
</tr>
<tr>
<td>$\text{C}_2\text{N}_2\text{H}^+ + \text{CH}_3\text{Cl}$ $\leftrightarrow \text{CH}_3\text{C}^H^+ + \text{C}_2\text{N}_2$</td>
<td>0.16</td>
<td>0.25</td>
<td>1.1</td>
<td>1.0</td>
<td>2.1</td>
<td>674.6 ± 4$^e$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5^+ + \text{CH}_3\text{Cl}$ $\leftrightarrow \text{CH}_3\text{C}^H^+ + \text{C}_2\text{H}_4$</td>
<td>0.063</td>
<td>0.83</td>
<td>6.5</td>
<td>1.0</td>
<td>7.5</td>
<td>672.5 ± 2$^f$</td>
</tr>
</tbody>
</table>

Notes:

- $k_f$ is the observed rate coefficient for proton transfer in the forward direction, $k_r$ is the proton transfer rate coefficient in the reverse direction.
- In units of kJ mol$^{-1}$.
- The entropy corrections are calculated on the basis of the rotational symmetry numbers detailed in Table 3.4.
- Proton affinity of neutral indicated, in kJ mol$^{-1}$, referenced to PA (C$_2$H$_4$) = 680 kJ mol$^{-1}$.
- An additional uncertainty in PA (C$_2$H$_4$), of ± 2 kJ mol$^{-1}$, is not included in the figures above. PAs quoted for the second equilibrium above are calculated with reference to the appropriate PAs derived from the first and third equilibria measurements: this illustrates the internal consistency of the results.
- PA(C$_2$N$_2$).
- PA(CH$_3$Cl).
Addition of C₂H₄ indicated the following as product ions:

m/z  28, 29, 41, 54, 56, 57, 69, 81.

Reduction of the injection energy allowed the breakup ion, m/z 27, to be eliminated: products observed in this instance, due solely to reactions of C₂N₂H⁺ and associated secondary reactions, were m/z 29, 57, 69, 81. It was possible to assign the signals at m/z 57 and 69 as products of secondary reactions, since the ratio of these ion signals to the total product ion signals converged towards zero at low C₂H₄ flows. Thus the reaction of C₂N₂H⁺ with C₂H₄ involves proton transfer and adduct formation:

\[
\text{C}_2\text{N}_2\text{H}^+ + \text{C}_2\text{H}_4 \rightarrow \quad \text{C}_2\text{H}_5^+ + \text{C}_2\text{N}_2 \quad [0.92] \\
\quad \rightarrow \quad \text{C}_2\text{N}_2.\text{H}^+.\text{C}_2\text{H}_4 \quad [0.08] \\
k_{3.18} = 9.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.
\]

Further reactions, of C₂H₅⁺ with C₂H₄, account for the products at m/z 57 and 69:

\[
\begin{align*}
\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_4 + \text{He} & \rightarrow \quad \text{C}_4\text{H}_9^+ + \text{He} \quad (3.19) \\
\text{C}_4\text{H}_9^+ + \text{C}_2\text{H}_4 & \rightarrow \quad \text{C}_5\text{H}_9^+ + \text{CH}_4 \quad (3.20) \\
\Delta H_{3.19} & = -188 \text{ kJ mol}^{-1} \\
\Delta H_{3.20} & = -96 \text{ kJ mol}^{-1}.
\end{align*}
\]

The enthalpies quoted above apply for formation and reaction of sec-C₄H₉⁺, the most probable ion structure for association of C₂H₅⁺ with C₂H₄ in the absence of
Formation of t-C$_4$H$_9^+$ is more exothermic (for reaction (3.19)) and gives $\Delta H_{3.20} = -24$ kJ mol$^{-1}$.

Reactions occurring from the breakup ion HCN$^+$/HNC$^+$ with C$_2$H$_4$ were responsible for product ions at m/z 28, 41, 54 and 56. The structure of the ion m/z 28 is uncertain:

$$
\text{HCN}^+ + \text{C}_2\text{H}_4 \rightarrow \text{HCNH}^+ + \text{C}_2\text{H}_3^+ \quad (3.21a)
$$

$$
\rightarrow \text{C}_2\text{H}_4^+ + \text{HCN} \quad (3.21b)
$$

$\Delta H_{3.21a} = -287$ kJ mol$^{-1}$

$\Delta H_{3.21b} = -298$ kJ mol$^{-1}$

$$
\text{HNC}^+ + \text{C}_2\text{H}_4 \rightarrow \text{HCNH}^+ + \text{C}_2\text{H}_3^+ \quad (3.22a)
$$

$$
\rightarrow \text{C}_2\text{H}_4^+ + \text{HCN} \quad (3.22b)
$$

$$
\rightarrow \text{C}_2\text{H}_4^+ + \text{HNC} \quad (3.22c)
$$

$\Delta H_{3.22a} = -213$ kJ mol$^{-1}$

$\Delta H_{3.22b} = -224$ kJ mol$^{-1}$

$\Delta H_{3.22c} = -159$ kJ mol$^{-1}$.

All of these possible processes, involving H-atom transfer and charge transfer, are exothermic. C$_2$H$_4^+$ can account for the signal at m/z 41:

$$
\text{C}_2\text{H}_4^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{CH}_3. \quad [0.9] \quad (3.23a)
$$

$$
\rightarrow \text{C}_4\text{H}_7^+ + \text{H}. \quad [0.1] \quad (3.23b)
$$

$k_{3.23} = 1.0 \times 10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$ \cite{208,209}$
however, a small signal at m/z 55 is also expected for this reaction, which was not detected. The origins of the ions at m/z 54 and m/z 56 are uncertain.

The rate coefficient which we observed for the reaction of $\text{C}_2\text{N}_2\text{H}^+ + \text{C}_2\text{H}_4$ compares well with the result of Deakyne et al.,$^{204}$ and in reasonable agreement with the result of Raksit and Bohme,$^{205}$ when allowance is made for the differences in experimental technique. Raksit and Bohme, using 0.20 Torr of H$_2$ as a buffer gas, reported a substantially larger product channel for adduct formation (30%) than we detected with He as a buffer at a pressure of 0.30 Torr. This difference can be accounted for by the greater efficiency of H$_2$ (in comparison to He) in collisional stabilisation of the collision complex to permit adduct formation.

$\text{C}_2\text{H}_5^+ + \text{C}_2\text{N}_2$ : To study the reaction of $\text{C}_2\text{H}_5^+$ with $\text{C}_2\text{N}_2$, $\text{C}_2\text{H}_5^+$ was produced as indicated above by chemical ionisation involving addition of CH$_4$ to the flow tube. Sufficient CH$_4$ was added to completely quench the injected m/z 15 signal (CH$_3^+$). The reactant ion profile, in addition to the ion of interest (m/z 29, $\text{C}_2\text{H}_5^+$), also contained impurity signals at m/z 41 (C$_3$H$_5^+$) and m/z 19 (H$_3$O$^+$, water contaminant):

$$\text{C}_2\text{H}_5^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{C}_2\text{H}_4$$

$$k_{3.24} = 3.5 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

The signal at m/z 41 is a mystery: $\text{C}_2\text{H}_5^+$ + CH$_4$ does not produce C$_3$H$_5^+$.$^{182,210}$ Possibly C$_3$H$_5^+$ arises from a C$_2$H$_4$ impurity in the methane.
\[ \text{CH}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2 \quad [0.5] \quad (3.25a) \]

\[ k_{3.25} = 1.0 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}, \]

but this reaction should produce a comparable signal at m/z 27 (C2H3+) which was not evident.\textsuperscript{210,211} In any event, as with H3O+, this contaminant ion signal was less than 5% of the intensity of the major ion C2H5+.

Upon addition of C2N2, product signals were detected at m/z 53, 62, 67 and 81. m/z 62 was attributed to an unidentified secondary reaction, because of its rapid disappearance at low C2N2 flows; m/z 67 was found to result from a side reaction involving CH3+ (arising from incomplete conversion from CH3+ to C2H5+ in the reaction distance between port 1, the CH4 inlet and port 2, the C2N2 inlet):

\[ \text{CH}_3^+ + \text{C}_2\text{N}_2 + \text{He} \rightarrow \text{CH}_3\text{C}_2\text{N}_2^+ + \text{He} \quad (3.26). \]

Having interpreted these additional products, the reaction between C2H5+ and C2N2 is found to consist of proton transfer and adduct formation channels:

\[ \text{C}_2\text{H}_5^+ + \text{C}_2\text{N}_2 \rightarrow \text{C}_2\text{N}_2\text{H}^+ + \text{C}_2\text{H}_4 \quad [0.4] \quad (3.27a) \]

\[ \rightarrow \text{C}_2\text{H}_4\text{H}^+.\text{C}_2\text{N}_2 \quad [0.6] \quad (3.27b) \]

\[ k_{3.27} = 2.1 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}. \]

The product ratio given here is that observed in the limiting case of low C2N2 flows. This ratio was not constant over the range of C2N2 partial pressures employed in the experiment: the ratio I\textsubscript{53} : I\textsubscript{81} decreased from 0.67 at low flows to
~ 0.1 at the highest flows used. This suggests that C_{2}N_{2}H^{+} participates in further unidentified reactions with C_{2}N_{2} or CH_{4}.

3.2.2. C_{2}N_{2}H^{+} + CH_{3}Cl \rightleftharpoons CH_{3}ClH^{+} + C_{2}N_{2}

A problem associated with the study of this equilibrium is that the ions C_{2}N_{2}H^{+} and CH_{3}^{37}ClH^{+} both give a signal at m/z 53. Therefore, the ion signal at m/z 51 (corresponding to CH_{3}^{35}ClH^{+}) was monitored in all experiments pertaining to this equilibrium, and the CH_{3}^{37}ClH^{+} content of the m/z 53 signal was calculated on the basis of the natural isotope ratio for ^{35}Cl:^{37}Cl (75.77 : 24.23).

C_{2}N_{2}H^{+} + CH_{3}Cl: For the reaction of C_{2}N_{2}H^{+} with CH_{3}Cl, the only product channel observed was proton transfer as shown in table 3.2.

CH_{3}ClH^{+} + C_{2}N_{2}: Reaction of CH_{3}ClH^{+} with C_{2}N_{2} presented some difficulties. Proton transfer was again the only channel apparent, but an accurate determination of the reaction rate was not obtainable. Since CH_{3}ClH^{+} was generated by chemical ionisation within the flow tube, the tube contained appreciable partial pressures of both the neutrals C_{2}N_{2} and CH_{3}Cl. Thus the reverse reaction was also able to occur, reducing the apparent rate of the forward reaction. Extrapolation of the slope of ln(CH_{3}ClH^{+} ion signal) versus C_{2}N_{2} partial pressure at low C_{2}N_{2} partial pressures yielded the rate coefficient reported here, which is best regarded as a lower limit. This rate is, however, well supported by an ICR measurement\textsuperscript{207} giving a rate for the proton transfer process
of $2.5 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$: thus the lower limit found by SIFT measurement appears to have reasonable accuracy.

3.2.3. $\text{C}_2\text{H}_5^+ + \text{CH}_3\text{Cl} \rightleftharpoons \text{CH}_3\text{ClH}^+ + \text{C}_2\text{H}_4$

$\text{C}_2\text{H}_5^+ + \text{CH}_3\text{Cl}$: Product analysis for this reaction was uncomplicated, with proton transfer and adduct formation channels seen:

\[
\begin{align*}
\text{C}_2\text{H}_5^+ + \text{CH}_3\text{Cl} & \rightarrow \text{CH}_3\text{ClH}^+ + \text{C}_2\text{H}_4 & [0.80] \quad (3.28a) \\
 & \rightarrow \text{CH}_3\text{ClH}^+.\text{C}_2\text{H}_4 & [0.20] \quad (3.28b)
\end{align*}
\]

$k_{3.28} = 7.9 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$

$\text{CH}_3\text{ClH}^+ + \text{C}_2\text{H}_4$: Proton transfer was the only channel observed here, with the rate for proton transfer found as listed in table 3.2. In this instance, although both $\text{C}_2\text{H}_4$ and $\text{CH}_3\text{Cl}$ were present in the tube, equilibration within the flow tube was not considered a significant problem (as it had been in the study of the proton transfer reactions involved in equilibrium (3.5)) since reaction of $\text{CH}_3\text{ClH}^+$ with $\text{C}_2\text{H}_4$ is much faster than the reaction of $\text{C}_2\text{H}_5^+$ with $\text{CH}_3\text{Cl}$.

Determination of symmetry factors for calculation of PA($\text{C}_2\text{N}_2$) and PA($\text{CH}_3\text{Cl}$):

Ion structures assumed, in the determination of entropy changes during proton transfer, are as shown in table 3.4.
A bond-protonated form is assumed in determination of $\sigma$ for $\text{C}_2\text{H}_5^+$. If this ion has, instead, the structure $\text{CH}_3-\text{CH}_2^+$, $\sigma = 1$ and the PA values determined from reactions involving $\text{C}_2\text{H}_4$ will be in error by 1.7 kJ mol$^{-1}$ owing to the change in entropy during the reaction. The bond-protonated form is, however, the most stable form of $\text{C}_2\text{H}_5^+$ according to ab initio calculations.\textsuperscript{212} An additional point to note from table 3.4 is that, although there are three perpendicular twofold rotational axes of symmetry for $\text{C}_2\text{H}_4$, $\sigma = 4$ (rather than 8) for this species since only four different and indistinguishable orientations exist for this molecule.\textsuperscript{187}

For protonated $\text{CH}_3\text{Cl}$, the Cl–H bond is assumed not to be colinear with the C–Cl bond: if these bonds are colinear, then $\sigma = 3$ for this species. However, this change in symmetry number would not alter the derived value of PA($\text{C}_2\text{N}_2$), since this quantity is not directly determined from PA($\text{CH}_3\text{Cl}$).

\textbf{Table 3.4: Rotational symmetry numbers for $X$ and $XH^+$, used in determining PA($\text{C}_2\text{N}_2$).}

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\sigma_X$</th>
<th>$XH^+$</th>
<th>$\sigma_{XH^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{C}≡\text{C}-\text{H}$</td>
<td>4</td>
<td>$\text{H}_2\text{C}≡\text{C}^+\text{C}=\text{H}$</td>
<td>2</td>
</tr>
<tr>
<td>$\text{N≡C–C≡N}$</td>
<td>2</td>
<td>$\text{N≡C–C≡N}^+\text{H}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{C–Cl}$</td>
<td>3</td>
<td>$\text{C–Cl}^+\text{H}$</td>
<td>1</td>
</tr>
</tbody>
</table>
Protonated C$_2$N$_2$ is assumed to be nonlinear: a recent ab initio calculation$^{191}$ indicates that NCCNH$^+$ may well be a linear ion, but $\sigma = 1$ whether this ion is linear or not. Thus our derived value of PA(C$_2$N$_2$) should not be in error even if this assumed structure is not correct.

Using these structures and the rate coefficients for proton transfer shown in table 3.3,

$$\text{PA(C}_2\text{N}_2) = 674.3 \pm 4 \text{ kJ mol}^{-1} \text{ from K}_{3.5},$$

and

$$\text{PA(CH}_3\text{Cl}) = 672.5 \pm 4 \text{ kJ mol}^{-1} \text{ from K}_{3.7}. $$

Using K$_{3.6}$ and the PA(CH$_3$Cl) value determined above, PA(C$_2$N$_2$) = 674.6 ± 6 kJ mol$^{-1}$: thus the thermochemical values determined from equilibria (3.5), (3.6) and (3.7) are consistent and in mutual agreement. These values are in agreement with the values determined earlier$^{185}$ but the uncertainties for PA(C$_2$N$_2$) and PA(CH$_3$Cl) are substantially less than for earlier determinations of these quantities.

Section 3.3: Some reactions of C$_2$N$_2^+$. 

The C$_2$N$_2^+$ ion was easily generated by electron bombardment of C$_2$N$_2$ within the ion source. Some reactions of this ion with various neutrals are presented in table 3.5.
As can be seen from the efficiency of the reaction with hydrogen, C$_2$N$_2^+$ will be depleted rapidly within interstellar clouds and thus its reactions with other neutral species will not be of significance to models of interstellar chemistry. Channels evident in the other reactions of C$_2$N$_2^+$ are principally charge transfer, association, and atom transfer processes. Charge transfer was seen in all the reactions where IP(C$_2$N$_2$) > IP(X), similar to earlier findings for the reactions of C$_2$N$_2^+$ with C$_4$H$_2$\textsuperscript{213} HC$_3$N,\textsuperscript{214} acetone and biacetyl,\textsuperscript{215,216} A more interesting finding, relating to the reaction of C$_2$N$_2^+$ with HCN, is discussed in chapter 5.

<table>
<thead>
<tr>
<th>X</th>
<th>Products</th>
<th>$k_{obs}$</th>
<th>$k_c$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>C$_2$N$_2$H$^+$ + H$^+$</td>
<td>0.96</td>
<td>1.51</td>
<td>235</td>
</tr>
<tr>
<td>CO</td>
<td>C$_2$N$_2$CO$^+$</td>
<td>0.11</td>
<td>0.79</td>
<td>–</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>C$_2$N$_2$O$^+$ + CO</td>
<td>[0.58]</td>
<td>0.0041</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>C$_2$N$_2$.CO$_2^+$</td>
<td>[0.42]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>H$_2$O$^+$ + C$_2$N$_2$</td>
<td>[0.09]</td>
<td>2.6</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>C$_2$N$_2$H$^+$ + OH$^-$</td>
<td>[0.91]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>C$_2$H$_2^+$ + C$_2$N$_2$</td>
<td>[≥0.95]</td>
<td>0.58</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>C$_2$N$_2$.C$_2$H$_2^+$</td>
<td>[≤0.05]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>C$_2$H$_4^+$ + C$_2$N$_2$</td>
<td>[≥0.95]</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_8$N$_2^+$ + H$^+$</td>
<td>[≤0.05]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes
a. Product channels reported in brackets, where more than one product was detected.
b. Observed rate coefficient, in units of 10$^9$ cm$^3$ molecule$^{-1}$ s$^{-1}$.
c. Calculated ADO collision rate coefficient, using the theory of Su and Chesnavich.\textsuperscript{172}
d. Reaction exothermicity in units of kJ mol$^{-1}$. Taken from the tabulation of Lias et al,\textsuperscript{184} unless otherwise stated.
Section 3.4: The proton affinity of C$_4$H$_2$.

H-C≡C-C≡C-H, diacetylene, is formed as a combustion intermediate in flames; ions derived from C$_4$H$_2$ have also been identified within flames, in connection with soot formation. Extraterrestrial occurrences of C$_4$H$_2$ include Titan's atmosphere. It is also considered partly responsible for stratospheric haze in the atmospheres of Uranus and Neptune. The molecule's lack of a permanent dipole moment renders it invisible to radio astronomers, but it is a very likely component of dark clouds: the detection of methylidiacetylene, CH$_3$C$_4$H, is very suggestive of the presence of diacetylene within interstellar clouds. Herbst has argued that the formation of diacetylene and more complex hydrocarbons in interstellar clouds requires a high abundance of neutral atomic carbon in the cloud's formative years, to permit reaction pathways such as

\[
\begin{align*}
C_3H_4^+ + C & \rightarrow C_4H_3^+ + H^· \\
C_4H_3^+ + e & \rightarrow C_4H_2 + H^·
\end{align*}
\]

\( \Delta H_{3.29} = -399 \text{ kJ mol}^{-1} \)

\( \Delta H_{3.30} = -568 \text{ kJ mol}^{-1}. \)

Reactions of protonated diacetylene, C$_4$H$_3^+$, with H$_2$, CO and hydrocarbons have been investigated, but there has been little study of the reactions of ions with C$_4$H$_2$. The work detailed in this section was undertaken as a result of the report by Deakyne et al of a value PA(C$_4$H$_2$) = 180 ± 1 kCal mol$^{-1}$ (≈ 753 ± 4 kJ mol$^{-1}$), obtained by ICR bracketing measurements, that was considerably higher than the value obtained by Knight et al. of PA(C$_4$H$_2$) = 738 ± 4 kJ mol$^{-1}$. This
latter value was obtained (on the University of Canterbury SIFT) by proton transfer equilibrium measurements involving BrCN and C4H2, and C2H5I and C4H2. A summary of the literature values of PA(C4H2) and related quantities is given in table 3.6.

In the present work, an attempt was made to determine PA(C4H2) by studying the three proton-transfer equilibria involving C4H2, BrCN and CH3NO2:

\[
\begin{align*}
C_4H_3^+ + CH_3NO_2 & \rightleftharpoons CH_3NO_2H^+ + C_4H_2 \\
BrCNH^+ + CH_3NO_2 & \rightleftharpoons CH_3NO_2H^+ + BrCN \\
C_4H_3^+ + BrCN & \rightleftharpoons BrCNH^+ + C_4H_2
\end{align*}
\] (3.31) (3.32) (3.33)

Table 3.6: Thermochemical values pertinent to determination of PA(C4H2).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value a</th>
<th>Method of determination</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA(CH3NO2)</td>
<td>750</td>
<td>PA standard value</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>751.5 ± 12</td>
<td>FA bracketing</td>
<td>229</td>
</tr>
<tr>
<td></td>
<td>756.1</td>
<td>ICR studies</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>748.5</td>
<td>ICR bracketing</td>
<td>231</td>
</tr>
<tr>
<td>PA(BrCN)</td>
<td>748 ± 2</td>
<td>SIFT studies</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td>746 ± 2</td>
<td>ICR bracketing</td>
<td>232</td>
</tr>
<tr>
<td></td>
<td>747 ± 2</td>
<td>SIFT studies</td>
<td>233b</td>
</tr>
<tr>
<td>PA(C4H2)</td>
<td>753 ± 4</td>
<td>ICR bracketing</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>777.4</td>
<td>MP3//6-31G** calculation</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>734</td>
<td>MP4SDQ/6-311G** calculation</td>
<td>233</td>
</tr>
<tr>
<td></td>
<td>741</td>
<td>CEPA-1/SCF calculation</td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>741 ± 4</td>
<td>SIFT studies</td>
<td>233b</td>
</tr>
</tbody>
</table>

Notes
a. in kJ mol⁻¹.
b. This work.
The reactant ions were all injected into the flow tube from the ion source, thus avoiding any problems with competing reverse reactions occurring in the tube (c.f. the reaction of \( \text{CH}_3\text{ClH}^+ \) with \( \text{C}_2\text{N}_2 \), in section 3.2.2).

\( \text{C}_4\text{H}_3^+ \) was produced from acetylene

\[
\begin{align*}
\text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_2 & \rightarrow \text{C}_4\text{H}_2^+ + \text{H}_2 & [0.35] \\
& \rightarrow \text{C}_4\text{H}_3^+ + \text{H}^- & [0.65]
\end{align*}
\]

\( k_{3.34} = 1.3 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) \( ^{208,210} \)

from vinyl acetylene, \( \text{CH}_2=\text{CH}−\text{C}≡\text{CH} \); and from a 1:10 mixture of diacetylene in hydrogen

\[
\begin{align*}
\text{H}_2^+ + \text{C}_4\text{H}_2 & \rightarrow \text{C}_4\text{H}_3^+ + \text{H}^- \\
\text{H}_3^+ + \text{C}_4\text{H}_2 & \rightarrow \text{C}_4\text{H}_3^+ + \text{H}_2
\end{align*}
\]

\( \Delta H_{3.35} = -484 \text{ kJ mol}^{-1} \)

\( \Delta H_{3.36} = -321 \text{ kJ mol}^{-1} \);

\[
\begin{align*}
\text{C}_4\text{H}_2^+ + \text{H}_2 & \nrightarrow \text{C}_4\text{H}_3^+ + \text{H}^- \\
k_{3.37} < 5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \)
\]

\( ^{226} \)

Knight et al.\textsuperscript{166} found that these various methods of \( \text{C}_4\text{H}_3^+ \) generation gave no evidence for the formation of different \( \text{C}_4\text{H}_3^+ \) isomers. Giles et al.\textsuperscript{226} also observed results consistent with the existence of only one stable \( \text{C}_4\text{H}_3^+ \) isomer. In the present work, we found the rate coefficients and product distributions for the reactions of \( \text{C}_4\text{H}_3^+ \) with \( \text{BrCN} \) and with \( \text{CH}_3\text{NO}_2 \) to be independent of the
method of ion generation, and thus we conclude that all of these techniques yield only protonated diacetylene as $C_4H_3^+$. 

$BrCNH^+$ was produced from a 1:10 mixture of $BrCN$ in $H_2$:

\[
\begin{align*}
H_2^+ + BrCN & \rightarrow BrCNH^+ + H^- \\
H_3^+ + BrCN & \rightarrow BrCNH^+ + H_2 \\
BrCN^+ + H_2 & \rightarrow BrCNH^+ + H^- \\
\end{align*}
\]
\[\Delta H_{3.38} = -486 \text{ kJ mol}^{-1}\]
\[\Delta H_{3.39} = -323 \text{ kJ mol}^{-1}\]
\[\Delta H_{3.40} = -140 \text{ kJ mol}^{-1}.\]

Injection of m/z 106 ($^{79}BrCNH^+$) from the ion source could not be accomplished without substantial contamination from neighbouring masses ($^{79,81}BrCN^+$). Instead, the mass spectrometer was set at m/z 112 and the resolution adjusted until a small signal at m/z 108 ($^{81}BrCNH^+$) was obtained without contamination.

$CH_3NO_2H^+$ was produced from a 1:10 mixture of $CH_3NO_2$ in $H_2$:

\[
\begin{align*}
H_2^+ + CH_3NO_2 & \rightarrow CH_3NO_2H^+ + H^- \\
H_3^+ + CH_3NO_2 & \rightarrow CH_3NO_2H^+ + H_2 \\
CH_3NO_2^+ + H_2 & \rightarrow CH_3NO_2H^+ + H^- \\
\end{align*}
\]
\[\Delta H_{3.41} = -490 \text{ kJ mol}^{-1}\]
\[\Delta H_{3.42} = -327 \text{ kJ mol}^{-1}\]
\[\Delta H_{3.43} = -64 \text{ kJ mol}^{-1}.\]
Injection of CH$_3$NO$_2$H$^+$ at m/z 62 was accompanied by contaminating signals due to CH$_3$NO$_2^+$, NO$_2^+$ and NO$^+$, the latter two species arising from breakup subsequent to injection:

\[
\begin{align*}
\text{CH}_3\text{NO}_2\text{H}^+ & \rightarrow \text{NO}_2^+ + \text{CH}_4 \quad (3.44a) \\
& \rightarrow \text{NO}^+ + \text{CH}_3\text{OH} \quad (3.44b)
\end{align*}
\]

\[\Delta H_{3.44a} = +194.5 \text{ kJ mol}^{-1}\]
\[\Delta H_{3.44b} = +78 \text{ kJ mol}^{-1}.
\]

Adjustment of the mass spectrometer resolution permitted elimination of the m/z 61 (CH$_3$NO$_2$+) signal, and operation at low repeller voltages allowed injection without detectable breakup to form NO$_2^+$, but formation of NO$^+$ by breakup was unavoidable. The NO$^+$ ion is generally unreactive, and there was no indication of any reaction of NO$^+$ with the neutrals used.

The results, for reaction of the ions CH$_3$NO$_2$H$^+$, BrCNH$^+$ and C$_4$H$_3^+$ with the appropriate neutrals, are given in table 3.7; the proton affinity values are calculated from these results in table 3.8, using the structures detailed in table 3.9 to determine the entropy changes as with the determination of PA(C$_2$N$_2$) in section 3.2. These results are interpreted below.

3.4.1 C$_4$H$_3^+$ + CH$_3$NO$_2$ $\rightleftharpoons$ CH$_3$NO$_2$H$^+$ + C$_4$H$_2$

CH$_3$NO$_2$H$^+$ + C$_4$H$_2$: The reaction between CH$_3$NO$_2$H$^+$ and C$_4$H$_2$ is fast, but does not exhibit proton transfer. Rather, the only product seen is at m/z 42,
corresponding to C$_2$H$_4$N$^+$, C$_2$H$_2$O$^+$, or CNO$^+$. Of these possibilities, all of which require complicated rearrangement of the reactants, the most exothermic channel corresponds to

$$\text{CH}_3\text{NO}_2\text{H}^+ + \text{C}_4\text{H}_2 \rightarrow \text{CH}_3\text{CNH}^+ + \text{C}_2\text{H}_2 + \text{CO}_2$$

$\Delta H_{3.45} = -494 \text{ kJ mol}^{-1}$,

Table 3.7: Proton transfer reactions studied to determine PA(C$_4$H$_2$).

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products $^a$</th>
<th>$k_{\text{obs}}$ $^a$</th>
<th>$k_{c}^{a,b}$</th>
<th>$k_{\text{lit}}^{a,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NO$_2$H$^+$ + C$_4$H$_2$</td>
<td>C$_2$H$_4$N$^+$ + C$_2$H$_2$ + CO$_2$ $^d$</td>
<td>[1.0]</td>
<td>1.1</td>
<td>1.20</td>
</tr>
<tr>
<td>C$_4$H$_5^+$ + CH$_3$NO$_2$</td>
<td>CH$_3$NO$_2$H$^+$ + C$_4$H$_2$</td>
<td>[0.45]</td>
<td>3.1</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_4$N$^+$ + C$_2$H$_2$ + CO$_2$ $^d$</td>
<td>[0.30]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>m/z 68$^f$</td>
<td>[0.25]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$NO$_2$H$^+$ + BrCN</td>
<td>BrCNH$^+$ + CH$_3$NO$_2$</td>
<td>[0.66]</td>
<td>0.80</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NO$_2$H$^+$·BrCN</td>
<td>[0.34]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{81}$BrCNH$^+$ + CH$_3$NO$_2$</td>
<td>CH$_3$NO$_2$H$^+$ + BrCN</td>
<td>[0.90]</td>
<td>1.5</td>
<td>2.87</td>
</tr>
<tr>
<td></td>
<td>m/z 121$^f$</td>
<td>[0.09]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$NO$_2$H$^+$·BrCN</td>
<td>[0.01]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{81}$BrCNH$^+$ + C$_4$H$_2$</td>
<td>C$_4$H$_3^+$ + BrCN</td>
<td>[0.20]</td>
<td>0.69</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_3^+$·BrCN</td>
<td>[0.80]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_4$H$_5^+$ + BrCN</td>
<td>BrCNH$^+$ + C$_4$H$_2$</td>
<td>[0.75]</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_3^+$·BrCN</td>
<td>[0.25]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes

a. See footnotes (a) - (c) for table 3.5.
b. Calculated using $\alpha$(C$_4$H$_2$) = 7.33 x 10$^{-24}$ cm$^3$, as determined theoretically by Fowler and Diercksen.$^{235}$
c. $k_{\text{lit}}$ is the literature value for the reaction rate, from the reference quoted.
d. The product ion at m/z 42 is identified as CH$_3$CNH$^+$ on the basis of this being the most exothermic channel. The neutral products were not established.
e. Taken from reference 166.
f. This product was not identified.
g. Taken from reference 167.
though CH₃NCH⁺ is another highly exothermic option (ΔH = -451 kJ mol⁻¹). Other possibilities are less likely on the basis of being less exothermic: formation of any product at m/z 42 requires extensive rearrangement, necessitating a long-lived collision complex, and for long complex lifetimes rearrangement is likely to yield the product having the lowest possible energy. Also, there exists a greater likelihood of activation energy barriers for such rearrangement if the eventual free energy gain is less. The absence of proton transfer in this reaction is not, in itself, at all conclusive: the reverse direction must be examined also.

Table 3.8: ΔG°, ΔH°, and PA values calculated from the proton transfer equilibria studied to determine PA(C₄H₂).

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>k_f a</th>
<th>k_r a</th>
<th>ΔG° a</th>
<th>TΔS° a,b</th>
<th>ΔH° a</th>
<th>PA c</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NO₂H⁺ + C₄H₂ ⇌ C₄H₃⁺ + CH₃NO₂</td>
<td>0</td>
<td>1.4</td>
<td>+d</td>
<td>0</td>
<td>+</td>
<td>&lt;750 e</td>
</tr>
<tr>
<td>CH₃NO₂H⁺ + BrCN ⇌ BrCNH⁺ + CH₃NO₂</td>
<td>0.53</td>
<td>1.35</td>
<td>2.3</td>
<td>0</td>
<td>2.3</td>
<td>748±2 f</td>
</tr>
<tr>
<td>BrCNH⁺ + C₄H₂ ⇌ C₄H₃⁺ + BrCN</td>
<td>0.14</td>
<td>1.8</td>
<td>6.4</td>
<td>0</td>
<td>6.4</td>
<td>741±4 e</td>
</tr>
</tbody>
</table>

Notes
a. See footnotes (a) - (b) for table 3.3.
b. The entropy corrections are calculated on the basis of the rotational symmetry numbers detailed in table 3.9.
c. Proton affinity of neutral indicated, in kJ mol⁻¹, referenced to PA (CH₃NO₂) = 750 kJ mol⁻¹.
d. Inferred ΔG > 0 from k_f < k_r (that is, K < 1).
e. PA(C₄H₂).
f. PA(BrCN).
$C_4H_3^+ + CH_3NO_2$: The observation of proton transfer as the major channel (45%) for the fast reaction between $C_4H_3^+$ and $CH_3NO_2$ is immediately in conflict with the finding, by Deakyne et al.\textsuperscript{204} that $PA(C_4H_2) > PA(CH_3NO_2)$. The existence, in addition to proton transfer, of competing exothermic channels

$$C_4H_3^+ + CH_3NO_2 \rightarrow C_2H_4N^+ + C_2H_2 + CO_2 \quad [0.30] \quad (3.46a)$$

$$\rightarrow m/z 68 \quad [0.25] \quad (3.46b)$$

$\Delta H_{3.46a} = -500 \text{kJ mol}^{-1}$ for $m/z 42 = CH_3CNH^+$

$\Delta H_{3.46b} = -457 \text{kJ mol}^{-1}$ for $m/z 42 = CH_3NCH^+$

(with the product at $m/z 68$ being unidentified) ensures that proton transfer cannot occur on every collision, but the observation of proton transfer in this direction and the absence of any proton transfer channel for the reaction of $CH_3NO_2H^+$ with $C_4H_2$ indicates that proton transfer is exothermic from $C_4H_3^+$ to $CH_3NO_2$. That is, $PA(CH_3NO_2) > PA(C_4H_2)$.

---

**Table 3.9:** Rotational symmetry numbers for $X$ and $XH^+$, used in determining $PA(C_4H_2)$.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\sigma_X$</th>
<th>$XH^+$</th>
<th>$\sigma_{XH^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H-C=N$</td>
<td>1</td>
<td>$H-C=N-H$</td>
<td>1</td>
</tr>
<tr>
<td>$H-C≡C-C≡C-H$</td>
<td>2</td>
<td>$H-C≡C-C≡C-H$</td>
<td>2</td>
</tr>
<tr>
<td>$Br-C≡N$</td>
<td>1</td>
<td>$Br-C≡N-H$</td>
<td>1</td>
</tr>
</tbody>
</table>

---

92
It is not possible, from the results for this equilibrium system, to calculate the difference in PAs from the equilibrium constant $K_{3,31}$ (because of the competing product channels observed for reaction in both directions). The absence of these channels from the earlier ICR measurements$^{204}$ can be explained in terms of the extensive rearrangement required for these channels, necessitating a long-lived (collisionally stabilised) collision complex. At ICR pressures, such collisional stabilisation is improbable and so proton transfer is the only channel detected. This explanation does not, however, resolve the conflict between the two sets of data: the ICR results indicate $\text{PA(C}_4\text{H}_2) > \text{PA(CH}_3\text{NO}_2)$, while our results indicate the reverse.

3.4.2 $\text{CH}_3\text{NO}_2\text{H}^+ + \text{BrCN} \rightleftharpoons \text{BrCNH}^+ + \text{CH}_3\text{NO}_2$

$\text{CH}_3\text{NO}_2\text{H}^+ + \text{BrCN}$: Proton transfer is the main product channel for this reaction (66%). The overall reaction rate coefficient ($8.0 \times 10^{-10}$ cm$^3$ mole$^{-1}$ s$^{-1}$) is below the calculated collision rate coefficient ($k_c = 2.34 \times 10^{-9}$ cm$^3$ mole$^{-1}$ s$^{-1}$), which suggests thermoneutral or endothermic proton transfer. The efficiency, $k_f / k_c$, of the proton transfer channel is 0.25: that is, 25% of collisions result in proton transfer.

$^{81}\text{BrCNH}^+ + \text{CH}_3\text{NO}_2$ : Proton transfer is again the main product channel, with an efficiency of 0.47. The sum of these efficiencies is substantially below the value of unity expected. This deficiency is not adequately explained by the presence of a minor product channel at m/z 121 (the nature of this product being
unidentified), since neither the forward nor the reverse reaction occurs at the collision rate - thus reaction is not saturated in either direction, and so proton transfer is not hindered by competition with the other channels evident. The low value of $r_f + r_r = 0.72$ indicates that the reaction is close to thermoneutral.\(^\text{236}\)

The absence of hindrances to the proton transfer channels permits calculation of the free energy difference:

$$K_{3,32} = \frac{k_f}{k_r} = 0.39$$

$$\Delta G^0_{3,32} = -RT \ln(K_{3,32})$$

$$\therefore \Delta G^0_{3,32} = 2.3 \text{ kJ mol}^{-1} \text{ at } 300K.$$  

An uncertainty of $\pm 20\%$ is ascribed to each rate coefficient, and $\pm 10\%$ to the determination of each product ratio, corresponding to an overall uncertainty of $\pm 1.2 \text{ kJ mol}^{-1}$ in the free energy calculation. From $\Delta G^0_{3,32}$, and from $T\Delta S^0$ as listed in table 3.9, it can be determined that

$$\text{PA(CH}_3\text{NO}_2) - \text{PA(BrCN)} = 2.3 \pm 2 \text{ kJ mol}^{-1}.$$  

This value is in good agreement, within the uncertainties of the respective techniques, with the difference in PAs for the two compounds as determined by bracketing\(^\text{185}\) and by an earlier SIFT measurement of this proton transfer equilibrium.\(^\text{167}\) The earlier SIFT study did not report the unidentified product at m/z 121 for the reaction of $^{81}\text{BrCNH}^+$ with CH$_3$NO$_2$. 

3.4.3  \[ \text{BrCNH}^+ + \text{C}_4\text{H}_2 \quad \rightarrow \quad \text{C}_4\text{H}_3^+ + \text{BrCN} \]

\[ ^{81}\text{BrCNH}^+ + \text{C}_4\text{H}_2: \] Adduct formation (80%) was the major product channel in evidence for this reaction, with (20%) proton transfer observed also. Competition between these channels is possible and is of concern in cases where adduct formation is the dominant channel, since the extent of proton transfer may be reduced by competition. However, the reaction is observed to be reproducibly slower than the calculated collision rate, suggesting that proton transfer is not hindered by competing association for this reaction.

\[ \text{C}_4\text{H}_3^+ + \text{BrCN}: \] Proton transfer accounts for 75% of the collisions for this fast reaction, with adduct formation as the alternative product channel. The overall reaction is seen to occur at the collision rate. The sum of the proton transfer efficiencies is seen to be close to unity \( (r_f + r_r = 0.91) \), indicating that proton transfer is not substantially influenced by competing processes in either direction. The energetics of proton transfer can be calculated:

\[
K_{3,33} = \frac{k_f}{k_r} = 0.077
\]

\[ \therefore \Delta G^\circ_{3,33} = 6.4 \pm 1.2 \text{ kJ mol}^{-1}. \]

\[ \therefore \text{PA(\text{BrCN}) - PA(\text{C}_4\text{H}_2)} = 6.4 \pm 2 \text{ kJ mol}^{-1} \]

(where the additional uncertainty is the ± 1 kJ mol\(^{-1}\) uncertainty in \( \Delta S^\circ \)). From the latter two equilibria, the difference in proton affinity between \( \text{CH}_3\text{NO}_2 \) and \( \text{C}_4\text{H}_2 \) can be determined:
PA(C₄H₂) = PA(CH₃NO₂) - 8.7 ± 4 kJ mol⁻¹.

This evaluation of PA(C₄H₂) = 741 ± 4 kJ mol⁻¹ is qualitatively supported by the conclusion, from the results obtained for equilibrium (3.31), that the proton affinity of C₄H₂ is below that of CH₃NO₂. Thus, while arithmetic triangulation of the results to achieve a self-consistent result is not possible because of the existence of competition for some of the proton transfer reactions, the results are seen to be in mutual agreement. The proton affinity determined for C₄H₂ is in good agreement with most of the values shown in table 3.6: the disagreement with the experimental value of Deakyne et al,²⁰⁴ and hence with the literature value,¹⁸⁴ suggests that this literature value needs to be revised.
CHAPTER 4.

ISOMERISM OF C$_2$N$^+$ AND C$_3$N$^+$.

Section 4.1: C$_2$N$^+$.

In 1981, Haese and Woods$^{237}$ proposed that the reactions

\[
\begin{align*}
C^+ + HCN & \rightarrow C_2N^+ + H^- \\
C^+ + HNC & \rightarrow C_2N^+ + H^- \\

k_{4,1} & = 3.5 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad (4.1)
\end{align*}
\]

would selectively produce the CNC$^+$ and CCN$^+$ isomers respectively, since these are the products expected on consideration of the ion-dipole interaction and since the products would have insufficient energy to overcome the isomerisation barrier. On the basis of these considerations, they suggested that these two C$_2$N$^+$ isomers would display differences in their reactivity which could be significant in the modelling of interstellar cloud chemistry.

Theoretical calculations$^{237,239-241}$ and experimental studies$^{237,241-245}$ have verified that there are two distinct isomers of the C$_2$N$^+$ ion. Calculations at varying levels of theory indicate that ground-state CCN$^+$ is substantially higher in energy than ground-state CNC$^+$, and that there exists a sizeable barrier to isomerisation. Thus, the two species CCN$^+$ and CNC$^+$ are expected to display differences in reactivity. A summary of experimental and theoretical results (including a set
of calculations performed by DeFrees and McLean\textsuperscript{241} as part of our study of the reactivity of the isomeric C$_2$N$^+$ system) is found in table 4.1.

The present study,\textsuperscript{241} which was undertaken to demonstrate the differing reactivity of the CCN$^+$/CNC$^+$ ions in a flow tube, represents a continuation of work originally conducted earlier in this laboratory.\textsuperscript{166} Other studies of C$_2$N$^+$ reactivity have been performed,\textsuperscript{245-247} including an independent study of C$_2$N$^+$ isomerism by Bohme and co-workers,\textsuperscript{245} but no earlier experimental investigations had dealt with the difference in reactivity of the two species.

Table 4.1: Experimental and theoretical heats of formation\textsuperscript{a} of C$_2$N$^+$ species.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$\Delta H_{\text{CCN}^+}$</th>
<th>$\Delta H_{\text{CNC}^+}$</th>
<th>$\Delta H_{(\text{CCN}^+ - \text{CNC}^+)}$</th>
<th>$\Delta H_{(\text{TS} - \text{CNC}^+)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>$1761 \pm 50$, $1720 \pm 17$</td>
<td>$1523 \pm 50$</td>
<td>$197 \pm 67$</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>$1761 \pm 105$</td>
<td>$1556 \pm 84$</td>
<td>$204 \pm 20$</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>$1715 \pm 29$</td>
<td>$1620 \pm 11$</td>
<td>$195 \pm 25$</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>$1726 \pm 12$</td>
<td>$1620 \pm 11$</td>
<td>$106 \pm 23$</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>$1615 \pm 29$</td>
<td>$1620 \pm 11$</td>
<td>$88 \pm 25$</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>$1715$</td>
<td>$1620$</td>
<td>$95$</td>
<td></td>
</tr>
</tbody>
</table>

Notes

- in kJ mol\textsuperscript{-1}.
- Electron impact upon HC$_3$N and C$_2$N$_2$, Dibeler et al.;\textsuperscript{242} as interpreted by Haese and Woods.\textsuperscript{257}
- 4-31G-SCF calculations, Hopkinson.\textsuperscript{239}
- DZ$^*$P-SCF and CI-SCF calculations, Haese and Woods.\textsuperscript{237}
- Electron impact on C$_2$N$_2$, Smith.\textsuperscript{243}
- CI(SDQ) calculations, Yoshimine and Kraemer.\textsuperscript{240}
- 'Monochromatic' electron impact on CH$_3$CN, CH$_3$NC and C$_2$N$_2$, Harland and McIntosh.\textsuperscript{244}
- MP4/6-311++G(df,pd) calculations, DeFrees and McLean.\textsuperscript{241}
- Tabulated literature values, Lias et al.\textsuperscript{184}
A variety of methods was employed to produce C$_2$N$^+$. Chemical ionisation techniques permitted the production of C$_2$N$^+$ in the flow tube by reaction of C$^+$ (injected from the ion source) with HCN and with C$_2$N$_2$:

$$\text{C}^+ + \text{HCN} \rightarrow \text{CCN}^+ + \text{H}^- \quad (4.1a)$$

$$\rightarrow \text{CNC}^+ + \text{H}^- \quad (4.1b)$$

$\Delta H_{4.1a} = -5 \text{ kJ mol}^{-1}$

$\Delta H_{4.1b} = -100 \text{ kJ mol}^{-1}$

$$\text{C}^+ + \text{C}_2\text{N}_2 \rightarrow \text{CCN}^+ + \text{CN}^- \quad (4.3a)$$

$$\rightarrow \text{CNC}^+ + \text{CN}^- \quad (4.3b)$$

$\Delta H_{4.3a} = +40 \text{ kJ mol}^{-1}$

$\Delta H_{4.3b} = -55 \text{ kJ mol}^{-1}$.

Alternatively, C$_2$N$^+$ was injected from the ion source where it was formed by electron bombardment upon the source gas C$_2$N$_2$, HC$_3$N or CH$_3$CN.

The reactions of CCN$^+$ and CNC$^+$ with several neutral reagent gases are detailed in tables 4.2 and 4.3. In view of the practical difficulties of obtaining pure CCN$^+$ or pure CNC$^+$, no attempts were made to characterise differences in the product distributions due to CCN$^+$/CNC$^+$, except where only one isomer was reactive (in which instance the products observed are clearly due solely to this isomer).

The reaction with CH$_4$ was used to distinguish between CCN$^+$ and CNC$^+$:

$$\text{CCN}^+ + \text{CH}_4 \rightarrow \text{products} \quad (4.4)$$

$$\text{CNC}^+ + \text{CH}_4 \rightarrow \text{products} \quad (4.5)$$

$k_{4.4} = 7.0 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$

$k_{4.5} = 4.0 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$.
A semilogarithmic graph of the ion signal at m/z 38 versus CH₄ concentration clearly showed a curved decay corresponding to the differing reactivity of two components of the m/z 38 ion signal (see figure 4.1). These components were identified as isomers since the addition of a substantial flow of N₂ from the first

<table>
<thead>
<tr>
<th>X</th>
<th>Products a</th>
<th>kₚₑₒᵇ b</th>
<th>kₑ c</th>
<th>ΔH d,e</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>CH₃N⁺ + C</td>
<td>0.90</td>
<td>1.53</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>C₂H₂N⁺</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>C₂H₄⁺ + HCN</td>
<td>0.70</td>
<td>1.12</td>
<td>399</td>
</tr>
<tr>
<td></td>
<td>CH₃N⁺ + C₂H₂</td>
<td>0.10</td>
<td></td>
<td>477</td>
</tr>
<tr>
<td></td>
<td>C₂H₂N⁺ + H₂</td>
<td>0.30</td>
<td></td>
<td>512</td>
</tr>
<tr>
<td>NH₃</td>
<td>CH₃N⁺ + HCN</td>
<td>1.9</td>
<td>2.29</td>
<td>598</td>
</tr>
<tr>
<td>H₂O</td>
<td>HCO⁺ + HCN</td>
<td>1.63</td>
<td>2.55</td>
<td>525</td>
</tr>
<tr>
<td></td>
<td>CH₂N⁺ + CO</td>
<td>0.08</td>
<td></td>
<td>648</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>C₂H⁺ + HCN</td>
<td>0.92</td>
<td>1.6</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>CH₂N⁺ + C₃</td>
<td>0.08</td>
<td>1.10</td>
<td>186</td>
</tr>
<tr>
<td>HCN</td>
<td>C₃H₂N⁺</td>
<td>0.42</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>no reaction</td>
<td>&lt;0.0001</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>
| O₂    | C₂NO⁺ + O                         | >0.97    | 0.4  | 0.70  | 6
|       | O₂⁺ + C₂N⁺                        | <0.03    |      |       |
| N₂O   | C₂NO⁺ + N₂ (or CN₃⁺ + CO)         | 0.73     | 1.0  | 0.93  | 6
|       | NO⁺ + C₂N₂                         | 0.22     |      | 518   |
|       | N₂O⁺ + C₂N⁺                       | 0.05     |      |       |
| CO₂   | C₂NO⁺ + CO                        | 1.1      | 0.83 |       |

Notes:
- a. Product channels reported in brackets, where more than one product was detected.
- b. Observed rate coefficient, in units of 10⁻⁹ cm³ mole⁻¹ s⁻¹.
- c. Calculated ADO collision rate coefficient, using the theory of Su and Chesnavich. ¹⁷²
- d. Reaction exothermicity in units of kJ mol⁻¹. Taken from the tabulation of Lias et al. ¹⁸⁴ unless otherwise stated.
- e. Calculated using ΔHᵢ(CC⁺) = 1726 kJ mol⁻¹.
inlet port did not alter the curved decay evident upon the subsequent addition of CH$_4$ from the second inlet port. In the case of curvature arising from a substantial extent of vibrational excitation of the ion at m/z 38, addition of N$_2$ should efficiently quench the vibrationally excited component. The fraction of the more reactive component at m/z 38 was not affected by the addition of N$_2$: thus vibrational excitation could be excluded as the cause of the observed reactivity.

**Table 4.3: Reactions of CNC$^+$ + X.**

<table>
<thead>
<tr>
<th>X</th>
<th>Products $^a$</th>
<th>$k_{\text{obs}}^a$</th>
<th>$k_e^a$</th>
<th>$-\Delta H^a,b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>no reaction</td>
<td>$&lt;$0.0001</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>C$_2$H$_3^+$ + HCN</td>
<td>0.60</td>
<td>0.004</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td>CH$_3$N$^+$ + C$_2$H$_2$</td>
<td>0.10</td>
<td>1.12</td>
<td>371</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_2$N$^+$ + H$_2$</td>
<td>0.30</td>
<td></td>
<td>406</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>CH$_3$N$^+$ + HCN</td>
<td>1.9</td>
<td>2.29</td>
<td>492</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>HCO$^+$ + HCN</td>
<td>[0.92]</td>
<td>0.07</td>
<td>419</td>
</tr>
<tr>
<td></td>
<td>CH$_3$N$^+$ + CO</td>
<td>[0.08]</td>
<td>2.55</td>
<td>542</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>C$_2$H$^+$ + HCN</td>
<td>[0.92]</td>
<td>0.7</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>CH$_3$N$^+$ + C$_3$</td>
<td>[0.08]</td>
<td>1.10</td>
<td>80</td>
</tr>
<tr>
<td>HCN</td>
<td>C$_3$HN$_2$+$</td>
<td>0.42</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>no reaction</td>
<td>$&lt;$0.0001</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>no reaction</td>
<td>$&lt;$0.0001</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>N$_2$O</td>
<td>C$_2$NO$^+$ + N$_2$</td>
<td>[0.73]</td>
<td>0.40</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>(or CN$_5^+$ + CO)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO$^+$ + C$_2$N$_2$</td>
<td>[0.22]</td>
<td></td>
<td>412</td>
</tr>
<tr>
<td></td>
<td>N$_2$O$^+$ + C$_2$N$^-$</td>
<td>[0.05]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>no reaction</td>
<td>$&lt;$0.0001</td>
<td>0.83</td>
<td></td>
</tr>
</tbody>
</table>

Notes

a. See footnotes (a) - (d) for table (4.2).
b. Calculated using $\Delta H(CNC^+) = 1620$ kJ mol$^{-1}$. 
The isomeric composition of the C$_2$N$^+$ ion signal, produced by a variety of techniques, was determined using the reactivity of m/z 38 with CH$_4$. These results are tabulated in Table 4.4. It should be noted that all of the chemical ionisation methods, employing reaction (4.3), produce approximately 10% CCN$^+$ whereas this reaction should produce CNC$^+$ only. Similarly, all the electron-impact techniques produce approximately 20% CCN$^+$. The occurrence of substantial CCN$^+$ arising from electron impact is to be expected given the structure of the source gases used and the highly energetic nature of the ionisation process, but the apparent formation of CCN$^+$ from reaction (4.3) is not thermodynamically feasible for ground-state reactants. It is therefore presumed

Figure 4.1: Experimentally observed decay curve for reaction of C$_2$N$^+$ (generated from electron impact upon C$_2$N$_2$) with CH$_4$. This graph of ln(reactant ion signal) versus reactant neutral flow is not well fitted by a single exponential decay, indicating that two C$_2$N$^+$ isomers are reacting at different rates with CH$_4$. These results show that the more reactive isomer, CCN$^+$ (which accounts for ~20% of the m/z 38 ion signal) reacts with CH$_4$ with a rate coefficient $k = 7.8 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$; the rate observed for reaction of the less reactive isomer, CNC$^+$, is $k = 2.4 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$.
that the CCN+ arises from an excited fraction of the C+ ion signal, rather than from ground state (2P) C+: the most likely metastable excited state of C+ is (4P).

\[
C^+(4P) + C_2N_2 \rightarrow (CNC^+)^* + CN^-. \tag{4.6}
\]

\[\Delta H_{4.6} = -565 \text{ kJ mol}^{-1}\]

\[
(CNC^+)^* \rightarrow (CCN^+)^* \tag{4.7a}
\]

\[
(CCN^+)^* \rightarrow (CNC^+)^* \tag{4.7b}.
\]

The excited-state C+ produces internally excited C2N+, which has sufficient internal energy to overcome the barrier to isomerisation: thus the immediate product ion resulting is able to oscillate between the CCN+ and CNC+ structures. The resulting distribution of CCN+:CNC+ might be expected to be governed by the thermal equilibrium constant for CCN+ ↔ CNC+:

<table>
<thead>
<tr>
<th>Method (^a)</th>
<th>Site (^b)</th>
<th>%CCN+ (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e + HCN)</td>
<td>IS</td>
<td>18</td>
</tr>
<tr>
<td>(e + CH_3CN)</td>
<td>IS</td>
<td>22</td>
</tr>
<tr>
<td>(e + C_2N_2)</td>
<td>IS</td>
<td>20</td>
</tr>
<tr>
<td>(C^+(CH_2)^d) + (C_2N_2)</td>
<td>FT</td>
<td>11</td>
</tr>
<tr>
<td>(C^+(CO)^d) + (C_2N_2)</td>
<td>FT</td>
<td>11</td>
</tr>
<tr>
<td>(C^+(CO/He)^d,e) + (C_2N_2)</td>
<td>FT</td>
<td>8</td>
</tr>
<tr>
<td>(C^+(CO_2)^d) + (C_2N_2)</td>
<td>FT</td>
<td>11</td>
</tr>
<tr>
<td>(C^+(C_2H_2)^d) + (C_2N_2)</td>
<td>FT</td>
<td>12</td>
</tr>
</tbody>
</table>

Notes
b. Site of m/z 38 production. IS = ion source; FT = flow tube.
c. Determined by reaction with CH4.
d. Gas from which C+ was produced by electron impact.
e. Using a 1:30 mixture of CO in He.
\[
\text{CNC}^+ + 195 \text{ kJ mol}^{-1} \leftrightarrow (\text{TS})^* \leftrightarrow \text{CCN}^+ + 89 \text{ kJ mol}^{-1} \quad (4.8),
\]

where \((\text{TS})^*\) denotes the transition state for isomerisation. The enthalpy values used here, and subsequently, are those tabulated by Lias et al.\textsuperscript{184} with the exception of \(\Delta H_f(\text{CNC}^+)\) and \(\Delta H_f(\text{TS})^*\), for which the values calculated by DeFrees and McLean\textsuperscript{241} are used in the calculations presented below. The equilibrium constant calculated here assumes that the transition state is the only barrier to isomerisation, and that the isomeric distribution can be explained in terms of an Arrhenius-type rate constant for crossing of this barrier in both directions (that is, for \(\text{CCN}^+ \rightarrow \text{CNC}^+\) and for \(\text{CNC}^+ \rightarrow \text{CCN}^+\)):

\[
\begin{align*}
K_{4,7} &= \frac{k_f}{k_b} \\
 k_f &= e^{-E_{a,f}/RT} \\
 k_b &= e^{-E_{a,r}/RT} \\
 E_{a,f} &= 195 \text{ kJ mol}^{-1} \\
 E_{a,r} &= 89 \text{ kJ mol}^{-1} \\
 \therefore K_{4,7} &= e^{(E_{a,r}-E_{a,f})/RT} \\
 \therefore K_{4,7} &= 2.9 \times 10^{-17} @ 300 \text{ K}.
\end{align*}
\]

It is clear, however, that this value drastically underestimates the observed \(\text{CCN}^+\) fraction, and this can be rationalised since the product ions at \(m/z\) 38 have far too short a residence time in the flow tube (\(t \sim 20 \text{ ms}\)) to achieve a thermal distribution in the face of such a large isomerisation barrier. Rather, the factor governing the \(\text{CCN}^+ / \text{CNC}^+\) distribution is the \(\text{CCN}^+ / \text{CNC}^+\) density-of-states ratio at the transition state energy: \(\text{C}_2\text{N}^+\) from reaction (4.6) is initially produced.
with ample energy to overcome the barrier, but loses this energy after repeated collisions with the He buffer gas in the flow tube.

Troe\textsuperscript{248} has determined the vibrational harmonic density of states to be

\[ \rho_{\text{vib},\text{h}}(E) = \frac{(E + a(E)E_Z)^{s-1}}{(s-1)! \prod_{i=1}^{s} (h\nu_i)} \]

where \( E \) is the energy of the species above the zero-point energy \( E_Z \), \( a(E) \) is a correction factor, \( S \) is the number of modes (including degenerate modes) of vibration, and \( \nu_i \) is the fundamental frequency of the \( i \)th vibrational mode. \( a(E) \) can be calculated according to the expression

\[ a(E) = 1 - B \omega \]

where

\[ B = (S - 1) \frac{(S + (r + d)/2)}{S} \frac{\sum_{i=1}^{s} \nu_i^2}{(\sum_{i=1}^{s} \nu_i)^2} \]

for which \( r = n_1 + 2n_2 \), where \( n_1 \) is the number of \( i \)-dimensional rotors, and \( d = 2 \) for linear molecules, \( d = 3 \) for nonlinear molecules;

and

\[ \log_{10} \omega = -1.0506(E/E_Z)^{0.25} \text{ for } E \geq E_Z \]

and

\[ \omega^{-1} = 5(E/E_Z) + 2.73\sqrt{E/E_Z} + 3.51 \text{ for } 0.1 \leq E/E_Z \leq 1 \]
This treatment neglects the contribution of rotational energy level spacings to the density of states. There is a general formula\textsuperscript{249} for the density of states

\[
N_{v_i}^r (E) = \frac{Q_r' (E + a_k E_z)^{v_{-1+\frac{1}{2}}} v_{\frac{v}{2}}}{\Gamma(v + \frac{1}{2}) \prod_{i=1}^{\nu} \hbar \nu_i}
\]

which includes vibrational and rotational contributions, but solution of this expression (in which \( Q_r' \) is the rotational partition function, \( E \) is the energy above the zero-point energy \( E_z \) of the \( v \) oscillators, and \( a_k \) is equivalent to the factor \( a(E) \) in equation (4.i) is not required since rotation will only affect the density of vibrational states if the molecule possesses rotational modes which contribute to its internal energy. In the case of a linear species such as \( \text{CCN}^+ \) or \( \text{CNC}^+ \), all the rotational energy is external and thus remains uncoupled from vibrational energy. This simplifies the density of states ratio \( \Psi \)

\[
\Psi(E, R) = \frac{\rho_{vibh}^1 (E) (1/\sigma_1 B_1)}{\rho_{vibh}^2 (E) (1/\sigma_2 B_2)}
\]

where \( E \) signifies internal, and \( R \), external, energy, and \( \sigma \) is the rotational symmetry number of the species in question, and for which

\[
B_i = \frac{\hbar}{8 \pi^2 c I_i}
\]

(where \( I \) is the moment of inertia) since for a harmonic-oscillator rigid-rotor, the density of rotational states is proportional to \( 1/\sigma B \).
Thus

\[ \Psi(E,R) = \frac{\rho_{^1vibh}(E)}{\rho_{^2vibh}(E)} \frac{(\sigma_2 h / 8 \pi^2 c I_2)}{(\sigma_1 h / 8 \pi^2 c I_1)} \]

\[ \therefore \quad \Psi(E,R) = \frac{\rho_{^1vibh}(E)}{\rho_{^2vibh}(E)} \frac{\sigma_2 I_1}{\sigma_1 I_2} \]  

This density-of-states ratio can now be calculated. Using the geometries calculated for CCN\(^+\) and for CNC\(^+\) by deFrees and McLean\(^{241}\) (see table 4.5), the required moments of inertia and the rotational symmetry numbers can be determined. From these values and from the calculated vibrational frequencies,\(^{241}\) \(\Psi\) can be determined as a function of \(C_2N^+\) energy:

---

**Table 4.5: Calculated geometries of CCN\(^+\) and CNC\(^+\).**

<table>
<thead>
<tr>
<th>Parameter (^a)</th>
<th>CCN(^+)</th>
<th>CNC(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1) (^b)</td>
<td>2257</td>
<td>1294</td>
</tr>
<tr>
<td>(v_2)</td>
<td>1077</td>
<td>1963</td>
</tr>
<tr>
<td>(v_3) (^c)</td>
<td>207</td>
<td>183</td>
</tr>
<tr>
<td>(r(C\text{-}N)) (^d)</td>
<td>1.149</td>
<td>1.227</td>
</tr>
<tr>
<td>(r(C\text{-}C))</td>
<td>1.383</td>
<td>–</td>
</tr>
<tr>
<td>(I) (^e)</td>
<td>6.879 x 10(^{-46})</td>
<td>6.000 x 10(^{-46})</td>
</tr>
<tr>
<td>(\sigma) (^f)</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

**Notes**

a. Calculated by DeFrees and McLean.\(^{241}\)
b. Vibrational frequencies, \(\text{cm}^{-1}\).
c. Doubly degenerate frequency.
d. Bond length, Angstroms.
e. Moment of inertia, \(\text{kg} \cdot \text{m}^2\).
f. Rotational symmetry number.
\[ \Psi(E,R) = 2.293 \frac{\rho_{\text{CCN}^+}}{\rho_{\text{CNC}^+}} \]  

The variation of \( \Psi \) with energy is illustrated in table 4.6. The resulting graph (see figure 4.2) shows that, at the calculated transition state energy, 1/4 of the \( \text{C}_2\text{N}^+ \) ions will be in the form \( \text{CCN}^+ \). This is very close to the isomeric ratio observed for the electron impact techniques in which \( \text{C}_2\text{N}^+ \) is injected from the ion source: at low pressures (\( P \approx 10^{-4} \) Torr) such as those in the ion source region, the time between collisions is long in comparison to the likely timescale for interconversion across the isomerisation barrier. In consequence, collisional deexcitation of the ions is inefficient and the isomer ratio produced is similar to the ratio at the transition state energy. In the case of \( \text{C}_2\text{N}^+ \) ions produced within the flow tube by the chemical reaction (4.6), the pressure is several orders of magnitude higher (\( P \approx 0.3 \) Torr) and so collision is much more frequent.

Table 4.6: \( \text{CCN}^+/\text{CNC}^+ \) density of states ratio, \( \Psi \), as a function of energy.

<table>
<thead>
<tr>
<th>Energy a</th>
<th>( \rho_{\text{CCN}^+} ) b</th>
<th>( \rho_{\text{CNC}^+} ) b</th>
<th>( \Psi(E,R) ) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>0.9645</td>
<td>8.6284</td>
<td>0.2563</td>
</tr>
<tr>
<td>-10</td>
<td>1.2846</td>
<td>10.0217</td>
<td>0.2939</td>
</tr>
<tr>
<td>0</td>
<td>1.6678</td>
<td>11.5570</td>
<td>0.3309</td>
</tr>
<tr>
<td>10</td>
<td>2.1197</td>
<td>13.2412</td>
<td>0.3671</td>
</tr>
<tr>
<td>20</td>
<td>2.6460</td>
<td>15.0810</td>
<td>0.4023</td>
</tr>
<tr>
<td>30</td>
<td>3.2521</td>
<td>17.0835</td>
<td>0.4365</td>
</tr>
<tr>
<td>40</td>
<td>3.9438</td>
<td>19.2554</td>
<td>0.4696</td>
</tr>
<tr>
<td>50</td>
<td>4.7266</td>
<td>21.6036</td>
<td>0.5017</td>
</tr>
<tr>
<td>60</td>
<td>5.6062</td>
<td>24.1349</td>
<td>0.5326</td>
</tr>
<tr>
<td>70</td>
<td>6.5882</td>
<td>26.8563</td>
<td>0.5625</td>
</tr>
<tr>
<td>80</td>
<td>7.6781</td>
<td>29.7746</td>
<td>0.5913</td>
</tr>
<tr>
<td>90</td>
<td>8.8816</td>
<td>32.8967</td>
<td>0.6191</td>
</tr>
<tr>
<td>100</td>
<td>10.2413</td>
<td>36.2294</td>
<td>0.6458</td>
</tr>
</tbody>
</table>

Notes
a. Energy, in kJ mol\(^{-1}\), relative to calculated transition state energy.
b. Density of states, in (cm\(^{-3}\))\(^{-1}\), for \( \text{CCN}^+ \) and for \( \text{CNC}^+ \).
c. Calculated density of states ratio \( \rho_{\text{CCN}^+}/\rho_{\text{CNC}^+} \).
Collisional deexcitation now competes much more efficiently with isomerisation, so the isomer ratio from reaction of C+(4P) reflects the density of states ratio at an energy significantly above the transition state energy, where \( \Psi > 0.33 \). The observed CCN⁺/CNC⁺ ratio from the reaction of C⁺ with C₂N₂ is thus consistent with less than 40% C⁺(4P) in the m/z 12 signal: determination of the exact fraction of metastable C⁺ required to account for the observed ratio is not possible given the uncertainty in the relative energy values and in the relative rates of isomerisation and collisional deexcitation.

The results of rate measurements and product analyses for CCN⁺/CNC⁺ reactions can be compared with those obtained in an independent study of C₂N⁺ chemistry by Bohme et al. The two studies are, in general, in good agreement, with few major differences. Bohme et al used the technique of electron impact upon

Figure 4.2: Calculated CCN⁺ / CNC⁺ density of states ratio.
C2N2 to produce C2N+: their observed isomeric ratio of 0.25:0.75 for CCN+:CNC+ is in good agreement with our findings for this method (see table 4.4), and with the ratio expected from the density-of-states ratio at the transition state energy. They used the reaction of C2N+ with O2

\[
\begin{align*}
\text{CCN}^+ + \text{O}_2 & \rightarrow \text{C}_2\text{NO}^+ + \text{O} \quad (4.9) \\
\text{CNC}^+ + \text{O}_2 & \rightarrow \text{no reaction} \quad (4.10)
\end{align*}
\]

\[k_{4.9} = 3.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]

\[k_{4.10} < 1.0 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]

(4.9) (4.10)

to distinguish the ions. Product analyses for CNC+ were conducted by addition of sufficient O2 to remove all CCN+: thus, in their study, differences in the product distributions for CCN+ and CNC+ are reported for the reactions with H2O, OCS and CS2. In our study, separate product analyses in this manner were not attempted due to the difficulties in allowing for the possible reactivity of the primary products with the O2 (or other titrant) added to remove CCN+.

Significant differences in the rate coefficients and product distributions obtained by the two studies are:

(i). For the reaction of CCN+ with H2, the rate coefficient which we obtained was \(9.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), significantly larger than the value \(k_{\text{obs}} = 3.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) reported by Bohme et al. The disagreement between these results is not covered by the estimated uncertainty of the rate coefficient determinations (±40% in the study of Knight et al,241 ±50% by Bohme et al245).
(ii). For the reactions of C$_2$N$^+$ with N$_2$O and C$_2$H$_2$, we observed slight but reproducible curvature evident in the experimental graphs for decay of the m/z 38 ion signal with added reactant, and on this basis determined $k_{CCN^+} > k_{CNC^+}$ for these reactions. Bohme et al reported $k_{CCN^+} = k_{CNC^+}$ for reaction with each of these reactants.

(iii). Bohme et al reported a 30% product channel for production of C$_2$NO$^+$ + H$_2$ from the reaction of CCN$^+$ with H$_2$O, which we did not observe.

(iv). Bohme et al reported a 20% product channel (C$_3$O$^+$ + NO$^-$) for the reaction CCN$^+$ + CO$_2$, which we did not observe.

Bohme et al also determined that the reaction of C$^+$ with HCN

$$\begin{align*}
C^+ + HCN &\rightarrow CCN^+ + H^- \\
&\rightarrow CNC^+ + H^-
\end{align*}$$

(4.1a) (4.1b)

$\Delta H_{4.1a} = -5$ kJ mol$^{-1}$

$\Delta H_{4.1b} = -100$ kJ mol$^{-1}$

produces CCN$^+$ and CNC$^+$ in a ratio ~ 1:3, in contrast to the expectations of Haese and Woods$^{237}$ that this reaction could only produce CNC$^+$. This result is in conflict also with the finding of Daniel et al,$^{250}$ in a crossed ion beam - molecular beam study, that CNC$^+$ is the sole product of the above reaction. The production of CCN$^+$ requires that reaction (4.1a) is exothermic, which is in doubt given the uncertainty in the tabulated heats of formation; it should also be noted that the
CCN\(^+\) fraction observed here may arise solely from, or be enhanced due to, reaction of the metastable C\(^+\) (\(^{4}\)P) with HCN.

The rapid reactivity which we observed for the reaction of CCN\(^+\) with H\(_2\) shows that this is the only reaction of CCN\(^+\) liable to be of importance in interstellar cloud chemistry, since this reaction will ensure that the ion is depleted before it can undergo reactions with any other cloud components. The lack of reactivity for CNC\(^+\) with H\(_2\) indicates that reactions of CNC\(^+\) with 'trace' cloud components (notably the rapid rates observed for its reactions with HCN, NH\(_3\) and C\(_2\)H\(_2\)) will be relevant to cloud chemistry. Reactions of CNC\(^+\) with CH\(_4\), C\(_2\)H\(_2\) and HCN are observed to result in lengthening of the carbon skeleton in the product ions: in this manner CNC\(^+\) is expected to contribute to the production of more complex molecules in interstellar clouds.

The interstellar chemistry of CCN\(^+\) is closely linked with that of HCN/HNC: reaction of C\(^+\) with CHN is likely to be the major source of interstellar CCN\(^+\)

\[
\begin{align*}
\text{C}^+ + \text{HCN} & \rightarrow \text{CCN}^+ + \text{H}^- & [0.25?]^{245} (4.1a) \\
\text{C}^+ + \text{HNC} & \rightarrow \text{CCN}^+ + \text{H}^- & [1.0?]^{237} (4.2a)
\end{align*}
\]

and the reaction of CCN\(^+\) with H\(_2\)

\[
\begin{align*}
\text{CCN}^+ + \text{H}_2 & \rightarrow \text{HCNH}^+ + \text{C} & [0.90] \quad (4.10a) \\
& \rightarrow \text{C}_2\text{H}_2\text{N}^+ & [0.10] \quad (4.10b)
\end{align*}
\]
indicates that most CCN+ is rapidly converted to protonated HCN/HNC. HCNH+ is unreactive with H2 and CO, and dissociative recombination of this ion is expected to yield both HCN and HNC:

\[
\begin{align*}
\text{HCNH}^+ + e^{-} & \rightarrow \text{HCN} + \text{H}^+ & \text{(4.11a)} \\
& \rightarrow \text{HNC} + \text{H}^+ & \text{(4.11b)} \\
& \rightarrow \text{CN}^+ + \text{H}_2 & \text{(4.11c)}.
\end{align*}
\]

In this context, the chemistry of CCN+ serves mainly to 'cycle' CHN between the molecular and protonated forms and hence is of no apparent synthetic significance to cloud chemistry, except for the small channel in reaction (4.10) leading to the adduct ion C2H2N+. The reactivity of this C2H2N+ ion has not yet been explored, but its apparent lack of reaction with H2 suggests that (assuming that channel (4.10b) occurs under interstellar, as well as laboratory, conditions) its reactivity with other interstellar molecules will be relevant to models of cloud chemistry.

**Section 4.2: \text{C}_3\text{N}^+**

The cyanoethynyl radical CCCN· was first reported, upon the basis of its calculated rotational spectrum,\textsuperscript{251} as a constituent of the circumstellar envelope IRC+10216.\textsuperscript{252} A subsequent detection of CCCN· within the cold cloud TMC-1 was reported by Friberg et al.;\textsuperscript{253} the isocyanoethynyl radical CCNC· has also been proposed as an interstellar species,\textsuperscript{254} but has not yet been detected.
$C_3N^-$ is likely to be formed in the interstellar environment by dissociative recombination of ionized or protonated cyanoacetylene

$$\begin{align*}
HC_3N^+ + e & \rightarrow C_3N^- + H^- \quad (4.12) \\
HC_3NH^+ + e & \rightarrow HCCCN + H^- \\
& \rightarrow C_3N^- + H_2 \quad (4.13a) \\
& \quad (4.13b)
\end{align*}$$

or by cosmic-ray-induced UV photodissociation of HC$_3$N (that is, resulting from UV radiation produced by the interaction of cosmic rays with other interstellar molecules). In this context, the UV photolysis of HC$_3$N has been explored by Halpern et al.$^{255}$ The molecular ion C$_3$N$^+$ can also be formed by high-energy phenomena involving HC$_3$N: for example, in the cosmic-ray ionisation of HC$_3$N within interstellar clouds.

In 1986 Knight$^{166}$ reported the preliminary results of measurements performed on the Canterbury SIFT demonstrating differing reactivity for two isomers of the formula C$_3$N$^+$. These ions, produced by electron impact upon HC$_3$N in the ion source, displayed differences in their reactivity with H$_2$ (see figure 4.3) and with CH$_4$. For reaction of the more reactive isomer ($\sim$90% of the m/z 50 ion signal) with H$_2$, $k_{\text{obs}} = 9.1 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$ was reported: the remaining isomer at m/z 50 appeared unreactive.

My initial studies of C$_3$N$^+$ reactivity, performed using HC$_3$N as the source gas, confirmed this pattern of reactivity: curvature characteristic of two isomeric forms at m/z 50 was seen in the reactions of C$_3$N$^+$ with CO$_2$, HCN and O$_2$ as well as with H$_2$ and CH$_4$. However, the product distributions of these reactions were
not easily characterized since injection of m/z 50 could not be accomplished without the accompanying injection of a signal at m/z 51, as large as (or larger than) the C₃N⁺ signal.

In most instances the reactivity of this HC₃N⁺

---

**Figure 4.3:** Experimentally observed decay curve for reaction of C₃N⁺ (generated from electron impact upon HC₃N) with H₂. (a) Graph covering the entire range of H₂ flows. (b) Graph highlighting the initial rapid decay. The absence of linearity in this decay curve very clearly demonstrates the existence of two forms of C₃N⁺, with k = 1.0 x 10⁹ cm³ molec⁻¹ s⁻¹ for the reactive form (accounting for 90% of the m/z 50 ion signal in this instance).

![Graph depicting the entire range of H₂ flows employed.](image)

![Graph showing the initial decay due to the more reactive isomer](image)
contaminant was almost as rapid as that of the more reactive C$_3$N$^+$ form, complicating product analysis. For this reason, and due to difficulties$^{256,257}$ in reproducing an earlier successful$^{258}$ synthesis of cyanoacetylene, alternative sources of the C$_3$N$^+$ ion were sought.

Methyl cyanoacetylene, CH$_3$–C≡C–C≡N, was initially chosen: it was felt that cleavage of the methyl group during ionisation would be likely to give rise to a "purer" C$_3$N$^+$ signal - that is, one less contaminated by a signal at m/z 51. However, when methylcyanoacetylene was employed as a source gas the signal at m/z 50 was accompanied by contaminating signals at m/z 51 (50% as large as at m/z 50) and at m/z 49 (20%). The signal at m/z 49 is a problem - improving the resolution of the upstream quadrupole mass spectrometer would allow injection of m/z 50 essentially uncontaminated by neighbouring masses, but m/z 49 can only be C$_4$H$^+$:

$$\text{CH}_3\text{C}≡\text{C}≡\text{N} + e → \text{C}_4\text{H}^+ + \text{H}_2 + \text{N}^− + 2e$$  \hspace{1cm} (4.14)

If a sizeable signal at m/z 49 is produced, then production of C$_4$H$_2^+$ and C$_4$H$_3^+$ is also very likely - and C$_4$H$_2^+$ cannot be distinguished from C$_3$N$^+$ on the basis of mass. For this reason, therefore, CH$_3$C$_3$N was not employed further as a source of C$_3$N$^+$.

Dicyanoacetylene, N≡C–C≡C–C≡N, was selected next: cleavage of either CN group during ionisation will produce C$_3$N$^+$, and since the source gas contains only C and N atoms, contamination at neighbouring masses should not be a significant problem.
Table 4.7: Reactions of C$_3$N$^+$ + X.

<table>
<thead>
<tr>
<th>X</th>
<th>Products $^{a,b}$</th>
<th>$k_1$$^{a,c}$</th>
<th>$k_2$$^{d}$</th>
<th>$k_3$$^{e}$</th>
<th>-ΔH $^{a,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>HCN$^+$ + H$^-$</td>
<td>[0.90]</td>
<td>0.81</td>
<td>&lt;0.0005</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>H$_2$CN$^+$</td>
<td>[0.10]</td>
<td></td>
<td></td>
<td>721</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>C$_2$H$_3$N$^+$ + C$_2$H$_2$</td>
<td>[0.18]</td>
<td>0.97</td>
<td>&lt;0.001</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>(or C$_3$H$_4^+$ + CN$^-$)</td>
<td></td>
<td></td>
<td></td>
<td>214$^f$</td>
</tr>
<tr>
<td></td>
<td>HCN$^+$ + CH$_3$</td>
<td>[0.50]</td>
<td></td>
<td></td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>H$_2$CN$^+$ + CH$_2$</td>
<td>[0.18]</td>
<td></td>
<td></td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>C$_2$NCH$_3^+$ + H$^.$</td>
<td>[0.14]</td>
<td></td>
<td></td>
<td>180$^g$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NH$_3^+$ + C$_3$N$^.$</td>
<td>[0.80]</td>
<td>2.0</td>
<td>2.0</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>CH$_2$N$^+$ + C$_2$HN</td>
<td>[0.20]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>CH$_3$N$^+$ + C$_2$O</td>
<td>[0.03]</td>
<td>0.90</td>
<td>0.05</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td>HCN$^+$ + OH$^.$</td>
<td>[0.67]</td>
<td></td>
<td></td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>HCN$^+$ + H$^-$.</td>
<td>[0.30]</td>
<td></td>
<td></td>
<td>&gt;317</td>
</tr>
<tr>
<td>N$_2$</td>
<td>C$_3$N$_2^+$</td>
<td>0.02</td>
<td>&lt;0.0005</td>
<td>0.73</td>
<td>-</td>
</tr>
<tr>
<td>O$_2$</td>
<td>C$_2$NO$^+$ + O</td>
<td>[0.58]</td>
<td>0.50</td>
<td>0.01</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>C$_2$N$^+$ + CO$_2$</td>
<td>[0.42]</td>
<td></td>
<td></td>
<td>529$^i$</td>
</tr>
<tr>
<td>CO</td>
<td>C$_3$NCO$^+$</td>
<td>0.54</td>
<td>&lt;0.001</td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>HCN$^+$ + H$^.$</td>
<td>[0.95]</td>
<td>1.02</td>
<td>&gt;0.06$^k$</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>H$_2$CN$^+$</td>
<td>[0.05]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>HCN$^+$ + CN$^-$</td>
<td>[0.98]</td>
<td>2.2</td>
<td>0.23</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>C$_3$N.HCN$^+$</td>
<td>[0.02]</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>C$_3$NO$^+$ + CO</td>
<td>0.35</td>
<td>&lt;0.001</td>
<td>0.79</td>
<td>-1</td>
</tr>
<tr>
<td>C$_2$N$_2$</td>
<td>C$_2$N$_2^+$ + CN$^.$</td>
<td>[0.21]</td>
<td>1.3</td>
<td>0.07</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>C$_3$N.C$_2$N$_2^*$</td>
<td>[0.79]</td>
<td></td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

Notes

a. See footnotes (a) - (d) for table (4.2).
b. Products and product ratios listed are for the reactions of the CCCN$^+$ isomer, generated by electron bombardment on a 1:20 mixture of C$_4$N$_2$ in He.
c. Rate coefficient observed for reaction of the more reactive C$_3$N$^+$ isomer, determined in this study as CCCN$^+$.
d. Rate coefficient observed for reaction of the less reactive C$_3$N$^+$ isomer, determined in this study as c-C$_3$N$^+$.
e. ΔH for the reaction CCCN$^+$ + X, calculated on the basis of ΔH$_f$(CCCN$^+$) = 1850 kJ mol$^{-1}$ according to Harland and Maclagan.$^{259}$
f. Assuming a CH$_2$=C=CH$_2^+$ structure for the C$_2$H$_4^+$ ion.
g. Calculated using ΔH$_f$(CH$_3$C=C=CH$_2^+$) = 1378 kJ mol$^{-1}$; a more likely product structure is C=C-C=NCH$_3^+$, which might be expected to have a lower heat of formation.
h. The occurrence of this channel requires ΔH$_f$(C$_2$O) < 661 kJ mol$^{-1}$. 
Ionisation of C₄N₂ in the ion source produced a large signal at m/z 76 (C₄N₂⁺, typically 2000 counts per second (cps)), with smaller sizeable signals at m/z 50 (C₃N⁺, ~ 250 cps), m/z 48 (C₄⁺, ~ 200 cps) and m/z 26 (CN⁺, ~ 200 cps). Injection of m/z 50 could be accomplished satisfactorily with negligible contamination by m/z 48. Most often, dicyanoacetylene was used as a source gas in the form of a 1:20 solution in helium, since neat C₄N₂ displayed a propensity to attack the ion-source filament to an excessive degree.

Rate coefficients and product distributions could be determined for C₃N⁺ + X for a wide variety of neutral reagents, as summarised in table 4.7. One surprising observation, apparent from the reaction of C₃N⁺ + H₂ (see figure 4.4), was that C₃N⁺ generated from C₄N₂ is essentially all (≥ 95%) in the more reactive form, and thus this method of generation cannot be used to determine the reactivity of the less reactive form with reagents X. For this reason it was felt necessary to synthesise further HC₃N, and this was done using the method of Moreu and Bongrand. ²⁶⁰,²⁶¹

Subsequently, problems were encountered in attempting to satisfactorily resolve between the signal at m/z 50 (C₃N⁺) and the substantially larger signal at m/z 51 (HC₃N⁺): the two adjacent signals could not be resolved except by operating the downstream quadrupole mass filter at an unacceptably high resolution (r = 8.9), at which setting the signal at m/z 50 was, at a few counts per second, too small to
permit accurate rate measurements or determination of the isomer ratio. The flow tube was then dismantled and cleaned: upon reassembly, the performance of the downstream mass spectrometer was substantially enhanced. The resolution at the appropriate mass range was investigated by injection (at m/z 52) of \( \text{C}_2\text{N}_2^+ \), generated by electron bombardment of \( \text{C}_2\text{N}_2 \) in the ion source. At a resolution setting of \( r=8.2 \) on the downstream mass spectrometer, the ion signal due to \( \text{C}_2\text{N}_2^+ \) was maximised at m/z 52.0 (I \( \sim \) 2000 cps) and decreased rapidly with decreasing m/z: at m/z 51.3 and below, I < 1 cps (see figure 4.5). This indicates that at this resolution setting, a reactant ion signal comprising both \( \text{C}_3\text{N}^+ \) and \( \text{HC}_3\text{N}^+ \) can be satisfactorily resolved: at a setting on the downstream mass spectrometer of m/z 50.0, no \( \text{HC}_3\text{N}^+ \) will be transmitted by the quadrupole. Subsequent injection of a 1:6 mixture of \( \text{C}_3\text{N}^+ \) and \( \text{HC}_3\text{N}^+ \) showed (see figure 4.6) that, although at m/z settings between 50.0 and 51.0 the ion signal did not

Figure 4.4: Experimental decay curve for reaction of \( \text{C}_3\text{N}^+ \) (generated from electron impact upon \( \text{C}_4\text{N}_2 \)) with \( \text{H}_2 \). For \( \text{C}_3\text{N}^+ \) produced by this method, less than 5% is unreactive towards \( \text{H}_2 \), as shown by the arrow which denotes the best-fit intercept for this isomer. Ionisation of \( \text{C}_4\text{N}_2 \) produces less c-\( \text{C}_3\text{N}^+ \) than does ionisation of \( \text{HC}_3\text{N} \).
decrease to zero, it did decrease to a low value consistent with two well-resolved adjacent-mass signals. This permitted us to determine the isomeric ratio for C₃N⁺, confident that the signal at m/z 50 contained no contamination from m/z 51. The reactivity of the C₃N⁺ ion signal thus obtained was consistent with that observed previously: 90% of the C₃N⁺ reacted at virtually the collision rate, whereas the remaining 10% was unreactive. The reactivity of this minority C₃N⁺ isomer with various neutrals X is also listed in table 4.7.

The observation that the largest proportion of the m/z 50 ion signal was the most reactive component suggested very strongly that this reactive component was CCCCCN⁺ and that this isomer is higher in energy than the less reactive component, for which CCNC⁺ and a cyclic C₃N⁺ ion are possible structures.

Figure 4.5: Mass spectrum obtained from C₂N₂⁺ in the region of m/z 52, using a resolution setting of 8.2 upon the downstream Q.M.S. The signal at m/z 53 is most probably due to C₂N₂H⁺ from reaction of C₂N₂⁺ with H₂O within the flow tube: alternatively, some contribution to this m/z 53 signal may arise from injection of ¹²C¹³CN₂⁺ from the ion source.
Harland and Maclagan\textsuperscript{259} have studied the C\textsubscript{3}N\textsuperscript{+} system both experimentally and theoretically. In their study, the appearance energy of the CCCN\textsuperscript{+} isomer was established by near-monochromatic electron impact ionisation of HC\textsubscript{3}N: AP(CCCN\textsuperscript{+}) = 17.78 ± 0.08 eV, corresponding to ΔH\textsubscript{f}(CCCN\textsuperscript{+}) = 1850 kJ mol\textsuperscript{-1}. A sharp break in the ionisation efficiency curve was observed at around 18.7 eV, which they interpreted as indicating the formation of a higher-energy isomer identified as c-C\textsubscript{3}N\textsuperscript{+} on the basis of this isomer's calculated heat of formation. Harland and Maclagan's identification of CCCN\textsuperscript{+} as the lowest-energy C\textsubscript{3}N\textsuperscript{+} isomer appears in serious disagreement with our observation that the more abundant isomer of C\textsubscript{3}N\textsuperscript{+} produced from HC\textsubscript{3}N is very substantially more reactive with a wide variety of neutral reagents than is the less abundant C\textsubscript{3}N\textsuperscript{+}.

Figure 4.6: Mass spectrum obtained from C\textsubscript{3}N\textsuperscript{+} and HC\textsubscript{3}N\textsuperscript{+} in the region of m/z 50, using a resolution setting of 8.2 upon the downstream Q.M.S. The shoulders of the m/z 50 and m/z 51 peaks are not completely resolved at m/z 50.5, but the spectrum seen for injection of C\textsubscript{2}N\textsubscript{2}\textsuperscript{+} (see figure 4.5) indicates that this resolution setting is suitable for complete separation of adjacent-mass ions in this mass range: that is, no HC\textsubscript{3}N\textsuperscript{+} ions will contribute to the signal at m/z 50. The signal at m/z 52 is probably a mixture of HC\textsubscript{3}NH\textsuperscript{+} and H\textsuperscript{12}C\textsubscript{2}\textsuperscript{13}CN\textsuperscript{+} ions.
isomer. The general characteristic that ion-molecule reactions usually lack activation energy barriers suggests very strongly that the more reactive an isomer, the higher its heat of formation. Indeed, the only previously reported ion-molecule reaction in which a higher-energy isomer is the less reactive form is in the reaction of \( \text{N}_2\text{OH}^+ \) isomers with \( \text{NO} \),\(^{262,263}\) where the collision complex from the higher-energy ion \( \text{HNNO}^+ \) must undergo substantially greater rearrangement than that of \( \text{NNOH}^+ \) to have access to the only available exothermic product channel.

The difference in heats of formation of the two \( \text{N}_2\text{OH}^+ \) isomers is much smaller than the difference in the heats of formation of the \( \text{C}_3\text{N}^+ \) isomers as determined from appearance potentials. For this reason, it is tempting to deduce that the appearance potential at 18.7 eV is indicative of the barrier height to isomerisation to the less reactive form of \( \text{C}_3\text{N}^+ \). This explanation reconciles the experimental results but leaves unresolved the discrepancy between theory and experiment: a higher-energy isomer should not be universally less reactive than the lowest-energy form. A test for this hypothesis (that the appearance potential for the less abundant isomer may represent the isomerisation barrier, rather than the heat of formation of this isomer) is to investigate the proportion of the \( \text{C}_3\text{N}^+ \) isomers produced in situations in which the structure of the reactants does not appear to favour formation of the CCCN\(^+\) isomer.

Reactions which have been reported\(^{167,214,238,247,264,265}\) to produce \( \text{C}_3\text{N}^+ \) are

\[
\text{He}^+ + \text{HC}_3\text{N} \rightarrow \text{C}_3\text{N}^+ + \text{H}^+ + \text{He} \quad [0.31] \quad (4.15)
\]

\[\Delta H_{4,15} = -655 \text{ kJ mol}^{-1}\]

\[k_{4,15} = 7.9 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]
\[ \text{CN}^+ + \text{C}_2\text{N}_2 \rightarrow \text{C}_3\text{N}^+ + \text{N}_2 \] \hspace{1cm} [0.10] (4.16)
\[ \Delta H_{4.16} = -251 \text{ kJ mol}^{-1} \]
\[ k_{4.16} = 1.4 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

\[ \text{C}_2^+ + \text{C}_2\text{N}_2 \rightarrow \text{C}_3\text{N}^+ + \text{CN}^- \] \hspace{1cm} [0.30] (4.17)
\[ \Delta H_{4.17} = -20 \text{ kJ mol}^{-1} \]
\[ k_{4.17} = 1.5 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

\[ \text{C}_2^+ + \text{HCN} \rightarrow \text{C}_3\text{N}^+ + \text{H}^- \] \hspace{1cm} [1.0] (4.18)
\[ \Delta H_{4.18} = -65 \text{ kJ mol}^{-1} \]
\[ k_{4.18} = 2.65 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

and

\[ \text{C}_2^+ + \text{HC}_3\text{N} \rightarrow \text{C}_3\text{N}^+ + \text{C}_2\text{H}^- \] \hspace{1cm} [0.50] (4.19)
\[ \Delta H_{4.19} = +66 \text{ kJ mol}^{-1} \]
\[ k_{4.19} = 4.8 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

where the \(\Delta H\) values are calculated using \(\Delta H_f(\text{CCCN}^+) = 1850 \text{ kJ mol}^{-1}\), as determined by Harland.\textsuperscript{266} Reaction (4.19) has been studied both by Raksit and Bohme\textsuperscript{214,247} and by Knight et al.\textsuperscript{167,267} the former determined \(\text{C}_3\text{N}^+\) to be the major product, whereas Knight et al detected products at m/z 48 (\(\text{C}_4^+\)), m/z 49 (\(\text{C}_4\text{H}^+\)) and m/z 51 (\(\text{HC}_3\text{N}^+\)) but did not find any \(\text{C}_3\text{N}^+\) to be produced by this reaction. Note that production of \(\text{C}_3\text{N}^+\) is quite sizeably endothermic, according to Harland's value for \(\Delta H_f(\text{CCCN}^+)\).
We determined the isomeric distribution of C₃N⁺ produced by reactions (4.16), (4.17) and (4.18). This was done by injection of the reactant ions (C₂⁺ from electron impact upon C₄N₂, CN⁺ from electron impact upon C₂N₂) from the ion source into the flow tube, addition of the reactant neutrals (HC₃N or C₂N₂) at portal 1, and addition of N₂ at portal 2. Since the C₃N⁺ ions are produced by reactions which occur throughout the tube's length, the rate of C₃N⁺ removal by addition of N₂ will not allow easy determination of the rate of reaction of the C₃N⁺ with N₂: however, since N₂ is unreactive with any of the other species in the flow tube, suppression of the m/z 50 ion signal by added N₂ indicates that CCCN⁺ formed by the reaction under consideration has reacted with nitrogen. This method thus ascribes a lower limit to the fraction of CCCN⁺ isomers within the C₃N⁺ ion signal. The results are summarised in table 4.8. These results clearly indicate that CCCN⁺ is the major or only form of C₃N⁺ to be produced by all of these reactions. Thus (contrary to our earlier suspicions) CCCN⁺ is indeed the lowest-energy isomer, supporting the relative C₃N⁺ energies calculated by Maclagan.²⁵⁹

<table>
<thead>
<tr>
<th>Method</th>
<th>Site</th>
<th>%CCCN⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + HC₃N</td>
<td>IS</td>
<td>90 ± 2 c</td>
</tr>
<tr>
<td>e + HC₃N/He</td>
<td>IS</td>
<td>90 ± 2 c</td>
</tr>
<tr>
<td>e + C₂N₂</td>
<td>IS</td>
<td>≥95 c</td>
</tr>
<tr>
<td>C₂⁺ + C₂N₂</td>
<td>FT</td>
<td>≥98 e</td>
</tr>
<tr>
<td>CN⁺ + C₂N₂</td>
<td>FT</td>
<td>≥95 e</td>
</tr>
<tr>
<td>C₂⁺ + HC₃N</td>
<td>FT</td>
<td>≥90 e</td>
</tr>
</tbody>
</table>

Notes
a. Method of C₃N⁺ generation employed.
b. Site of m/z 50 production. IS = ion source; FT = flow tube.
c. Determined by reaction with H₂.
d. Using a 1:20 mixture of HC₃N in He.
e. Determined by reaction with N₂.
Having demonstrated that CCCN$^+$ is indeed the lowest-energy isomer, it then becomes necessary to explain how this ion can be more reactive than the higher-energy form, to which we ascribe, in accordance with the findings of Harland and Maclagan$^{259}$ the structure c-C$_3$N$^+$. A species with higher $\Delta H_f$ will be less reactive than a lower energy species if there are significantly higher barriers to the reaction of this high-energy species. Similar arguments have been presented for the lability and stability of transition metal complexes. There are, however, no apparent precedents in ion-molecule chemistry to explain why the barriers for reaction of c-C$_3$N$^+$ with the majority of reagents used here should be so much larger than those for CCCN$^+$. An alternative explanation is that the isomer with higher $\Delta H_f$ will be less reactive if its product channels are endothermic while the lower-energy isomer has exothermic channels possible. Such a scenario requires that the reaction products from the higher-energy isomer have unusually high heats of formation. Why should this be so?

One possible rationale is found in the structure of the c-C$_3$N$^+$ ion as determined by Harland and Maclagan.$^{259}$ The bond lengths of the C$_3$N$^+$ ring (see figure 4.7) are very similar to those expected for an aromatic heterocycle, and very different from the expected values for a singly- or doubly-bonded system. If the c-C$_3$N$^+$ ion were aromatic - that is, if it possessed 6 $\pi$ electrons delocalised around the 4-membered ring - then it might well have a lower heat of formation than that expected upon the basis of ring strain (which must be considerable, since the ion seems to have a bicyclo structure: compare the length of bond c with that expected for a C–C single bond). Formation of products, or of a stable collision complex, might involve the loss of this aromatic character, and thus necessitate an endothermic reaction to give products. Theoretical calculations exploring
the structures, and heats of formation, of possible products such as c-C₃NH⁺ and c-C₃NH₂⁺, would be very useful in testing this hypothesis. A problem with this hypothesis is that the existence of a 6 π electron cloud in a four-centre molecular orbital seems implausible, and is not reflected by the calculated electronic configuration.²⁵⁹ An alternative explanation, involving two 2 π systems associated with the two rings present, is also unsatisfactory since the 'central' C–C bond would be a part of both π systems, which would suggest a shorter C–C bond length than has been calculated in this instance. It seems more probable, though less helpful in explaining the observed unreactivity of the cyclic species, that c-C₃N⁺ is not aromatic but possesses equivalent bond order (1.5) to aromatic species.

![Figure 4.7: c-C₃N⁺ structure. Comparison of calculated bond lengths with literature values for various bond types.](image)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Angstroms)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.350</td>
<td>259</td>
</tr>
<tr>
<td>b</td>
<td>1.386</td>
<td>259</td>
</tr>
<tr>
<td>c</td>
<td>1.542</td>
<td>259</td>
</tr>
<tr>
<td>C–N single bond</td>
<td>1.472 - 1.479</td>
<td>186</td>
</tr>
<tr>
<td>C=N double bond</td>
<td>1.30</td>
<td>260</td>
</tr>
<tr>
<td>C–N bond (aromatic heterocycle)</td>
<td>1.352 ± 0.005</td>
<td>186</td>
</tr>
<tr>
<td>C–C single bond</td>
<td>1.541 ± 0.003</td>
<td>186</td>
</tr>
<tr>
<td>C=C double bond</td>
<td>1.337 ± 0.006</td>
<td>186</td>
</tr>
<tr>
<td>C–C bond (aromatic compound)</td>
<td>1.395 ± 0.003</td>
<td>186</td>
</tr>
</tbody>
</table>
Our studies of C₃N⁺ reactivity indicate that CCCN⁺ is exceptionally reactive - it reacted with near-unit efficiency with virtually all of the reagents tested (see table 4.7). The rapid reaction with hydrogen shows that CCCN⁺ will be rapidly depleted within interstellar clouds; the products of this reaction

$$\text{CCCN}^+ + \text{H}_2 \rightarrow \text{HC}_3\text{N}^+ + \text{H}^- \quad [0.90] \quad (4.20a)$$

$$\rightarrow \text{HC}_3\text{NH}^+ \quad [0.10] \quad (4.20b)$$

$$k_{4.20} = 8.1 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

are both of importance in the interstellar synthesis of cyanoacetylene.¹⁶⁷,²⁶⁷ The reaction of CCCN⁺ with CO may also be of some interstellar significance: this reaction

$$\text{CCCN}^+ + \text{CO} \rightarrow \text{C}_3\text{N.CO}^+ \quad (4.21)$$

$$k_{4.21} = 5.4 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

$$k_{4.21} > 5.1 \times 10^{-26} \text{ cm}^6 \text{molec}^{-2} \text{s}^{-1}$$

is observed to occur at an appreciable fraction of the apparent bimolecular collision rate at 0.3 Torr, so the analogous radiative association process may also occur rapidly under interstellar conditions.

Other CCCN⁺ reactions are unlikely to play a significant rôle in interstellar cloud chemistry, although they may be important in the chemistry of hydrogen-free planetary atmospheres such as that of Titan. The reaction with C₂H₂, for example, is of relevance to the synthesis of cyanodiacylene, HC₅N, in such an
environment: Kunde et al\textsuperscript{194} have reported the detection of several polyyne\textsubscript{s}, including HC\textsubscript{3}N, in the Titanian atmosphere.

Although apparently too slow to be of any relevance to the chemistry of extraterrestrial environments, the reaction with N\textsubscript{2} is notable: to our knowledge, this reaction is the only such association reaction yet reported. The structure of the C\textsubscript{3}N\textsubscript{3}\textsuperscript{+} ion formed, which must represent an adduct ion collisionally stabilised with reasonable efficiency ($k_{\text{obs}} \sim 0.03$ $k_{c}$), is a matter for conjecture (and worth theoretical investigation). The only reaction for which a C\textsubscript{3}N\textsubscript{3}\textsuperscript{+} product has been reported previously is

\[
\text{C}_4\text{N}_4\textsuperscript{+} + \text{C}_2\text{N}_2 \rightarrow \text{C}_3\text{N}_3\textsuperscript{+} + \text{C}_3\text{N}_3. \quad (4.22a)
\]
\[
\rightarrow \text{C}_5\text{N}_5\textsuperscript{+} + \text{CN}. \quad (4.22b)
\]

described by Raksit and Bohme\textsuperscript{247} as part of a SIFT study of C\textsubscript{2}N\textsubscript{2} ion-molecule chemistry: no product ratio or rate coefficient is reported for this reaction, but it appears from the data given\textsuperscript{247} to be slow, $k_{4,22} < 0.1$ $k_{c}$. The same study of C\textsubscript{2}N\textsubscript{2} chemistry reported also the reaction of the CCCN\textsuperscript{+} ion with C\textsubscript{2}N\textsubscript{2}, giving C\textsubscript{5}N\textsubscript{3}\textsuperscript{+} as the major product with some production of C\textsubscript{4}N\textsubscript{2}\textsuperscript{+} also. Raksit and Bohme's product analysis for this reaction is in excellent agreement with the products determined in our own experiments: however, our rate coefficient is larger than their value of $\sim 4.5 \times 10^{-10}$ cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1}.

The reaction with CH\textsubscript{4} may be compared with the reactions of C\textsubscript{5}N\textsuperscript{+} and C\textsubscript{7}N\textsuperscript{+} with methane, which have been studied using Fourier transform mass spectrometry.\textsuperscript{269,270} C\textsubscript{5}N\textsuperscript{+} and C\textsubscript{7}N\textsuperscript{+} have structures very similar to that of
CCCN$^+$ (differing merely by the number of C≡C− linkages present), and so a similar reactivity is expected. In fact, few similarities in reactivity are observed, although the major channel for reaction of all three ions is H−atom abstraction. The product ion at m/z 40 may be accompanied by C$_2$H$_2$ formation, showing a parallel to a minor channel seen for C$_5$N$^+$ and C$_7$N$^+$. Prominent channels for the reaction of C$_5$N$^+$ and C$_7$N$^+$ which were not observed in the present study are hydride transfer (23% of products for each of C$_5$N$^+$ and C$_7$N$^+$) and formation of C$_3$H$_3^+$ accompanied by neutral cyano(poly)yne formation (5% and 10% for C$_5$N$^+$ and C$_7$N$^+$, respectively). These reaction channels are substantially exothermic for C$_3$N$^+$ also, so their absence in this instance suggests differences in the mechanism of reactivity of C$_3$N$^+$ when compared with these larger C$_5$N$^+$ ions. These differences may in fact arise because of the differences in experimental technique: the studies involving C$_5$N$^+$ and C$_7$N$^+$ ions use an ICR-based technique, in which reactant ions are not thermalised because of the low pressures. This is illustrated by the occurrence of hydride transfer in the reactions of C$_4$N$^+$ and C$_6$N$^+$. Thus the differences in product channels may merely reflect the more quiescent conditions and longer collision complex lifetimes pertinent to SIFT studies.

In the present study, determination of the products due to the less reactive isomer, c-C$_3$N$^+$, was not attempted due to the difficulties associated with obtaining a pure signal of this isomer. No source of C$_3$N$^+$ gave better than 10% of c-C$_3$N$^+$ at m/z 50, and the only convenient technique (electron impact upon cyanoacetylene) also gave very large signals at m/z 51. It was not, therefore, thought to be feasible to attempt to determine which of the observed products
were due to \( c-C_3N^+ \) rather than to \( CCCN^+ \) or \( HCCCN^+ \) or various secondary reactions. A far better technique in this respect would be one involving electron impact upon some cyclic \( C_3N \)-containing species such as azetidine

\[
\begin{align*}
  &\text{H}_2\text{C} - \text{NH} \\
  &\text{H}_2\text{C} - \text{CH}_2
\end{align*}
\]

or some less saturated analogue. Alternatively, if injection of m/z 50 from \( HC_3N \) could be accomplished cleanly (without contamination at m/z 51), addition of sufficient \( N_2 \) upstream would remove all the CCCN\(^+\) allowing an unfettered glimpse of the \( c-C_3N^+ \) reactivity.

**Figure 4.8:** Experimentally observed decay curve for reaction of \( C_3N^+ \) (generated from electron impact upon \( HC_3N \)) with \( NH_3 \). The interpolated line describes the decay curve expected for \( k = 2.0 \times 10^{-9} \ cm^3 \ \text{molec}^{-1} \ \text{s}^{-1} \). No difference in reactivity between the two isomers is apparent.
Figure 4.9: Experimentally observed decay curves for reaction of $\text{C}_3\text{N}^+$ (generated from electron impact upon $\text{HC}_3\text{N}$) with $\text{C}_2\text{H}_2$. Analysis is complicated by the production of $\text{C}_4\text{H}_2^+$ (also at m/z 50) from the reaction of $\text{HC}_3\text{N}^+$ with $\text{C}_2\text{H}_2$. The line plotted in graph (b) is for c-$\text{C}_3\text{N}^+$ (10% of the initial m/z 50 ion signal) reacting with $\text{C}_2\text{H}_2$ at a rate $k = 6.1 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$, which represents a lower limit for this reaction rate.

(a). Typical experimental data set.

(b). Experimental graph showing interpolated lower limit for reaction of c-$\text{C}_3\text{N}^+$ with $\text{C}_2\text{H}_2$. (The arrow denotes further experimental points, out of graph range, below the interpolated line).
Although a satisfactory product analysis was too difficult in the circumstances prevailing, \( \text{c-C}_3\text{N}^+ \) is plainly much less reactive than \( \text{CCCN}^+ \): its complete unreactivity with \( \text{H}_2 \) and \( \text{CO} \) indicates that, once produced in the interstellar medium - for example, by cosmic-ray ionisation of \( \text{HC}_3\text{N} \) - it should persist for a substantial length of time, aiding detection. The most important interstellar reactions involving \( \text{c-C}_3\text{N}^+ \) are likely to be those with \( \text{NH}_3 \) (see figure 4.8), \( \text{HCN} \) and \( \text{C}_2\text{H}_2 \) as well as dissociative recombination with an electron. The rate of reaction of \( \text{c-C}_3\text{N}^+ \) with \( \text{C}_2\text{H}_2 \) could not be accurately determined in our study: a major product of the reaction of \( \text{HC}_3\text{N}^+ + \text{C}_2\text{H}_2 \) is \( \text{C}_4\text{H}_2^+ (+ \text{HCN}) \) at m/z 50, and the contribution from this product during the course of the reaction precluded a rate determination. However, a lower limit of \( k \geq 6.0 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \) can be ascribed on the basis of the amount of \( \text{C}_2\text{H}_2 \) required for complete removal of all forms of m/z 50 (see figure 4.9): thus the reaction of \( \text{c-C}_3\text{N}^+ \) with \( \text{C}_2\text{H}_2 \) is presumed to occur rapidly.

Section 4.3: \( \text{C}_4\text{N}_2^+ \).

Having synthesised dicyanoacetylene to investigate the chemistry of \( \text{C}_3\text{N}^+ \), we performed a brief study of the reactivity of the ion \( \text{C}_4\text{N}_2^+ \) with various neutrals (see table 4.9). Neither \( \text{C}_4\text{N}_2 \) nor its molecular ion have been detected in the interstellar environment, but this is not surprising in view of the symmetry of these species which would render them invisible at radio wavelengths. Yung\textsuperscript{272} has proposed that the reaction of \( \text{CN}^- \) with \( \text{HC}_3\text{N} \) should lead to the production of \( \text{C}_4\text{N}_2 \) in the atmosphere of Titan. This reaction has since been studied by Halpern et al.\textsuperscript{196}
\[
\begin{align*}
\text{CN}^- + \text{HC}_3\text{N} & \rightarrow \text{C}_4\text{N}_2 + \text{H}^+ \quad (4.23a) \\
& \rightarrow \text{HCN} + \text{C}_3\text{N}^- \\
\Delta H_{4.23a} &= -33 \text{ kJ mol}^{-1} \\
\Delta H_{4.23b} &= -21 \text{ kJ mol}^{-1} \\
k_{4.23} &= (1.70 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>(X)</th>
<th>Products (^a)</th>
<th>(k_{\text{obs}}) (^a)</th>
<th>(k) (^a)</th>
<th>(-\Delta H) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2)</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>1.49</td>
<td>–</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>(\text{C}_4\text{N}_2\text{H}^+ + \text{CH}_3^-)</td>
<td>0.46</td>
<td>1.04</td>
<td>&gt;205 (^b)</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>(\text{NH}_3^+ + \text{C}_4\text{N}_2)</td>
<td>1.8</td>
<td>2.12</td>
<td>159</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>(\text{C}_4\text{N}_2\text{H}^+ + \text{OH}^-)</td>
<td>0.56</td>
<td>2.35</td>
<td>&gt;144 (^b)</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>0.69</td>
<td>–</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>(\text{C}_4\text{N}_2\text{O}^+ + \text{O})</td>
<td>[0.70]</td>
<td>0.004</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>(\text{C}_4\text{N}_2\text{O}_2^+)</td>
<td>[0.30]</td>
<td>–</td>
<td>–</td>
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<tr>
<td>(\text{CO})</td>
<td>(\text{C}_4\text{N}_2\text{CO}^+)</td>
<td>0.075</td>
<td>0.74</td>
<td>–</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_2)</td>
<td>(\text{C}_2\text{H}_2^+ + \text{C}_4\text{N}_2)</td>
<td>[0.20]</td>
<td>1.2</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>(\text{C}_4\text{N}_2\text{C}_2\text{H}_2^+)</td>
<td>[0.80]</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(\text{HCN})</td>
<td>(\text{C}_4\text{N}_2\text{HCN}^+)</td>
<td>1.2</td>
<td>3.12</td>
<td>–</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
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<td>&lt;0.001</td>
<td>0.72</td>
<td>–</td>
</tr>
<tr>
<td>(\text{C}_2\text{N}_2)</td>
<td>(\text{C}_4\text{N}_2\text{C}_2\text{N}_2^+)</td>
<td>0.40</td>
<td>0.94</td>
<td>–</td>
</tr>
</tbody>
</table>

**Notes**

a. See footnotes (a) - (d) for table (4.2).

b. Based on an upper limit \(\Delta H_f(\text{C}_4\text{N}_2\text{H}^+ ) > 1248 \text{ kJ mol}^{-1}\). \(^{271}\)

c. Calculated assuming a \((\text{N=})_2\text{C}=\text{C}=\text{O}^+\) structure for \(\text{C}_4\text{N}_2\text{O}^+\).
The products of reaction (4.23) were not determined in the study by Halpern et al, but C₄N₂ is assumed to be the major product. The apparent existence of a small activation energy barrier (Eₐ ~ 6 kJ mol⁻¹) implies that this reaction will not be a significant source of interstellar C₄N₂, but it is able to account for C₄N₂ production in the warmer (T ~ 150K) atmosphere of Titan.

Very few ion-molecule studies involving C₄N₂ or C₄N₂⁺ have been reported. Raksit and Bohme²⁴⁷ determined that C₄N₂⁺, presumably having the structure C₂⁺·C₂N₂, is a minor product of the reaction of C₃N⁺ with C₂N₂ (see also table 4.7). Bohme et al²⁷¹ also studied the reaction

\[
C_4N^+ + CH₃CN \rightarrow C_2H_3^+ + C_4N₂ \quad [0.60] \quad (4.24a)
\]

\[
\rightarrow C_4N₂H^+ + C₂H₂ \quad [0.40] \quad (4.24b)
\]

\[k_{4.24} = 3.1 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]

in which the products appear to include neutral and protonated dicyanoacetylene. The C₄N₂H⁺ produced in this reaction was observed to proton-transfer rapidly to CH₃CN, suggesting Pₐ(C₄N₂) < Pₐ(CH₃CN) (788.0 kJ mol⁻¹).¹⁸⁵ This reaction suggests that C₄N₂ is indeed a likely constituent of interstellar clouds, since CH₃CN has been identified within dark clouds and since C₄N⁺ is formed rapidly by the reaction of C⁺ with HC₃N and is likely to be unreactive with H₂ at cloud temperature:

\[
C^+ + HC₃N \rightarrow C_4N^+ + H^+ \quad (4.25)
\]

\[
C_4N^+ + H₂ \rightarrow C_3H^+ + CHN \quad (4.26)
\]

\[k_{4.25} = 6.1 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \quad 167,267\]

\[k_{4.26} = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ at } 296\text{K}\]
The low rate constant observed for reaction (4.26) suggests that a barrier exists to inhibit this reaction. $\text{C}_4\text{N}^+$ should thus persist to allow reaction (4.24) to occur to some extent. For this reason, the reactions of $\text{C}_4\text{N}_2$ with various ions, and $\text{C}_4\text{N}_2\text{H}^+$ with various neutrals, are relevant to interstellar chemistry. The reactivity of $\text{C}_4\text{N}_2^+$, as described here, is also of potential interstellar relevance.

In the present study, $\text{C}_4\text{N}_2^+$ was generated in the ion source by electron impact on a 1:20 mixture of dicyanoacetylene in helium.

As demonstrated in table 4.9, the product channels evident in the reactions of $\text{C}_4\text{N}_2^+$ with the neutrals surveyed are adduct formation, atom abstraction and charge transfer. In this respect, the reactivity of $\text{C}_4\text{N}_2^+$ is similar to that of $\text{C}_2\text{N}_2^+$ generated from dicyanogen (as was seen in section 3.3). One unexpected observation is that $\text{C}_4\text{N}_2^+$ is unreactive with $\text{H}_2$, even though H-atom abstraction is highly exothermic:

$$\text{C}_4\text{N}_2^+ + \text{H}_2 \rightarrow \text{C}_4\text{N}_2\text{H}^+ + \text{H}.$$ (4.27)

$\Delta H_{4.27} < -207 \text{ kJ mol}^{-1}$.

The exothermicity of this reaction is calculated using Bohme's experimental upper limit to $\Delta H_f(\text{C}_4\text{N}_2\text{H}^+)$. The failure of this reaction suggests that it is inhibited by a substantial activation barrier: if this is so, then $\text{C}_4\text{N}_2^+$ should be unreactive with interstellar hydrogen also. H-atom abstraction does occur in the reactions with $\text{CH}_4$ and $\text{H}_2\text{O}$, which are exothermic to a similar degree - there does not appear to be any barrier in these instances, though the reactions proceed with less than unit efficiency. Prodnuk et al. have commented that H-atom
abstraction reactions are commonly barrier-inhibited when the neutral reactant is H₂, but not otherwise: this is in accord with the results reported here.

Adduct formation is the most common channel, evident in the reactions with O₂, CO, HCN, C₂H₂ and C₂N₂. The rapidity of the termolecular association channels with CO, C₂H₂ and HCN indicate that radiative association may be an important reactive process of C₄N₂⁺ within interstellar clouds. Cyclization of such adducts might well lead to aromatic ions which could be involved in gas-phase production of polycyclic aromatic hydrocarbons (PAHs) - though this is highly conjectural, especially since the structure of these adduct ions is not known from these SIFT studies. A major channel in the reaction with O₂ is O-atom abstraction: note that O-atom abstraction from CO₂ does not occur, perhaps indicating that this is an endothermic channel (there is no guarantee that the structure ascribed to C₄N₂O⁺, based on the only structure explored in the compilation of ion thermochemistry¹⁸⁴ is correct in this instance: a more likely form is ONCCCCN⁺, for which no thermochemical information is available) but more likely showing that the reaction with CO₂ is inhibited by a more substantial activation barrier than is the reaction with O₂.

Charge-transfer occurs in the reactions with C₂H₂ and NH₃: these represent pathways for neutralization of C₄N₂⁺ in dense clouds. Since C₄N₂⁺ does not react with H₂ and may not react rapidly with CO under interstellar conditions, dissociative recombination is an important reaction for removal of the ion: the most likely product channel is obviously
\[
\text{C}_4\text{N}_2^+ + e \rightarrow \text{C}_2\text{N}_2^- + \text{CN}^-
\]
(4.28)
\[
\Delta H_{428} = -609 \text{ kJ mol}^{-1},
\]

since this is the most exothermic channel not involving rearrangement.
CHAPTER 5.

ISOMERISM OF CHN$^+$ AND CH$_2$N$^+$.

Section 5.1: CHN$^+$.

During the course of our brief study of C$_2$N$_2^+$ chemistry, we investigated the reaction of C$_2$N$_2^+$ with HCN:

$$
\begin{align*}
\text{C}_2\text{N}_2^+ + \text{HCN} & \rightarrow \text{CHN}^+ + \text{C}_2\text{N}_2 & [0.20] \\
& \rightarrow \text{C}_2\text{N}_2\text{H}^+ + \text{CN}^- & [0.75] \\
& \rightarrow [\text{C}_2\text{N}_2\text{H.CN}]^+ & [0.05]
\end{align*}
$$

$$k_{5.1} = 2.7 \times 10^{-9} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}.$$

The reaction rate and product distribution observed are both in serious disagreement with the findings of Inoue and Cottin, who reported

$$
\begin{align*}
\text{C}_2\text{N}_2^+ + \text{HCN} & \rightarrow \text{C}_3\text{N}_3^+ + \text{H}^- & [1.0] \\
k_{5.1} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}. 
\end{align*}
$$

The discrepancies between these results arise from the differences in the experimental techniques used. Inoue and Cottin's experiments were performed in a mass spectrometer chamber containing C$_2$N$_2$ and HCN. Reactions were assigned upon the basis of the signals observed for various ions as a function of pressure: clearly, since the reaction chamber contained a multiplicity of possible
reactant ions at all pressures, the possibility for misinterpretation of the reaction chemistry involved was fairly high. In the SIFT, in contrast, a C₂N₂⁺ ion signal can be injected free of contamination by any other ions and thus the product distribution obtained is much more reliable.

The product channels observed by us for reaction (5.1) appear, initially, to all be very straightforward processes. The major channel is hydrogen atom abstraction to form protonated dicyanogen (5.1b), and charge-transfer (5.1a) and adduction (5.1c) processes account for minor products. However, the apparent charge-transfer channel presents a problem. The ionisation potential of HCN is higher than that of C₂N₂ (IP(HCN) = 1312 ± 1 kJ mol⁻¹, while IP(C₂N₂) = 1290 ± 1 kJ mol⁻¹) and, therefore, charge-transfer in this manner is endothermic. An endothermic channel could not be expected to account for such a large fraction (20%) of the products of a collision-rate reaction, especially when the major product is strongly exothermic as is the case here (ΔH₅.1b = -140 kJ mol⁻¹). The existence of sufficient metastable excited C₂N₂⁺ to account for the apparent charge-transfer channel is unlikely: therefore the product signal at (m/z = 27) is interpreted not as HCN⁺ but as HNC⁺. Formation of HNC⁺ is energetically favourable (see Table 5.1) but requires a substantially more complicated mechanism than merely the transfer of an electron. HNC⁺ could be accounted for by the initial formation of a collision complex

\[
\text{C}_2\text{N}_2^+ + \text{HCN} \rightarrow [\text{C}_2\text{N}_2^+\cdot\text{HCN}]
\]  

(5.2)

with substantial internal rearrangement of the complex preceding its dissociation into the observed products C₂N₂H⁺ (+ CN⁻) and HNC⁺ (+ C₂N₂). This type of
mechanism is supported by the detection of a primary product at m/z = 79, corresponding to the collisionally stabilised addition product HC₃N₃⁺.

Having proposed that HNC⁺ and not HCN⁺ is being produced in this reaction, it becomes necessary to demonstrate this, and to this end we require a method of distinguishing HCN⁺ from HNC⁺. The different energies of HNC⁺ and HCN⁺ suggest that HCN⁺ will display a higher gas-phase acidity than will HNC⁺ - thus, HCN⁺ should undergo proton transfer reactions more readily than HNC⁺:

\[
\begin{align*}
\text{HCN}^+ + X & \rightarrow \text{XH}^+ + \text{CN}^- \quad (5.3) \\
\text{HNC}^+ + X & \rightarrow \text{no reaction} \quad (5.4)
\end{align*}
\]

provided \( \text{PA (CN}^- \text{ at C) < PA (X) < PA (CN}^- \text{ at N).} \)

---

**Table 5.1:** Experimental and theoretical thermochemistry of CHN⁺.

<table>
<thead>
<tr>
<th>( \Delta H_f(\text{HCN}^+) ) ( ^a )</th>
<th>( \Delta H_f(\text{HNC}^+) ) ( ^a )</th>
<th>( \Delta H_f(\text{TS}) ) ( ^{a,b} )</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1447</td>
<td>-</td>
<td>-</td>
<td>from IP(HCN)</td>
<td>184</td>
</tr>
<tr>
<td>-</td>
<td>1407</td>
<td>-</td>
<td>experimental bracketing</td>
<td>275</td>
</tr>
<tr>
<td>1437</td>
<td>1350</td>
<td>-</td>
<td>theoretical calculation ( ^c )</td>
<td>276</td>
</tr>
<tr>
<td>-</td>
<td>1360</td>
<td>-</td>
<td>theoretical calculation ( ^d )</td>
<td>277</td>
</tr>
<tr>
<td>-</td>
<td>1370</td>
<td>1572</td>
<td>theoretical calculation ( ^e )</td>
<td>278</td>
</tr>
<tr>
<td>-</td>
<td>( \leq 1373 )</td>
<td>-</td>
<td>experimental value ( ^f )</td>
<td>279,280</td>
</tr>
</tbody>
</table>

**Notes**

\( ^a \) Heats of formation are expressed in kJ mol\(^{-1}\).

\( ^b \) TS = transition state for isomerisation of CHN⁺.

\( ^c \) Green's function calculation of ionization potentials, using literature values\(^{184} \) for \( \Delta H_f(\text{HCN}) \) and \( \Delta H_f(\text{HNC}) \)

\( ^d \) SCF calculation, adjusted to experimental \( \Delta H_f(\text{HCN}^+) \).\(^{184} \)

\( ^e \) MP2/6-31G**/6-31G+ZPE calculations, adjusted to experimental \( \Delta H_f(\text{HCN}^+) \).\(^{184} \)

\( ^f \) This work (see text for discussion).
The proton affinities of \( \text{CN}^- \) have not been measured directly, but can be calculated from known heats of formation:

\[
\begin{align*}
\text{H}^+ + \text{CN}^- & \rightarrow \text{HCN}^+ \\
& \rightarrow \text{HNC}^+
\end{align*}
\]

(5.5a)

(5.5b).

\[ \text{PA(\text{CN}^-)} = -\Delta H_{5.5a} \quad \text{and} \quad \text{PA(\text{CN}^-)} = -\Delta H_{5.5b} \] [where the underlined character indicates the site of protonation]. Using the appropriate \( \Delta H_f \) values,\(^{184}\) \( \text{PA(\text{CN}^-)} = 518 \pm 10 \text{ kJ mol}^{-1} \) and \( \text{PA(\text{CN}^-)} = 592 \pm 10 \text{ kJ mol}^{-1} \). On the basis of these values, reaction with a species \( X \) for which \( \text{PA}(X) \) is between 518 and 592 kJ mol\(^{-1}\) should serve to distinguish \( \text{HCN}^+ \) from \( \text{HNC}^+ \), and may additionally allow refinement of \( \Delta H_f(\text{HCN}^+) \) and \( \Delta H_f(\text{HNC}^+) \).

The expectation that proton transfer would allow discrimination between \( \text{HCN}^+ \) and \( \text{HNC}^+ \) was not initially borne out by the experiments which were attempted (see table 5.2). Various neutrals with proton affinities within the appropriate range were tested for reaction with \( \text{CHN}^+ \), and none showed any proton-transfer reaction channels, or any reproducible curvature in the graph of \( \ln(\text{ion signal}) \) versus reactant neutral pressure. The \( \text{CHN}^+ \) signal was obtained by various techniques (chiefly chemical ionisation and electron bombardment methods - see table 5.3) in an effort to find a technique which produced observable fractions of each isomer. The main method of \( \text{CHN}^+ \) production used was electron impact on \( \text{HCN} \): this method was chosen partly for its simplicity and partly because it was felt that the ionisation process would produce initially \( \text{HCN}^+ \), with subsequent isomerisation to the more stable \( \text{HNC}^+ \) (provided that the initially formed \( \text{HCN}^+ \) possessed sufficient energy to overcome the barrier to
The expectation was, therefore, that the m/z = 27 signal from this method should contain appreciable fractions of each isomer, simplifying the task of detecting curvature in the experimental graphs for reaction of CHN⁺ with the neutral, X.

That this was not observed to be the case was most perplexing: reactions of CHN⁺ with CO, CO₂, O₂, N₂O and C₂N₂ were studied in an effort to differentiate HCN⁺ and HNC⁺. Curvature was not seen in the semilogarithmic plots of ion signal against reactant neutral flows in any of these reaction studies, indicating either that only one isomer was present or that there was no observable difference in the reactivity of the two isomers. Of the reactants listed in table 5.2, CO, CO₂ and

**Table 5.2:** Reactions of CHN⁺ + X, which failed to distinguish between HCN⁺ and HNC⁺.

<table>
<thead>
<tr>
<th>X</th>
<th>Products</th>
<th>k_{obs}</th>
<th>k_c</th>
<th>PA(X)</th>
<th>IP(X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>HCO⁺ + CN⁻</td>
<td>0.0029</td>
<td>0.91</td>
<td>594</td>
<td>14.0139</td>
</tr>
<tr>
<td>O₂</td>
<td>O₂⁺ + HCN</td>
<td>[.70]</td>
<td>0.50</td>
<td>0.77</td>
<td>422</td>
</tr>
<tr>
<td></td>
<td>HCNO⁺ + O</td>
<td>[.20]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO⁺ + HCO⁻</td>
<td>[.10]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂N₂</td>
<td>C₂N₂H⁺ + CN⁻</td>
<td>1.7</td>
<td>1.24</td>
<td>674</td>
<td>13.37 ± .01</td>
</tr>
<tr>
<td>N₂O</td>
<td>N₂O⁺ + HCN</td>
<td>[.54]</td>
<td>1.2</td>
<td>1.04</td>
<td>581</td>
</tr>
<tr>
<td></td>
<td>HCNO⁺ + N₂</td>
<td>[.44]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO⁺ + CHN₂</td>
<td>[.02]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>CO₂⁺ + HCN</td>
<td>[.60]</td>
<td>0.0015</td>
<td>0.98</td>
<td>548</td>
</tr>
<tr>
<td></td>
<td>CHN.CO₂⁺</td>
<td>[.40]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes**

a. Product channels reported in brackets, where more than one product was detected.
b. Observed rate coefficient, in units of 10^{-9} cm³ molec⁻¹ s⁻¹.
c. Calculated ADO collision rate coefficient, using the theory of Su and Chesnavich.¹⁷²
d. Proton affinity in units of kJ mol⁻¹. Taken from the tabulation of Lias et al,¹⁸⁵ unless otherwise stated.
e. Ionisation potential in units of kJ mol⁻¹. Taken from the tabulation of Lias et al,¹⁸⁴ unless otherwise stated.
f. Taken from reference 203.
N$_2$O were chosen on the basis of PA; O$_2$ and C$_2$N$_2$ were selected on the basis of IP, so that different rates were expected for proton transfer and/or for charge transfer with these reactants. The failure to see the desired channels for N$_2$O, O$_2$, and C$_2$N$_2$ was readily explained by the presence of other exothermic product channels for these reactants, but the very slow reaction rates seen for reaction of CHN$^+$ with CO and CO$_2$ were much more mysterious. Proton transfer from HCN$^+$ to CO or to CO$_2$ should occur rapidly, especially in the absence of competing product channels.

The dilemma posed by this apparent unreactivity of CHN$^+$ with CO and CO$_2$ was eventually resolved by recognising the following reaction mechanism occurred.

Table 5.3: Methods used for generating CHN$^+$ for reaction studies.

<table>
<thead>
<tr>
<th>Code</th>
<th>Method</th>
<th>Site</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Ar$^+$ + HCN $\rightarrow$ CHN$^+$</td>
<td>FT</td>
<td>CN$^+$ a minor product channel; CH$_2$N$^+$ formed from subsequent rapid reaction with HCN. Not a 'clean' source.</td>
</tr>
<tr>
<td>ii</td>
<td>Ar$^+$ + HCN $\rightarrow$ CHN$^+$</td>
<td>IS</td>
<td>from a 10:1 mixture of Ar and HCN. Satisfactory in terms of size of CHN$^+$ ion signal: little contamination from adjacent masses.</td>
</tr>
<tr>
<td>iii</td>
<td>CN$^+$ + H$_2$ $\rightarrow$ CHN$^+$</td>
<td>FT</td>
<td>CN$^+$ from e + C$_2$N$_2$ in ion source. Problems with CH$_2$N$^+$ contamination, small CHN$^+$ signal. Should give mostly HNC$^+$.</td>
</tr>
<tr>
<td>iv</td>
<td>CN$^+$ + H$_2$ $\rightarrow$ CHN$^+$</td>
<td>IS</td>
<td>from a 20:1 mixture of H$_2$ and C$_2$N$_2$. Satisfactory.</td>
</tr>
<tr>
<td>v</td>
<td>e + C$_6$H$_5$NH$_2$ $\rightarrow$ CHN$^+$</td>
<td>IS</td>
<td>Aniline used in an effort to generate HNC$^+$ free from HCN$^+$. Contamination at m/z = 27 by C$_2$H$_3^+$. Small signal obtained. Unsatisfactory.</td>
</tr>
<tr>
<td>vi</td>
<td>e + HCN $\rightarrow$ CHN$^+$</td>
<td>IS</td>
<td>Satisfactory. Large signal at m/z = 27, little contamination from neighbouring masses.</td>
</tr>
</tbody>
</table>

Notes
a. Site of CHN$^+$ production. (FT = within the flow tube; IS = within the ion source)
A reactant $X$ capable of accepting a proton from HCN$^+$ but not from HNC$^+$ may, upon collision with HCN$^+$, produce HNC$^+$ rather than $XH^+$. Such a process can take place because the collision complex has a sufficiently long lifetime for a second proton transfer to occur after proton transfer from HCN$^+$ to $X$ - that is, proton transfer from $XH^+$ to NC:

$$
\begin{align*}
\text{HCN}^+ &+ X \rightarrow (XH^+.CN)^* \quad (5.6a) \\
(XH^+.CN)^* &\rightarrow (XH^+.NC)^* \quad (5.6b) \\
(XH^+.NC)^* &\rightarrow X + \text{HNC}^+ \quad (5.6c).
\end{align*}
$$

Thus when no product channels apart from proton transfer are available for a reaction of HCN$^+$ with $X$ (as is essentially the case for CO and CO$_2$), the major product channel will be isomerisation from HCN$^+$ to HNC$^+$. This change in the composition of the m/z= 27 ion signal is not detectable by the mass spectrometer and thus this isomerisation is not directly observable in the SIFT.

To demonstrate this isomerisation process, a reaction is required which distinguishes between HCN$^+$ and HNC$^+$ in some observable manner. The reactions of CHN$^+$ with CF$_4$ and with SF$_6$ were finally found to distinguish satisfactorily between HCN$^+$ and HNC$^+$:

$$
\begin{align*}
\text{HCN}^+ &+ \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{HF} + \text{CN}. \quad (5.7) \\
\text{HNC}^+ &+ \text{CF}_4 \rightarrow \text{no reaction} \quad (5.8) \\

k_{5.7} &= 1.2 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \\
k_{5.8} &< 1.0 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}
\end{align*}
$$
The reaction with CF₄ (5.7 & 5.8) was especially useful because it allowed direct determination of the HCN⁺ / HNC⁺ ratio in the m/z = 27 ion signal: the HCN⁺ was that fraction of the m/z = 27 signal which disappeared upon addition of (sufficient) CF₄. Figure 5.1 demonstrates the degree of curvature evident in the semilogarithmic graphs.

Figure 5.1: Experimental graph showing the reaction of CHN⁺ with CF₄. HCN⁺ reacts at the collision rate, while HNC⁺ is unreactive: thus the isomeric ratio can be very easily determined. In this experiment, HCN⁺ constituted 64% of the m/z 27 ion signal.
Reaction (5.7) may occur via proton-transfer \((\text{PA(CF}_4) \sim 527 \text{ kJ mol}^{-1})\):\(^{185}\)

\[
\begin{align*}
\text{HCN}^+ + \text{CF}_4 & \rightarrow (\text{CF}_4\text{H}^+.\text{CN})^* \quad (5.7a) \\
(\text{CF}_4\text{H}^+.\text{CN})^* & \rightarrow (\text{CF}_4\text{H}^+)^* + \cdot\text{CN} \quad (5.7b) \\
(\text{CF}_4\text{H}^+)^* & \rightarrow \text{CF}_3^+ + \text{HF} \quad (5.7c)
\end{align*}
\]

involving a mechanism in which isomerisation of HCN\(^+\) to HNC\(^+\) does not occur because the collision complex is weakly bound and so has too short a lifetime to permit the intramolecular rearrangement required for HNC\(^+\) formation. Note that the mechanism above is one of several possible: others include fluoride ion transfer from CF\(_4\) to HCN\(^+\) (producing HCNF, which subsequently rearranges and dissociates as HF + CN\(^-\)) and loss of HF rather than CN\(^-\) in step (5.7b) above (followed by dissociation of CF\(_3\)CN\(^+\) to give CF\(_3^+\) + CN\(^-\)). The mechanism for reaction of HCN\(^+\) with SF\(_6\) is similarly uncertain (\(\text{PA(SF}_6)\) has not been determined) but most likely is analogous to that for reaction (5.7).

Reactions (5.7) to (5.10) permitted determination of the rate of isomerisation of HCN\(^+\) by CO or by CO\(_2\), by a method analogous to that detailed by Freeman et al.\(^ {206}\) For an experiment in which CHN\(^+\) is injected into the flow tube, the isomerising gas \(\text{CO}_x\) \((x = 1 \text{ or } 2)\) is introduced at portal 1 with ensuing reaction

\[
\text{HCN}^+ + \text{CO}_x \rightarrow \text{HNC}^+ + \text{CO}_x \quad (5.11),
\]

and the titrating gas CF\(_4\) is added at portal 2, the relevant equations for the changing concentrations of the ionic species involved are
\[ [\text{HCN}^+]_{z_2} = [\text{HCN}^+]_0 (e^{jk_{5.11} z_1}) (e^{jk_{7} z_2}) \]  \hspace{1cm} (5.i) \\
\[ [\text{HNC}^+]_{z_2} = [\text{HNC}^+]_0 + \left( [\text{HCN}^+]_0 (1-e^{-jk_{5.11} (z_1-z_2)}) \right) \] \\
\[ + \left( [\text{HCN}^+]_0 (e^{-jk_{5.11} (z_1-z_2)}) (1-e^{-jk_{7} z_2/(jk_{7}+jk_{5.11})}) \right) \]  \hspace{1cm} (5.ii) \\
\[ [\text{CF}^+]_{z_2} = [\text{HCN}^+]_0 e^{-jk_{5.11} (z_1-z_2)} \left( 1 - e^{jk_{7} z_2/(jk_{7}+jk_{5.11})} \right) \]  \hspace{1cm} (5.iii) \\

(where \( z_i \) is the reaction length for portal \( i \), and \\

\[ j_i = C k_i f_B \]

(5.iv)

where \( f_B \) is the flux, in molec s\(^{-1}\), of the reactant neutral \( B \) added to the tube and \( C \) has the form \\

\[ C = \frac{\gamma (1-e)}{\omega \pi r^2 v_{\text{buff}}^2} \]  \hspace{1cm} (5.v) \\

(for which \( \frac{\gamma}{\omega} \) and \( e \) are flow coefficients as defined in section 2.2, \( r \) is the flow tube radius, and \( v_{\text{buff}} \) is the buffer gas velocity within the flow tube). Solution of equations (5.i)-(5.iii)\(^{281}\) yields the expression \\

\[ C k_{5.11} f_{\text{CO}_x} z_1 = \ln(X_{\text{HCN}^+}^0) - \ln(X_{\text{HCN}^+} (1 - \beta)) \]  \hspace{1cm} (5.vi) \\

\[ \therefore k_{5.11} = \frac{[\ln(X_{\text{HCN}^+}^0) - \ln(X_{\text{HCN}^+} (1 - \beta))]}{C f_{\text{CO}_x} z_1} \]  \hspace{1cm} (5.vii) \\

\[ X_{\text{HCN}^+} = \frac{[\text{HCN}^+]}{[\text{HCN}^+] + [\text{HNC}^+]}, \quad X = X^0 \text{ at } f_{\text{CO}_x} = 0 \]  \hspace{1cm} (5.viii),
\[ \beta = X_{HCN+} (K'_{CO} - K_{CO}) \]  \hspace{1cm} (5.ix)

with \[ K_{CO} = e^{k_{5,11}z} \]  \hspace{1cm} (5.x)

and \[ K'_{CO} = e^{k_{5,11}(1-z)} \]  \hspace{1cm} (5.xi).

From equations (5.v), (5.vii), (5.ix) and (5.x) above, it can be seen that solution of \( k_{5,11} \) requires prior solution of \( \beta \), and solution of \( \beta \) requires prior solution of \( k_{5,11} \). Thus solution of \( k_{5,11} \) must be an iterative process, with some approximate value of \( k_{5,11} \) initially being chosen to define approximately the parameter \( \beta \). Since isomerisation was seen to be rapid, with relatively small flows of \( CO_x \) being required to effect noticeable changes in the \( HCN^+ / HNC^+ \) isomer ratio, the ADO rate coefficients\(^{172} \) for collision of \( CHN^+ + CO_x \) were selected as the initial approximation to \( k_{5,11} \):

\[ k_{c,5,11} = 9.19 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ for } CO_x = CO \]
\[ k_{c,5,11} = 9.28 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ for } CO_x = CO_2. \]

Under the operating conditions employed in the Canterbury SIFT (\( T = 300K, P = 0.300 \text{ Torr of He} \)), values of the other parameters required were

\( r = 3.66 \text{ cm} \)
\( v_{buff} = 8133 \text{ cm s}^{-1} \)
\( z_1 = 82.7 \text{ cm} \)
\( z_2 = 42.7 \text{ cm} \)
\( \Upsilon_0 = 0.6465 \)
\( \epsilon = 5.385 \times 10^{-3} \)
\[ \therefore C = 2.310 \times 10^{-10} \text{ s cm}^{-3}. \]
The isomerisation experiments were performed by establishing a CHN\(^+\) signal by injection of m/z 27 from HCN in the ion source and varying the flow of CF\(_4\) in order to determine X\(_{\text{HCN}^+}\) for the flow of CO\(_x\) being applied. A range of CO flows, from f\(_{\text{CO}}\) = 0 to 2.7 \times 10^{17} \text{ molec s}^{-1}, was employed; CO\(_2\) flows used ranged from f\(_{\text{CO}_2}\) = 0 to 1.6 \times 10^{17} \text{ molec s}^{-1} (see tables 5.4 & 5.5). k\(_{5.11}\) was determined as the slope of the resulting graph (see figures 5.2 & 5.3) of \([\ln(X_{\text{HCN}^+}^0) - \ln(X_{\text{HCN}^+}(1 - \beta))]\) versus Cf\(_{\text{CO}_x}\). 

The values found after three iterations (convergence was obtained rapidly) were 

\[ k_{5.11} = (4.63 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ for } \text{CO}_x = \text{CO}, \]

and 

\[ k_{5.11} = (5.01 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ for } \text{CO}_x = \text{CO}_2. \]

Once the rate of isomerisation by CO\(_x\) was established, the reactions of HNC\(^+\) with various neutrals (see table 5.6) were studied by addition at portal 1 of sufficient CO\(_x\) to convert >99% of HCN\(^+\) to HNC\(^+\). Product channels then identified for the reaction of the ion signal at m/z = 27 with the relevant neutrals were inferred to be entirely due to HNC\(^+\) (though care was taken to verify that none of the products observed arose from reaction of some primary product with the isomerising gas CO\(_x\)).

Having assigned the products due to HNC\(^+\), products due to HCN\(^+\) were inferred (see table 5.7) by studying the product ratios for reaction of the m/z = 27 ion signal (in the absence of the isomerising gas) with various neutrals: the proportion of HNC\(^+\) to HCN\(^+\) in the reactant ion signal was determined by titration with CF\(_4\) or SF\(_6\) and the proportions of each product channel due to HNC\(^+\) were subtracted.
from the observed total for each product channel. In some cases (because of cumulative uncertainties), product ions could not be ruled out as minor product channels for the reaction of HCN$^+$ with the neutral in question - for example,

\[ \text{HCN}^+ + \text{N}_2 \text{O} \rightarrow \text{N}_2\text{O}^+ + \text{HCN} \ [>0.90] \quad (5.12a) \]

\[ \rightarrow \text{HCNO}^+ + \text{N}_2 \ [<0.10] \quad (5.12b) \]

<table>
<thead>
<tr>
<th>Table 5.4: Calculation of the rate of HCN$^+$ isomerisation by CO.</th>
</tr>
</thead>
<tbody>
<tr>
<td>First iteration: using $k_{\text{isom}} = 9.19 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ (calculated collision rate)</td>
</tr>
<tr>
<td>$C f_{\text{CO}} z_1$</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>4.11 x 10^8</td>
</tr>
<tr>
<td>7.53 x 10^8</td>
</tr>
<tr>
<td>1.316 x 10^9</td>
</tr>
<tr>
<td>2.961 x 10^9</td>
</tr>
<tr>
<td>5.215 x 10^9</td>
</tr>
</tbody>
</table>

Second iteration: using $k_{\text{isom}} = 4.38 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ (from first iteration)

<table>
<thead>
<tr>
<th>$C f_{\text{CO}} z_1$</th>
<th>$j_{\text{isom}}$</th>
<th>$X_{\text{HCN}^+}$</th>
<th>$\beta$</th>
<th>$\ln(X_{\text{HCN}^+}^\beta) - \ln(X_{\text{HCN}^+}^{1-\beta})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.7325</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.11 x 10^8</td>
<td>2.175 x 10^{-3}</td>
<td>0.631</td>
<td>0.0596</td>
<td>0.211</td>
</tr>
<tr>
<td>7.53 x 10^8</td>
<td>3.986 x 10^{-3}</td>
<td>0.547</td>
<td>0.0977</td>
<td>0.395</td>
</tr>
<tr>
<td>1.316 x 10^9</td>
<td>6.971 x 10^{-3}</td>
<td>0.434</td>
<td>0.1427</td>
<td>0.677</td>
</tr>
<tr>
<td>2.961 x 10^9</td>
<td>1.568 x 10^{-2}</td>
<td>0.232</td>
<td>0.1920</td>
<td>1.363</td>
</tr>
<tr>
<td>5.215 x 10^9</td>
<td>2.762 x 10^{-2}</td>
<td>0.0851</td>
<td>0.1680</td>
<td>2.337</td>
</tr>
</tbody>
</table>

Third iteration: using $k_{\text{isom}} = 4.68 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ (from second iteration)

<table>
<thead>
<tr>
<th>$C f_{\text{CO}} z_1$</th>
<th>$j_{\text{isom}}$</th>
<th>$X_{\text{HCN}^+}$</th>
<th>$\beta$</th>
<th>$\ln(X_{\text{HCN}^+}^\beta) - \ln(X_{\text{HCN}^+}^{1-\beta})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.7325</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.11 x 10^8</td>
<td>2.32 x 10^{-3}</td>
<td>0.631</td>
<td>0.063</td>
<td>0.214</td>
</tr>
<tr>
<td>7.53 x 10^8</td>
<td>4.26 x 10^{-3}</td>
<td>0.547</td>
<td>0.103</td>
<td>0.401</td>
</tr>
<tr>
<td>1.316 x 10^9</td>
<td>7.45 x 10^{-3}</td>
<td>0.434</td>
<td>0.148</td>
<td>0.684</td>
</tr>
<tr>
<td>2.961 x 10^9</td>
<td>1.68 x 10^{-2}</td>
<td>0.232</td>
<td>0.192</td>
<td>1.363</td>
</tr>
<tr>
<td>5.215 x 10^9</td>
<td>2.95 x 10^{-2}</td>
<td>0.0851</td>
<td>0.161</td>
<td>2.328</td>
</tr>
</tbody>
</table>

Notes
a. See text for definition of parameters.
\[
\begin{align*}
\text{HNC}^+ + \text{N}_2\text{O} & \rightarrow \text{HNCO}^+ + \text{N}_2 \quad [0.55] \quad (5.13a) \\
& \rightarrow \text{NO}^+ + \text{HNCN} \quad [0.45] \quad (5.13b).
\end{align*}
\]

In these experiments, CHN\(^+\) was produced by electron impact upon HCN and the resultant m/z = 27 ion signal was found to contain 70% HCN\(^+\), by titration with CF\(_4\). The product signal at m/z = 43, corresponding to HCNO\(^+\) / HNCO\(^+\), was probably due to reaction of HNC\(^+\) only, but a small product channel at this mass due to HCN\(^+\) could not be ruled out given the uncertainty in the product ratio determination and in the HCN\(^+\) / HNC\(^+\) ratio, or on the basis of available energy (\(\Delta H_{5.12b} = -266 \text{ kJ mol}^{-1}\)). The structures of the ions at m/z = 43 are those conjectured to be most likely on the grounds of minimal rearrangement to products.

**Figure 5.2:** Graph showing calculated rate of isomerisation of HCN\(^+\) by CO. The parameters calculated are from table 5.4, and yield a slope of \((4.63 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\); this slope is equal to the rate coefficient for isomerisation to HNC\(^+\), and is about half the calculated collision rate. The results shown are from the third iteration, and reflect a change of 1.1% from the rate determined from the second iteration: since the convergence at this stage appeared sufficiently rapid, no further iterations were performed.
For the reactions with \( \text{C}_2\text{H}_2 \), both isomers were observed to react at the collision rate:

\[
\begin{align*}
\text{HCN}^+ + \text{C}_2\text{H}_2 & \rightarrow \text{C}_2\text{H}_2^+ + \text{HCN} \quad [>0.85] \quad (5.14a) \\
& \rightarrow \text{C}_2\text{H}_3^+ + \text{CN}^- \quad [<0.15] \quad (5.14b) \\
\text{HNC}^+ + \text{C}_2\text{H}_2 & \rightarrow \text{C}_2\text{H}_2^+ + \text{HCN} \quad [>0.50] \quad (5.15a) \\
& \rightarrow \text{C}_2\text{H}_3^+ + \text{CN}^- \quad [<0.15] \quad (5.15b) \\
& \rightarrow \text{C}_3\text{H}_2\text{N}^+ + \text{H}^- \quad [>0.35] \quad (5.15c).
\end{align*}
\]

---

**Table 5.5: Calculation of the rate of HCN\(^+\) isomerisation by \( \text{CO}_2 \).**

First iteration: using \( k_{\text{isom}} = 9.28 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) (calculated collision rate)

<table>
<thead>
<tr>
<th>( C_f\text{CO}_2 )</th>
<th>( \lambda_{\text{isom}} )</th>
<th>( X_{\text{HCN}^+} )</th>
<th>( \beta )</th>
<th>( \ln(X_{\text{HCN}^+}^0) - \ln(X_{\text{HCN}^+}^0/(1-\beta)) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.7325</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4.55 \times 10^8</td>
<td>5.102 \times 10^{-3}</td>
<td>0.591</td>
<td>0.1420</td>
<td>0.339</td>
</tr>
<tr>
<td>8.58 \times 10^8</td>
<td>9.625 \times 10^{-3}</td>
<td>0.519</td>
<td>0.1905</td>
<td>0.669</td>
</tr>
<tr>
<td>1.685 \times 10^9</td>
<td>1.891 \times 10^{-2}</td>
<td>0.381</td>
<td>0.1680</td>
<td>0.865</td>
</tr>
<tr>
<td>3.076 \times 10^9</td>
<td>3.451 \times 10^{-2}</td>
<td>0.209</td>
<td>0.1169</td>
<td>1.408</td>
</tr>
</tbody>
</table>

Second iteration: using \( k_{\text{isom}} = 5.42 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) (from first iteration)

<table>
<thead>
<tr>
<th>( C_f\text{CO}_2 )</th>
<th>( \lambda_{\text{isom}} )</th>
<th>( X_{\text{HCN}^+} )</th>
<th>( \beta )</th>
<th>( \ln(X_{\text{HCN}^+}^0) - \ln(X_{\text{HCN}^+}^0/(1-\beta)) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.7325</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4.55 \times 10^8</td>
<td>2.980 \times 10^{-3}</td>
<td>0.591</td>
<td>0.0777</td>
<td>0.295</td>
</tr>
<tr>
<td>8.58 \times 10^8</td>
<td>5.621 \times 10^{-3}</td>
<td>0.519</td>
<td>0.1248</td>
<td>0.478</td>
</tr>
<tr>
<td>1.685 \times 10^9</td>
<td>1.104 \times 10^{-2}</td>
<td>0.381</td>
<td>0.1770</td>
<td>0.848</td>
</tr>
<tr>
<td>3.076 \times 10^9</td>
<td>2.016 \times 10^{-2}</td>
<td>0.209</td>
<td>0.1888</td>
<td>1.463</td>
</tr>
</tbody>
</table>

Third iteration: using \( k_{\text{isom}} = 5.01 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) (from second iteration)

<table>
<thead>
<tr>
<th>( C_f\text{CO}_2 )</th>
<th>( \lambda_{\text{isom}} )</th>
<th>( X_{\text{HCN}^+} )</th>
<th>( \beta )</th>
<th>( \ln(X_{\text{HCN}^+}^0) - \ln(X_{\text{HCN}^+}^0/(1-\beta)) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.7325</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4.55 \times 10^8</td>
<td>2.75 \times 10^{-3}</td>
<td>0.591</td>
<td>0.0725</td>
<td>0.290</td>
</tr>
<tr>
<td>8.58 \times 10^8</td>
<td>5.20 \times 10^{-3}</td>
<td>0.519</td>
<td>0.119</td>
<td>0.471</td>
</tr>
<tr>
<td>1.685 \times 10^9</td>
<td>1.02 \times 10^{-2}</td>
<td>0.381</td>
<td>0.172</td>
<td>0.842</td>
</tr>
<tr>
<td>3.076 \times 10^9</td>
<td>1.86 \times 10^{-2}</td>
<td>0.209</td>
<td>0.191</td>
<td>1.466</td>
</tr>
</tbody>
</table>

**Notes**

a. See text for definition of parameters.
Product channels (5.14b) and (5.15b) were not observable, since the product ions have m/z = 27 and are thus indistinguishable from CHN⁺. These product channels could not be excluded, given the uncertainty in the rate coefficient determination and upon the basis of exothermicity (ΔH₅.₁₄b = -128 kJ mol⁻¹; ΔH₅.₁₅b ≥ -54 kJ mol⁻¹). The channels positively identified for reactions (5.14) and (5.15) are more exothermic than these possible proton-transfer channels, but proton transfer is often able to compete efficiently with more exothermic processes: for example, in the reaction of C₄H₃⁺ with CH₃NO₂ as described in section 3.4, a barely exothermic proton transfer channel was seen to accompany production of CH₃CNH⁺ with an exothermicity of several hundred kJ mol⁻¹.²⁸²

Figure 5.3: Graph showing calculated rate of isomerisation of HCN⁺ by CO₂, using parameters from table 5.5. The rate coefficient for isomerisation to HNC⁺ is (5.01 ± 0.7) x 10⁻¹⁰ cm³ molec⁻¹ s⁻¹. As with figure 5.2, the graph shows the results of the third and final iteration.
Similarly, C$_2$H$_3^+$ could not be excluded as a product of the reactions with CH$_4$:

\[
\begin{align*}
\text{HCN}^+ + \text{CH}_4 & \rightarrow \text{HCNH}^+ + \text{CH}_3^+ \quad [>0.85] \quad (5.16a) \\
& \rightarrow \text{C}_2\text{H}_3^+ + \text{NH}_2^* \quad [<0.15] \quad (5.16b) \\
\text{HNC}^+ + \text{CH}_4 & \rightarrow \text{HCNH}^+ + \text{CH}_3^+ \quad [>0.85] \quad (5.17a) \\
& \rightarrow \text{C}_2\text{H}_3^+ + \text{NH}_2^* \quad [<0.15] \quad (5.17b). 
\end{align*}
\]

### Table 5.6: Reactions of HNC$^+$ + X.

<table>
<thead>
<tr>
<th>X</th>
<th>Products $^a$</th>
<th>$k_{\text{obs}}$</th>
<th>$k_e$</th>
<th>$-\Delta H$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_6$</td>
<td>HNCP$^+$ + SF$_5^*$</td>
<td>1.2</td>
<td>1.2</td>
<td>$-132$</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>no reaction</td>
<td>$&lt;0.005$</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>no reaction</td>
<td>$&lt;0.002$</td>
<td>0.91</td>
<td>-</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>products $^c$</td>
<td>0.0012</td>
<td>0.98</td>
<td>-</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>HNCO$^+$ + N$_2$</td>
<td>[0.55]</td>
<td>1.1</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>NO$^+$ + HNCN</td>
<td>[0.45]</td>
<td>1.04</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>O$_2$</td>
<td>HNCO$^+$ + O</td>
<td>[0.75]</td>
<td>0.36</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>NO$^+$ + HCO$^-$</td>
<td>[0.25]</td>
<td>0.77</td>
<td>344</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>HCNH$^+$ + CH$_3^+$</td>
<td>[≥ 85%]$^d$</td>
<td>1.1</td>
<td>134</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>C$_2$H$_3^+$ + HCN</td>
<td>[≥ 50%]$^d$</td>
<td>1.5</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_2$N$^+$ + H$^*$</td>
<td>[≥ 35%]$^d$</td>
<td>1.2</td>
<td>255</td>
</tr>
<tr>
<td>N$_2$</td>
<td>no reaction</td>
<td>&lt; 0.001</td>
<td>0.84</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$</td>
<td>CH$_2$N$^+$ + H$^*$</td>
<td>0.70</td>
<td>1.54</td>
<td>208</td>
</tr>
</tbody>
</table>

### Notes

a. See footnotes (a) - (c) for table (5.2).
b. Reaction exothermicity in units of kJ mol$^{-1}$. Taken from the tabulation of Lias et al.$^{184}$ unless otherwise stated.
c. See text for discussion.
d. A minor channel (≤ 15%) is also possible for C$_3$H$_3^+$ formation. See text.
These reactions (excluding the "invisible" channels (5.16b) and (5.17b)) were observed to occur upon virtually every collision, which means that channels leading to C2H3+ could not exceed 15% of the product distribution given the uncertainty in the rate coefficient determination. Production of C2H3+ is exothermic for HCN+ (ΔH5.16b = -72 kJ mol⁻¹) and possibly exothermic for HNC+, within experimental uncertainty (ΔH5.17b ≥ +2 ± 12 kJ mol⁻¹), but is unlikely in view of the high exothermicity of the competing H-atom transfer (5.16a, 5.17a) and the improbability of breakage of the C-N bond during reaction.

### Table 5.7: Reactions of HCN+ + X.

<table>
<thead>
<tr>
<th>X</th>
<th>Products</th>
<th>(k_{obs}^a)</th>
<th>(k^a)</th>
<th>(-\Delta H^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₆</td>
<td>SF₅⁺ + HF + CN⁻</td>
<td>1.3</td>
<td>1.2</td>
<td>49</td>
</tr>
<tr>
<td>CF₄</td>
<td>CF₃⁺ + HF + CN⁻</td>
<td>1.2</td>
<td>1.0</td>
<td>? b</td>
</tr>
<tr>
<td>CO</td>
<td>HNC⁺ + CO</td>
<td>[0.99]</td>
<td>0.46</td>
<td>-74</td>
</tr>
<tr>
<td></td>
<td>HCO⁺ + CN⁻</td>
<td>[0.01]</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>HNC⁺ + CO₂</td>
<td>[&gt; 0.99]</td>
<td>0.50</td>
<td>-74</td>
</tr>
<tr>
<td></td>
<td>CO₂⁺ + HCN</td>
<td>[0.003]</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>N₂O⁺ + HCN</td>
<td>[&gt; 0.90]</td>
<td>1.2</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>HCNO⁺ + N₂</td>
<td>[&lt; 0.10]</td>
<td>1.04</td>
<td>266</td>
</tr>
<tr>
<td>O₂</td>
<td>O₂⁺ + HCN</td>
<td>0.50</td>
<td>0.77</td>
<td>147</td>
</tr>
<tr>
<td>CH₄</td>
<td>HCNH⁺ + CH₃⁺</td>
<td>[&gt; 0.85] c</td>
<td>1.1</td>
<td>208</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>C₂H₃⁺ + HCN</td>
<td>[&gt; 0.85] c</td>
<td>1.5</td>
<td>212</td>
</tr>
<tr>
<td>N₂</td>
<td>no reaction</td>
<td>&lt; 0.001</td>
<td>0.84</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>CH₃N⁺ + H⁺</td>
<td>[&gt; 0.90]</td>
<td>0.86</td>
<td>282</td>
</tr>
<tr>
<td></td>
<td>HNC⁺ + H₂</td>
<td>[&lt; 0.10]</td>
<td>1.54</td>
<td>74</td>
</tr>
</tbody>
</table>

**Notes**

a. See footnotes (a) - (c) for table (5.2), (b) for table (5.6).
b. See text for discussion.
c. A minor channel (≤ 15%) is also possible for C₂H₃⁺ formation: see text.
For the reactions with $O_2$, both isomers were observed to react with similar efficiencies: only $HCN^+$ displayed charge transfer, suggesting $IP(HNC) < IP(O_2)$ since the rate coefficient observed for $HNC^+ + O_2$ was only half the calculated rate coefficient.

$$HNC^+ + O_2 \rightarrow HNCO^+ + O \quad [0.75] \quad (5.18a)$$

$$\rightarrow NO^+ + HCO^- \quad [0.25] \quad (5.18b)$$

$$\leftrightarrow O_2^+ + HNC \quad (5.18c)$$

The absence of channel (5.18c) thus implies $IP(HNC) < 12.071$ eV, which is lower than a value of $12.5 \pm 0.2$ eV obtained by charge exchange bracketing from $HNC^+$ generated from CH$_3$NC,$^{275}$ but which is in agreement with our determination of $\Delta H_f(HNC^+) \leq 1373$ kJ mol$^{-1}$ from the proton-transfer isomerisation of $HCN^+$ by CO.

The similarity of the rate coefficients for reaction of $HCN^+$ and $HNC^+$ with $O_2$ ($k_{HCN^+} = 1.4 k_{HNC^+}$) ensured that there was insufficient curvature evident [in the experimentally obtained graph of $\ln$(ion signal at m/z 27) versus $O_2$ concentration] to identify two reactive components. For this reason $O_2$ could not be used as a means of distinguishing $HCN^+$ from $HNC^+$, hence its position in table 5.2 among the other reagents that did not, by themselves, permit discrimination of $HCN^+$/HNC$^+$.

The reactions with CO$_2$ deserve further mention. In the absence of CO (added, to effect isomerisation, from the first inlet port), a very slow decay in the m/z 27 ion signal was evident, with a product signal at m/z 44 indicating the presence of
charge transfer to CO$_2$. This is, of course, in competition with a fairly rapid isomerisation:

\[
\begin{align*}
\text{HCN}^+ + \text{CO}_2 & \rightarrow \text{HNC}^+ + \text{CO}_2 & [0.997] & (5.19a) \\
& \rightarrow \text{CO}_2^+ + \text{HCN} & [0.003] & (5.19b).
\end{align*}
\]

The very slow charge-transfer process represented by channel (5.19b) is entirely consistent with known thermochemical values. IP(CO$_2$) - IP(HCN) = 17 ± 1 kJ mol$^{-1}$, and on the basis of the Arrhenius expression for the upper limit to the rate of an endothermic process,

\[
k_{5.19b} \leq k_c e^{-\Delta H_{5.19b}/RT}
\]

\[
\therefore \quad k_{5.19b} \leq 2.0 \times 10^{-3} k_c \ @ 300K
\]

\[
\therefore \quad k_{5.19b} \leq 2.0 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1},
\]

which is in accord with the observed effective rate coefficient $k_{5.19b} = 1.5 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Upon the addition of CO, essentially complete conversion of HCN$^+$ to HNC$^+$ could be effected: reaction of the m/z 27 ion signal with CO$_2$ then exhibited an adduct signal only (HNC.CO$_2^+$, m/z = 71). This product signal was not evident in the absence of CO, which suggests that it may have arisen by a ligand-switching mechanism

\[
\begin{align*}
\text{HNC}^+ + \text{CO} + \text{He} & \rightarrow \text{HNC.CO}^+ + \text{He} & (5.20) \\
\text{HNC.CO}^+ + \text{CO}_2 & \rightarrow \text{HNC.CO}_2^+ + \text{CO} & (5.21)
\end{align*}
\]
rather than by simple termolecular association of HNC\(^+\) with CO\(_2\). The adduct produced by the proposed reaction (5.20), HNC.CO\(^+\) (m/z = 55), was not detected, but a weakly-bound adduct might not survive the ion sampling system downstream from the flow tube.

The absence of proton transfer from HNC\(^+\) to CO indicates that this process is endothermic (as indeed is required by the forth-and-back proton transfer mechanism invoked for isomerisation of HCN\(^+\) by CO). A mildly endothermic proton-transfer process might still be observable, in the absence of competing product channels, so the absence of such a proton-transfer channel in the case of HNC\(^+\) with CO suggests that this process is considerably endothermic (\(\Delta H \geq +10 \text{ kJ mol}^{-1}\)). However, the absence of an expected product channel is not an adequate basis for establishing thermochemistry and so the threshold for \(\Delta H_f(\text{HNC}^+)\) is best expressed as \(\leq 1373 \text{ kJ mol}^{-1}\).

Other systems in which ion-molecule reactions are involved in isomerisation are HCO\(^+\)/HOC\(^+\) and HNNO\(^+\)/NNOH\(^+\). HOC\(^+\), which has been studied by Freeman et al.,\(^{166,206}\) is seen to undergo conversion to the lower-energy isomer HCO\(^+\) by reaction with CO and with H\(_2\):

\[
\begin{align*}
\text{HOC}^+ + \text{CO} & \rightarrow \text{HCO}^+ + \text{CO} \\
k_{5.22} &= 6.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \\
\text{HOC}^+ + \text{H}_2 & \rightarrow \text{H}_3^+ + \text{CO} \\
& \rightarrow \text{HCO}^+ + \text{H}_2 \\
k_{5.23} &= 4.7 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}. 
\end{align*}
\]
The reaction with H₂ is interpreted as involving initial proton transfer (which is endothermic by ~ 3 kJ mol⁻¹)²⁶³ to H₂, followed by rotation of CO within the collision complex and subsequent proton transfer back to CO, yielding HCO⁺. The low efficiency of this isomerisation process reflects the endothermicity of the initial proton transfer to H₂ and the relatively low probability of CO rotation within the complex before fragmentation: CO has a very small dipole moment (μ = 0.112 debye), so the forces inducing rotation will be weak compared with those for HCN⁺ isomerisation by X: rotation of the (NC···HX⁺) complex is favoured by the large dipole moment (μ = 1.45 debye) of CN.

Conversion of HNNO⁺ to the more stable isomer NNOH⁺ has not been directly observed,²⁶² but this isomerisation has been implicated in the reaction with NO which has been analysed by Ferguson:²⁶³

\[
HNNO^+ + NO \rightarrow NO^+ + N_2 + OH^-
\]

\[k_{5.24} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.
\]

This reaction, which is observed to proceed more slowly than the corresponding reaction of the lower-energy isomer NNOH⁺,²⁶² is interpreted in terms of a mechanism involving exothermic proton transfer to NO, rotation of NNO within the collision complex, exothermic proton transfer to NNO, and subsequent dissociative charge transfer:

\[
\text{ONNH}^+ + \text{NO} \rightarrow (\text{ONN}···\text{HNO})^+
\]

\[(\text{ONN}···\text{HNO})^+ \rightarrow (\text{NNO}···\text{HNO})^+
\]

\[(\text{NNO}···\text{HNO})^+ \rightarrow (\text{NNOH}···\text{NO})^+
\]

\[(\text{NNOH}···\text{NO})^+ \rightarrow \text{NO}^+ + N_2 + \text{OH}^-
\]
The necessity for such a complicated mechanism is that thermochemistry constrains the neutral products to be N₂ and OH·, the formation of which requires substantial rearrangement of the collision complex. It is quite conceivable that this reaction also results in the direct conversion of a fraction of the HNNO⁺ to NNOH⁺ via dissociation of the complex following step (5.24c), but this has not been experimentally verified.

In the present work, further experiments were performed to investigate the ratio of HCN⁺/HNC⁺ isomers produced in various reactions. The results of these experiments are summarised in table 5.8. It might intuitively be expected that any reaction of the form

\[
\begin{align*}
X^+ + HCN & \rightarrow HCN^+ + X \quad (5.25a) \\
& \rightarrow HNC^+ + X \quad (5.25b)
\end{align*}
\]

would tend to form predominantly HCN⁺, since this higher-energy ion can be produced by a simple charge exchange while HNC⁺ can only be produced by rearrangement of an excited HCN⁺ product (or within an X···HCN⁺ collision complex). If the barrier to isomerisation is high, as Koch et al.²⁷⁸ have calculated, then isomerisation can occur only within the collision complex unless reaction (5.25a) is sufficiently exothermic to allow the unimolecular reaction

\[
(HCN^+)^* \rightarrow (HNC^+)^* \quad (5.26)
\]

\[E_a \sim 120 \text{ kJ mol}^{-1}\]

to occur also. For a simple charge transfer reaction, collision complexes should be comparatively short-lived, and much of the excess energy released by charge
Table 5.8: Miscellaneous other reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>$k_{obs}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$k$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>-ΔH&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
<td>Ar&lt;sup&gt;+&lt;/sup&gt; + SF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>SF&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt; + Ar + F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>[&gt; 0.99]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.54</td>
<td>1.0</td>
</tr>
<tr>
<td>CN&lt;sup&gt;+&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>HCN&lt;sup&gt;+&lt;/sup&gt; + H&lt;sup&gt;-&lt;/sup&gt;</td>
<td>[0.57]&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.79</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>HNC&lt;sup&gt;+&lt;/sup&gt; + H&lt;sup&gt;-&lt;/sup&gt;</td>
<td>[0.43]&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt; + HCN</td>
<td>HNC&lt;sup&gt;+&lt;/sup&gt; + C&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>[0.20]</td>
<td>2.7</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;H&lt;sup&gt;+&lt;/sup&gt; + CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>[0.75]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>[0.05]</td>
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<td></td>
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<tr>
<td>O&lt;sup&gt;+&lt;/sup&gt; + HCN</td>
<td>NO&lt;sup&gt;+&lt;/sup&gt; + CH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>[0.55]</td>
<td>3.9</td>
<td>4.4</td>
</tr>
<tr>
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<td>HCN&lt;sup&gt;+&lt;/sup&gt; + O</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>[0.06]&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
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</tr>
<tr>
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<td>CHO&lt;sup&gt;+&lt;/sup&gt; + N&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>HCN&lt;sup&gt;+&lt;/sup&gt; + N</td>
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<td>[0.09]&lt;sup&gt;c&lt;/sup&gt;</td>
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</tr>
<tr>
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<td>HCN&lt;sup&gt;+&lt;/sup&gt; + N&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>0.39&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>[0.22]&lt;sup&gt;c&lt;/sup&gt;</td>
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<td></td>
</tr>
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<td>Kr&lt;sup&gt;+&lt;/sup&gt; + HCN</td>
<td>HCN&lt;sup&gt;+&lt;/sup&gt; + Kr</td>
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<td>3.1</td>
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<tr>
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<td>HNC&lt;sup&gt;+&lt;/sup&gt; + Kr</td>
<td>[0.22]&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt; + HCN</td>
<td>HCN&lt;sup&gt;+&lt;/sup&gt; + CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>[0.59]&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>HNC&lt;sup&gt;+&lt;/sup&gt; + CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>[0.41]&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN&lt;sup&gt;+&lt;/sup&gt; + HCN</td>
<td>HCN&lt;sup&gt;+&lt;/sup&gt; + CN&lt;sup&gt;-&lt;/sup&gt;</td>
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<td></td>
<td>HNC&lt;sup&gt;+&lt;/sup&gt; + CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>[0.55]&lt;sup&gt;c&lt;/sup&gt;</td>
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<td></td>
</tr>
<tr>
<td>CN&lt;sup&gt;+&lt;/sup&gt; + CO</td>
<td>CO&lt;sup&gt;+&lt;/sup&gt; + CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>[0.39]</td>
<td>0.39</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Notes

a. See footnotes (a) - (c) for table (5.2), (b) for table (5.6).
b. Minor product seen [-0.001] at m/z = 89, corresponding to SF<sub>3</sub><sup>+</sup>.
c. Product ratio determined by reaction of CHN<sup>+</sup> with CF<sub>4</sub>.
d. Calculated exothermicity for formation of HCO<sup>+</sup>. -ΔH = 262 kJ mol<sup>-1</sup> for production of COH<sup>+</sup>.
e. Rate coefficient not determined.
f. Rate coefficient not determined in this work. Literature value quoted from the compilation of Anichich & Huntress.<sup>182</sup>
transfer should be localised within the ionic product: thus, isomerisation should occur reasonably efficiently for those charge-transfer reactions which have an exothermicity greater than \( E_a \). The efficiency of HNC\(^+\) production by this method will depend upon the competition between the unimolecular isomerisation (5.26) and the collisional quenching of internally excited CHN\(^+\) by He. Charge-transfer reactions less exothermic than \( E_a \) should not result in noticeable isomerisation of HCN\(^+\).

Of the reactions \( X^+ + \text{HCN} \) in table 5.8, those with \( X = \text{N}_2 \) and Ar have sufficiently exothermic charge-transfer channels to allow subsequent isomerisation; for \( X = \text{N}^+, \text{O}, \text{Kr}, \text{CO}_2 \) and \( \text{CN}^- \), no HNC\(^+\) should be produced if the reaction initially occurs as the transfer of an electron from HCN to \( X^+ \). This expectation is not well met by the data observed.

The observation of \(~20-25\%\) HNC\(^+\) formation in the reactions of Ar\(^+\) and N\(_2^+\) is quite consistent with the expectation that some HNC\(^+\) should be produced by charge-transfer in these instances, but several of the other reactions also produce comparable yields of HNC\(^+\). How?

One possibility is that the reactant ions may possess vibrational or rotational excitation. In all cases, ions were produced in the ion source by electron bombardment: the high energies of the electrons emitted from the filament easily permit production of excited ions, which might not be adequately quenched by repeated collisions with the He buffer gas. Metastable electronic excitation, for example, might account for the production of some HNC\(^+\) in the reactions with \( \text{N}^+ \) and Kr\(^+\). The lowest metastable electronic state of \( \text{N}^+ \) is the
\(^1D_2\) state, which lies 183 k\(\text{J mol}^{-1}\) above the ground state \((^3P_0)\). The lowest such states for \(\text{Kr}^+\) are the \(^2P_0\) and \(^4P_2\) states, which are 64.3 k\(\text{J mol}^{-1}\) and 1350 k\(\text{J mol}^{-1}\), respectively, above the ground state \((^2P_{1/2})\).\(^{283}\)

Other factors are likely to apply in the reactions of \(\text{O}^+, \text{CN}^+\) and \(\text{CO}_2^+\). With \(\text{O}^+\), several product channels are evident, and some of the products (\(\text{NH}, \text{HCO}^+\)) require rearrangement. If such rearrangement can occur for these products, it is reasonable to expect that it can occur also to produce \(\text{HNC}^+\).

The reaction of \(\text{CN}^+\) may involve charge-transfer or H-atom abstraction: the latter process will tend to favour \(\text{HNC}^+\) production, so the \(\text{HNC}^+\) formed in this reaction can be taken as a lower limit of the extent of H-atom transfer in this reaction. Similarly, the reaction of \(\text{CN}^+\) with \(\text{H}_2\) (which we have studied also) appears to produce a \(\sim 1:1\) mixture of the two isomers.

Charge-transfer from \(\text{CO}_2\) is only slightly exothermic, and for this reason (and since a \(\text{CO}_2\cdot\text{HCN}^+\) complex features many vibrational and rotational modes among which internal energy may be partitioned) the collision complex may be relatively long-lived. \(\text{HNC}^+\) can be produced by forth-and-back proton transfer within such a complex:

\[
\begin{align*}
\text{CO}_2^+ + \text{HCN} &\rightarrow (\text{OCO}\cdots\text{HCN})^+ \quad (5.27a) \\
(\text{OCO}\cdots\text{HCN})^+ &\rightarrow (\text{OCOH}\cdots\text{CN})^+ \quad (5.27b) \\
(\text{OCOH}\cdots\text{CN})^+ &\rightarrow (\text{OCOH}\cdots\text{NC})^+ \quad (5.27c) \\
(\text{OCOH}\cdots\text{NC})^+ &\rightarrow (\text{OCO}\cdots\text{HNC})^+ \quad (5.27d) \\
(\text{OCO}\cdots\text{HNC})^+ &\rightarrow \text{HNC}^+ + \text{CO}_2 \quad (5.27e).
\end{align*}
\]
This mechanism seems satisfactory to account for the especially high efficiency of HNC\(^+\) production in this charge-transfer process.

Another factor which must be addressed is that the HCN\(^+\)/HNC\(^+\) ratio might be dependent upon the quantity of HCN added in the above experiments. Specifically, is HCN\(^+\) converted to HNC\(^+\) in reactions with neutrals such as HCN? A mechanism of forth-and-back proton transfer suggests that HCN should be efficient in isomerising HCN\(^+\)

\[
\text{HCN} + \text{HCN}^+ \rightarrow (\text{HCNH} \cdots \text{CN})^+ \quad (5.28a)
\]

\[
(\text{HCNH} \cdots \text{CN})^+ \rightarrow (\text{HCNH} \cdots \text{NC})^+ \quad (5.28b)
\]

\[
(\text{HCNH} \cdots \text{NC})^+ \rightarrow \text{HCN} + \text{HNC}^+ \quad (5.28c)
\]

\[\Delta H_{5.28a-c} = 74 \text{ kJ mol}^{-1},\]

since PA(HCN) > PA(CN), but in practice the formation of HCNH\(^+\) + CN\(^-\) is substantially more exothermic than formation of HNC\(^+\) and so HCNH\(^+\) is seen to be the major product:

\[
\text{HCN}^+ + \text{HCN} \rightarrow \text{HCNH}^+ + \text{CN}^- \quad (5.28d)
\]

\[\Delta H_{5.28d} = 413 \text{ kJ mol}^{-1}\]

\[k_{5.28d} = 2.50 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}.\]

A small difference between the rate of reaction (5.28d) and the corresponding reaction rate for HNC\(^+\)

\[
\text{HNC}^+ + \text{HCN} \rightarrow \text{HCNH}^+ + \text{CN}^- \quad (5.29)
\]

\[\Delta H_{5.29} = 339 \text{ kJ mol}^{-1}\]

\[k_{5.29} = 3.22 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}.\]
suggests that the two ions may react differently. Furthermore, since the higher energy isomer is observed to react at a slightly slower rate than the lower-energy isomer (although the difference in rates is within the ascribed uncertainty of the measurements) and significantly below the calculated ADO collision rate \( k_c = 3.8 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \), there exists the possibility that some apparently unreactive HCN\(^+\) + HCN collisions do result instead in forth-and-back isomerisation to HNC\(^+\). Experiments which were performed by us attempted to examine this possibility, using CF\(_4\) to investigate the HCN\(^+\)/HNC\(^+\) ratio as a function of HCN flow, but the results are not conclusive. A rate coefficient of \( k_{5.28a-c} = (2.75 \pm 3) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) was obtained: clearly, the uncertainty of this value (derived principally from the large uncertainties in \( k_{5.28d} \) and \( k_{5.29} \)) is too great to exclude the possibility that channel (5.28d) is the only channel accessible in reaction of HCN\(^+\) with HCN.

Further experiments with isotopically substituted reactants attempted to resolve this issue. The reaction

\[
\text{DCN}^+ + \text{HCN} \rightarrow \text{HNC}^+ + \text{DCN} \quad (5.30a)
\]

is exothermic by a similar degree to the isomerisation of HCN\(^+\) by HCN, although differences in the zero-point energies of the respective reactants and products will have a small thermochemical effect. Channel (5.30a) is, of course, in competition with the more exothermic process

\[
\text{DCN}^+ + \text{HCN} \rightarrow \text{DCNH}^+ + \text{CN}^- \quad (5.30b)
\]
as well as the channels

\[
\begin{align*}
\rightarrow & \quad \text{DNC}^+ + \text{HCN} & (5.30c) \\
\rightarrow & \quad \text{HCN}^+ + \text{DCN} & (5.30d),
\end{align*}
\]

although in view of the near-thermoneutral nature of reaction (5.30d), this channel is likely to be of very low efficiency. An estimate of \(\Delta H_{5.30d} \sim 6 \text{ kJ mol}^{-1}\) can be obtained from the literature values of ZPE(HCN)\(^{284}\) and ZPE(HCN\(^{+}\))\(^{285}\) and the estimated values for the deuterated isotopomers of these species\(^{286}\) the endothermicity of this reaction, with so many exothermic channels available, ensures that channel (5.30d) will be of very little importance. Any observed products at m/z 27 are thus likely to originate from channel (5.30a), while products at m/z 29 arise from channel (5.30b). A small channel corresponding to reaction (5.30c) is likely to be unobservable because of the rapid subsequent reaction of this isomer with HCN. In our experiments, channel (5.30a) was found to account for less than 2% of the total disappearance of m/z 28: therefore, it appears that proton-transfer isomerisation (if it occurs here) does not also involve H/D scrambling in the collision complex.

The reaction of DCND\(^{+}\) (generated by electron impact on DCN in the ion source) with HCN is observed to result in rapid H/D scrambling:

\[
\text{DCND}^+ + \text{HCN} \rightarrow \text{HCND}^+ + \text{DCN} \quad (5.31)
\]

\[k_{5.31} = 1.47 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}.\]
The high efficiency of this process shows that this reaction is not greatly endothermic (that is, the differences in zero-point energy of the reactants and products only marginally favour the reactants over formation of products). In fact, $\Delta H_{5.31} \sim 4 \text{ kJ mol}^{-1}$ according to experimental, calculated, and estimated zero-point vibrational energies for the various reactants. An estimate for $\Delta H_{5.31} \leq 3.3 \text{ kJ mol}^{-1}$ can be obtained from the Arrhenius expression: this is in reasonable agreement with the value calculated from zero-point energies, considering that the calculated value is not of high accuracy. Note that the structure of the product ion is expected to be HCND$^+$ rather than DCNH$^+$ since a simple deuteron-transfer reaction to HCN is the most straightforward mechanism available.

The experiments described here do not conclusively answer the problem of whether HCN can convert HCN$^+$ to HNC$^+$: however, the studies to date suggest that such a process (if it occurs) is very inefficient in comparison with formation of HCNH$^+$ in the same reaction. For this reason, the product ratios reported in table 5.8 are not likely to be significantly in error due to such an isomerisation process.

Finally, the charge-transfer reaction involving CN$^+$ and CO (also listed in table 5.8) may help to refine the thermochemistry of CN$^-$: this reaction is calculated to be $7 \text{ kJ mol}^{-1}$ exothermic, but the total uncertainties on this value are very large. The observation that this reaction does indeed proceed reasonably rapidly suggests that it is exothermic, which allows some reduction of the uncertainties of $\Delta H_f(\text{CN}^+)$ and $\Delta H_f(\text{CN}^-)$. 
Section 5.2: CH$_2$N$^+$. 

Hydrogen cyanide$^{287}$ and hydrogen isocyanide$^{288}$ are the first pair of isomers to be reported in the interstellar environment. Protonation of this pair of isomers yields three possible structures:

\[
\begin{align*}
XH^+ + HCN &\rightarrow HCNH^+ + X \\
&\rightarrow H_2CN^+ + X \\
XH^+ + HNC &\rightarrow HCNH^+ + X \\
&\rightarrow CNH_2^+ + X
\end{align*}
\]

(5.32a) (5.32b) (5.33a) (5.33b).

Ab initio calculations by Pearson and Schaefer$^{289}$ on the relative energies of H$_2$CN$^+$ and HCNH$^+$ (see table 5.9) indicated that HCNH$^+$ was the more stable of this pair of isomers and would therefore be the most likely form of CH$_2$N$^+$ to be produced by reactions in interstellar clouds. However, these authors cautioned, "... there is some uncertainty as to whether [HCNH$^+$] would be observable, even if a radioastronomer were to stumble upon its proper frequency ... the electric dipole moment ... is 0.63 debyes".

The proper frequency was stumbled upon by Ziurys and Turner,$^{294}$ who reported a detection of HCNH$^+$ in the giant molecular cloud Sgr B2, with a calculated abundance (relative to H$_2$) of 3 x 10$^{-10}$. CNH$_2^+$ has also been searched for, but not detected. Brown$^{295}$ has suggested that the reaction

\[ C^+ + NH_3 \rightarrow CH_2N^+ + H^- \] (5.34)
should preferentially produce the CNH$_2^+$ isomer, which should yield HNC rather than HCN upon dissociative recombination:

\[
\begin{align*}
\text{CNH}_2^+ + e & \rightarrow \text{HNC} + \text{H}^- \quad (5.35a) \\
& \rightarrow \text{CN}^- + \text{H}_2 \quad (5.35b).
\end{align*}
\]

Schaefer$^{291,292}$ has countered that reaction (5.34) is very exothermic and should deposit sufficient internal energy in any CNH$_2^+$ product to effect the isomerisation of this ion to the more stable HCNH$^+$ isomer. If this isomerisation occurs, the HCN/HNC ratio is dependent principally upon the branching ratio of the dissociative recombination process.

Table 5.9: Experimental and theoretical thermochemistry of CH$_2$N$^+$.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\Delta H_f$(HCNH$^+$)$^a$</th>
<th>$\Delta H_f$(H$_2$CN$^+$)$^a$</th>
<th>$\Delta H_f$(CNH$_2^+$)$^a$</th>
<th>$\Delta H_f$(TS)$^a,b$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>947</td>
<td>$-$</td>
<td>1109</td>
<td>$-$</td>
<td>1248</td>
<td>c</td>
</tr>
<tr>
<td>947</td>
<td>1257</td>
<td>1165</td>
<td>1175</td>
<td>$-$</td>
<td>d</td>
</tr>
<tr>
<td>947</td>
<td>$-$</td>
<td>1140</td>
<td>1265</td>
<td>$-$</td>
<td>e</td>
</tr>
<tr>
<td>947</td>
<td>1248</td>
<td>1114</td>
<td>$-$</td>
<td>$-$</td>
<td>f</td>
</tr>
</tbody>
</table>

Notes:

a. Heats of formation are expressed in kJ mol$^{-1}$.
b. TS = transition state for the isomerisation HCNH$^+ \leftrightarrow$ CNH$_2^+$.
c. Literature values.$^{184}$
d. MP4SDTQ/6-311G(d,p)//MP2/6-31G(d) calculations, adjusted to the accepted literature value for $\Delta H_f$(HCNH$^+$).
e. MP2/6-31G**//4-31G+ZPVE calculations, adjusted to the accepted literature value for $\Delta H_f$(HCNH$^+$).
f. DZ SCF calculations, adjusted to the accepted literature value for $\Delta H_f$(HCNH$^+$).
g. SCF/6-31G** calculations, adjusted to the accepted literature value for $\Delta H_f$(HCNH$^+$).
HCNH\(^+\) + e \rightarrow HCN + H\(^-\) \hspace{1cm} (5.36a)

\rightarrow HNC + H\(^-\) \hspace{1cm} (5.36b)

\rightarrow CN\(^-\) + H\(_2\) \hspace{1cm} (5.36c).

One aspect of understanding the observed HCN/HNC abundances is, therefore, a knowledge of the reactivity of HCNH\(^+\) and of CNH\(_2^+\). A requirement for studying these isomers in the SIFT is that some diagnostic reagent be found to distinguish between them. This in turn requires that a satisfactory method can be found for generating a CH\(_2^+\) ion signal which contains some observable proportion of the CNH\(_2^+\) isomer. As explained below, this proved not to be an easy task.

The experimental techniques unsuccessfully used to generate CNH\(_2^+\) are summarised in table 5.10. Of these methods, only (i) and (vi) resulted in injection of satisfactorily large signals of CH\(_2^+\) at m/z 28 from the ion source, and the predominant isomer produced in these instances is expected to be HCNH\(^+\).

Several of the methods employed the reaction of C\(^+\) or CCl\(^+\) with NH\(_3\), in the hope that CNH\(_2^+\) would be the major product. Of these methods, (iv), (v) and (viii) failed to produce substantial m/z 28 signals in the ion source: (ix) produced appreciable m/z 28, but this appeared, from its subsequent reactivity, to be almost entirely due to CO\(^+\) from electron impact upon CO.

Methods (ii) and (iii) produced sizeable m/z 28 signals within the flow tube, but no reactivity conclusively due to CNH\(_2^+\) was observed in these instances.
Production of CH$_2$N$^+$ from NH$_3$ within the flow tube was problematic, since optimum m/z 28 signals were obtained when only a small flow of NH$_3$ was

Table 5.10: Methods of CNH$_2^+$ generation employed unsuccessfully.

<table>
<thead>
<tr>
<th>Source cpds. $^a$</th>
<th>Reaction(s) involved</th>
<th>Site $^{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>i HCN</td>
<td>CHN$^+$ + HCN → CH$_2$N$^+$ + CN$^-$</td>
<td>IS</td>
</tr>
<tr>
<td>ii CCl$_4$ (IS); NH$_3$ (FT)</td>
<td>CCl$^+$ + NH$_3$ → CH$_2$N$^+$ + HCl</td>
<td>FT</td>
</tr>
<tr>
<td>iii CO (IS); NH$_3$ (FT)</td>
<td>C$^+$ + NH$_3$ → CH$_2$N$^+$ + H$^+$</td>
<td>FT</td>
</tr>
<tr>
<td>iv CCl$_4$, NH$_3$ $^c$</td>
<td>CCl$^+$ + NH$_3$ → CH$_2$N$^+$ + HCl</td>
<td>IS</td>
</tr>
<tr>
<td>v He, CCl$_4$, NH$_3$ $^d$</td>
<td>CCl$^+$ + NH$_3$ → CH$_2$N$^+$ + HCl</td>
<td>IS</td>
</tr>
<tr>
<td>vi HCN, H$_2$ $^e$</td>
<td>CHN$^+$ + HCN → CH$_2$N$^+$ + CN$^-$</td>
<td>IS</td>
</tr>
<tr>
<td>vii CS$_2$ (IS); NH$_3$ (FT)</td>
<td>C$^+$ + NH$_3$ → CH$_2$N$^+$ + H$^+$</td>
<td>FT</td>
</tr>
<tr>
<td>viii He, C$_2$N$_2$, NH$_3$ $^d$</td>
<td>C$^+$ + NH$_3$ → CH$_2$N$^+$ + H$^+$</td>
<td>IS</td>
</tr>
<tr>
<td>ix He, CO, NH$_3$ $^f$</td>
<td>C$^+$ + NH$_3$ → CH$_2$N$^+$ + H$^+$</td>
<td>IS</td>
</tr>
<tr>
<td>x C$_2$H$_5$NO$_3$ $^g$</td>
<td>e + C$_2$H$_5$NO$_3$ → CH$_2$N$^+$ + 3CO + CH$_3^+$ + 2e</td>
<td>IS</td>
</tr>
<tr>
<td>xi He, C$_2$H$_5$NO$_3$ $^g$</td>
<td>e + C$_2$H$_5$NO$_3$ → CH$_2$N$^+$ + 3CO + CH$_3^+$ + 2e</td>
<td>IS</td>
</tr>
<tr>
<td>xii CCl$_4$, C$_2$H$_5$NO$_3$ $^g$</td>
<td>e + C$_2$H$_5$NO$_3$ → CH$_2$N$^+$ + 3CO + CH$_3^+$ + 2e</td>
<td>IS</td>
</tr>
<tr>
<td>xiii C$_3$H$_6$NH$_2$</td>
<td>e + C$_3$H$_6$NH$_2$ → CH$_2$N$^+$ + C$_3$H$_5^+$ + 2e</td>
<td>IS</td>
</tr>
<tr>
<td>xiv H$_2$NCN $^k$</td>
<td>e + H$_2$NCN → CH$_2$N$^+$ + N + 2e</td>
<td>IS</td>
</tr>
<tr>
<td>xv He (IS), H$_2$NCN $^l$ (FT)</td>
<td>He$^+$ + H$_2$NCN → CH$_2$N$^+$ + N + He</td>
<td>FT</td>
</tr>
<tr>
<td>xvi C$_2$N$_2$ (IS), H$_2$ (FT)</td>
<td>CN$^+$ + H$_2$ → CHN$^+$ + H.</td>
<td>FT</td>
</tr>
<tr>
<td></td>
<td>CHN$^+$ + H$_2$ → CH$_2$N$^+$ + H.</td>
<td>FT</td>
</tr>
</tbody>
</table>

Notes
a. IS = ion source; FT = flow tube. Unless specified, all reagents are added at the ion source.
b. Site of CH$_2$N$^+$ generation.
c. 1:1 mixture.
d. 10:1:1 mixture.
e. 1:10 mixture.
f. 30:1:2 mixture.
g. Introduced into source at $T \sim 120^\circ$C.
h. A dilute solution of C$_2$H$_5$NO$_3$ in CCl$_4$.
i. Introduced entrained in helium or dissolved in CCl$_4$, CHCl$_3$ or tetrahydrofuran.
j. Dissolved in CCl$_4$. 

\[
\text{CH}_3\text{O} \quad \text{C} \quad \text{C} \quad \text{O} \\
\text{H}_2\text{N} \quad \text{C} \quad \text{C} \quad \text{O}
\]
established: under these conditions the signal detected due to the C+ or CCl+ primary ion was sizeable, and so CH₂N+ production was occurring throughout the length of the flow tube from the point of NH₃ injection at portal 1 to the exit orifice. A titrating gas X could not be found which would apparently distinguish between HCNH⁺ and CNH₂⁺ without reacting also with C+ or CCl+, and under these conditions addition of a large flow of X would reduce the m/z 28 signal by approximately half due to removal of all C+ or CCl+ downstream of portal 2 by reaction with X. Identification of an additional decrease in m/z 28 due to the reaction of CNH₂⁺ with X in a manner distinct from the reaction of HCNH⁺ with X was, in these circumstances, not possible.

Method (vii) resulted in too small a signal of C+ to be serviceable.

Methods (x), (xi) and (xii) attempted to exploit the demonstration, by Burgers et al.,²⁹⁶ that electron bombardment of the squaric acid derivative 1-methoxy 2-amino cyclobutenedione produces CNH₂⁺, and not HCNH⁺, at m/z 28. 1-methoxy 2-amino cyclobutenedione was prepared by the method of Cohen and Cohen¹⁸⁰ and its purity determined by ms, gc-ms and IR spectroscopy. For method (x) the crystalline solid was placed in a U-tube immediately upstream of the ion source and heated while a stream of argon was maintained through the tube to entrain the vapourised compound. For method (xi) the solid was stored in a glass bulb under helium and heated prior to injection into the ion source. For method (xii) the solid was dissolved (sparingly) in CCl₄ which was then vacuum-distilled and the resultant vapour was admitted to the ion source. In all these cases, heating of the glass vessel containing the compound resulted in the introduction of a reasonable pressure of C₅H₅NO₃ into the ion source, but
electron impact upon this vapour gave rise to much larger signals at m/z 27, 29 and 31 than at m/z 28. This is in disagreement with the observation by Burgers et al that a peak at m/z 28 due to CNH$_2^+$ dominated this region of the mass spectrum. In our experiment, it appeared that the peaks at m/z 27, 29 and 31 (C$_2$H$_3^+$, C$_2$H$_5^+$, CH$_3$O$^+$ ?) arose mainly from secondary reactions of ions produced within the ion source, since these signals diminished in intensity relative to m/z 28 as the pressure in the ion source was reduced. However, the m/z 28 signal did not exceed about 3 counts per second at any point over the whole range of pressures tested in our experiment: it was not felt to be worthwhile attempting to determine the isomeric purity of such a small signal, especially since the increased resolution required to remove the contaminant ion signals at m/z 27 and 29 would have resulted in a further signal attenuation. It appears that, though electron impact upon C$_5$H$_5$NO$_3$ at a pressure of approximately 10$^{-7}$ Torr does produce large signals due to CNH$_2^+$ as shown by Burgers et al.,$^{296}$ the higher operating pressure (P > 10$^{-4}$ Torr) required in the SIFT ion source to generate detectable signals results in the loss of most of the m/z 28 initially generated, due to secondary reactions.

Method (xiii) also attempted to favour CNH$_2^+$ formation by virtue of the structure of the source gas, aniline. However, injection of aniline into the ion source resulted in only a very small signal due to m/z 28, which we did not attempt to study further.

Methods (xiv) and (xv) attempted to favour CNH$_2^+$ formation from cyanamide, H$_2$NCN. The low-pressure mass spectrum of cyanamide$^{297}$ does feature a m/z 28 peak, which may well be CNH$_2^+$ on the basis of the parent neutral's structure.
However, none of the methods for introducing H$_2$NCN into the SIFT resulted in a usable m/z 28 ion signal. At 30°C, the vapour pressure of cyanamide is very low (~ 1 Torr) and so an attempt to add the vapour from solid cyanamide (stored under helium in a gas bulb) was not successful. Attempts with dissolved cyanamide were more successful - when CCl$_4$ was employed as the solvent, a sizeable m/z 42 signal could be obtained when the vapour was introduced into the ion source, and this appears a good method for studying the reactions of the cyanamide ion CN$_2$H$_2$+. CHCl$_3$ and THF (tetrahydrofuran) were less useful solvents - although they dissolved cyanamide more readily, they also produced many unidentified ion signals in the mass range m/z 25 - 55: in the chloroform solution, these signals were most probably due to organic contaminants. The reaction of He$^+$ with cyanamide (introduced as the vapour from a saturated solution of H$_2$NCN in CCl$_4$) was also studied, in the hope that this might produce some m/z 28, but this did not eventuate - in this experiment, there was a background of ~ 10 counts per second at m/z 28 (most probably from the reaction of He$^+$ with an N$_2$ impurity within the tube), while complete reaction of He$^+$ with the added reactant gas did not produce any change at m/z 28, nor any observable signal at m/z 42.

Method (xvi) was studied in the hope that some observable fraction of the resulting CH$_2$N$^+$ signal might be CNH$_2$+, the formation of which is energetically feasible:

\[
\begin{align*}
\text{CN}^+ & \quad + \quad \text{H}_2 & \rightarrow \quad \text{HCN}^+ & \quad + \quad \text{H}^- & \quad [0.50] & \quad (5.37a) \\
& \quad \rightarrow \quad \text{HNC}^+ & \quad + \quad \text{H}^- & \quad [0.50] & \quad (5.37b) \\
\end{align*}
\]

\[k_{5,37} = 1.1 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\]
\[
\text{HNC}^+ + \text{H}_2 \rightarrow \text{HCNH}^+ + \text{H}_2^+ \quad (5.38a) \\
\rightarrow \text{CNH}_2^+ + \text{H}_\cdot \\
\]

\[k_{5,38} = 7 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

\[\Delta H_{5,38a} = -209 \text{ kJ mol}^{-1} \]

\[\Delta H_{5,38b} = -47 \text{ kJ mol}^{-1}. \]

It might be expected that some of the HNC\(^+\) produced in reaction (5.37b) can produce CNH\(_2^+\), which should be left with insufficient energy to isomerise by unimolecular rearrangement since the calculated barrier is substantial. If CNH\(_2^+\) is unreactive with H\(_2\), addition of large flows of H\(_2\) to the flow tube should result in complete conversion of CN\(^+\) to CH\(_2\)N\(^+\), containing a minority signal due to CNH\(_2^+\) which should then undergo further reaction with an appropriate reagent. Unfortunately, this method too proved ineffective: no recognisable reaction was observed that might be due only to CNH\(_2^+\) within this m/z 28 ion signal.

Reactions of CH\(_2\)N\(^+\) which were studied to attempt to distinguish between HCNH\(^+\) and CNH\(_2^+\) are listed in table 5.11. Many of these reactions were selected in the hope that proton transfer would be observed due to the reaction of CNH\(_2^+\), but not due to HCNH\(^+\). This requires that the proton affinity of the neutral reactant be intermediate between PA (HNC) and PA (HCN), that is, 622 kJ mol\(^{-1}\) < PA(X) < 717 kJ mol\(^{-1}\). The lower boundary condition here is necessarily vague because of the substantial uncertainty in \(\Delta H_f\) (CNH\(_2^+\)), and a further uncertainty exists since a proton-transfer reaction involving isomerisation of the product neutral CHN can also be postulated:
\[
\begin{align*}
\text{CNH}_2^+ + X & \rightarrow XH^+ + \text{HCN} & \text{(5.39a)} \\
& \rightarrow XH^+ + \text{HNC} & \text{(5.39b)} \\
\Delta H_{5.39a} = \Delta H_{5.39b} - 66 \text{ kJ mol}^{-1}.
\end{align*}
\]

If product channel (5.39a) is accessible to any proton transfer reactions under consideration, the range of compounds \( X \) which may have an appropriate PA to distinguish between \( \text{CNH}_2^+ \) and \( \text{HCNH}^+ \) is substantially increased \( (556 \text{ kJ mol}^{-1} < \text{PA}(X) < 717 \text{ kJ mol}^{-1}) \). It is not known if this channel is accessible. Another problem is isomerisation of the \( \text{CH}_2\text{N}^+ \) ions. Since, in the preceding section, \( \text{HCN}^+ \) is seen to be converted to \( \text{HNC}^+ \) by reactants with intermediate PA, it is entirely possible that a similar mechanism can also operate to efficiently convert \( \text{CNH}_2^+ \) to \( \text{HCNH}^+ \) by a two-step proton transfer process analogous to reaction

<table>
<thead>
<tr>
<th>X</th>
<th>Product channel sought</th>
<th>(-\Delta H_{\text{CNH}_2^+}^a)</th>
<th>(-\Delta H_{\text{HCNH}^+}^a)</th>
<th>Reaction seen?^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>HNO(^+) + HCN (HNC)</td>
<td>-25 (-91)</td>
<td>-186</td>
<td>N</td>
</tr>
<tr>
<td>CO</td>
<td>HCO(^+) + HCN (HNC)</td>
<td>38 (-28)</td>
<td>-123</td>
<td>N</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>C(_2)H(_3^+) + HCN (HNC)</td>
<td>85 (19)</td>
<td>-76</td>
<td>A(^c)</td>
</tr>
<tr>
<td>C(_2)N(_2)</td>
<td>C(_2)N(_2^+) + HCN (HNC)</td>
<td>118 (52)</td>
<td>-43</td>
<td>N</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>C(_2)H(_5^+) + HCN (HNC)</td>
<td>124 (58)</td>
<td>-37</td>
<td>A(^c)</td>
</tr>
<tr>
<td>C(_2)</td>
<td>CS(_2^+) + HCN (HNC)</td>
<td>143 (77)</td>
<td>-18</td>
<td>N</td>
</tr>
<tr>
<td>CH(_3)Cl</td>
<td>CH(_3)ClH(^+) + HCN (HNC)</td>
<td>147 (81)</td>
<td>-14</td>
<td>N</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>HNCO(^+) + N(_2^+) + H(^+)</td>
<td>-42</td>
<td>-204</td>
<td>N</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>SF(_5^+) + HF + HCN (HNC)</td>
<td>-7 (-73)</td>
<td>-168</td>
<td>N</td>
</tr>
<tr>
<td>CF(_4)</td>
<td>CF(_3)CNH(^+) + HF</td>
<td>106</td>
<td>-55</td>
<td>N</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>CH(_3^+) + HCN (HNC)</td>
<td>-4 (-70)</td>
<td>-165</td>
<td>N</td>
</tr>
<tr>
<td>CH(_3)CNH(^+) + H(_2)</td>
<td>217</td>
<td>56</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>CCl(_3^+) + HCl + HCN (HNC)</td>
<td>137 (71)</td>
<td>-24</td>
<td>Y(^c)</td>
</tr>
</tbody>
</table>

Notes
a. Reaction exothermicity, calculated using \( \Delta H_f(\text{CNH}_2^+) = 1109 \text{ kJ mol}^{-1}; \Delta H_f(\text{HNC}) = 201 \text{ kJ mol}^{-1}\). Other energies are as tabulated by Lias et al.,\(^{104}\) except \( \Delta H_f(\text{SF}_5^+) = 32 \pm 6 \text{ kJ mol}^{-1}\).\(^{298}\)
b. N = no reaction observed; A = adduct formation only observed; Y = reaction observed as shown.
c. See text for discussion.
(5.6). For this reason, proton affinity was not the only criterion by which appropriate reactant neutrals were selected. As with the reactions (5.7) - (5.10) which allowed discrimination of HCN+ and HNC+, special consideration was given to those reactions likely to result in rapid fragmentation of the initial collision complex: such reactivity should reduce the possibility for proton-transfer-based isomerisation of the CH2N+ ions concerned. This was the rationale behind the selection of SF6 and CCl4. Additionally, attention was given to reactions which might be exothermic for both ions but which required substantial rearrangement, as in the proposed reactions of CH4, N2O and CF4. As Table 5.11 shows, none of these reactions allowed discrimination of CNH2+ and HCNH+.

Table 5.12 shows the results for the reactivity observed. The rates observed for adduct formation with C2H2 and with C2H4 are in reasonable agreement with the rates observed for these processes by Herbst et al.55

The product distribution for the reaction with CCl4 is very surprising and will be discussed in some detail in the next section: suffice to say that the products observed appear due to HCNH+ rather than to CNH2+, since CCl3+ was observed

<table>
<thead>
<tr>
<th>Table 5.12: Reactions of HCNH+ + X.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>M</td>
</tr>
<tr>
<td>C2H4</td>
</tr>
<tr>
<td>C2N2</td>
</tr>
<tr>
<td>CCl4</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Notes
a. See footnotes (a) - (c) for table (5.2), (b) for table (5.6).
b. M = CO, NO, CS2, CF4, SF6, NO2, CH4, C2H2, CH3Cl.
to be the major product of the reaction for all methods of CH$_2$N$^+$ formation and CNH$_2^+$ is not expected to dominate the m/z 28 ion signal in all of these methods.

The inability to observe any evidence for the existence of CNH$_2^+$, in the experiments described here, does not allow us to resolve what is actually happening. Two possibilities exist: either that in no instance have the techniques detailed in table 5.10 produced sufficient CNH$_2^+$ to detect, or that CNH$_2^+$ has been produced in some instances but not detected because of the unsuitability of the reactions detailed in table 5.11. I shall now examine these options in turn.

It seems likely that, given the energetic parameters detailed in table 5.9, some of the methods employed should produce some CNH$_2^+$: this ion exists in a deep potential well and has a very substantial barrier to isomerisation. The situation is complicated by the uncertainty in the heats of formation of the ion and its transition state to isomerisation, and by the very low efficiencies of the formation processes in some instances. For example, the attempt to generate CNH$_2^+$ from H$_2$NCN requires, to be successful, a C≡N bond to be broken during electron impact ionisation. In many instances, the yields of m/z 28 were too low for any study of the reactivity of this ion to be worthwhile: this does not indicate that these methods did not produce CNH$_2^+$, or that a substantially enhanced signal might not be obtained by a slight refinement in technique. Further attempts to generate CNH$_2^+$ by these or similar methods, using similar or modified equipment, therefore seem justified.
It is quite possible that the reactions detailed in table 5.11 are unable to distinguish CNH$_2^+$ and HCNH$^+$, because these ions do not react with any observable differences. For example, in our study of CHN$^+$ chemistry, the means of distinguishing between the HCN$^+$ and HNC$^+$ isomers remained elusive until an appropriate titrant (CF$_4$) was found. A mechanism involving proton-transfer isomerisation of CNH$_2^+$ to HCNH$^+$ would, as has been explained earlier, help to account for the inability to detect CNH$_2^+$ using reagents such as CO, CS$_2$ and CH$_3$Cl. Note that, if CNH$_2^+$ is converted to HCNH$^+$ by reaction with CO, then CNH$_2^+$ cannot have much influence on the observed interstellar abundances of HCN and HNC, since rapid isomerisation by CO represents a more efficient loss mechanism for CNH$_2^+$ than does dissociative recombination with an electron. This proposed isomerisation is highly speculative, and given the uncertainty in $\Delta H_f$(CNH$_2^+$) ($\pm$ 40 kJ mol$^{-1}$) might be exothermic for both channels (5.40a) and (5.40b), for channel (5.40a) only, or for neither:

$$\text{CNH}_2^+ + \text{CO} \rightarrow (\text{HNC}\cdots\text{OCH}^+)$$  \hspace{1cm} (5.40a)

$$\rightarrow (\text{HCN}\cdots\text{OCH}^+)$$  \hspace{1cm} (5.40b)

$\Delta H_{5.40a} = 28 \text{ kJ mol}^{-1}$

$\Delta H_{5.40b} = -38 \text{ kJ mol}^{-1}$

$$(\text{CHN}\cdots\text{OCH}^+) \rightarrow \text{HCNH}^+ + \text{CO}$$  \hspace{1cm} (5.41)

The formula CHN is used in reaction (5.41) to denote that this reaction may occur for both HCN and HNC. The quoted values $\Delta H_{5.40a}$ and $\Delta H_{5.40b}$ relate to the heats of formation of HCN/HNC and HCO$^+$ at infinite separation, and may very well not relate closely to the heat of formation of the collision complex formed.
Channel (5.40b), although favoured upon the basis of enthalpy values, may not be practical given the greater degree of rearrangement required - migration of both H atoms is necessary for this channel to occur. An ab initio study would help resolve whether either of the reaction channels (5.40a) or (5.40b) are accessible to reactants under interstellar conditions.

Given the results obtained in this study, it is difficult to assert with confidence what chemistry is occurring here. The strong possibility that isomerisation of CNH$_2^+$ may be the dominant reaction channel for the reaction of this ion with many neutral reagents deserves further study: similar isomerisation has been observed now for HCN$^+$/HNC$^+$, HCO$^+$/HOC$^+$ and HNNO$^+$/NNOH$^+$ as has been discussed in the preceding section. The prospect for such isomerisation in this system should be seriously considered since both CNH$_2^+$ and HCNH$^+$ have been widely invoked as important ions in interstellar synthesis.

Section 5.3: Does a fast reaction have to be exothermic?

The reaction of HCN$^+$ with CF$_4$ (see section 5.1)

\[
\text{HCN}^+ + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{HF} + \text{CN}^- \tag{5.7}
\]

\[k_{5.7} = 1.15 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\]
is of interest not only because it distinguishes between HCN+ and HNC+ by virtue of its reactivity, but also because it occurs rapidly despite its apparent endothermicity. Tabulated heats of formation for the reactants and products are

\[
\begin{align*}
\Delta H_f(\text{HCN}^+) & = 1447 \pm 10 \text{ kJ mol}^{-1} \\
\Delta H_f(\text{CF}_4) & = -934.5 \pm 0.4 \text{ kJ mol}^{-1} \\
\Delta H_f(\text{CF}_3^+) & = 399.0 \pm 5 \text{ kJ mol}^{-1} \\
\Delta H_f(\text{HF}) & = -272.5 \pm 0.8 \text{ kJ mol}^{-1} \\
\Delta H_f(\text{CN}^-) & = 435.1 \pm 10 \text{ kJ mol}^{-1}. 
\end{align*}
\]

Using these values, the calculated enthalpy of reaction is \( \Delta H_{5,7} = +49.1 \pm 26.2 \text{ kJ mol}^{-1} \). The large uncertainty in this value can be considerably reduced: the main contributions to this uncertainty arise from the tabulated uncertainty in \( \Delta H_f(\text{HCN}^+) \) and \( \Delta H_f(\text{CN}^-) \). In fact the appearance potentials \( \text{AP}(\text{HCN}^+/\text{HCN}) \) and \( \text{AP}(\text{H}^+ + \text{CN}^-/\text{HCN}) \) are each known with much higher precision than \( \pm 10 \text{ kJ mol}^{-1} \); this uncertainty arises from the heat of formation of HCN itself. Using these appearance potentials \(^3\) and considering the process

\[
\text{HCN}^+ \rightarrow \text{H}^+ + \text{CN}^- 
\]

\( \Delta H_{5,42} = +521 \pm 2 \text{ kJ mol}^{-1} \),

the enthalpy for reaction (5.7) can be recalculated:

\[
\begin{align*}
\Delta H_{5,7} & = \Delta H_{5,42} + \Delta H_f(\text{CF}_3^+) + \Delta H_f(\text{HF}) - \Delta H_f(\text{CF}_4) - \Delta H_f(\text{H}^+) \\
\therefore \Delta H_{5,7} & = +52 \pm 8 \text{ kJ mol}^{-1}. 
\end{align*}
\]
From these values, reaction (5.7) is apparently very endothermic. Such an endothermic reaction should not occur at the collision rate, since not all collisions of reactants will feature sufficient internal energy to overcome such an enthalpy barrier. Ferguson and co-workers\textsuperscript{302,303} have argued that, clearly, the reaction is instead exothermic: this requires that one of the tabulated enthalpy values is dramatically incorrect. The heats of formation of CF\textsubscript{4}, HF and H\textsuperscript{+} have all been determined to high accuracy and are not open to question; similarly, AP(HCN\textsuperscript{+}/HCN) and AP(H\textsuperscript{+} + CN\textsuperscript{-}/HCN) have been very precisely determined. The only thermochemical value in doubt is thus $\Delta H_f(CF_3\textsuperscript{+})$.

There is considerable evidence that the tabulated heat of formation of CF\textsubscript{3}$\textsuperscript{+}$ is too high. The earliest determination of this quantity, by photoionisation of CF\textsubscript{4}, gave AP(CF\textsubscript{3}$\textsuperscript{+}$/CF\textsubscript{4}) = 15.30 eV which corresponds to $\Delta H_f(CF_3\textsuperscript{+}) = 463$ kJ mol\textsuperscript{-1}.\textsuperscript{304} However, CF\textsubscript{3}$\textsuperscript{+}$ in this instance is produced via dissociation of the unstable ion CF\textsubscript{4}$\textsuperscript{+}$:

\[
\text{CF}_4\textsuperscript{+} \rightarrow \text{CF}_3\textsuperscript{+} + \text{F}. \quad (5.43)
\]

Since CF\textsubscript{4}$\textsuperscript{+}$ is unstable with respect to CF\textsubscript{3}$\textsuperscript{+}$ + F\textsuperscript{-}, the appearance potential for CF\textsubscript{3}$\textsuperscript{+}$/CF\textsubscript{4} can only provide an upper limit to $\Delta H_f(CF_3\textsuperscript{+})$. Other experiments indicate that this upper limit is an electron volt or more too high. Langford et al\textsuperscript{305} performed charge-stripping experiments on CF\textsubscript{3}$\textsuperscript{+}$ produced by electron bombardment upon a variety of source gases including CF\textsubscript{4}. In these experiments, highly-accelerated reactant ions were allowed to collide with gas molecules which effected ionisation:
By measuring accurately the amount of translational energy lost, the energy required to further ionise CF$_3^+$ could be determined. Langford et al found that charge-stripping of CF$_3^+$ from CF$_3$Cl, CF$_3$Br, C$_2$F$_6$, C$_2$F$_5$H, CF$_3$CH$_3$ and CF$_2$HCFH$_2$ gave no evidence for population of excited states of CF$_3^+$, but that charge-stripping of the CF$_3^+$ produced from CF$_4$ did show such evidence. They concluded that CF$_3^+$ produced from CF$_4$ is initially vibrationally excited by ~ 0.5 eV and that this vibrational excitation is long-lived: this can be compared to the suggestion by Fisher et al$^{306}$ that ionisation of CF$_4$ produces pyramidal CF$_3^+$, which subsequently relaxes to the planar CF$_3^+$ ground state.

Tichy et al$^{307}$ have studied the reaction

\[
\text{HCl}^+ + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{HF} + \text{Cl.} \tag{5.45}
\]

\[k_{5.45} = 1.0 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\]

which is very similar to reaction (5.7) except that it does not occur at the collision rate. Upon the basis of this reaction, they concluded that the correct 'adiabatic' appearance potential $\text{AP}_A(\text{CF}_3^+ / \text{CF}_4)$ [where the adiabatic potential is that for production of ground-state products from ground-state reactants: it should be distinguished from the 'vertical' appearance potential, which may be influenced by Franck-Condon effects] could not exceed 14.23 eV, which requires $\Delta H_f(\text{CF}_3^+) \leq 364 \text{ kJ mol}^{-1}$. The displacement between the vertical and adiabatic potentials is known as the kinetic shift. Vertical potentials, obtained from photoionisation and similar techniques, can be significantly higher than adiabatic potentials.
Methods such as photoionisation occur on too short a timescale to permit rearrangement of the product to its ground-state geometry: if this geometry differs significantly from that of the reactant, the potential thus obtained will not relate well to the heat of formation of the product in its ground state.

Babcock and Streit\textsuperscript{308} have investigated the equilibrium

\[
\text{CF}_3^+ + \text{SF}_6 \rightleftharpoons \text{SF}_5^+ + \text{CF}_4
\]  \hspace{1cm} (5.46)

in a flow-tube experiment: they determined \(K_{5.46} \approx (5.9 \pm 0.9) \times 10^3\), from which they derived \(\Delta P_A(\text{CF}_3^+/\text{CF}_4) - \Delta P_A(\text{SF}_5^+/\text{SF}_6) = 0.17\) eV. The heat of formation of \(\text{SF}_5^+\) is also very much lower than its vertical appearance potential \(\Delta P_v(\text{SF}_5^+/\text{SF}_6) = 15.33 \pm 0.3\) eV would suggest, as reaction studies by Tichy et al\textsuperscript{303,307} and double-charge-transfer experiments by Langford et al\textsuperscript{309} have shown: the currently-accepted value for the adiabatic potential is \(\Delta P_A(\text{SF}_5^+/\text{SF}_6) = 13.65\) eV. This should, in conjunction with the equilibrium reaction (5.46), yield a value of \(\Delta H_f(\text{CF}_3^+)\); however, subsequent studies by Fisher and Armentrout\textsuperscript{310} have shown the results of Babcock and Streit to be in error. There is no accurately determined value of \(K_{5.46}\) - therefore, determination of \(\Delta P_A(\text{SF}_5^+/\text{SF}_6)\) cannot provide an accurate indication of \(\Delta P_A(\text{CF}_3^+/\text{CF}_4)\). Notwithstanding this, there is still a large amount of evidence which demonstrates that \(\Delta H_f(\text{CF}_3^+)\) is substantially below the currently tabulated value.

If reaction (5.7) is, as Ferguson claims, exothermic\textsuperscript{302} then an upper limit of \(\Delta H_f(\text{CF}_3^+) < 347\) kJ mol\(^{-1}\) can be ascribed. This is lower than any other value yet determined for this heat of formation.
An alternative proposal is that reaction (5.7) is endothermic but exergonic: that is, the enthalpy change $\Delta H$ is positive while the free energy change $\Delta G$ for the reaction is negative. This can be so if the reaction is "entropy-driven" by virtue of the formation of three products from only two reactants - for such reactions the entropic contribution (-T$\Delta S$) to $\Delta G$ can amount to $\sim 20$ kJ mol$^{-1}$ at 300 K, so a reaction which is endothermic by less than this can still proceed efficiently if 'assisted' by the change in entropy.

The rôle of entropy in ion-molecule reactions is still a subject of debate. Traditionally, the enthalpy change $\Delta H$ has been considered as the deciding factor in ion-molecule reactions: convention holds that if $\Delta H$ is positive for a reaction, then this reaction will have less than unit efficiency. Henchman has suggested that this perspective arose from the tendency to regard ion-molecule reactions observed in an experiment as 'single-collision' events in which a loss of energy is not permissible, with energy equating to enthalpy. In addition, the much more widespread tabulation of ionic heats of formation, than of free energies of formation of ions, has favoured the use of $\Delta H$ rather than $\Delta G$ in interpretation of ion-molecule reactions.

There are now several ion-molecule reaction studies which very strongly suggest the involvement of entropy in reaction rate enhancement or inhibition. Henchman et al have studied systems such as $\text{H}^+(\text{D}^+) + \text{H}_2(\text{D}_2)$ and $\text{CH}_4^+(\text{CD}_4^+) + \text{CH}_4(\text{CD}_4)$ in a VT-SIFT, over appreciable temperature ranges. The observed variation in the equilibrium constant $K$ with $T$ for these reactions is clearly characteristic of a temperature-dependent change in the entropy of reaction. Mautner has studied many proton-transfer equilibria in HP-MS
experiments. For some such systems, K displays a clear temperature
dependence consistent with entropy changes due to changing symmetry, ring
opening and closing, etc. King et al\(^{316}\) have studied, in a SIFT, the reaction

\[
\begin{align*}
\text{CH}_3\text{ONO} + F^- & \rightarrow \text{NO}^- + \text{HF} + \text{H}_2\text{CO} \quad [0.18] \quad (5.47a) \\
& \rightarrow \text{NO.HF}^- + \text{H}_2\text{CO} \quad [0.03] \quad (5.47b) \\
& \rightarrow \text{NO}_2^- + \text{CH}_3\text{F} \quad [0.79] \quad (5.47c)
\end{align*}
\]

\[k_{5.47} = 2.1 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\]

\[\Delta H_{5.47a} = +25 \text{ kJ mol}^{-1}\]

\[\Delta G_{5.47a} < 0 \text{ kJ mol}^{-1},\]

for which channel (5.47a) proceeds efficiently despite its endothermicity. This
reaction closely parallels reaction (5.7) - if the latter reaction is entropy-driven.
A problem connected with the reported occurrence of reaction (5.47a) is that this
channel is not directly observable because the NO\(^-\) ion is not stable, rapidly
undergoing detachment:

\[
\text{NO}^- + \text{He} \rightarrow e + \text{NO} + \text{He} \quad (5.48).
\]

In the study by King et al, this channel was deduced as a product channel by the
assumption that the ratio of products for channels (5.47a) and (5.47b) was equal to
the ratio of the analogous product channels (5.49a) and (5.49b)\(^{316}\)

\[
\begin{align*}
\text{F}^- + \text{XCH}_2\text{ONO} & \rightarrow \text{NO}^- + \text{HF} + \text{XCHO} \quad [0.85] \quad (5.49a) \\
& \rightarrow \text{NO.HF}^- + \text{XCHO} \quad [0.15] \quad (5.49b)
\end{align*}
\]

\[k_{5.49} = 3.1 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\]
where \( X = (\text{CH}_3)_3\text{C} \). This reaction presents a more convincing case for the existence of the endothermic, entropy-driven channel (5.49a) \((\Delta H_{5.49a} = +29 \text{ kJ mol}^{-1})\), since the only product channel seen accounts for only 15% of the F\(^-\) lost through reaction: however, the uncertainties in \(\Delta H_{5.49a}\) will be larger owing to the greater complexity of the reactants and products. The uncertainties in product ratios and thermodynamic quantities relevant to channels (5.47a) and (5.49a) appear sufficiently large to make questionable the claim that these reactions are entropy-driven.

Mautner and Tsang\(^{189}\) present a model for 'intrinsically fast' entropy-driven reactions (that is, in the absence of activation energy barriers and involving merely the formation of a single collision complex) of the form

\[
A^+ + B \xrightarrow{k_c/k_b} (AB^+)\dagger \xrightarrow{k_p/k_c'} C^+ + D \tag{5.50}
\]

If \( A^+ + B \) and \( C^+ + D \) are the only possible product channels accessible from the collision complex \((AB^+)\dagger\), then the forward and reverse rate coefficients for the reaction

\[
A^+ + B \rightarrow C^+ + D \tag{5.51}
\]

can be defined in terms of the fraction of \((A^+ + B)\) collisions producing \((C^+ + D)\) and vice versa:
\[ k_f = k_c \frac{k_p}{k_p + k_b} \quad (5.\text{xii}) \]

and
\[ k_r = k_c' \frac{k_b}{k_p + k_b} \quad (5.\text{xiii}). \]

By application of the definition of the equilibrium constant \( K_{5.51} \)
\[ K_{5.51} = \frac{k_f}{k_r} \quad (5.\text{xiv}), \]

Mautner and Tsang\(^{189} \) show that the reaction efficiency \( r_f \) - that is, the fraction of \( A^+ + B \) collisions which result in the successful production of \( C^+ + D \) - has the relation
\[ r_f = \frac{K}{K + k_c/k_c'} \quad (5.\text{xv}) \]

which simplifies to
\[ r_f = \frac{K}{K + 1} \quad (5.\text{xvi}) \]

with the approximation that \( k_c = k_c' \).

A problem in attempting to describe reaction (5.7), and similar reactions, as entropy-driven is the possible confusion between thermodynamic and kinetic effects. A common view of entropy in chemical systems is as a measure of disorder or probability: by extension of such a view, a system which is initially in
a condition of order will move naturally to a condition of greater disorder insofar as this is compatible with a low expenditure of energy. Thus, an equilibrium involving two reactants and three products will naturally favour the formation of three products (despite a minor endothermicity) because of the much greater probability of a bimolecular collision of the two reactants than the required termolecular collision of the three products. In terms of the model outlined above, this corresponds to an extreme case where \( k_c \gg k_c' \), since \( k_c' \) must represent the effective collision rate for the termolecular process \( C^+ + D + E \). This event is more properly regarded as a close succession of two bimolecular collisions, involving a model of the form

\[
C^+ + D + E \xrightleftharpoons[k_2']{k_2} (CD^+) + E \xrightleftharpoons[k_1']{k_1} (AB^+) +
\]

\[
\xrightleftharpoons[k_b']{k_b} A^+ + B
\]

(5.52).

In this model (for which \( A^+ \) and \( B \) appear as products as shown here, rather than as reactants in reaction (5.50)) the rate law for removal of \( C^+ \) by reaction is

\[
\frac{-d[C^+]}{dt} = k_c' [C^+] [D][E] \frac{k_c'}{k_2 + k_c[E]} \frac{k_b}{k_1 + k_b} + \frac{k_2}{k_1 + k_b k_2 + k_c[E]}
\]

(5.xvii).

In the case where the concentrations of the reactants \( C^+ \), \( D \) and \( E \) are in vast excess to the concentrations of the products \( A^+ \) and \( B \), this expression can be simplified to

\[
\frac{-d[C^+]}{dt} \approx k_c' [C^+] [D][E] \frac{k_c'}{k_2 + k_c[E]} \frac{k_b}{k_1 + k_b}
\]
This simplification approximates to the situation in a SIFT experiment, where the occurrence of the reverse reaction is generally negligible because of the extremely low concentrations of the products. The rate coefficient for reaction of $C^+$ with $D$ and $E$ can now be expressed as

$$\frac{-d[C^+]}{dt} = k_c [C^+][D][E] \frac{k_c}{k_2 + k_c[E]} \frac{k_b}{k_1 + k_b} \quad (5.xviii).$$

while the rate coefficient $k_r$ for reaction of $A^+$ with $B$ has the form

$$k_f = k_c \frac{k_c}{k_2 + k_c[E]} \frac{k_b}{k_1 + k_b} \quad (5.xix),$$

and

$$k_r \approx k_c \frac{k_1}{k_1 + k_b} \quad (5.xxii).$$

Using the terminology of Mautner and Tsang,\textsuperscript{189} the efficiency $\tau_r$ (which defines the fraction of $A^+ + B$ collisions which successfully form $C^+ + D + E$) is
Similarly, the efficiency $r_f$ can be defined as the fraction of $C^+ + D + E$ collisions resulting in formation of $A^+ + B$:

$$r_f = \frac{k_f}{k_c(k_c/k_2)} = \frac{k_b}{k_1 + k_b}$$  \hspace{1cm} (5.xxiv).

This method of expression is, however, misleading. $r_f$ and $r_r$ have similar forms, but it must be remembered that $r_f$ denotes the efficiency of a termolecular process while $r_r$ refers to the reverse, bimolecular process. An alternative expression, $r'_f$, can be derived. This quantity denotes the efficiency of $C^+ + D$ collisions - that is, the fraction of $C^+ + D$ collisions which result in $A^+ + B$ formation:

$$r'_f = \frac{k_f [E]}{k_c} = \frac{k_c [E]}{k_2} \frac{k_b}{k_1 + k_b}$$  \hspace{1cm} (5.xxv).

Now, $r_f + r_r < 1$ and $r_f << r_r$ for $k_b \sim k_1$ (providing $k_c' [E] << k_2$, which holds if the concentration of $E$ is negligible - as in, for example, our SIFT studies of reaction (5.7)). This model shows that the rate of conversion of $A^+ + B$ to $C^+ + D + E$ can greatly exceed the rate of the opposite process while still proceeding on only a small fraction of $A^+ + B$ collisions (those in which the reactants have sufficient energy to overcome the reaction endothermicity). This yields a system in which $K_{5.51}$ favours formation of the three particles $C^+ + D + E$ in spite of the low efficiency of this process.
This model of the 'entropy-driven' system is contested by Mautner, who claims that K in this case does not relate to the relative probabilities of collision in the two opposing directions, but to the likely disproportionation of the collision complex (AB+)‡. In the instances where an ion-molecule reaction is seen as being entropy-driven, the entropy change is rationalised by Mautner in terms of a density-of-states argument. A reaction may be endothermic but still efficient provided that the density of states for products is large in comparison to the available density of states for reactants. This situation can occur, for example, when symmetry factors limit the available density of states for reactants. In the case of a reaction such as (5.7) where a change in the number of particles occurs due to reaction, it is argued that the available density of states for products will be large because of the larger number of permutations available for energy dispersal within three particles. Figure 5.4 illustrates this concept. For such a reaction to occur on every collision, the endothermicity must be exceeded by the thermal energy of the reactants, and the products will be internally cold.

An approximate value for the thermal energy available in reaction (5.7) can be easily calculated. Using \( E = nRT/2 \) as the total quantity of thermal energy distributed among the n modes accessible, and \( T = 300 \text{ K} \), it becomes necessary to determine n. Each reactant has three translational degrees of freedom: but in a collision, one reactant can be considered as fixed (both reactants must occupy the same position, essentially, for a collision to occur) so the total number of accessible translational modes is three. HCN⁺ is linear and has two rotational modes; CF₄ has three, so there are five accessible rotational modes. Several vibrational modes exist for each reactant, but the lowest vibrational frequency of HCN⁺ is at \( v = 712 \text{ cm}^{-1} \), while the smallest vibrational frequency of CF₄ is \( v = \)
437 cm⁻¹ these frequencies are too large for these levels to be substantially populated at T = 300 K, so the vibrationally excited population of reactants is too small for these vibrational modes to contribute significantly to the available thermal energy. No electronic levels are low enough to be worth consideration, so n = 8. There is thus a total of 10 kJ mol⁻¹ thermal energy available for reaction (5.7): therefore, this reaction cannot feasibly be endothermic to a greater extent than this. If all of this thermal energy is expended in driving this reaction, the products will have an effective internal temperature of zero - although, in a SIFT experiment, thermalisation following reaction would occur owing to repeated collision with bath gas molecules.

Figure 5.4: A diagram illustrating the model of Mautner,¹⁸⁹ which states that endothermic reactions can occur rapidly if they are entropy-driven. In this model, the endothermicity is exceeded by the available thermal energy (the dotted line in this diagram), and the 3-product channel is favoured by a greater density of available rovibrational states than the 2-reactant channel.
There is some experimental evidence to support the notion that reaction (5.7) is endothermic. We have studied the reaction

\[
\text{CF}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3^+ + \text{CF}_3\text{H} \quad [0.25] \quad (5.53a)
\]

\[
\rightarrow \text{C}_3\text{F}_2\text{H}_3^+ + \text{HF} \quad [0.75] \quad (5.53b)
\]

\[ k_{5.53} = 1.0 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \]

\[ \Delta H_{5.53a} < 0 \text{ kJ mol}^{-1} , \]

for which the product channel (5.53a) is clearly exothermic from the observation of a rate coefficient close to the collision rate. We were initially concerned that this product channel might have arisen through a substantial population of vibrationally excited CF$_3^+$, but this possibility was eliminated after using CF$_3$Br instead of CF$_4$ as a source gas (Langford et al.\textsuperscript{305} have determined that CF$_4$ produces excited-state CF$_3^+$ while CF$_3$Br does not) and additionally using N$_2$ as a quenching gas added upstream of the C$_2$H$_4$. Using the following tabulated heats of formation\textsuperscript{184}

\[
\Delta H_f(\text{C}_2\text{H}_4) = 52.2 \pm 1 \text{ kJ mol}^{-1} \\
\Delta H_f(\text{C}_2\text{H}_3^+) = 1112 \pm 4 \text{ kJ mol}^{-1} \\
\Delta H_f(\text{CF}_3\text{H}) = -695 \pm 8 \text{ kJ mol}^{-1} ,
\]

a lower limit of \( \Delta H_f(\text{CF}_3^+) > 352 \text{ kJ mol}^{-1} \) is required if channel (5.53a) is to be exothermic. This is in conflict with the \( \Delta H_f(\text{CF}_3^+) \) required for the exothermicity of reaction (5.7): thus, it appears that one of these reactions must be endothermic. Since the expected \( T \Delta S_{5.53a} \) is negligible, reaction (5.7) must be an endothermic process.
The determination that reaction (5.7) is not exothermic does not, however, demonstrate that this reaction is driven by entropy in the style proposed by Mautner. Ferguson has speculated that the apparent generation of three products is illusory: if one of the products was a weakly-bound cluster ion such as CF₃.HF⁺, this ion might well be too fragile to survive the acceleration induced by electrostatic focussing prior to mass selection and detection. This proposal is related, by the principle of microscopic reversibility, to the model (5.52) in which the reaction C⁺ + D + E is viewed as two successive bimolecular collisions: if the fragmentation of (AB⁺) occurs as two successive fragmentations, one of which is not necessarily spontaneous, then there is no immediate entropy gain accessible to the collision complex. Fisher and Armentrout have also considered this proposal, and favour the formation of CF₃.CN⁺ or CF₃.HF⁺, or of the van der Waal's complex [FH···CN] as the neutral product in reaction (5.7). They estimate a binding energy for this neutral complex of ~ 14 kJ mol⁻¹ by analogy with the binding energy of the HF dimer: under these criteria, the exothermicity of the reaction of HCN⁺ with CF₄ requires an upper limit to Δⱼ(CF₃⁺) of 361 kJ mol⁻¹ (for production of FH···CN; a higher limit is obtained if CF₃.CN⁺ or CF₃.HF⁺ is formed) which would resolve the discrepancy apparent in the occurrence of reactions (5.7) and (5.53a). In the absence of a detailed study of the binding energy of such a complex as that formed in reactions (5.7) and (5.47a), this possibility cannot be dismissed.

It is of interest also to note the similarity of the reaction

\[
\text{HCNH}^+ + \text{CCl}_4 \rightarrow \text{CCl}_3^+ + \text{HCN} + \text{HCl} \quad [0.88] \quad (5.54a)
\]

\[
\rightarrow \text{CCl}_3\text{CNH}^+ + \text{HCl} \quad [0.12] \quad (5.54b)
\]

\[k_{5.54} = 8.0 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\]

\[\Delta H_{5.54a} = + 24 \text{ kJ mol}^{-1}\]
to reaction (5.7). This reaction was studied as part of our unsuccessful foray into CNH$_2^+$ chemistry (see the preceding section): channel (5.54a) is, as can be seen, substantially endothermic according to the available thermochemical data. This indicates either

(i). that this channel (which is an appreciable product channel of a fast reaction, and therefore exergonic) is driven by entropy changes in the same manner as reaction (5.7),

(ii). that the formation of a van der Waal's complex (HCN···HCl) with sufficient binding energy drives the reaction, or

(iii). that the thermochemical information is incorrect. The latter rationalisation most readily requires a lower value of $\Delta H_f(\text{CCl}_3^+)$, which has been determined from ICR and FA bracketing:\textsuperscript{318}

$$\begin{align*}
\text{H}_3\text{O}^+ + \text{CFCl}_3 &\rightarrow \text{CCl}_3^+ + \text{HF} + \text{H}_2\text{O} \quad (5.55) \\
\text{sec-C}_3\text{H}_7^+ + \text{CFCl}_3 &\rightarrow \text{CCl}_3^+ + \text{C}_3\text{H}_7\text{F} \quad (5.56) \\
k_{5.56} &< 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\end{align*}$$

If $\Delta H_f(\text{CCl}_3^+)$ had been determined in the same manner as $\Delta H_f(\text{CF}_3^+)$, - that is, by appearance potentials from photoionisation methods - it might be expected to be too high for similar reasons. Note, however, that in this case the upper limit for $\Delta H_f(\text{CCl}_3^+)$ is obtained from the occurrence of an ion-molecule reaction (5.55) in a flowing-afterglow apparatus, which should therefore give a value appropriate to the truly thermalised CCl$_3^+$ ion. An additional complicating factor is that reaction (5.55) is also of the '2→3' form of reactions (5.7), (5.47a) and (5.54a), which (if the entropy-driven argument is to be heeded) might rather be
expected in this instance to yield an underestimate of $\Delta H_f(CCl_3^+)$. Further studies involving $CCl_3^+$ ions might help resolve this issue.
CHAPTER 6.

ION-MOLECULE CHEMISTRY OF ACRYLONITRILE, CH₂CHCN.

Section 6.1: Introduction.

Acrylonitrile, CH₂CHCN, is structurally closely related to H—(C≡C)ₙ—C≡N, the cyanopolyynes, which form a prominent series of interstellar molecules. The interstellar chemistry of the cyanopolyynes has been extensively studied⁶⁴,¹⁶⁷,²⁰⁵,²¹⁴,²⁵⁵,²⁶⁵,²⁶⁷ and discussed²⁷,³⁹,⁴⁰,⁹⁹,²²⁴,²³⁸ but the interstellar chemistry of acrylonitrile has to date received little attention.

Acrylonitrile was first detected in the dense cloud TMC-1 by Matthews and Sears³¹⁹ in 1982. Herbst⁵⁴ has suggested that acrylonitrile is formed in such clouds as a result of the radiative association process

\[
\text{HCNH}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_4\text{N}^+ + \text{hv} \quad (6.1)
\]

for which a rate coefficient \( k_{6.1} = 2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) at 10 K has been estimated.⁵⁴ A possible additional pathway involves the reaction of hydrocarbon ions with nitrogen atoms²⁷,¹⁵⁰

\[
\text{C}_n\text{H}_m^+ + \text{N} \rightarrow \text{C}_n\text{H}_{m-x}\text{N}^+ + x\text{H} \quad (6.2).
\]
Very few such reactions have yet been studied experimentally, and none of those studied to date provides a useful method of generating interstellar CH₂CHCN. Millar and Nejad suggested that reactions of N atoms with hydrocarbon radicals and molecules might provide a route to the formation of cyanopolyyynes and related species, but this reaction type may feature activation energy barriers and would, in consequence, be prohibitively inefficient under interstellar conditions.

Acrylonitrile has also been proposed as a likely trace constituent of the atmosphere of Titan, as well as of other planetary atmospheres, though it has not yet been detected in such environments. The proposed atmospheric synthesis of acrylonitrile involves a termolecular association of HCNH⁺ and C₂H₂, analogous to reaction (6.1). Abundances of acrylonitrile in the atmospheres of the outer planets will necessarily be low because of photodissociation and the high condensation point for such compounds: some support for the formation of nitriles, in Titan's atmosphere at least, is seen in the observation of cyanoacetylene by Kunde et al.

The present chapter reports results for some ion-molecule reactions relating to the interstellar chemistry of acrylonitrile.

The ions C₃H₂N⁺ and C₃H₃N⁺ were produced in the ion source by electron impact upon a dilute solution (1:20) of acrylonitrile in helium, since it was found that the ion signal was unstable against fluctuations in size when pure acrylonitrile was used as the source gas. C₃H₄N⁺ was generated by electron bombardment upon a dilute solution (1:10) of acrylonitrile in hydrogen:
\[
\begin{align*}
\text{H}_2^+ + \text{C}_2\text{H}_3\text{CN} & \rightarrow \text{CH}_2\text{CCHCNH}^+ + \text{H}^- & (6.3) \\
\text{H}_3^+ + \text{C}_2\text{H}_3\text{CN} & \rightarrow \text{CH}_2\text{CCHCNH}^+ + \text{H}_2 & (6.4) \\
\text{C}_3\text{H}_2\text{N}^+ + \text{H}_2 & \rightarrow \text{CH}_2\text{CCHCNH}^+ + \text{H}^- & (6.5) \\
\text{C}_3\text{H}_2\text{N}^+ + \text{C}_2\text{H}_3\text{CN} & \rightarrow \text{CH}_2\text{CCHCNH}^+ + \text{C}_3\text{HN} & (6.6)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{6.3} & = -534 \text{ kJ mol}^{-1} \\
\Delta H_{6.4} & = -371 \text{ kJ mol}^{-1} \\
\Delta H_{6.5} & = -99 \text{ kJ mol}^{-1} \\
\Delta H_{6.6} & = -41 \text{ kJ mol}^{-1}.
\end{align*}
\]

Reaction (6.3) has not been studied to date; results for reactions (6.4), (6.5) and (6.6) are described within this chapter.

Acrylonitrile was also used as a dilute solution in helium for the studies of reactions of various ions with acrylonitrile, since the rate coefficients observed for these reactions were almost invariably too rapid to acquire satisfactorily accurate measurements from pure acrylonitrile used as a neutral reactant.

**Section 6.2: Reactions of C\(_3\)H\(_3\)N\(^+\).**

The reactions of C\(_3\)H\(_3\)N\(^+\) with various neutrals are summarised in table 6.1.

In the context of interstellar cloud chemistry, C\(_3\)H\(_3\)N\(^+\) may be formed by cosmic-ray ionization, cosmic-ray-induced photoionization, electron bombardment or chemical ionization of acrylonitrile. C\(_3\)H\(_3\)N\(^+\) has been reported as the major
product (80%), at a pressure of 0.30 Torr, of the reaction of C$_2$H$_2^+$ with HCN:$^{166,267}$

\[ k_{\text{obs}} = 3.7 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \text{ at } 305K. \]

Adduct formation in this instance is ascribed to termolecular association: under interstellar conditions, the analogous

<table>
<thead>
<tr>
<th>X</th>
<th>Products $^a$</th>
<th>$k_{\text{obs}}$</th>
<th>$k_c$</th>
<th>$-\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>C$_3$H$_4$N$^+$ + H·</td>
<td>0.0012</td>
<td>1.50</td>
<td>99</td>
</tr>
<tr>
<td>CO</td>
<td>C$_3$H$_3$N$^+$CO</td>
<td>0.007</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>N$_2$</td>
<td>none</td>
<td>&lt;0.0005</td>
<td>0.73</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>CH$_2$CNH$^+$ + C$_3$H$_4^g$</td>
<td>[0.70]</td>
<td>0.026</td>
<td>1.08 106</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_4$N$^+$ + CH$_3^+$</td>
<td>[0.25]</td>
<td>97</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_6$N$^+$ + H·</td>
<td>[0.05]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>C$_2$H$_4$O$^+$ + HCN$^g$</td>
<td>[0.68]</td>
<td>0.21</td>
<td>2.42 -</td>
</tr>
<tr>
<td></td>
<td>(or H$_2$NCO$^+$ + C$_2$H$_3^+$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_4$NO$^+$ + H·</td>
<td>[0.31]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_3$N$^+$,OH$_2$</td>
<td>[0.01]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NH$_3$ + CH$_2$CHCN</td>
<td>[0.66]</td>
<td>1.9</td>
<td>2.18 73</td>
</tr>
<tr>
<td></td>
<td>NH$_4^+$ + C$_3$H$_2$N$^+$</td>
<td>[0.34]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>C$_3$H$_3^+$ + CH$_2$CN$^a$</td>
<td>[0.08]</td>
<td>0.93</td>
<td>1.02 145$^f$</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_4^+$ + HCN$^g$</td>
<td>[0.55]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(or HC$_3$NH$^+$ + C$_3$H$_3^+$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HC$_3$NH$^+$ + H$_2$ + H·</td>
<td>[0.21]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_4$N$^+$ + H·</td>
<td>[0.16]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HCN</td>
<td>C$_4$HN$_2^+$ + H$_2$ + H·</td>
<td>[0.09]</td>
<td>0.19</td>
<td>3.28 -</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_3$N$_2^+$ + H$_2$</td>
<td>[0.38]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_3$N$_2^+$ + H·</td>
<td>[0.20]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_4$N$_2^+$</td>
<td>[0.33]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH$_2$CHCN</td>
<td>C$_3$H$_3$N$^+$CH$_2$CHCN</td>
<td>2.0</td>
<td>3.62</td>
<td>-</td>
</tr>
</tbody>
</table>

Notes

a. Product channels reported in brackets, where more than one product was detected.
b. Observed rate coefficient, in units of $10^{-9}$ cm$^3$ mole$^{-1}$ s$^{-1}$.
c. Calculated ADO collision rate coefficient, using the theory of Su and Chesnavich.$^{172}$
d. Reaction exothermicity in units of kJ mol$^{-1}$. Taken from the tabulation of Lias et al.$^{184}$ unless otherwise stated.
e. See text for discussion of ion identification.
f. Calculated assuming a protonated cyclopropenylidene structure for C$_3$H$_3^+$.
radiative association reaction could occur. C$_3$H$_3$N$^+$ has also been reported as a minor product of the reaction of C$_3$H$^+$ with NH$_3$,$^{329-331}$ although this may not represent an efficient method of C$_3$H$_3$N$^+$ production depending upon the low-temperature reactivity of C$_3$H$^+$ with H$_2$ and other cloud species more abundant than NH$_3$.

The reaction of C$_3$H$_3$N$^+$ with H$_2$, which occurs via H-atom abstraction, is very slow. The product ion is presumed to be protonated acrylonitrile, in accordance with the calculations of Heerma et al.$^{332}$ which establish H$_2$C=CH—C=NH$^+$ ↔ H$_2$C=CH—C≡NH$^+$ as the most stable C$_3$H$_4$N$^+$ isomer. The slow rate observed for this exothermic channel suggests that C$_3$H$_3$N$^+$ will be totally unreactive with H$_2$ under cold cloud conditions, although the low rate in this instance is not necessarily a consequence of an activation energy barrier. Atom abstraction reactions are generally fast if exothermic.$^{333}$ A dramatic exception is

\[
\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}^- \quad (6.7)
\]

\[\Delta H_{6,3} = -86 \text{kJmol}^{-1}.\]

This reaction occurs very slowly at room temperature ($k_{6,7} \sim 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$ at 300K)$^{333}$ but proceeds much more rapidly at low temperature. The mechanism invoked to explain this behaviour involves formation of a weakly-bound complex prior to rearrangement to products. At elevated temperature, complex fragmentation occurs more rapidly than complex rearrangement, explaining the large negative temperature dependence seen for reaction (6.7) below 80K. A similar mechanism, to explain an even more marked negative temperature dependence, has been proposed for the reaction$^{334,335}$
\[ \text{O}_2^+ + \text{CH}_4 \rightarrow \text{CH}_3\text{O}_2^+ + \text{H} \quad (6.8). \]

In the face of such counterexamples, and in the absence of a study of the temperature dependence of the reaction of C_3H_3N^+ with H_2 (the current version of the Canterbury SIFT permitting only room-temperature study of reactions), it is not possible to state that this reaction will necessarily be slow at low cloud temperatures. If the reaction is slow, then reaction of C_3H_3N^+ with other neutrals will be of some relevance in modelling of cloud chemistry.

The reaction of C_3H_3N^+ with CH_4 yields primary products at m/z 41, 54 and 68 as shown in table 6.1. The product ion at m/z 41 can be C_3H_5^+ or C_2H_3N^+ on the basis of its mass: however, all channels involving C_3H_5^+ are endothermic by at least 136 kJmol\(^{-1}\), while channels involving CH_3CN^+ and CH_3NC^+ are also endothermic to a similar extent upon the basis of tabulated heats of formation.\(^{184}\) The products are thus designated as CH_2CNH^+ + C_2H_4, since this is the only exothermic channel evident. The product ion at m/z 54 is protonated acrylonitrile, C_3H_4N^+: the other possible structure, C_4H_6^+, is rejected since all channels yielding C_4H_6^+ are very substantially endothermic. The product ion at m/z 68 is C_4H_6N^+. The structure of this C_4H_6N^+ ion cannot be reliably determined upon the basis of heats of formation. Production of the branched structure (CH_3)_2CCN^+ is endothermic by 15 kJmol\(^{-1}\), but could well be exothermic within the combined uncertainties of the \(\Delta H_f\) values used.\(^{184}\) The formation of a cyclic isomer is also an exothermic channel, two such isomers (protonated pyrrole, and protonated cyclopropylcarbonitrile, c-C_3H_5CNH^+) having been reported.\(^{184}\)
Identification of the main product of the reaction with H₂O is again difficult. The major product at m/z 42 can be either C₂H₄O⁺ or CH₂NO⁺, with the most exothermic possibility being the formation of CH₂CHOH⁺ + HCN (ΔH = -103 kJ mol⁻¹). Formation of H₂NCO⁺ is possible (ΔH = -30 kJ mol⁻¹) but unlikely in view of the low exothermicity and the substantial degree of rearrangement required. The other product channels are adduct formation with, and without, the loss of H⁺.

For the fast reaction with NH₃, charge transfer and proton transfer compete. The presence of the latter channel establishes PA(C₃H₂N) < PA(NH₃), corresponding to ΔHᵣ(C₃H₂N) < 561 kJ mol⁻¹. This is in comfortable agreement with ΔHᵣ(CH₂CHCN) = 184 kJ mol⁻¹ and the expected value for D(H—C₃H₂N), since D(H—C₂H₃) = 213.1 kJ mol⁻¹.

The reaction with C₂H₂ proceeds at the collision rate, with several product channels. The major channel at m/z 52 is probably H-atom transfer to yield protonated cyanoacetylene (HC₃NH⁺) and C₂H₃ (ΔH = -72 kJ mol⁻¹), although formation of C₄H₄⁺ + HCN is exothermic also for both linear and cyclic isomers of C₄H₄⁺. The product ion at m/z 39 is identified as C₃H₃⁺ + CH₂CN, since all channels to C₂HN⁺ + C₃H₄ are endothermic. C₃H₃⁺ produced in this reaction is most probably the cyclopropenylidenium cation, although a less exothermic channel to a linear isomer exists also. The minor channel at m/z 76 is very interesting, since this ion, C₅H₂N⁺, may well be protonated cyanodiacetylene (HC₅NH⁺). Alternative structures for this ion are less likely, since HC₅NH⁺ is the protonated form of a known compound while other structures must represent linear ions with unsatisfied valences or cyclic ions with high strain due
to their extreme unsaturation. The cyclic structure with the lowest ring strain would be a structure related to pyridine. Bews and Glidewell\textsuperscript{337} have calculated the heats of formation of six isomeric C\textsubscript{5}H\textsubscript{2}N\textsuperscript{+} pyridine analogues: \( \Delta H_f \geq 1777 \text{ kJ mol}^{-1} \) for all of these isomers. Given the accuracy of these calculations (agreement for the \( \Delta H_f \) values calculated for ions in this study, where experimental values exist, is within \( \pm 100 \text{ kJ mol}^{-1} \) in all instances), such a cyclic structure for the ion formed in this reaction can be ruled out as endothermic. The study of Bews and Glidewell does not include N-protonated ions, but it seems intuitively unlikely that an N-protonated cyclic ion would have a heat of formation sufficiently far below those of the isomers covered by the study to permit generation of such an ion in the reaction considered here. The existence of the m/z 52 product channel thus establishes \( \Delta H_f(\text{HC}_5\text{NH}^+) < 1247 \text{ kJ mol}^{-1} \), and would also yield a lower limit to the proton affinity of HC\textsubscript{5}N except that, to date, no experimental value exists for \( \Delta H_f(\text{HC}_5\text{N}) \). A theoretical calculation\textsuperscript{336} using a STO-3G basis set yields an atomisation energy for HC\textsubscript{5}N of 26.49 eV, corresponding to \( \Delta H_f(\text{HC}_5\text{N}) = 1718 \text{ kJ mol}^{-1} \); but since the same analysis drastically underestimates the atomisation energies for HCN and C\textsubscript{2}H\textsubscript{2}, this value for \( \Delta H_f(\text{HC}_5\text{N}) \) is clearly far too high. The fourth channel evident for this reaction is formation of C\textsubscript{5}H\textsubscript{4}N\textsuperscript{+}, for which both linear and cyclic structures are energetically feasible: \( \Delta H_f(\text{C}_5\text{H}_4\text{N}^+) < 1247 \text{ kJ mol}^{-1} \), within the range of values given for pyridine-like C\textsubscript{5}H\textsubscript{4}N\textsuperscript{+} ions.\textsuperscript{337}

The reaction with HCN results in adduct formation with varying degrees of hydrogen loss, as listed in table 6.1. This reaction is evidently exothermic in view of the multiplicity of product channels observed, yet occurs at substantially below the calculated collision rate.
The reaction with CH₂CHCN is fast and results solely in adduct formation.

The exact structure of the C₃H₃N⁺ ion exploited in these reactions is unknown. A CCCN skeletal structure is assumed, in view of its formation from acrylonitrile, and ΔHᵣ(C₃H₃N⁺) = 1237 kJ mol⁻¹ is assumed in accordance with IP(CH₂CHCN). ¹⁸⁴, ³³⁸ Several isomeric forms of C₃H₃N⁺ probably exist as stable ionic structures: Heerma et al.³³² postulate the existence of at least six stable C₃H₄N⁺ isomers, and experiments on the Canterbury SIFT have demonstrated isomerism in a number of systems involving CN-containing ions (see chapters 4 & 5).¹⁶₆, ²₄₁, ²₇⁹, ²₈₀, ³³⁹ In view of these considerations, and of the highly energetic method of C₃H₃N⁺ production, the isomeric purity of the reactant ion signal at m/z 53 cannot be certain: however, none of the reactions listed in table 6.1 gave any evidence to support the presence of multiple isomers in the reactant ion signal. It can also be assumed that the reactant ion signal was free of any effects from vibrational excitation: it would be unprecedented for an ion containing more than four atoms²²₆ to exhibit any metastable vibrational excitation.

Section 6.3: Reactions of C₃H₄N⁺, C₃H₂N⁺ and HC₃N⁺.

In interstellar chemistry, C₃H₄N⁺ can arise via protonation of CH₂CHCN as well as by the reactions detailed in section 6.1. C₃H₄N⁺ is the ion which is central to acrylonitrile production in clouds:
\[
\begin{align*}
\text{CH}_2\text{CHCNH}^+ + X & \rightarrow \text{C}_2\text{H}_3\text{CN} + \text{XH}^+ \quad (6.9) \\
\text{CH}_2\text{CHCNH}^+ + e & \rightarrow \text{C}_2\text{H}_3\text{CN} + \text{H}^\cdot \quad (6.10)
\end{align*}
\]
\[\Delta H_{6.10} = -518 \text{ kJ mol}^{-1}.\]

Dissociative recombination (6.10) may also lead to other products, for example \(\text{C}_3\text{H}_2\text{N}^\cdot + \text{H}_2.\)

The reactions of \(\text{C}_3\text{H}_4\text{N}^+\) with various neutrals are summarised in table 6.2.

<table>
<thead>
<tr>
<th>(X)</th>
<th>Products (a)</th>
<th>(k_{\text{obs}}^a)</th>
<th>(k_c^a)</th>
<th>(-\Delta H^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2)</td>
<td>none</td>
<td>(&lt; 0.0005)</td>
<td>1.50</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>none</td>
<td>(&lt; 0.0005)</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>none</td>
<td>(&lt; 0.0005)</td>
<td>0.72</td>
<td>-</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>none</td>
<td>(&lt; 0.0005)</td>
<td>0.65</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>none</td>
<td>(&lt; 0.0005)</td>
<td>1.07</td>
<td>-</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>(\text{CH}_2\text{CHCN.OH}^+ + \text{H}^\cdot)</td>
<td>0.018</td>
<td>2.42</td>
<td>-</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>(\text{NH}_4^+ + \text{C}_3\text{H}_2\text{N})</td>
<td>1.7</td>
<td>2.18</td>
<td>60</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_2)</td>
<td>none (b)</td>
<td>(&lt; 0.01)</td>
<td>1.02</td>
<td>-</td>
</tr>
<tr>
<td>(\text{HCN})</td>
<td>(\text{CH}_2\text{CHCN.H.NCH}^+)</td>
<td>0.034</td>
<td>3.27</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CH}_2\text{CHCN})</td>
<td>((\text{CH}_2\text{CHCN})_2\text{H}^+)</td>
<td>1.30</td>
<td>3.60</td>
<td>-</td>
</tr>
</tbody>
</table>

Notes
a. See footnotes (a-d) for table (6.1).
b. See text for discussion.
C₃H₄N⁺ is substantially less reactive than C₃H₃N⁺, exhibiting no reaction with H₂, CO, N₂, CH₄ or O₂, and slow adduct-forming reactions with HCN and H₂O. A reaction with C₂H₂ is possible, but the reaction (if it occurs) is very slow: products from such a reaction could not be detected due to the multiplicity of products formed by the rapid reaction of a small contaminant signal at m/z 53 (C₃H₃N⁺) with C₂H₂, with additional products from secondary reactions in evidence also. Proton transfer is the only channel seen for the rapid reaction with NH₃. Adduct formation is the only channel seen for the reaction with the parent neutral, acrylonitrile.

Attempts were made to identify the C₃H₄N⁺, generated in the manner described here, as protonated acrylonitrile on the basis of the known proton affinity of acrylonitrile. Staley et al. established PA(CH₂CHCN) = 790.0 kJ mol⁻¹ by ICR bracketing using 1,3-dioxolane, C₂H₅CHO and CH₃CN. Lias et al. adjusted this value to 794.0 kJ mol⁻¹, in good agreement with the value derived from a calculation by Heerma et al. of ΔH₁(CH₂CHCNH⁺) = 925 kJ mol⁻¹ which establishes this as the lowest-energy C₃H₄N⁺ isomer.

Unfortunately, attempts to use proton-transfer bracketing techniques to characterise the m/z 54 ion signal were thwarted by the occurrence of competing adduct formation in the reactions between C₃H₄N⁺ and toluene (PA(C₆H₅CH₃) = 794.0 kJ mol⁻¹) and C₃H₄N⁺ and CH₃CN (PA(CH₃CN) = 788 kJ mol⁻¹). These reagents were chosen on the basis of their PA values, which are close to the literature value (794 kJ mol⁻¹) for acrylonitrile. Proton transfer was observed as a minor channel in each of these reactions (less than 5% for C₃H₄N⁺ + CH₃CN)
but in view of the competing adduction processes it was not felt useful to quantify the product distributions for these reactions.

Some studies were also made of the reactivity of $\text{C}_3\text{H}_2\text{N}^+$ with various neutrals: these results are presented in table 6.3.

<table>
<thead>
<tr>
<th>X</th>
<th>Products$^a$</th>
<th>$k_{\text{obs}}^a$</th>
<th>$k_e^a$</th>
<th>$-\Delta H^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>none</td>
<td>&lt;0.0005</td>
<td>1.50</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>none</td>
<td>&lt;0.001</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>N$_2$</td>
<td>none</td>
<td>&lt;0.0005</td>
<td>0.73</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>none</td>
<td>&lt;0.005</td>
<td>1.08</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>none</td>
<td>&lt;0.05</td>
<td>2.42</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>none</td>
<td>&lt;0.01</td>
<td>1.02</td>
<td>-</td>
</tr>
<tr>
<td>HCN</td>
<td>$\text{C}_3\text{H}_2\text{N}.\text{HCN}^+$</td>
<td>0.06</td>
<td>3.28</td>
<td>-</td>
</tr>
<tr>
<td>CH$_2$CHCN</td>
<td>$\text{CH}_2\text{CHCNH}^+ + \text{HC}_3\text{N}^b$</td>
<td>[0.81]</td>
<td>1.6</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_3\text{H}_4^+ + \text{HCN}$</td>
<td>[0.19]</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>CH$_3$NO$_2$</td>
<td>$\text{CH}_3\text{NO}_2^+ + \text{HC}_3\text{N}$</td>
<td>[0.60]</td>
<td>1.2$^b$</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_3\text{H}_2\text{N} .\text{CH}_3\text{NO}_2^+$</td>
<td>[0.40]</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>CH$_3$NO$_2$</td>
<td>$\text{CH}_3\text{NO}_2^+ + \text{HC}_3\text{N}$</td>
<td>[0.60]</td>
<td>1.37$^d$</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_3\text{H}_2\text{N} .\text{CH}_3\text{NO}_2^+$</td>
<td>[0.40]</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

Notes

a. See footnotes (a-d) for table (6.1).

b. Results obtained for $\text{C}_3\text{H}_2\text{N}^+$ generated by electron impact upon CH$_2$CHCN.

c. Calculated assuming a protonated cyanacetylene structure for $\text{C}_3\text{H}_2\text{N}^+$; see text for discussion.

d. Results obtained for $\text{C}_3\text{H}_2\text{N}^+$ generated by electron impact upon a HC$_3$N / H$_2$ mixture (1:30).
HC$_3$NH$^+$ is the precursor ion to the prominent interstellar species HC$_3$N, and should also be detectable within dense clouds although attempts at its detection have to date proved fruitless.$^{39,40}$ Many interstellar pathways to HC$_3$NH$^+$ exist,$^{182}$ and its reactivity (with reference especially to proton transfer) has been previously studied in SIFT instruments by bracketing$^{205}$ and by determination of proton-transfer equilibrium constants.$^{167,267}$

A small signal at m/z 52, due to C$_3$H$_2$N$^+$, was present in all cases when the reactions of C$_3$H$_3$N$^+$ were being studied. In consequence, it was necessary to study the reactivity of this m/z 52 ion to ensure that it was not giving rise to any signals ascribed to C$_3$H$_3$N$^+$ + X reaction products, and to determine also whether the C$_3$H$_2$N$^+$ ion signal was protonated cyanoacetylene. This possibility was strongly suggested by the reaction

$$
\text{C}_3\text{H}_2\text{N}^+ + \text{C}_2\text{H}_3\text{CN} \rightarrow \text{C}_3\text{H}_4\text{N}^+ + \text{C}_3\text{HN} \quad [0.81] \quad (6.6a)
$$

$$
\rightarrow \text{C}_5\text{H}_4\text{N}^+ + \text{CHN} \quad [0.19] \quad (6.6b)
$$

for which $k_{6.6} = 1.6 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ was found. The presence of channel (6.6a) as the major product channel is consistent with rapid proton transfer from HC$_3$N to acrylonitrile ($\Delta H = -41 \text{ kJ mol}^{-1}$)$^{184}$ Channel (6.6b) requires $\Delta H_f(\text{C}_5\text{H}_4\text{N}^+) < 1177 \text{ kJ mol}^{-1}$, a lower value than the upper limit for C$_5$H$_4$N$^+$ production from the reaction of C$_3$H$_3$N$^+$ with C$_2$H$_2$ (see table 6.1). The structure of the C$_5$H$_4$N$^+$ ion produced in this reaction is not known.

C$_3$H$_2$N$^+$ was not reactive with most of the neutral reagents tested: for X = H$_2$, CO, N$_2$, CH$_4$, H$_2$O, HCN and C$_2$H$_2$, C$_3$H$_2$N$^+$ was unreactive or exhibited
$k_{\text{obs}}(\text{C}_3\text{H}_2\text{N}^+) < 0.1 k_{\text{obs}}(\text{C}_3\text{H}_3\text{N}^+)$, while for $X = \text{NH}_3$, proton transfer was the only product channel observed:

$$\text{C}_3\text{H}_2\text{N}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{HC}_3\text{N} \quad (6.11),$$

with $k_{6.11} = 2.0 \times 10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Adduct formation was observed to occur in the slow reaction with HCN; adduct formation may also be occurring with C$_2$H$_2$, although an upper limit of $k < 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ was assigned for this reaction. The C$_3$H$_2$N$^+$ ion was also seen to react with CH$_3$NO$_2$:

$$\text{C}_3\text{H}_2\text{N}^+ + \text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3\text{NO}_2\text{H}^+ + \text{HC}_3\text{N} \quad [0.60] \quad (6.12a)$$

$$\rightarrow \text{CH}_3\text{NO}_2.\text{HN}_\text{C}_3\text{H}^+ \quad [0.40] \quad (6.12b),$$

with $k_{6.12} = 1.2 \times 10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$. The product ratio determined here may be mildly distorted due to mass discrimination effects. Nevertheless, the observed product ratio is in excellent agreement with that observed for the reaction of protonated cyanoacetylene with nitromethane; the rate coefficient observed is somewhat lower than the value of $1.8 \times 10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$ reported by Knight et al for reaction (6.12) using protonated cyanoacetylene, but in very good agreement with the value of $k_{6.12} = 1.37 \times 10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$ obtained when we repeated Knight's measurement using HC$_3$N / H$_2$ as the source gas. The agreement between these two values, which are significantly below the collision rate expected for reaction (6.12), indicates that C$_3$H$_2$N$^+$ generated by electron impact upon acrylonitrile has the same structure as protonated cyanoacetylene.
Ions at the neighbouring masses, m/z 51 (HC$_3$N$^+$) and 53 (C$_3$H$_3$N$^+$), were also present when C$_3$H$_2$N$^+$ was injected to study the reaction with CH$_3$NO$_2$. By varying the mass setting on the upstream mass spectrometer, the ratios of the reactant ion signals at m/z 51, 52 and 53 could be altered, and thus it was possible to assign products also for the reactions of C$_3$HN$^+$ and C$_3$H$_3$N$^+$ with CH$_3$NO$_2$:

\[
\begin{align*}
C_3HN^+ + CH_3NO_2 & \rightarrow CH_3NO^+ + HC_3NO \quad (6.13) \\
C_3H_3N^+ + CH_3NO_2 & \rightarrow C_4H_6N^+ + NO_2 \quad (6.14)
\end{align*}
\]

\[k_{6.13} = 1.9 \times 10^{-9} \text{ cm}^3 \text{ mole}^{-1} \text{s}^{-1}\]

\[k_{6.14} = 1.0 \times 10^{-9} \text{ cm}^3 \text{ mole}^{-1} \text{s}^{-1}.
\]

A secondary product peak at m/z 76, especially prominent when m/z 51 was the largest reactant ion signal, was attributed to the reaction

\[
CH_3NO^+ + CH_3NO_2 \rightarrow (CH_3)_2NO_2^+ + NO \quad (6.15)
\]

for which a rate determination was not attempted (although the reaction appeared to occur rapidly).

Although not directly related to the ion-molecule chemistry of acrylonitrile, some further reactions of HC$_3$N$^+$ with prominent interstellar neutrals were also studied. These reactions have not been included in previous investigations of cyanoacetylene ion-molecule chemistry,\textsuperscript{64,167,205,214,255,265,267} since HC$_3$N$^+$ displays little reactivity with H$_2$, these reactions (which are presented in \textbf{table 6.4}) are likely to be important as loss processes of HC$_3$N$^+$ within interstellar clouds.
The reaction with CH₄ shows some parallels with the reaction of C₃H₃N⁺ with methane: channels involving H-atom abstraction and formation of CH₂CNH⁺ appear common to both ions, although the ion at m/z 41 can also be CH₂CHCH₂⁺ since this channel is slightly exothermic also. A channel at m/z 40 is attributed to C₃H₄⁺, since production of any ion of the form C₂H₂N⁺ is endothermic. The structure of the C₃H₄⁺ product is not known: several possible structures exist, each of which corresponds to an exothermic channel.

The reaction with C₂H₂ displays adduct formation and a small charge-transfer channel in addition to a larger channel producing C₄H₂⁺: this reaction has already been discussed in section 4.2.

<table>
<thead>
<tr>
<th>X</th>
<th>Products a</th>
<th>k_{obs} b</th>
<th>k_c c</th>
<th>-ΔH a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>C₃H₄⁺ + HCN</td>
<td>[0.11]</td>
<td>0.83</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>CH₂CHCH₂⁺ + CN⁻</td>
<td>[0.56]</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(or CH₂CNH⁺ + C₂H₂)</td>
<td></td>
<td>168</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCN⁺ + CH₃⁻</td>
<td>[0.35]</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>C₂H₂</td>
<td>C₂H₂⁺ + HC₃N</td>
<td>[0.05]</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>C₄H₂⁺ + HCN</td>
<td>[0.60]</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HC₃N.C₂H₂⁺</td>
<td>[0.30]</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>HC₃N.CO⁺</td>
<td></td>
<td>0.055</td>
<td>0.80</td>
</tr>
<tr>
<td>NH₃</td>
<td>NH₃⁺ + HC₃N</td>
<td></td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>HCN</td>
<td>HCNH⁺ + C₃N⁻</td>
<td>[0.32]</td>
<td>1.32</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>C₄N₂H⁺ + H⁻</td>
<td>[0.17]</td>
<td>&lt;143 c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HC₃N.HCN⁺</td>
<td>[0.51]</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Notes

a. See footnotes (a) - (d) for table (6.1).
b. See text for discussion.
c. Calculated assuming a structure NCCCCNH⁺ for the product ion (see section 4.3).
Charge-transfer (which occurs rapidly) is the only product channel seen with NH₃. The apparent absence of proton transfer (ΔH = -170 kJ mol⁻¹) as a competing product channel in this reaction is surprising, given the usual rapidity of proton transfer when exothermic.

The reaction with HCN exhibits adduct formation, proton transfer, and production of a C₄N₂H⁺ ion: this ion may have the same structure as the protonated dicyanoacetylene species seen in several reactions of the C₄N₂⁺ ion investigated in section 4.3.

All of these reactions occur rapidly at 300 K: they are likely to represent efficient reactions under interstellar conditions also, and should thus be considered in models of cyanopolyyne chemistry. The adduct formation channel evident with CO, although inefficient as a termolecular association process at 0.3 Torr, is likely also (as a radiative association process) to be of some significance to the loss of HC₃N⁺ within clouds.

Section 6.4: Reactions of various ions with acrylonitrile.

Reactions of several ions with acrylonitrile are displayed in table 6.5.

Although a detailed survey of ions of astrophysical interest was not attempted, many of the reactions detailed in table 6.5 are of relevance to interstellar
Table 6.5: Reactions of X⁺ + CH₂CHCN.

<table>
<thead>
<tr>
<th>X⁺</th>
<th>Products</th>
<th>k_{obs}[^a]</th>
<th>k_c[^a]</th>
<th>-ΔH[^a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃⁺</td>
<td>CH₂CHCNH⁺ + H₂</td>
<td>9.9</td>
<td>11.1</td>
<td>370</td>
</tr>
<tr>
<td>He⁺</td>
<td>C₂H₂⁺ + HCN + He[^b]</td>
<td>[0.33]</td>
<td>10.5</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>C₂H₂⁺ + CN⁻ + He</td>
<td>[0.05]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(or CHN⁺ + C₂H₂ + He)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c-C₃H₃⁺ + N⁻ + He[^b]</td>
<td>[0.05]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCN⁺ + H₂ + He</td>
<td>[0.29]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₂N⁺ + H⁻ + He</td>
<td>[0.12]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂CHCN⁺ + He</td>
<td>[0.16]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C⁺</td>
<td>C₃H₃⁺ + HCN[^b]</td>
<td>[0.24]</td>
<td>4.1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>c-C₃H₃⁺ + CN⁻[^b]</td>
<td>[0.44]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₄H₂N⁺ + H⁻</td>
<td>[0.29]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₄H₃N⁺</td>
<td>[0.03]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N⁺</td>
<td>C₂H₂⁺ + HNCN⁻[^d]</td>
<td>[0.20]</td>
<td>4.3</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>CHN⁺ + CH₂CN⁻</td>
<td>[0.07]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(or C₂H₂⁺ + N₂⁺ + C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₂⁺ + N₂ + H⁻</td>
<td>[0.48]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₂N⁺ + NH</td>
<td>[0.10]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂CHCN⁺ + N⁻</td>
<td>[0.15]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂⁺</td>
<td>C₂H₂⁺ + HCN + N₂</td>
<td>[0.57]</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>CHN⁺ + N₂ + C₂H₂</td>
<td>[0.08]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(or C₂H₂⁺ + N₂ + CN⁻)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₂N⁺ + N₂ + H⁻</td>
<td>[0.26]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂CHCN⁺ + N₂</td>
<td>[0.09]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar⁺</td>
<td>C₂H₂⁺ + HCN + Ar</td>
<td>[0.46]</td>
<td>3.1</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>CH₂CHCN⁺ + Ar</td>
<td>[0.54]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>c-C₄H₃⁺ + CH₃NH[^b]</td>
<td>[0.15]</td>
<td>4.4</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>C₄H₂N⁺ + CH₄</td>
<td>[0.29]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂CHCN.CH₃⁺</td>
<td>[0.56]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H⁺</td>
<td>C₂H₂N⁺ + C₂H₂</td>
<td>4.8</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(or C₄H₄⁺ + CN⁻)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂⁺</td>
<td>c-C₃H₃⁺ + C₂H₂N⁻[^b]</td>
<td>[0.15]</td>
<td>4.3</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>CH₂CHCN⁺ + C₂H₂</td>
<td>[0.55]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂CHCNH⁺ + C₂H⁻</td>
<td>[0.15]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂CHCN.C₂H₂⁺</td>
<td>[0.15]</td>
<td></td>
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<tr>
<td>C₂H₃⁺</td>
<td>products[^b]</td>
<td>4.4</td>
<td>4.4</td>
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<tr>
<td></td>
<td>c-C₃H₂⁺ products[^b]</td>
<td>4.5</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Products</td>
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</tr>
<tr>
<td>1-C_3H_2^+</td>
<td>4.5</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c-C_3H_5^+</td>
<td>CH_2CHCN.C_3H_5^+</td>
<td>0.11</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>1-C_3H_5^+</td>
<td>products^b</td>
<td>4.0</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>CO^+</td>
<td>C_2H_2^+ + HCN + CO</td>
<td>4.1</td>
<td>4.4</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>CH_2CHCN^+ + CO</td>
<td>0.65</td>
<td>0.35</td>
<td>340</td>
</tr>
<tr>
<td>CN^+</td>
<td>C_3H_5^+ + N_2 +C</td>
<td>4.5</td>
<td>4.4</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>CH_2CHCN^+ + CN^-</td>
<td>0.16</td>
<td>0.75</td>
<td>187</td>
</tr>
<tr>
<td></td>
<td>(or C_3N_2H^+ + C_2H_2)</td>
<td>307</td>
<td>586^e</td>
<td>586</td>
</tr>
<tr>
<td></td>
<td>CH_2CHCN.CN^+</td>
<td>0.09</td>
<td>0.11</td>
<td>307</td>
</tr>
<tr>
<td>HCN^+</td>
<td>products^b</td>
<td>4.6</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>HNC^+</td>
<td>products^b</td>
<td>4.6</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>HCNH^+</td>
<td>CH_2CHCNH^+ + HCN</td>
<td>4.5</td>
<td>4.4</td>
<td>77</td>
</tr>
<tr>
<td>CCN^+</td>
<td>C_3H_5^+ + C_2N_2^b</td>
<td>3.6</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>CNC^+</td>
<td>C_3H_5^+ + C_2N_2^b</td>
<td>3.6</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>HC_2N^+</td>
<td>CH_2CHCNH^+ + C_2N^-</td>
<td>2.9</td>
<td>3.9</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td>C_4H_3N^+ + HCN</td>
<td>0.70</td>
<td>0.15</td>
<td>315</td>
</tr>
<tr>
<td></td>
<td>(or C_3HN_2^+ + C_2H_2)</td>
<td>0.15</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH_2CHCN.C_3H_2^+</td>
<td>0.15</td>
<td>g</td>
<td></td>
</tr>
</tbody>
</table>

Notes:

a. See footnotes (a) - (d) for table (6.1).
b. See text for discussion.
c. Calculated assuming a structure HCCCNH^+ for C_3H_3N^+.
d. Neutral products not established. The exothermicity of this product channel requires \( \Delta H_f(HNCN^-) < 731 \text{ kJ mol}^{-1} \), consistent with an upper limit of \( \Delta H_f(HNCN^-) < 471 \text{ kJ mol}^{-1} \) upon the evidence of the product channel HNC^+ + N_2O \rightarrow NO^+ + HCN (see chapter 5). Alternatively, the neutrals here may be HCN + N^- (\( \Delta H = -123 \text{ kJ mol}^{-1} \)) or CH^- + N_2 (\( \Delta H = -135 \text{ kJ mol}^{-1} \)).
e. Calculated using a value \( \Delta H_f(C_2N_2H^+) = 1165 \text{ kJ mol}^{-1} \) (see chapter 3).
f. The exothermicity of this product channel requires \( \Delta H_f(C_4H_3N^+) < 1580 \text{ kJ mol}^{-1} \).
g. The exothermicity of this product channel requires \( \Delta H_f(C_3HN_2^+) < 1450 \text{ kJ mol}^{-1} \).

chemistry, since the ions H_3^+, He^+, C^+, CH_3^+, C_2H_3^+, C_3H_2^+, C_3H_3^+, N^+, HCNH^+ and CNC^+ are all unreactive (or react only slowly) with H_2. All of the ions studied,
except c-C$_3$H$_3^+$, were observed to react very rapidly ($k > 2.5 \times 10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$) with CH$_2$CHCN.

Where applicable, reactivity of the ions concerned is compared to their reactivity with other CN-containing neutrals such as HCN and C$_2$N$_2$.

**He$^+$, N$_2^+$, CO$^+$, Ar$^+$.** For these ions the major products from reaction with acrylonitrile were at m/z 26 and m/z 53. For $X = N_2^+$, CO$^+$, Ar$^+$, production of CN$^+$ + C$_2$H$_3^+$ + X is endothermic and so the product ion at m/z 26 for these reactions is clearly C$_2$H$_2^+$; for He$^+$, production of CN$^+$ is energetically possible but C$_2$H$_2^+$ production is more likely upon energetic grounds and by analogy with the reactions of N$_2^+$, CO$^+$ and Ar$^+$. Attempts were made to distinguish between CN$^+$ and C$_2$H$_2^+$ upon the basis of the reactivity of these ions with CH$_2$CHCN, but it was not possible to positively identify the m/z 26 ion product for the reaction of He$^+$. Other fragmentary ions were produced in the reactions of He$^+$ and N$_2^+$: these include c-C$_3$H$_3^+$ (identified by its lack of reactivity with CH$_2$CHCN) and C$_3$H$_2$N$^+$, presumably protonated cyanoacetylene. The production in these reactions of protonated cyclopropenylidene, and HC$_3$NH$^+$, is of interest because these ions are integral to ion-molecule models of interstellar chemistry. Furthermore, He$^+$ reacts only slowly with H$_2$ and thus its reaction with acrylonitrile should be considered in such models.

The multiplicity of fragmentary products seen in these reactions suggests that these reactions occur by a mechanism of dissociative charge transfer. Charge transfer in all these instances is highly exothermic, and collisional stabilisation of the charge-transfer product may be in competition with unimolecular
dissociation of the initial, highly excited, product. The greatest multiplicity of product channels is seen in the reaction with He+, corresponding to the very high exothermicity of charge-transfer in this instance. Reaction of He+ with HCN and HC₃N also results in several fragmentation products,¹⁶⁷,³⁴¹ whereas N₂⁺ is observed¹⁶⁷,²¹⁴,³⁴¹ to undergo only charge-transfer with HCN and HC₃N.

C⁺, N⁺, CN⁺. These ions all generated product ions at m/z 38 and/or m/z 39. Possible product ions at m/z 38 are c-C₃H₂⁺, l-C₃H₂⁺, CCN⁺ and CNC⁺; possible products at m/z 39 are c-C₃H₃⁺, l-C₃H₃⁺, HCCN⁺ and HCNC⁺. In all these instances, production of cyano-containing ions could be eliminated on energetic grounds or upon the basis of the reactivity of these product ions with acrylonitrile. The major product channel for the reaction of CN⁺ with acrylonitrile, at m/z 53, is probably charge-transfer: it should be noted, however, that production of C₂N₂H⁺ (protonated dicyanogen) requires only a slight degree of rearrangement and is more exothermic. Adduct formation was a minor channel for the reactions of C⁺ and CN⁺.

A parallel is evident between the reaction of C⁺ with acrylonitrile, and those of C⁺ with HCN, HC₃N and C₂N₂: in the latter reactions, as with CH₂CHCN, loss of H⁻ and of CN⁻ are the dominant product channels observed.¹⁴⁹,¹⁶⁷,²¹⁴,²²⁵,²³⁸,²⁴⁷,³⁴³ Similarly, the occurrence of charge-transfer as the major product channel for the reactions of CN⁺ + HCN, HC₃N, CD₃CN and C₂N₂ ²¹⁴,²⁴⁶,²⁴⁷,³⁴⁴ mirrors the tendency observed in the reaction of CN⁺ with acrylonitrile. There are fewer similarities evident in the case of the reaction of N⁺: a wider range of product channels in the reaction with CH₂CHCN, in comparison with the reactions¹⁶⁷,²⁴⁷
\[
\begin{align*}
\text{N}^+ + \text{HC}_3\text{N} & \rightarrow \text{C}_3\text{H}^+ + \text{N}_2 & [0.50] & (6.16a) \\
& \rightarrow \text{HC}_3\text{N}^+ + \text{N}^- & [0.50] & (6.16b) \\
\text{N}^+ + \text{C}_2\text{N}_2 & \rightarrow \text{C}_2\text{N}^+ + \text{N}_2 & [0.70] & (6.17a) \\
& \rightarrow \text{C}_2\text{N}_2^+ + \text{N}^- & [0.30] & (6.17b),
\end{align*}
\]

probably reflects the greater structural complexity of the acrylonitrile molecule.

**H_3^+, C_2H_3^+, HCNH^+.** Proton transfer was the major channel evident in these reactions, which is consistent with the proton affinity of acrylonitrile (\(\text{PA(}CH_2\text{CHCN}) = 794\) kJ mol\(^{-1}\)). In the case of \(C_2H_3^+\), some adduct formation (~20%) was also seen: a rigorous product analysis for this reaction was not attempted since we were unable to produce an adequately large, clean signal of \(C_2H_3^+\).

**HCN^+, HNC^+.** These ions were injected together from the ion source, using HCN as a source gas. Under these conditions, HCN^+ accounts for ~70% of the m/z 27 ion signal.\(^{279}\) No attempt was made in this instance to distinguish between the reactivity of HCN^+ and of HNC^+ with \(CH_2\text{CHCN}\) - the intent was, rather, to ascertain differences in the reactivity of CHN^+ and \(C_2H_3^+\) with \(CH_2\text{CHCN}\), so that product ions at m/z 27 could be characterised. The product channels observed for reaction of CHN^+ with acrylonitrile were at m/z 53 (60%) and m/z 54 (40%), corresponding to charge-transfer and proton-transfer respectively (these are also the only product channels seen in the reactions of CHN^+ with HCN and HC_3N).
As it happened, the reactions of He\(^+\), N\(^+\) and N\(_2\)^+ produced too little m/z 27 (≤ 8\% of total products) to be able to distinguish between C\(_2\)H\(_3\)^+ and CHN\(^+\) in these instances.

**CH\(_3\)^+**. The major product observed for this reaction was the adduct. The other products were identified as the protonated forms of cyclopropenylidene and cyanoacetylene. In view of the lack of reactivity of CH\(_3\)^+ with H\(_2\) and with CO, this reaction represents an important loss process for CH\(_2\)CHCN within interstellar clouds: although the minor products suggest that c-C\(_3\)H\(_2\) and HC\(_3\)N will be eventual products of such reaction, it is possible also that radiative association may be more prominent under interstellar conditions.\(^{60}\)

Association is also observed as the dominant channel for the reactions of CH\(_3\)^+ with HCN, CH\(_3\)CN and HC\(_3\)N, even at the low pressures pertinent to ICR experiments.\(^{60,63}\) This indicates that CH\(_3\)^+ forms very long-lived and stable collision complexes with CN-containing compounds.

**C\(_2\)H\(^+\), C\(_2\)H\(_2\)^+**. These ions were produced from electron impact upon C\(_2\)H\(_2\). The sole product channel observed for the reaction of C\(_2\)H\(^+\), at m/z 52, is presumed to be hydride transfer (\(\rightarrow\) HC\(_3\)NH\(^+\) + C\(_2\)H\(_2\)) since the alternative, production of C\(_4\)H\(_4\)^+ + CN\(^-\), is substantially less exothermic and requires more rearrangement. Charge-transfer is the major product from C\(_2\)H\(_2\)^+; other product channels are at m/z 39 (c-C\(_3\)H\(_3\)^+, identified by its lack of reactivity with CH\(_2\)CHCN) and at m/z 54, corresponding to proton transfer.
$C_3H_2^+$, $C_3H_3^+$. These ions were produced by electron bombardment upon propyne, CH$_3$CCH. Smith and Adams$^{345}$ have shown that electron impact upon propyne produces $\sim80\%$ of $C_3H_2^+$, and $\sim35\%$ of $C_3H_3^+$, in the higher-energy linear forms: the cyclic isomers account for the remainder. In the present studies, reactions of $C_3H_2^+$ and $C_3H_3^+$ were investigated to aid identification of m/z 38 and m/z 39 products from other reactions with acrylonitrile. No attempt was made to distinguish between the cyclic and linear forms of $C_3H_2^+$. Adduct formation was the dominant channel seen for all of the reactive ions: the reaction profile for m/z 39 with acrylonitrile displayed distinct curvature (see figure 6.1), indicating a difference in reactivity of the two isomers of $C_3H_3^+$. The more reactive ion, which accounted for $\sim30\%$ of the m/z 39 ion signal, is identified as l-$C_3H_3^+$, since it could be removed by addition of C$_2$H$_2$ (see figure 6.2): the reactivity of the m/z 39 ion remaining was consistent with its reactivity in the absence of C$_2$H$_2$. The cyclic isomer reacted on only a few percent of collisions, exhibiting only adduct formation. The absence of proton transfer from c-$C_3H_3^+$ to CH$_2$CHCN suggests that PA(c-$C_3H_2$) exceeds 794 kJ mol$^{-1}$, the proton affinity of CH$_2$CHCN: PA(c-$C_3H_2$) has not been determined, but a value PA(c-$C_3H_2$) > 794 kJ mol$^{-1}$ is in agreement with the findings of Smyth et al.$^{346}$ who studied the reactions of $C_3H_3^+$ with several hydrocarbons in an ICR experiment.

A minor product at m/z 54, corresponding to proton transfer, was in evidence in our experiments: we were unable to determine whether it arose from c-$C_3H_2^+$, l-$C_3H_2^+$ or l-$C_3H_3^+$ since we could not inject m/z 39 from propyne without some contamination from m/z 38, and vice versa. This peak at m/z 54 was not in evidence when C$_2$H$_2$ was added to remove l-$C_3H_3^+$ (and also C$_3H_2^+$, since both isomers are reactive with acetylene), so the possibility of proton transfer from c-$C_3H_3^+$ can be eliminated.
Figure 6.1: Experimental decay curves observed for the reaction of \( \text{C}_3\text{H}_3^+ \) with \( \text{CH}_2\text{CHCN} \). (a). Graph over the entire flow range. (b). Graph highlighting the initial decay at low \( \text{CH}_2\text{CHCN} \) flows. The curvature evident in these graphs indicates that two isomers of \( \text{C}_3\text{H}_3^+ \) react at distinctly different rates with \( \text{CH}_2\text{CHCN} \): the solid curve fitted to the experimental data points describes the sum of two exponential terms, yielding \( k = 3.97 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for the more reactive \( \text{C}_3\text{H}_3^+ \) isomer (which accounts for 29% of the m/z 39 ion signal in this graph) and \( k = 1.10 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for the less reactive isomer.
C$_2$N$^+$, HC$_2$N$^+$. The reactions of these ions were studied so that products at m/z 38 (39) could be identified as C$_3$H$_2$(3)$^+$ or (H)C$_2$N$^+$.

CCN$^+$ and CNC$^+$ were produced by electron impact upon C$_2$N$_2$: we have previously shown$^{241}$ that this technique produces approximately 20% CCN$^+$ : 80% CNC$^+$. The only product seen (for reaction of both isomers of C$_2$N$^+$ with acrylonitrile) was at m/z 39, which was observed to react further with acrylonitrile to form an adduct at m/z 92. We suppose the product ions at m/z 39 to be a mixture of l-C$_3$H$_3^+$ and c-C$_3$H$_3^+$, since these channels are more exothermic than production of HC$_2$N$^+$ and since generation of C$_3$H$_3^+$ would be accompanied by C$_2$N$_2$ formation, in keeping with the reactions

Figure 6.2: Experimental decay curve observed for the reaction of C$_3$H$_3^+$ with CH$_2$CHCN (added at port 2), subsequent to the addition of a large flow of C$_3$H$_2$ at port 1. C$_2$H$_2$ reacts rapidly with l-C$_3$H$_3^+$ but is unreactive with c-C$_3$H$_3^+$; thus, this graph indicates the reaction due to c-C$_3$H$_3^+$ with acrylonitrile. The slope from this graph gives $k = (1.014 \pm 0.025) \times 10^{-10}$ cm$^3$ mole$^{-1}$ s$^{-1}$ for this reaction, in excellent agreement with the rate coefficient determined for the reaction of the less reactive C$_3$H$_3^+$ isomer in the graph in figure 6.1.
\[
\begin{align*}
\text{C}_2\text{N}^+ + \text{CH}_3\text{CN} & \rightarrow \text{C}_2\text{H}_3^+ + \text{C}_2\text{N}_2 \\
\text{C}_2\text{N}^+ + \text{HC}_3\text{N} & \rightarrow \text{C}_3\text{H}^+ + \text{C}_2\text{N}_2
\end{align*}
\] (6.18, 6.19).

HC\(_2\)N\(^+\) was generated from a 5% mixture of C\(_2\)N\(_2\) in H\(_2\). The major product channel seen was proton transfer, with adduct formation also in evidence.

HCNC\(^+\) was produced from methyl isocyanide, CH\(_3\)NC. Only a very small ion signal at m/z 39 could be obtained, and the isomeric nature of this ion could not be established. A rate coefficient for the reaction of HCNC\(^+\) with CH\(_2\)CHCN could not be reliably obtained in view of the signal size and since m/z 39 was also the sole product from the contaminating signal at m/z 38. However, a lower limit of \(k \geq 1.5 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) suggests that this isomer reacts rapidly, probably at the collision rate, with CH\(_2\)CHCN.

**Section 6.5: Production of CH\(_2\)CHCN and cyanopolyynes in interstellar clouds.**

Few of the reactions listed in tables 6.1 to 6.5 shed any light on the processes involved in acrylonitrile formation in interstellar clouds, beyond demonstrating that protonated acrylonitrile C\(_3\)H\(_4\)N\(^+\) (which is the likely main precursor ion to acrylonitrile in the interstellar environment) is unreactive with the predominant interstellar species. In an effort to explore an additional possible pathway to CH\(_2\)CHCN production, the reactions of N\(^+\) with C\(_2\)H\(_2\) and CH\(_3\)CCH
were studied: the reactions of N\(^+\) with alkynes represent an ion-molecule reaction class not previously investigated, and alkynes and their derivatives are prominent interstellar cloud constituents.

\[
\begin{align*}
N^+ + C_2H_2 & \rightarrow C_2H_2^+ + N^- [0.65] \quad (6.20a) \\
& \rightarrow CH_2N^+ + C [0.19] \quad (6.20b) \\
& \rightarrow C_2N^+ + H_2 [0.09] \quad (6.20c) \\
& \rightarrow HC_2N^+ + H_2 [0.07] \quad (6.20d)
\end{align*}
\]

\[k_{6.20} = 1.5 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]

\[
\begin{align*}
N^+ + CH_3CCH & \rightarrow C_2H_2^+ + HCN + H^- [0.20] \quad (6.21a) \\
& \rightarrow C_3H_3^+ + NH [0.47] \quad (6.21b) \\
& \rightarrow C_3H_4^+ + N^- [0.32] \quad (6.21c) \\
& \rightarrow C_3HN^+ + H_2 + H^- [0.01] \quad (6.21d)
\end{align*}
\]

\[k_{6.21} = 1.4 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.\]

The products reported here are those calculated as the most exothermic product channels corresponding to the product ion masses: in the reaction of propyne, product channels to CN\(^+\) + C\(_2\)H\(_4\) and to HC\(_2\)N\(^+\) + CH\(_3\) are possible also but are less exothermic than the products assigned for channels (6.21a) and (6.21b), respectively. Charge transfer is a prominent channel for each reaction. None of the major product channels suggest any promise for CH\(_2\)CHCN synthesis by such reactions, although the appearance of a very small C\(_3\)HN\(^+\) channel (6.21d) for the reaction with propyne is of interest since this ion could be ionized cyanoacetylene.
On the topic of HC$_3$N production, Turner has commented$^{18,39,347}$ that the non-detection$^{39,40}$ of the HC$_3$NH$^+$ ion in interstellar sources such as TMC-1 and Sagittarius B2 indicates a flaw in the ion-molecule modelling of cyanopolyynesynthesis in these sources. A discrepancy in the abundances of HCN and HC$_3$N is apparent relative to their protonated ions, since HCNH$^+$ is seen to be very abundant while HC$_3$NH$^+$ is, at present, below the detection limit. Given the broadly similar processes for interconversion of HC$_n$N and HC$_n$NH$^+$ for any $n$, and the broadly similar formation and destruction processes for these species, the ratio of HC$_n$NH$^+$ to HC$_n$N should, Turner argues, be essentially independent of the carbon skeleton length $n$ - and yet this ratio is much larger for $n=1$ than for $n=3$. Turner interprets this in terms of a possible grain-surface process whereby HCN is absorbed and undergoes processing to form HC$_3$N which is then, in some manner, desorbed. It should be noted, however, that since HC$_3$N has a dipole moment larger than HCN, it is more likely to adhere strongly to dust grains. It is difficult to postulate a method of efficiently desorbing$^{83}$ HC$_3$N from grain surfaces, and thus this mechanism seems more likely to result in HC$_3$N depletion than in its formation.

It should also be noted that the products of the crucial dissociative recombination reactions

\[
\begin{align*}
\text{HCNH}^+ + e & \rightarrow \text{products} \quad (6.22) \\
\text{HC}_3\text{NH}^+ + e & \rightarrow \text{products} \quad (6.23)
\end{align*}
\]

have not been determined: if reaction (6.22) were found to produce mainly CN$^- + H_2$, while reaction (6.23) yielded predominantly HC$_3$N + H, the discrepancy
detailed above would be resolved. Turner argues that reactions (6.22) and (6.23) should both produce predominantly $\text{C}_n\text{HN}$, in accordance with the Bates theory of dissociative recombination. However, recent experiments on the dissociative recombination of $\text{H}_3\text{O}^+$ have indicated that a major product is $\text{OH}$, in apparent conflict with the Bates theory which holds that only one existing bond should be broken in the recombination event. Further work on the products of dissociative recombination reactions is needed to adequately test the theories of Bates and others, with regard to dissociative recombination product channels.

A further point to note is that, while the reactions of HCN$^+$ and HNC$^+$ with H$_2$ are rapid at room temperature, the reaction of HC$_3$N$^+$ with H$_2$ is very slow if this reaction possesses an activation barrier it will not occur at interstellar temperatures, and thus charge-transfer from HC$_3$N$^+$ to various neutrals could constitute a method of HC$_3$N production not available in the analogous case of HCN production, thus permitting resolution (if these charge-transfer processes occurred efficiently enough) of the apparent discrepancy in HC$_n$N/HC$_n$NH$^+$ observed abundances. An example is seen in the reaction of HC$_3$N$^+$ with NH$_3$, featured in table 6.4.

\[
\begin{align*}
\text{H}_3\text{O}^+ + e & \rightarrow \text{H}_2\text{O} + \text{H} \quad (6.24a) \\
& \rightarrow \text{OH} + \text{H}_2 \quad (6.24b) \\
& \rightarrow \text{OH} + \text{H} + \text{H} \quad (6.24c) \\
& \rightarrow \text{O} + \text{H}_2 + \text{H} \quad (6.24d)
\end{align*}
\]
This point is of some relevance to acrylonitrile formation, if the reaction of \( \text{C}_3\text{H}_3\text{N}^+ \) with \( \text{H}_2 \) is prohibitively slow under interstellar conditions (as suggested by the room temperature measurements reported here). Charge transfer processes, for example involving \( \text{NH}_3 \) (see table 6.1), could well represent a significant source of interstellar \( \text{CH}_2\text{CHCN} \), though this would naturally depend on the abundance of the \( \text{C}_3\text{H}_3\text{N}^+ \) ion. Reactions producing \( \text{C}_3\text{H}_3\text{N}^+ \), which may be of interstellar significance and which do not require \( \text{CH}_2\text{CHCN} \) as a precursor, are the association of \( \text{C}_2\text{H}_2^+ \) with \( \text{HCN} \) and the reaction of \( \text{C}_3\text{H}^+ \) with \( \text{NH}_3 \) \(^{329-331}\):

\[
\begin{align*}
\text{C}_2\text{H}_2^+ + \text{HCN} &\rightarrow \text{CH}_2\text{N}^+ + \text{C}_2\text{H}^+ & [0.05] \quad (6.25a) \\
&\rightarrow \text{C}_3\text{H}_2\text{N}^+ + \text{H}^+ & [0.15] \quad (6.25b) \\
&\rightarrow \text{C}_3\text{H}_3\text{N}^+ & [0.80] \quad (6.25c)
\end{align*}
\]

\[k_{6.25} = 3.7 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]

\[
\begin{align*}
\text{C}_3\text{H}^+ + \text{NH}_3 &\rightarrow \text{NH}_3^+ + \text{C}_3\text{H}^+ & [0.25] \quad (6.26a) \\
&\rightarrow \text{NH}_4^+ + \text{C}_3 & [0.40] \quad (6.26b) \\
&\rightarrow \text{CH}_2\text{N}^+ + \text{C}_2\text{H}_2 & [0.20] \quad (6.26c) \\
&\rightarrow \text{C}_3\text{H}_3\text{N}^+ + \text{H}^+ & [0.15] \quad (6.26d)
\end{align*}
\]

\[k_{6.26} = 1.7 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\].

These and other processes (such as radiative association of \( \text{CH}_2\text{N}^+ \) and \( \text{C}_2\text{H}^- \)) can be considered likely sources of interstellar \( \text{C}_3\text{H}_3\text{N}^+ \).

To some extent, the arguments detailed above are of secondary importance in resolving Turner's discrepancy. Very recently, Herbst and Leung\(^{42}\) have
considered the reactions of CN· radicals with unsaturated hydrocarbons in the context of interstellar synthesis. These reactions are known to occur rapidly at room temperature\(^{348}\) and are thought to lack activation energy barriers, so they should also occur rapidly under interstellar conditions. If this is so, then this accounts for the apparent discrepancy in HC\(_n\)N/HC\(_n\)NH\(^+\) ratios, since HC\(_3\)NH\(^+\) is not necessarily the major source of HC\(_3\)N if the reaction

\[
\text{CN·} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H}· \tag{6.27}
\]

proceeds at a significant rate within cold clouds. Similarly, the reaction

\[
\text{CN·} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{CHCN} + \text{H}· \tag{6.28}
\]

\[k_{6.28} = 2.1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} (\text{@ } 300 \text{ K})\]

could well represent the dominant source of acrylonitrile if this reaction proceeds efficiently, and if acrylonitrile represents a significant product channel: products for this reaction have yet to be determined.\(^{42}\)

Another possible source of organic nitriles is from reaction of hydrocarbon radicals with HCN

\[
\text{C}_2\text{H}· + \text{HCN} \rightarrow \text{HC}_3\text{N} + \text{H}· \tag{6.29}
\]

\[k_{6.29} = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} (\text{@ } 300 \text{ K})\]

\[
\text{C}_2\text{H}_3· + \text{HCN} \rightarrow \text{CH}_2\text{CHCN} + \text{H}· \tag{6.30}
\]

\[\Delta H_{6.30} = 1.6 \pm 15 \text{ kJ mol}^{-1},\]
although it appears from the low rate observed for reaction (6.29) that this reaction is inhibited by a sizeable activation barrier. Nevertheless, reaction (6.29) has been considered as a significant source of HC$_3$N within shocked clouds and circumstellar shells. Reaction (6.30), which has not yet been studied experimentally, is of doubtful significance in acrylonitrile synthesis: even if this reaction lacks an activation barrier, it may well be endothermic.

It is of interest to note also that Brown et al (1990) have very recently proposed a greater importance for reactions of the type

$$
C_nH_2 + N^- \rightarrow HC_nN + H^-
$$

(6.31)

in the synthesis of cyanopolyynes, if hot-ion hydrogen atom abstraction reactions between C$_n$H$_2^+$ and H$_2$ are considered. Brown et al. argue that hot-ion reactions can produce greater abundances of C$_n$H$_3^+$ ions than most ion-molecule models normally consider, resulting in higher abundances of C$_n$H$_2$ hydrocarbons from dissociative recombination of C$_n$H$_3^+$. These authors have commented that reactions such as (6.31) can help account for observed cyanopolyyne abundances, and the production of cyanopolyynes in this fashion (since HC$_n$NH$^+$ is not involved as a precursor) can also be invoked to explain Turner's observational discrepancy regarding HC$_n$NH$^+/HC_nN$ abundances. Note that reactions of the type (6.31) are unlikely to influence the acrylonitrile abundance, since production of acrylonitrile in an analogous fashion would require the reactions

$$
\text{CH}_3\text{CCH} + N^- \rightarrow \text{CH}_2\text{CHCN} + H^-
$$

(6.32)

$\Delta H_{6.32} = -257 \text{ kJ mol}^{-1}$
and/or

\[ \text{CH}_2\text{CCH}_2 + \text{N}^- \rightarrow \text{CH}_2\text{CHCN} + \text{H}^- \]  
\( \Delta H_{6.33} = -261 \text{ kJ mol}^{-1} \).

An increase in the interstellar abundance of C\(_3\)H\(_4\) owing to hot-ion reactions, in the manner described by Brown et al, requires the successive occurrence of three endothermic or barrier-inhibited reactions:

\[ \text{C}_3\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{H}^- \]  
\( \Delta H_{6.34} \approx 0 \text{ kJ mol}^{-1} \)

\[ \text{C}_3\text{H}_3^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_4^+ + \text{H}^- \]  
\( \Delta H_{6.35} = 165 \text{ kJ mol}^{-1} \)

\[ \text{C}_3\text{H}_4^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}^- \]  
\( \Delta H_{6.36} = 38 \text{ kJ mol}^{-1} \).

These endothermicities relate to formation and reaction of the lowest-energy linear isomer of C\(_3\)H\(_n^+\). The insurmountable endothermicities of the latter two reactions indicate that hot-ion reactions cannot directly affect the C\(_3\)H\(_4\) abundance, and thus these reactions cannot directly affect the acrylonitrile abundance either.
CHAPTER 7.

REACTIONS OF $\text{H}_n\text{C}_3\text{O}^+$ AND THE ION-MOLECULE CHEMISTRY OF $\text{C}_3\text{O}_2$.

Section 7.1: Introduction.

Tricarbon monoxide (\(\text{C}=\text{C}=\text{C}=\text{O}\)) and propynal are among the largest oxygen-containing molecules to have yet been detected within interstellar clouds. $\text{C}_3\text{O}$, whose microwave spectrum was observed in the laboratory by Brown et al.,\textsuperscript{349} was subsequently detected in TMC-1 in 1984.\textsuperscript{350,351} Propynal was also first detected in this source.\textsuperscript{352} The presence of these molecules in such a cold, quiescent environment implies a gas-phase process for their production, in the absence of effective grain-surface processing.

For $\text{C}_3\text{O}$, Matthews et al.\textsuperscript{350} proposed the reaction

\[
\text{C}_3\text{H}_2^+ + \text{O} \rightarrow \text{C}_3\text{HO}^+ + \text{H}^-
\]  

(7.1)

followed by dissociative recombination

\[
\text{C}_3\text{HO}^+ + e^{-} \rightarrow \text{C}_3\text{O} + \text{H}^-
\]  

(7.2),
with the main loss mechanisms being charge transfer and proton transfer from reactions with positive ions. Brown et al\textsuperscript{351} suggested

\begin{equation}
C_4 + O \rightarrow C_3O + C \tag{7.3}
\end{equation}

and the sequence

\begin{align*}
C_3O^+ + H_2 &\rightarrow C_3HO^+ + H^+ \tag{7.4} \\
C_3HO^+ + H_2 &\rightarrow C_3H_2O^+ + H^+ \tag{7.5} \\
C_3H_2O^+ + H_2 &\rightarrow C_3H_3O^+ + H^+ \tag{7.6} \\
C_3H_3O^+ + e &\rightarrow C_3O + H_2 + H^+ \tag{7.7}.
\end{align*}

Herbst et al\textsuperscript{353} have suggested that the radiative association processes

\begin{align*}
C_2H_2^+ + CO &\rightarrow C_3H_2O^+ + hv \tag{7.8} \\
C_2H_3^+ + CO &\rightarrow C_3H_3O^+ + hv \tag{7.9}
\end{align*}

are the major sources of C\textsubscript{3}O: these reactions have been estimated\textsuperscript{354} to occur with effective bimolecular rate coefficients of $k_{7.8} \sim 10^{-12}$ cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1} and $k_{7.9} \sim 10^{-11}$ cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1} at 10 K, upon the basis of their observed rates for termolecular association.\textsuperscript{141} Herbst et al\textsuperscript{353} note also that reactions of C\textsubscript{3}H\textsuperscript{+} with oxygen-containing neutrals also yield C\textsubscript{3}HO\textsuperscript{+} as products,\textsuperscript{329-331,355} but consider such reactions as being less important due to the presumed rapid depletion\textsuperscript{356} of C\textsubscript{3}H\textsuperscript{+} by reaction with H\textsubscript{2} at interstellar temperatures. A contribution to the interstellar C\textsubscript{3}O abundance has also been suggested from the reaction sequence
The radiative association reaction (7.10) is presumed to be fast as the analogous termolecular association is also fast \((k_{7.10} = 2 \times 10^{-26} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}, @ 80 \text{ K})\)\(^{353}\) the product distribution of the dissociative recombination (7.11) is unknown. Formation of \(\text{C}_3\text{O}\) by reaction (7.11) is disfavoured as a major product channel according to the dissociative recombination theories of Herbst\(^{69}\) and Green and Herbst\(^{83}\) who consider that breaking of a multiple bond is unlikely to compete with single-bond cleavage. Bates, however, considers that breakage of a multiple bond can occur during dissociative recombination\(^{82}\). The feasibility of reaction (7.11) as a source of interstellar \(\text{C}_3\text{O}\) cannot be assessed until considerably more is known of the product distributions of dissociative recombination reactions.

Reactions (7.8) and (7.9) have also been considered by Nejad and Millar\(^{100}\) in the chemistry of the circumstellar shell of IRC+10216 as a source of \(\text{C}_3\text{O}\) in this object, although a detection of circumstellar \(\text{C}_3\text{O}\) has yet to be reported.

Three \(\text{C}_3\text{H}_2\text{O}\) isomers, propynal (\(\text{HC}≡\text{C}-\text{CHO}\)), propadienone (\(\text{H}_2\text{C}=\text{C}=\text{C}=\text{O}\)) and cyclopropenone have been proposed as potential interstellar molecules. To date, only propynal has been detected within interstellar clouds.

Propynal is though to be formed principally by the dissociative recombination of \(\text{C}_3\text{H}_3\text{O}^+\)\(^{352,357}\) although the product distribution for this reaction is not known. Most theories of dissociative recombination favour cleavage of one bond only,
indicating a bias towards \( \text{C}_3\text{H}_2\text{O} \) formation. Irvine et al\(^{352} \) have searched TMC-1 unsuccessfully for propadienone (\( \text{H}_2\text{C}≡\text{C}=\text{C}=\text{O} \)), and argue that the apparent absence of this molecule indicates that it is not formed by dissociative recombination of \( \text{C}_3\text{H}_3\text{O}^+ \). Adams et al\(^{357} \) support this proposal, suggesting that propadienone is not formed because interstellar \( \text{C}_3\text{H}_3\text{O}^+ \) does not have two hydrogens on the terminal carbon atom. This suggestion seems at variance with the theoretical and experimental findings of Holmes et al\(^{358} \) who determined the lowest-energy isomer of \( \text{C}_3\text{H}_3\text{O}^+ \) to be protonated propadienone, \([\text{H}_2\text{C}=\text{CH}=\text{C}=\text{O}]^+\) with other isomers having a calculated heat of formation at least 100 \( \text{kJ mol}^{-1} \) greater than this form. Furthermore, this lowest-energy isomer would appear to be the predominant product of reaction (7.9), which is the principal source of \( \text{C}_3\text{H}_3\text{O}^+ \) within models of cloud chemistry. Guillemin et al\(^{359} \) propose that the isomer cyclopropenone may also be detectable within clouds, following an earlier unsuccessful search for this species\(^{360} \) the three isomers propynal, cyclopropenone and propadienone have similar heats of formation, so production of all three isomers within clouds should be at least energetically feasible.

Adams et al\(^{357} \) have also considered the formation of larger analogues of \( \text{C}_n\text{O} \) and \( \text{C}_n\text{H}_2\text{O} \) in interstellar clouds, by virtue of the general class of radiative association reactions

\[
\text{C}_{n-1}\text{H}_m^+ + \text{CO} \rightarrow \text{C}_n\text{H}_m\text{O}^+ + \text{hv}
\]  

(7.12)

followed by dissociative recombination. The termolecular association processes related to reaction (7.12) have been studied by Giles et al\(^{226} \) and mostly proceed
rapidly for \( m \leq 2 \): hydrocarbon ions having \( n > 1 \) and \( m = 2 \) or \( 3 \) are considered to be relatively abundant in interstellar clouds, by virtue of their unreactivity with \( \text{H}_2 \). These considerations suggest that \( \text{C}_n\text{O} \) and \( \text{C}_n\text{H}_2\text{O} \) may form an abundant class of interstellar molecules: Adams et al\(^{357} \) propose that \( \text{C}_4\text{O}, \text{C}_5\text{O}, \text{C}_6\text{O} \) and \( \text{C}_7\text{O} \) should be observable in TMC-1, once their microwave spectra have been determined. To this end, Brown et al\(^{361} \) and DeFrees and McLean\(^{362} \) have recently calculated the rotational constants of \( \text{C}_5\text{O} \); Ewing\(^{363} \) has calculated the structures of \( \text{C}_4\text{O} \) and \( \text{C}_6\text{O} \), finding that even-\( n \) \( \text{C}_n\text{O} \) species (over the short series from \( n = 3 \) to 6) are substantially less stable against fragmentation to products than are odd-\( n \) \( \text{C}_n\text{O} \). This suggests that \( \text{C}_5\text{O} \) is a more likely candidate for interstellar detection than \( \text{C}_4\text{O} \) and \( \text{C}_6\text{O} \).

The present chapter reports some results for reactions of the "\( \text{C}_3\text{O} \) precursor" ions \( \text{C}_3\text{H}_1\text{O}^+ \) with prominent interstellar molecules, as well as some reactions of the ions \( \text{C}_3\text{O}^+ \) and \( \text{C}_3\text{O}_2^+ \). The interstellar implications of these results are discussed.

**Section 7.2:** The ion-molecule chemistry of \( \text{H}_n\text{C}_3\text{O}^+ \) (\( n = 1 \) to 3).

\( \text{C}_3\text{HO}^+ \) and \( \text{C}_3\text{H}_2\text{O}^+ \) were generated in the ion source by electron bombardment upon fumaroyl dichloride, (1).

![Fumaroyl dichloride](1)
$\text{C}_3\text{H}_5\text{O}^+$ was produced by electron bombardment upon acrylic anhydride, (2).

\[
\begin{array}{c}
\text{H}_2\text{C}=\text{C} \quad \text{O} \\
\text{C}=\text{O} \\
\text{H}_2\text{C}=\text{C} \quad \text{H}
\end{array}
\] (2).

The mass spectra obtained when injecting at m/z 53, 54 and 55 for these three ions are tabulated in table 7.1. As can be seen from this table, the attainable signal for $\text{C}_3\text{H}_5\text{O}^+$ was much larger than for $\text{C}_3\text{HO}^+$ and $\text{C}_3\text{H}_2\text{O}^+$, most probably because only one bond of (2) needs to be broken to produce $\text{C}_3\text{H}_5\text{O}^+$; production of the other ions from (1) requires the breakage of two or three bonds and is hence less probable. None of the ions could be injected without contamination. $\text{C}_3\text{HO}^+$ could not be injected without contamination by sizeable signals at m/z 52 and / or m/z 54. $\text{C}_3\text{H}_2\text{O}^+$ and $\text{C}_3\text{H}_3\text{O}^+$ could be injected with only minor contamination from neighbouring ion masses, but contamination from $\text{C}_2\text{H}_n^+$ arising from the breakup process

\[
\text{C}_3\text{H}_n\text{O}^+ \rightarrow \text{C}_2\text{H}_n^+ + \text{CO} \quad (7.13)
\]

$\Delta H_{7.13} = +611 \text{ kJ mol}^{-1} \ (n=1)$

$\Delta H_{7.13} = +242 \text{ kJ mol}^{-1} \ (n=2)$

$\Delta H_{7.13} = +250 \text{ kJ mol}^{-1} \ (n=3)$

accounted for a significant fraction of the total reactant ion signal. In some instances, products initially attributed to reactions of $\text{C}_3\text{H}_n\text{O}^+$ were later discovered to arise from these breakup ions. The lack of breakup of $\text{C}_3\text{HO}^+$ can
Table 7.1: Mass spectra obtained under optimal conditions for injecting the ions C\(_3\)H\(_4\)O\(^+\) (n = 1 → 3).

<table>
<thead>
<tr>
<th>m/z</th>
<th>I/I_{max} (^a)</th>
<th>Ion formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.4</td>
<td>C(_2^+)</td>
</tr>
<tr>
<td>25</td>
<td>0.8</td>
<td>C(_2)H(^+)</td>
</tr>
<tr>
<td>26</td>
<td>3.9</td>
<td>C(_2)H(_2^+)</td>
</tr>
<tr>
<td>27</td>
<td>&lt;0.1</td>
<td>-</td>
</tr>
<tr>
<td>46</td>
<td>&lt;0.1</td>
<td>-</td>
</tr>
<tr>
<td>47</td>
<td>0.3</td>
<td>C(<em>3)S(</em>\text{Cl}^+)</td>
</tr>
<tr>
<td>48</td>
<td>2.5</td>
<td>C(_4^+)</td>
</tr>
<tr>
<td>49</td>
<td>5.6</td>
<td>C(<em>3)S(</em>\text{Cl}^+); C(_4H^+)</td>
</tr>
<tr>
<td>50</td>
<td>2.2</td>
<td>C(_4)H(_2^+)</td>
</tr>
<tr>
<td>51</td>
<td>2.1</td>
<td>O(<em>3)S(</em>\text{Cl}^+) ?</td>
</tr>
<tr>
<td>52</td>
<td>23.0</td>
<td>C(_5^+)</td>
</tr>
<tr>
<td>53</td>
<td>100</td>
<td>C(_3)HO(^+)</td>
</tr>
<tr>
<td>54</td>
<td>7.7</td>
<td>C(_3)H(_2)O(^+); 12C(_2)(_3)CHO(^+)</td>
</tr>
<tr>
<td>55</td>
<td>&lt;0.1</td>
<td>-</td>
</tr>
<tr>
<td>ii.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1.5</td>
<td>C(_2)H(^+)</td>
</tr>
<tr>
<td>26</td>
<td>23.2</td>
<td>C(_2)H(_2^+)</td>
</tr>
<tr>
<td>27</td>
<td>1.1</td>
<td>C(_2)H(_3^+); 12C(_3)(_3)CH(_2^+)</td>
</tr>
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<td>28</td>
<td>0.4</td>
<td>CO(^+)</td>
</tr>
<tr>
<td>52</td>
<td>&lt;0.1</td>
<td>-</td>
</tr>
<tr>
<td>53</td>
<td>4.5</td>
<td>C(_3)HO(^+)</td>
</tr>
<tr>
<td>54</td>
<td>100</td>
<td>C(_3)H(_2)O(^+)</td>
</tr>
<tr>
<td>55</td>
<td>12.0</td>
<td>C(_3)H(_3)O(^+); 12C(_2)(_3)CH(_2)O(^+)</td>
</tr>
<tr>
<td>56</td>
<td>3.0</td>
<td>C(_2)O(_2^+) ?</td>
</tr>
<tr>
<td>57</td>
<td>&lt;0.1</td>
<td>-</td>
</tr>
<tr>
<td>iii.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.1</td>
<td>C(_2)H(^+)</td>
</tr>
<tr>
<td>26</td>
<td>&lt;0.1</td>
<td>-</td>
</tr>
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<td>27</td>
<td>5.0</td>
<td>C(_2)H(_3^+)</td>
</tr>
<tr>
<td>28</td>
<td>0.1</td>
<td>12C(_3)(_3)CH(_3^+); CO(^+)</td>
</tr>
<tr>
<td>53</td>
<td>2.5</td>
<td>C(_3)HO(^+)</td>
</tr>
<tr>
<td>54</td>
<td>0.4</td>
<td>C(_3)H(_2)O(^+)</td>
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<td>55</td>
<td>100</td>
<td>C(_3)H(_2)O(^+)</td>
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<tr>
<td>56</td>
<td>2.9</td>
<td>12C(_2)(_3)CH(_2)O(^+)</td>
</tr>
</tbody>
</table>

Notes

a. Ion signal, expressed as a percentage of the maximum peak height, using the mean value from 3 ten-second counts.

b. Derived by electron bombardment (50V electron energy) upon fumaroyl dichloride.

c. m/z 53 (71.2 counts per second) accounts for 66.8% of the total reactant ion signal. This spectrum was obtained with a setting of m/z 50.5 on the upstream QMS.

d. m/z 54 (77.8 counts per second) accounts for 68.6% of the total reactant ion signal. This spectrum was obtained using a setting of m/z 56.6 on the upstream QMS.

e. Derived by electron bombardment (30V electron energy) upon acrylic anhydride.

f. m/z 55 (2389.0 counts per second) accounts for 90.1% of the total reactant ion signal. This spectrum was obtained using a setting of m/z 56.2 on the upstream QMS.
be easily understood in terms of the much higher amounts of kinetic energy to drive reaction (7.13) in this case. Examination of the mass spectrum for C$_3$H$_3$O$^+$ also suggests that C$_3$HO$^+$ in this spectrum arises principally from the breakup process

$$ \text{C}_3\text{H}_3\text{O}^+ \rightarrow \text{C}_3\text{H}_2^+ + \text{H}_2 $$

(7.14)

$$ \Delta H_{7,14} = +220 \text{ kJ mol}^{-1} $$

rather than from insufficient mass resolution, since the signal at the intermediate mass (m/z 54) is very much smaller.

The ions C$_3$HO$^+$, C$_3$H$_2$O$^+$ and C$_3$H$_3$O$^+$ generated by the above techniques are all assumed to exist as the lowest-energy isomers listed in the tabulation of Lias et al.$^{184}$ The heats of formation of C$_3$H$_n$O$^+$ isomers, and related species, are detailed in table 7.2.

Only one form of C$_3$HO$^+$, HCCCO$^+$, has been reported to date: the equivalence of this ion with C$_3$HO$^+$ generated from fumaroyl dichloride can be reasonably assumed given the lack of rearrangement required to produce HCCCO$^+$ from the parent compound.

Several structures of C$_3$H$_2$O$^+$ have been reported$^{367-369}$ and proposed$^{368}$ of those for which the appearance potentials have been experimentally determined, the isomer H$_2$C=C=C=O$^+$ (corresponding to ionized propadienone) has substantially the lowest heat of formation. This isomer can be formed by a 1,2 hydrogen shift during electron-impact ionization of fumaroyl dichloride. Schaefer$^{292}$ has noted
Table 7.2: Thermochemistry of \( \text{C}_3\text{H}_n\text{O}^+ \) (\( n = 0 \rightarrow 3 \)) and \( \text{C}_3\text{O}_2^+ \), and related neutrals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H_f ) a</th>
<th>Method b</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}=\text{C}=\text{C}=\text{O}^+ )</td>
<td>( &gt;1252 )</td>
<td>R</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>1393</td>
<td>MO</td>
<td>364</td>
</tr>
<tr>
<td>( \text{C}=\text{C}=\text{C}=\text{O} )</td>
<td>282</td>
<td>MO</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td>326</td>
<td>PA</td>
<td>366</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>MO</td>
<td>363</td>
</tr>
<tr>
<td>( \text{HC}=\text{C}-\text{C}=\text{O}^+ )</td>
<td>971</td>
<td>AP</td>
<td>367</td>
</tr>
<tr>
<td>( \text{HC}=\text{C}=\text{C}=\text{O}^- )</td>
<td>(&lt;299 )</td>
<td>R</td>
<td>c</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{C}=\text{C}=\text{O}^+ )</td>
<td>975</td>
<td>IP</td>
<td>367</td>
</tr>
<tr>
<td>( \text{HC}=\text{CH}^-\text{CO}^+ )</td>
<td>996</td>
<td>MO (^d)</td>
<td>368</td>
</tr>
<tr>
<td>( \text{HC}=\text{CH}^-\text{C}=\text{O}^+ )</td>
<td>1052</td>
<td>IP</td>
<td>367</td>
</tr>
<tr>
<td></td>
<td>1089</td>
<td>MO (^d)</td>
<td>368</td>
</tr>
<tr>
<td>( \text{HC}=\text{C}^-\text{C}=\text{OH}^+ )</td>
<td>1120</td>
<td>MO (^d)</td>
<td>368</td>
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<tr>
<td>( \text{HC}=\text{C}=\text{CHO}^+ )</td>
<td>1157</td>
<td>IP</td>
<td>369</td>
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<tr>
<td></td>
<td>1216</td>
<td>MO (^d)</td>
<td>368</td>
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<tr>
<td>( \text{H}_2\text{C}=\text{C}=\text{C}=\text{O} )</td>
<td>95</td>
<td>EST</td>
<td>184</td>
</tr>
<tr>
<td>( \text{HC}=\text{C}=\text{CHO} )</td>
<td>115</td>
<td>EST</td>
<td>184</td>
</tr>
<tr>
<td>( \text{HC}=\text{CH}^-\text{C}=\text{O} )</td>
<td>138±8</td>
<td>EST</td>
<td>184</td>
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<tr>
<td>( \text{HC}=\text{CH}^-\text{CO} )</td>
<td>251</td>
<td>MO (^e)</td>
<td>368</td>
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<tr>
<td>( \text{H}_2\text{C}=\text{CH}^-\text{CO}^+ )</td>
<td>749</td>
<td>MNDO</td>
<td>358</td>
</tr>
<tr>
<td></td>
<td>751</td>
<td>AP</td>
<td>370</td>
</tr>
<tr>
<td>( \text{HC}=\text{C}=\text{CH}=\text{OH}^+ )</td>
<td>833</td>
<td>EST</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>MNDO (^f)</td>
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</tr>
<tr>
<td>( \text{HC}=\text{CH}^-\text{C}=\text{OH}^+ )</td>
<td>858</td>
<td>EST</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>866</td>
<td>MNDO (^f)</td>
<td>358</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{C}=\text{COH}^+ )</td>
<td>882</td>
<td>EST</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>977</td>
<td>MNDO (^f)</td>
<td>358</td>
</tr>
<tr>
<td>( \text{HC}=\text{C}=\text{CH}_2\text{O}^+ )</td>
<td>950</td>
<td>AP</td>
<td>371</td>
</tr>
<tr>
<td>( \text{O}=\text{C}=\text{C}=\text{O}^+ )</td>
<td>832</td>
<td>MNDO</td>
<td>364</td>
</tr>
<tr>
<td></td>
<td>929</td>
<td>IP</td>
<td>372,373</td>
</tr>
<tr>
<td>( \text{O}=\text{C}=\text{C}=\text{O} )</td>
<td>-94±2</td>
<td></td>
<td>374</td>
</tr>
</tbody>
</table>
that such 1,2 shifts are facile in energised species such as ions produced by bombardment of high-energy electrons: an example of such a 1,2 shift is in the isomerisation of HCN$^+$ to HNC$^+$ (see chapter 5). Bouchoux et al$^{368}$ have proposed that the ion HC=CH–CO$^+$ is also a stable isomer of C$_3$H$_2$O$^+$, with a heat of formation only 21 kJ mol$^{-1}$ higher than $\Delta H_f$(H$_2$CCCO$^+$) according to ab initio calculations. The HCCHCO$^+$ ion can be formed without rearrangement from fumaroyl dichloride, and so it is also a likely component of the m/z 54 ion signal: the ratio of these two isomeric forms will depend upon their actual relative energies as well as on the height of the isomerisation barrier (as has been discussed at length for the case of C$_2$N$^+$ isomerisation, in chapter 4). In our studies of C$_3$HO$^+$ and of C$_3$H$_2$O$^+$ reactivity, no evidence was found for the existence of more than one isomer of each ion mass in the flow tube.

The lowest energy isomer of C$_3$H$_3$O$^+$, H$_2$C=CH–CO$^+$, can be generated without rearrangement by cleavage of the H$_2$CCHC(O)–OC(O)CHCH$_2$ bond in acrylic anhydride. For this reason, and since $\Delta H_f$(H$_2$CCHCO$^+$) is 199 kJ mol$^{-1}$ lower in energy than the next lowest-energy isomer, the contribution from higher-energy isomeric forms in the m/z 55 ion signal is expected to be minimal.
The reactions of $C_3H_nO^+$ with various neutrals are summarised in tables 7.3, 7.4 and 7.5. It is immediately apparent from these tables that all of these ions are remarkably unreactive.

$C_3HO^+$ was seen to react only with NH$_3$, HCN and CH$_3$CCH. Adduct formation was a significant channel in the reaction with NH$_3$ and the sole product in the (very slow) reaction with HCN.

### Table 7.3: Reactions of $C_3HO^+$ + $X$.

<table>
<thead>
<tr>
<th>$X$</th>
<th>Products *</th>
<th>$k_{obs}$ b</th>
<th>$k_c$ c</th>
<th>$-\Delta H$ d</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>no reaction</td>
<td>$&lt;0.0005$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CO</td>
<td>no reaction</td>
<td>$&lt;0.001$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>N$_2$</td>
<td>no reaction</td>
<td>$&lt;0.001$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>O$_2$</td>
<td>no reaction</td>
<td>$&lt;0.001$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>no reaction</td>
<td>$&lt;0.001$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>CH$_3$CO$^+$ + HCN</td>
<td>[0.55]</td>
<td>0.21</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>$C_3HO.NH_3^+$</td>
<td>[0.45]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>no reaction</td>
<td>$&lt;0.01$</td>
<td>2.4</td>
<td>–</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>no reaction</td>
<td>$&lt;0.001$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HCN</td>
<td>$C_3HO.HCN^+$</td>
<td>0.004</td>
<td>3.28</td>
<td>–</td>
</tr>
<tr>
<td>CH$_3$CCH</td>
<td>$C_5H_5^+ + CO$ (or $C_4HO^+ + C_2H_2$)</td>
<td>0.92</td>
<td>1.40</td>
<td>– f</td>
</tr>
</tbody>
</table>

**Notes**

a. Product channels reported in brackets, where more than one product was detected.
b. Observed rate coefficient, in units of $10^{-9}$ cm$^3$ molec$^{-1}$ s$^{-1}$.
c. Calculated ADO collision rate coefficient, using the theory of Su and Chesnavich,172
d. Reaction exothermicity in units of kJ mol$^{-1}$. Taken from the tabulation of Lias et al,184 unless otherwise stated.
e. Production of CH$_2$CO$^+$ is endothermic by 13 kJ mol$^{-1}$.
f. Formation of several $C_5H_5^+$ isomers is energetically possible.
g. This product channel requires $\Delta H_f(C_4HO^+) < 1105$ kJ mol$^{-1}$. 
The occurrence of a significant product signal at m/z 18 in the reaction with NH$_3$ was initially attributed to proton transfer from C$_3$HO$^+$, in disagreement with Botschwina's$^{366}$ calculation of PA(C$_3$O) which indicates that such a proton

Table 7.4: Reactions of C$_3$H$_2$O$^+$ + X.

<table>
<thead>
<tr>
<th>X</th>
<th>Products $^a$</th>
<th>$k_{obs}^a$</th>
<th>$k_e^a$</th>
<th>$-\Delta H^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>no reaction</td>
<td>&lt;0.0005</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N$_2$</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O$_2$</td>
<td>CHO$^+$ + C$_2$HO$_2$; C$_2$H$_2$O$^+$ + CO$_2$</td>
<td>[0.60]</td>
<td>0.036</td>
<td>0.66</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NH$_4^+$ + C$_3$HO$^-$</td>
<td>1.3</td>
<td>2.19</td>
<td>$^{d}$ -</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>no reaction</td>
<td>&lt;0.01</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>HCN</td>
<td>C$_3$H$_2$O.HCN$^+$</td>
<td>0.19</td>
<td>3.27</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>C$_3$O$^+$ + 2H$_2$; C$_3$HO$^+$ + H$_2$ + H; C$_2$H$_2$O$^+$ + H$_2$</td>
<td>[0.28]</td>
<td>0.43</td>
<td>1.02</td>
</tr>
<tr>
<td>C$_3$C$_2$H</td>
<td>C$_3$H$_4^+$ + CO; (or C$_3$H$_2$O$^+$ + C$_2$H$_4$); C$_2$H$_2$O$^+$ + CH$_4$; C$_3$H$_2$O.CH$_3$C$_2$H$^+$</td>
<td>[0.32]</td>
<td>1.2</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Notes:

a. See footnotes (a) - (d) for table 7.3.

b. The observation of this channel requires $\Delta H(C_2H_2O) < 149$ kJ mol$^{-1}$ for production of HCO$^+$ + C$_2$HO$_2$. Alternatively, $-\Delta H = 215$ kJ mol$^{-1}$ for production of HCO$^+$ + HCO$^+$ + CO.

c. Calculated for production of H$_2$CCO$^+$. $-\Delta H = 336$ kJ mol$^{-1}$ for production of HCCOH$^+$ + CO$_2$.

d. Proton-transfer in this instance is only exothermic if $\Delta H(C_3H_2O) < 299$ kJ mol$^{-1}$.

e. Requires $\Delta H(C_3O^+) < 1203$ kJ mol$^{-1}$.

f. Requires $\Delta H(C_2H_2O^+) < 985$ kJ mol$^{-1}$.

g. Requires $\Delta H(C_2H_2O^+) < 1203$ kJ mol$^{-1}$.

h. Calculated for ionized cyclopentadiene, c-C$_3$H$_4^+$, but production of several other C$_3$H$_6^+$ species is exothermic also.

i. Requires $\Delta H(C_3H_2O^+) < 1109$ kJ mol$^{-1}$.

j. Calculated using $\Delta H(C_3H_2O^+) < 1203$ kJ mol$^{-1}$. 
transfer reaction is endothermic by approximately 30 kJ mol⁻¹. Subsequently, this reaction was re-examined to reveal that the signal at m/z 18 arose, at low flows, via a side reaction involving a contaminant ion at m/z 52 (C₃O⁺) or 54 (C₃H₂O⁺). NH₄⁺ also dominated the product distribution at high flows, indicating that C₃HO⁺ was responsible for its formation via a secondary reaction: the most likely explanation is that CH₃CO⁺ undergoes rapid proton transfer to NH₃, and this accounts for the observed loss of CH₃CO⁺ with increasing flow of NH₃.

<table>
<thead>
<tr>
<th>Table 7.5: Reactions of C₃H₃O⁺ + X.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>H₂</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>N₂</td>
</tr>
<tr>
<td>O₂</td>
</tr>
<tr>
<td>CH₄</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td>C₂H₂</td>
</tr>
<tr>
<td>HCN</td>
</tr>
<tr>
<td>CH₃C₂H</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Notes
a. See footnotes (a) - (d) for table (7.3).
b. Requires ΔH₂(C₃H₃O⁺) < 1012 kJ mol⁻¹.
The absence of any apparent reaction between C\textsubscript{3}HO\textsuperscript{+} and H\textsubscript{2}, CO or N\textsubscript{2} indicates that C\textsubscript{3}HO\textsuperscript{+} is likely to be persistent within interstellar clouds: in particular, the lack of reaction with H\textsubscript{2} suggests that C\textsubscript{3}O cannot arise via the mechanism of Brown et al\textsuperscript{351} which supposes that stepwise H-atom abstraction in reactions (7.4)-(7.6) precedes dissociative recombination to C\textsubscript{3}O. The low upper limit, k\textsubscript{7.5} \leq 5.0 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}, suggests that C\textsubscript{3}HO\textsuperscript{+} is not involved in the production of C\textsubscript{3}H\textsubscript{2}O isomers within the interstellar environment. The radiative association process

\begin{equation}
\text{C}\textsubscript{3}\text{HO}\textsuperscript{+} + \text{H}_2 \rightarrow \text{C}\textsubscript{3}\text{H}_3\text{O}\textsuperscript{+} + \text{hv} \tag{7.15}
\end{equation}

is unlikely to be fast as the termolecular association channel is not observed for this reaction. Similarly, the absence of any apparent association between C\textsubscript{3}HO\textsuperscript{+} and CO indicates that the neutral species O=\text{C}=\text{C}=\text{C}=\text{C}=\text{O} (which might have been expected to result from from dissociative recombination following such an association process) cannot be formed in this manner. The absence of any visible reaction with H\textsubscript{2}O and C\textsubscript{2}H\textsubscript{2}, as well as the very slow rate coefficient observed for the reaction with HCN, underlines the lack of reactivity of the C\textsubscript{3}HO\textsuperscript{+} ion.

C\textsubscript{3}H\textsubscript{2}O\textsuperscript{+} is a somewhat more reactive species, although only the reactions with NH\textsubscript{3} and CH\textsubscript{3}CCH proceeded at more than half the collision rate. As with C\textsubscript{3}HO\textsuperscript{+}, the absence of reactivity with H\textsubscript{2}, CO and N\textsubscript{2} indicates that C\textsubscript{3}H\textsubscript{2}O\textsuperscript{+} will have a long lifetime within clouds: also, since C\textsubscript{3}H\textsubscript{2}O\textsuperscript{+} does not appear to react via H-atom abstraction, it is unlikely to play a significant part in C\textsubscript{3}H\textsubscript{2}O formation.
The reactions with acetylene and propyne indicate that such reactions between C$_3$H$_2$O$^+$ and interstellar alkynes may be significant in terms of the synthesis of larger species. These reactions clearly produce precursors to C$_5$O (although not, apparently, to C$_5$H$_2$O - unless C$_5$H$_2$O$^+$ reacts further with H$_2$); the product at m/z 66, from reaction with CH$_3$CCH, is uncertain. This ion is either C$_5$H$_6^+$ or C$_4$H$_2$O$^+$: several possible channels to C$_5$H$_6^+$ isomers are exothermic, while production of C$_4$H$_2$O$^+$ by an exothermic channel requires $\Delta H_f$(C$_4$H$_2$O$^+$) < 1109 kJ mol$^{-1}$ (which seems plausible). The ion at m/z 78 is identified as C$_5$H$_2$O$^+$ since formation of each known C$_6$H$_6^+$ isomer is endothermic (by $\geq$ 63 kJ mol$^{-1}$), and the possibility of some unknown C$_6$H$_6^+$ product having lower energy seems remote.

The occurrence of proton transfer to NH$_3$ establishes $\Delta H_f$(C$_3$HO·) < 299 kJ mol$^{-1}$: no other measurement of this quantity has been previously reported.

C$_3$H$_3$O$^+$ was observed to display very little reactivity with any of the neutrals (see table 7.5), indicating its probable persistence in interstellar clouds. Reaction occurred only with NH$_3$, HCN and CH$_3$CCH, did not exceed 5% of the collision rate in any of these cases, and involved adduct formation as the major (or only) product channel in these reactions. In the reaction with CH$_3$CCH, which was the only case in which a product channel other than adduct formation was evident, the 16% channel at m/z 79 was identified as formation of C$_5$H$_3$O$^+$ (ion structure not known) + CH$_4$ since all channels leading to formation of C$_6$H$_7^+$ + O are exothermic by $>166$ kJ mol$^{-1}$.\textsuperscript{184}

Although the C$_3$H$_n$O$^+$ ions are clearly sufficiently unreactive with the predominant interstellar neutrals for these ions to persist within cold clouds,
their significance with respect to C₃O and C₃H₂O production cannot be accurately determined since their dissociative recombination chemistry is not known. The possible consequences of dissociative recombination of the C₃HₙO⁺ ions, using a simple model allowing breakage of only one or two bonds of the parent ion without subsequent rearrangement, are summarised in table 7.6.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>-ΔH a</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–C=C=C=O⁺ + e</td>
<td>:C₃O + H⁺</td>
<td>427</td>
</tr>
<tr>
<td></td>
<td>C₂O + CH⁺</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>CO + C₂H⁺</td>
<td>517</td>
</tr>
<tr>
<td></td>
<td>O + C₃H⁺</td>
<td>c</td>
</tr>
<tr>
<td>H₂C=C=C=O⁺ + e</td>
<td>HC₃O⁺ + H⁺</td>
<td>&gt;458</td>
</tr>
<tr>
<td></td>
<td>:C₃O + H₂</td>
<td>649</td>
</tr>
<tr>
<td></td>
<td>C₂O + CH₂</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>CO + H₂C=C=CH</td>
<td>689 e</td>
</tr>
<tr>
<td></td>
<td>O + H₂C=C=CH</td>
<td>189 f</td>
</tr>
<tr>
<td>H₂C=CH–C=O⁺ + e</td>
<td>H₂C=CH–C=O + H⁺</td>
<td>438</td>
</tr>
<tr>
<td></td>
<td>HC₃O⁺ + H₂</td>
<td>&gt;452</td>
</tr>
<tr>
<td></td>
<td>:C₃O + H₂ + H⁺</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>HC₂O⁺ + CH₂</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td>C₂O + CH₂ + H⁺</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>CO + C₂H₃</td>
<td>596 h</td>
</tr>
<tr>
<td></td>
<td>O + C₃H₅</td>
<td>159</td>
</tr>
</tbody>
</table>

Notes
a. Exothermicity in kJ mol⁻¹.
b. Not known. The exothermicity of this channel requires ΔHₐ(C₂O) < 375 kJ mol⁻¹.
c. Not known. The exothermicity of this channel requires ΔHₐ(C₂H⁺) < 722 kJ mol⁻¹.
d. The exothermicity of this channel requires ΔHₐ(C₂O) < 585 kJ mol⁻¹.
e. Calculated using ΔHₐ(H₂CC) = 397 kJ mol⁻¹, from reference 375.
f. Calculated using ΔHₐ(H₂CCC) = 544 kJ mol⁻¹, from reference 376.
g. Unlikely. The exothermicity of this channel requires ΔHₐ(C₂O) < 143 kJ mol⁻¹.
h. -ΔH for formation of linear C₃H₅⁺.
C$_3$HO$^+$ cannot produce C$_3$H$_2$O, so all dissociative recombination channels not leading to C$_3$O are best regarded as destruction channels for tricarbon monoxide. The most exothermic channel is dissociation to the ethynyl radical and carbon monoxide: the enthalpy of reaction for other channels, apart from production of C$_3$O + H·, is not known and the other channels may well be endothermic. Since C$_3$HO$^+$ is so unreactive, it is likely that the interstellar chemistry of C$_3$O and C$_3$HO$^+$ is very tightly coupled. C$_3$O produces HC$_3$O$^+$ upon protonation (virtually all H-bearing ions should serve to protonate C$_3$O, given the high value of PA(C$_3$O) = 885 kJ mol$^{-1}$ calculated by Botschwina$^{366}$) and upon ionization:

\[
\begin{align*}
\text{C}_3\text{O} + \text{hv} & \rightarrow \text{C}_3\text{O}^+ + \text{H}_2 \quad (7.16) \\
\text{C}_3\text{O}^+ + \text{H}_2 & \rightarrow \text{C}_3\text{HO}^+ + \text{H}· \quad (7.17)
\end{align*}
\]

C$_3$HO$^+$ can arise through other reactions not involving C$_3$O, as has been discussed in section 7.1, but these reactions are not likely to be as significant in determining the C$_3$HO$^+$ abundance as will be protonation of C$_3$O. C$_3$HO$^+$, therefore, probably serves mainly to recycle C$_3$O rather than to produce it. Given the high dipole moment which Botschwina$^{366}$ has determined for this ion, the high PA(C$_3$O), and the probable long lifetime of C$_3$HO$^+$ within clouds, an interstellar search for protonated tricarbon monoxide appears justified.

C$_3$H$_2$O$^+$ can recombine to form HC$_3$O$^+$ and C$_3$O, but not C$_3$H$_2$O. (Radiative recombination processes have very low efficiencies.) As Herbst et al$^{353}$ have suggested, C$_3$H$_2$O$^+$ is likely to be a major ion precursor of C$_3$O by virtue of the efficient association reaction, (7.8), between C$_2$H$_2^+$ and CO.
C$_3$H$_3$O$^+$ can produce C$_3$O, HC$_3$O$^-$ and C$_3$H$_2$O upon recombination. A major channel competing with these possible products is likely to be CO + C$_2$H$_3^-$, which appears to be the most exothermic channel. Herbst et al$^{353}$ contend, on the basis of interstellar detection of propynal (HCCCHO) but not of propadienone (H$_2$CCCO), that propynal is a major product of this recombination process. A possible mechanism to account for the observation of propynal but not propadienone would require initial production of the biradical HC=CH–CO rather than the more stable H$_2$C=C=C=O, followed by a 1,2 hydrogen shift to yield propynal - though such a shift could, of course, also yield propadienone unless precluded by some energetic constraint. No information is available concerning the barriers to 1,2 hydrogen shifts in this system, although Kaneti et al$^{377}$ have determined that considerable barriers exist for another rearrangement of propynal:

\[
\text{HC}≡\text{C–CHO} \leftrightarrow :\text{C}≡\text{CH–CHO} \quad (7.18).
\]

An alternative hypothesis to explain the presence of propynal and the apparent absence of propadienone is that propynal is less reactive in the interstellar environment than is propadienone, the abundance of propadienone being maintained below the observational limit by, say, a rapid reaction with an abundant interstellar radical such as CN$^-$ or OH$^-$.

Further reactions of the C$_3$H$_n$O$^+$ ions (especially C$_3$H$_2$O$^+$, which appears the most reactive) with higher alkynes such as C$_4$H$_2$ and CH$_3$C$_4$H may represent a source of higher-order interstellar C$_n$O and C$_n$H$_2$O molecules, as indicated by the reactions
of these ions with CH₃CCH. A further investigation of C₃HₙO⁺ reactivity with hydrocarbons thus seems warranted.

Section 7.3: Ion-molecule chemistry of C₃O₂.

Electron impact upon carbon suboxide was used to generate the ions C₃O⁺ and C₃O₂⁺. The mass spectrum obtained by 50 V electron bombardment upon C₃O₂ is tabulated in table 7.7. Peaks due to CO₂⁺, CO⁺ and C⁺ are attributed (in part) to a large CO₂ impurity, which was not eliminated from the C₃O₂ sample prepared.

The heats of formation of C₃O and C₃O⁺ have not yet been determined experimentally. Brown and Rice³⁶⁵ have performed MP3/6-31G* calculations upon the stability of C₃O relative to dissociation to the fragments C₂ + CO: their calculations yield an estimate of ΔHf₀(C₃O) = 282 kJ mol⁻¹. Ewing³⁶³ has used MP4/DZP//HF/DZP calculations to determine C₃O's stability in a similar manner, calculating ΔHf(C₃O) = 390 kJ mol⁻¹. Botschwina³⁶⁶ has performed detailed ab initio calculations upon C₃O and HC₃O⁺: these calculations yield PA(C₃O) = 885 ± 5 kJ mol⁻¹. Terlouw et al³⁶⁷ have determined ΔH(HC₃O⁺) = 971 ± 5 kJ mol⁻¹ from the experimental appearance potential for this ion. These values permit calculation of ΔHf(C₃O) = 326 ± 10 kJ mol⁻¹, a value which lies between the other theoretical values. McElvany et al³⁶⁴ have performed MNDO calculations on the species Cₙ⁺, CₙH⁺, CₙH₂⁺, CₙO⁺ and CₙO₂⁺ for n = 3 → 9. Their calculated value for C₃O⁺ is ΔHf(C₃O⁺) = 1393 kJ mol⁻¹, with a substantial uncertainty: they calculate also ΔHf(C₃⁺) = 1979 kJ mol⁻¹ and ΔHf(C₃O₂⁺) =
832 kJ mol\(^{-1}\), which differ appreciably from the experimental literature values of \(\Delta H_f(C_3^+) = 2004\) kJ mol\(^{-1}\) and \(\Delta H_f(C_3O_2^+) = 929\) kJ mol\(^{-1}\).

Table 7.7: Mass spectrum obtained by electron impact ionisation (50V electron energy) of \(C_3O_2\).

<table>
<thead>
<tr>
<th>m/z</th>
<th>I/I\text{max}</th>
<th>Ion formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.1</td>
<td>C(^+)</td>
</tr>
<tr>
<td>16</td>
<td>0.8</td>
<td>O(^+)</td>
</tr>
<tr>
<td>24</td>
<td>0.3</td>
<td>C(_2^+)</td>
</tr>
<tr>
<td>28</td>
<td>3.8</td>
<td>CO(^+)</td>
</tr>
<tr>
<td>32</td>
<td>0.5</td>
<td>O(_2^+)</td>
</tr>
<tr>
<td>36</td>
<td>0.3</td>
<td>C(_3^+)</td>
</tr>
<tr>
<td>40</td>
<td>6.7</td>
<td>C(_2O^+)</td>
</tr>
<tr>
<td>44</td>
<td>54.4(^b)</td>
<td>CO(_2^+)</td>
</tr>
<tr>
<td>48</td>
<td>&lt;0.1</td>
<td>C(_4^+)</td>
</tr>
<tr>
<td>52</td>
<td>5.0</td>
<td>C(_3O^+)</td>
</tr>
<tr>
<td>56</td>
<td>0.8</td>
<td>C(_2O_2^+)</td>
</tr>
<tr>
<td>60</td>
<td>&lt;0.1</td>
<td>C(_5^+)</td>
</tr>
<tr>
<td>64</td>
<td>0.6</td>
<td>O(_4^+); C(_4O^+)</td>
</tr>
<tr>
<td>68</td>
<td>100.0(^c)</td>
<td>C(_3O_2^+)</td>
</tr>
</tbody>
</table>

Notes:

a. Ion signal, expressed as a percentage of the m/z 68 peak height, using the mean value from 3 ten-second counts.

b. Attributed principally to a large CO\(_2\) impurity: the signals at m/z 12, 16 and 28 may also contain some contribution from CO\(_2\) dissociative ionisation products.

c. 867 counts per second was obtained for m/z 68 in this experiment.
Thermochemical values for reactions of $\text{C}_3\text{O}^+$ presented here (see Table 7.8) are calculated using $\Delta H_f(\text{C}_3\text{O}) = 326 \pm 10 \text{ kJ mol}^{-1}$ as described above, and $\Delta H_f(\text{C}_3\text{O}^+) > 1252 \text{ kJ mol}^{-1}$ based upon the observed occurrence of the rapid reaction

$$\text{C}_3\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C}_3\text{O}^+ + \text{OH}^- \tag{7.19}$$

$k_{7.19} = 5.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

| Table 7.8: Reactions of $\text{C}_3\text{O}^+ + \text{X}$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\text{X}$     | Products         | $k_{obs}^a$     | $k_c^a$         | $-\Delta H^a$   |
| H$_2$           | $\text{C}_3\text{H}_4^+ + \text{H}^+$ | 0.8             | 1.50             | $> 63$           |
| CO              | $\text{C}_3\text{O}.\text{CO}^+$ | 0.072           | 0.79             | $-$              |
| N$_2$           | no reaction      | $<0.001$        | 0.73             | $-$              |
| O$_2$           | $\text{CO}^+ + 2\text{CO}$ | [0.20]          | 0.22             | $> 232$          |
|                 | $\text{C}_3\text{O}_2^+ + \text{O}$ | [0.80]          | 0.67             | $> 74$           |
| CH$_4$          | $\text{C}_3\text{H}_4^+ + \text{CH}_3^+$ | 0.83            | 1.08             | $> 60$           |
| NH$_3$          | $\text{C}_3\text{H}_4^+ + \text{NH}_2$ | 1.9             | 2.20             | $> 46$           |
|                 | $\text{C}_3\text{O}.\text{NH}_3^+$ | $-$             | $-$              | $-$              |
| H$_2$O          | $\text{C}_3\text{H}_4^+ + \text{OH}^-$ | 0.50            | 2.44             | $> 0$            |
| C$_2$H$_2$      | $\text{C}_3\text{H}_5^+ + \text{CO}$ | [0.45]          | 1.08             | $> 69$           |
|                 | $\text{C}_3\text{O}.\text{C}_2\text{H}_2^+$ | [0.55]          | 1.03             | $-$              |
| HCN             | $\text{HC}_3\text{N}^+ + \text{CO}$ | 2.9             | 3.30             | $> 24$           |
|                 | $\text{C}_3\text{O}.\text{CN}^+ + \text{H}^+$ | $-$             | $-$              | $-$              |
| CO$_2$          | no reaction      | $<0.001$        | 0.78             | $-$              |

**Notes**

a. See footnotes (a) - (d) for table (7.3).

b. Product ratio not determined. See text for discussion.
Accurate product distributions for the reactions of C$_3$O$^+$ with NH$_3$ and HCN could not be determined under the experimental conditions. The occurrence of two major product channels in each of these reactions, with one channel leading to formation of a product ion at m/z 51 (HC$_3$N$^+$) or m/z 53 (HC$_3$O$^+$), meant that a higher resolution was required to satisfactorily resolve the m/z 52 ion signal from this product ion: under these conditions, signals at m/z 52 (C$_3$O$^+$) were too small (~5 cps) and too erratic to permit determination of the relative proportions of the two product channels concerned. In the case of the reaction with NH$_3$, H-atom transfer appeared to be the major channel (~75% of products), while for the reaction with HCN, both product channels observed appeared to be of comparable size.

The main product channels observed in the reactions of C$_3$O$^+$ are atom-transfer and adduct formation. Hydrogen atom transfer, to form HC$_3$O$^+$, was observed as the major or only product channel for the rapid reactions with H$_2$, CH$_4$, NH$_3$ and H$_2$O. Adduct formation was observed as a minor channel in the reactions with NH$_3$ and C$_2$H$_2$, and as the only channel in the slow reaction with CO. The most interesting reactions, from a mechanistic point of view, are those in which rearrangement or substantial fragmentation has occurred, as in the reactions with C$_2$H$_2$, HCN and O$_2$:

\[
\begin{align*}
\text{C}_3\text{O}^+ + \text{C}_2\text{H}_2 & \rightarrow \text{C}_4\text{H}_2^+ + \text{CO} \\
& \rightarrow \text{C}_3\text{O.C}_2\text{H}_2^+ \\
\Delta H_{7.20a} & < -69 \text{ kJ mol}^{-1} \\
k_{7.20} & = 1.08 \times 10^{-9} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}
\end{align*}
\]
\[ \text{C}_3\text{O}^+ + \text{HCN} \rightarrow \text{HC}_3\text{N}^+ + \text{CO} \]  \hspace{1cm} (7.21a)  \\
\[ \rightarrow \text{C}_3\text{O.CN}^+ + \text{H}^+ \]  \hspace{1cm} (7.21b)  \\
\[ \Delta H_{7.21a} < -24 \text{ kJ mol}^{-1} \]  \\
\[ k_{7.21} = 2.9 \times 10^{-9} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \]

\[ \text{C}_3\text{O}^+ + \text{O}_2 \rightarrow \text{CO}^+ + \text{CO} + \text{CO} \]  \hspace{1cm} [0.20]  \hspace{1cm} (7.22a)  \\
\[ \rightarrow \text{C}_3\text{O}_2^+ + \text{O} \]  \hspace{1cm} [0.80]  \hspace{1cm} (7.22b)  \\
\[ \Delta H_{7.22a} < -232 \text{ kJ mol}^{-1} \]  \\
\[ \Delta H_{7.22b} < -74 \text{ kJ mol}^{-1} \]  \\
\[ k_{7.22} = 2.2 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \].

The reaction with \( \text{O}_2 \) has also been studied by McElvany et al\textsuperscript{364} using a Fourier Transform ICR technique. They observed only channel (7.22b), for which they reported a rate coefficient \( k_{7.22} = 1.3 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \). The occurrence of channel (7.22b) in the SIFT experiment suggests that dissociation of a weakly-bound collision complex is responsible for this channel. McElvany et al\textsuperscript{364} have proposed that reaction (7.22) occurs as a complexation of \( \text{O}_2 \) at the carbene end of \( \text{C}_3\text{O}^+ \), followed by loss of an oxygen atom:

\[ \text{OC}_{3}\text{O}^+ + \text{O}_2 \rightarrow \text{OC}_3\text{O}_2^+ \rightarrow \text{OC}_3\text{O}^+ + \text{O.} \]

Partial collisional stabilisation of the \( (\text{C}_3\text{O}_3)^+ \) complex would increase the complex lifetime and allow a greater degree of rearrangement. A longer complex lifetime would, therefore, be expected to be accompanied by an increase in the more exothermic channel (7.22a) which requires a greater degree of rearrangement.
The occurrence of channels (7.20a) and (7.21a) also suggests a mechanism involving dissociation of a weakly-bound collision complex. If the reactions of C₃O⁺ are viewed as carbene-insertion reactions by analogy to the reactivity of :C₃H⁺ and :C₄N⁺, then those reactions of C₃O⁺ involving H-atom transfer will have a mechanism which features carbene insertion into the H-X σ bond:

\[
\begin{align*}
\text{O}=\text{C}=\text{C}=\text{O} & \xrightarrow{\text{H}} \text{C}=\text{C}=\text{C}=\text{O} \rightarrow \text{O}=\text{C}=\text{C}=\text{H}^+ + \text{X}^-. \\
\end{align*}
\]

This product channel (loss of X from the collision complex) is not evident in the reactions with C₂H₂ or HCN, where H-atom transfer is not so energetically favourable: for the product channels

\[
\begin{align*}
\text{C}_3\text{O}^+ + \text{C}_2\text{H}_2 & \rightarrow \text{HC}_3\text{O}^+ + \text{C}_2\text{H}^- \quad (7.20c) \\
\text{C}_3\text{O}^+ + \text{HCN} & \rightarrow \text{HC}_3\text{O}^+ + \text{CN}^- \quad (7.21c)
\end{align*}
\]

the calculated upper limits to the enthalpy of reaction are \(\Delta H_{7.20c} < +19\ \text{kJ mol}^{-1}\) and \(\Delta H_{7.21c} < +56\ \text{kJ mol}^{-1}\). These channels may be endothermic: they are certainly less energetically feasible than H-atom transfer for H₂, CH₄, NH₃ and H₂O. A possible additional factor is that the lifetime of the collision complex formed with C₂H₂ or HCN is longer than that of the complex formed with the lighter reactants H₂, CH₄, NH₃ or H₂O, thus permitting the more exothermic channel (rearrangement accompanied by loss of CO) to dominate.

Although these reactions with HCN and C₂H₂ appear mechanistically interesting, the very rapid reaction of C₃O⁺ with H₂ ensures that C₃O⁺ will not have a
sufficiently long lifetime in interstellar clouds to make its reactivity with other cloud constituents significant.

\( \text{C}_3\text{O}_2^+ \) (see Table 7.9) appeared to be less reactive than \( \text{C}_3\text{O}^+ \). Of the neutrals employed in our study, only \( \text{NH}_3 \) and \( \text{C}_2\text{H}_2 \) displayed collision-rate reactions with \( \text{C}_3\text{O}_2^+ \):

\[
\begin{align*}
\text{C}_3\text{O}_2^+ + \text{NH}_3 & \rightarrow \text{NH}_3^+ + \text{C}_3\text{O}_2 & [0.75] & (7.23a) \\
& \rightarrow \text{C}_2\text{H}_2\text{O}^+ + \text{HNCO} & [0.25] & (7.23b)
\end{align*}
\]

\( \Delta H_{7.23a} = -43 \text{ kJ mol}^{-1} \)

\( \Delta H_{7.23b} = -108 \text{ kJ mol}^{-1} \)

\( k_{7.23} = 2.0 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \)

\[
\text{C}_3\text{O}_2^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2\text{O}^+ + \text{CO} \quad (7.24)
\]

\( k_{7.24} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \).

Channel (7.24) requires a degree of rearrangement, but less than is evident in channel (7.23b): the rapidity of these reactions, and the extent of rearrangement evident, argues for the involvement of a 'tight' collision complex in these reactions. The existence of channel (7.23b) as a substantial product channel of a fast reaction requires that the products have the structure \( \text{HC}≡\text{COH}^+ + \text{HNCO} \). All other possible channels involving production of m/z 42 (e.g. \( \text{H}_2\text{CCO}^+ + \text{HNCO}, \text{CNO}^+ + \text{C}_2\text{H}_3\text{O}, \text{C}_2\text{H}_2\text{O}^+ + \text{HCNO} \)) are substantially endothermic.

The reaction with \( \text{O}_2 \) also displays fragmentation and rearrangement:
$$\text{C}_3\text{O}_2^+ + \text{O}_2 \rightarrow \text{CO}^+ + \text{CO} + \text{CO}_2 \quad [0.09] \quad (7.25\text{a})$$

$$\rightarrow \text{CO}_2^+ + \text{CO} + \text{CO} \quad [0.76] \quad (7.25\text{b})$$

$$\rightarrow \text{C}_2\text{O}_2^+ + \text{CO}_2 \quad [0.15] \quad (7.25\text{c})$$

$k_{7.25} = 1.2 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$.

These product channels can be interpreted by a mechanism involving formation of the collision complex (C$_3$O$_4$)$^+$ followed by rearrangement and loss of the stable neutrals CO and/or CO$_2$.

### Table 7.9: Reactions of C$_3$O$_2^+$ + X.

<table>
<thead>
<tr>
<th>X</th>
<th>Products$^a$</th>
<th>$k_{\text{obs}}$</th>
<th>$k_e$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>no reaction</td>
<td>&lt;0.0001</td>
<td>1.49</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>C$_3$O$_2$H$^+$ + CH$_3^+$</td>
<td>0.3</td>
<td>1.05</td>
<td>b</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NH$_3^+$ + C$_3$O$_3$</td>
<td>[0.75]</td>
<td>2.0</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_2$O$^+$ + HNCO</td>
<td>[0.25]</td>
<td>2.12</td>
<td>109$^c$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>C$_3$O$_2$.H$_2$O$^+$</td>
<td>0.001</td>
<td>1.97</td>
<td>-</td>
</tr>
<tr>
<td>N$_2$</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>0.70</td>
<td>-</td>
</tr>
<tr>
<td>O$_2$</td>
<td>CO$^+$ + CO + CO$_2$</td>
<td>[0.09]</td>
<td>0.12</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>CO$_2^+$ + 2CO</td>
<td>[0.76]</td>
<td>0.63</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>C$_2$O$_2^+$ + CO$_2$</td>
<td>[0.15]</td>
<td></td>
<td>288$^d$</td>
</tr>
<tr>
<td>CO</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>0.76</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>C$_4$H$_2$O$^+$ + CO</td>
<td>1.2</td>
<td>0.99</td>
<td>e</td>
</tr>
<tr>
<td>HCN</td>
<td>C$_3$O$_2$.HCN$^+$</td>
<td>0.015</td>
<td>3.16</td>
<td>-</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>no reaction</td>
<td>&lt;0.001</td>
<td>0.74</td>
<td>-</td>
</tr>
</tbody>
</table>

**Notes**

a. See footnotes (a) - (d) for table (7.3).
b. This channel yields $\Delta H$ for (C$_3$O$_2$.H$^+$) $< 709$ kJ mol$^{-1}$; PA(C$_3$O$_2$) $> 727$ kJ mol$^{-1}$.
c. Calculated for the products H$_2$C=CO$^+$ + HNCO. Production of HC=COH$^+$ is 44 kJ mol$^{-1}$ endothermic; production of HCNO is 214 kJ mol$^{-1}$ endothermic.
d. Calculated using $D$(OC.CO$^+$) $= 22.4 \pm 1.0$ kCal mol$^{-1}$.$^{578}$
e. This channel yields $\Delta H$ for (C$_4$H$_2$O$^+$) $< 1268$ kJ mol$^{-1}$.
In view of the lack of reactivity with H₂ and CO, the reaction with O₂ (which may be the major oxygen-containing species within clouds, excepting CO) may be the dominant loss process for any interstellar C₃O₂⁺: note that this reaction serves to reduce the molecular complexity of the ion, thus suggesting that C₃O₂⁺ cannot aid in the synthesis of more complex cloud constituents.
CHAPTER 8.

A CONSIDERATION OF RADICAL-\( \text{H}_2 \) REACTIONS IN INTERSTELLAR SYNTHESIS.

Section 8.1: Introduction.

Processes involved in interstellar synthesis are most commonly characterised by a lack of activation energy or of endothermicity, since under interstellar conditions the only processes which can occur without hindrance are exothermic reactions lacking energetic barriers. Ion-molecule reactions most usually adhere to this criterion, but certain categories of neutral-neutral reactions may also be of interstellar relevance. A recent review by Smith\(^{32}\) distinguishes four types of bimolecular neutral reactions: molecule-molecule, radical-saturated molecule, radical-unsaturated molecule, and radical-radical, as characterised by reactions (8.1) to (8.4).

\[
\text{H}_2 + \text{D}_2 \rightarrow \text{HD} + \text{HD} \quad (8.1) \\
E_a > 250 \text{ kJ mol}^{-1}
\]

\[
\text{OH}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^- \quad (8.2) \\
E_a = 17.5 \text{ kJ mol}^{-1}
\]

\[
\text{OH}^- + \text{CO} \rightarrow \text{CO}_2 + \text{H}^- \quad (8.3) \\
E_a \sim 0 \text{ kJ mol}^{-1}
\]
\[ \text{OH}^+ + \text{O} \rightarrow \text{O}_2 + \text{H}^+ \]  
\( E_a = -100 \text{ kJ mol}^{-1} \).  

The occurrence of a negative activation energy for the biradical reaction of \( \text{O} + \text{OH}^- \), as determined from studies of the dependence of reaction rate on temperature, implies that these reactions are not well explained in terms of an Arrhenius rate law. Biradical reactions are, however, usually fast and usually exhibit a negative temperature dependence, both factors underlining their importance in interstellar synthesis. In this context, the prospect for radiative association between interstellar free radicals has been explored.  

Radical-unsaturated molecule reactions such as reaction (8.3) may also lack activation energy barriers, but may be slow nevertheless, since the transition state to product formation is 'tighter' than in the instance of radical-radical reactions. Only a narrow channel (on the potential energy surface describing the bimolecular interaction) may lead to product formation, and so these types of reaction are less efficient than radical-radical processes. However, as discussed in section (6.5), such reactions are also important in interstellar chemistry.  

Reactions of types (8.1) and (8.2) are so hindered by activation energy barriers that they have been considered of no interstellar relevance\(^{32}\) except in the case of shock chemistry, where very high prevailing temperatures permit such reactions to occur rapidly. I propose that under some conditions, reactions of type (8.2) may be significant in the chemistry of cold, dark clouds in the absence of shock effects. This may be compared with the suggestion\(^{41,86,87}\) that endothermic ion-
molecule reactions may serve a useful purpose in the interstellar synthesis of ammonia:

\[
\begin{align*}
\text{He}^+ + N_2 & \rightarrow (N_2^+)\# + \text{He} \quad \text{(1.16a)} \\
(N_2^+)\# & \rightarrow (N^+)\star + N^- \quad \text{(1.16b)} \\
(N^+)_{\text{fast}} + H_2 & \rightarrow \text{NH}^+ + H^- \quad \text{(1.17a)} \\
& \rightarrow N^+ + (H_2)_{\text{fast}} \quad \text{(1.17b)}
\end{align*}
\]

Formation of NH\(^+\) by the endothermic reaction (1.17a) avoids a bottleneck in the synthesis of NH\(_3\)\(^4\)\(_1\),\(^8\)\(_6\).

Section 8.2: General considerations.

The occurrence, within cold dense interstellar clouds, of reactions of the type

\[
X + AB \rightarrowXA + B \quad \text{(8.5)},
\]

where the translational energy \(E_{T(X)}\) of the radical \(X\) is sufficient to overcome the activation energy \(E_a\), has not previously been explored in models of cloud chemistry. The factors relevant to the efficiency and importance of these reactions will now be considered.

Under the conditions prevailing within cold molecular clouds, AB is most likely to be H\(_2\) or He, with a translational energy appropriate to the background temperature of the cloud (typically \(T \sim 20\) K). Only collisions between X and H\(_2\) are likely to be of any interest in terms of chemistry resulting from
translationally excited X, since H\textsubscript{2} is so much more abundant than any other reactant molecule of interest (CO, the next most abundant interstellar molecule, typically has an abundance n(CO) \leq 10^{-4} n(H\textsubscript{2})). Collisions with atoms such as H· and He are not, in this context, chemically interesting: these collisions will serve only to cool the translationally excited reactant X, as will unreactive collisions involving H\textsubscript{2}. Since H\textsubscript{2} is the only reactant molecule that need be considered, and since H-atom abstraction is the only product channel feasible for such a reaction, reaction (8.5) may be rewritten:

\[
X + H\textsubscript{2} \rightarrow XH + H\cdot
\]  

(8.6).

Reaction (8.6) will only occur if a collision features sufficient energy to exceed the activation energy barrier $E_\text{a}$. The major source of such energy is the translational excitation of the fragment X: since the H\textsubscript{2} 'target' is expected to be thermalised at $T \sim 20$ K, the contribution from translational and internal excitation of H\textsubscript{2} is very small. Similarly, the contribution from internal excitation of X is negligible. If X is produced by a dissociative recombination process

\[
XY^+ + e \rightarrow X + Y
\]  

(8.7),

then in a cold cloud with a particle density of n(H\textsubscript{2}) \sim 10^3 \text{ cm}^{-3}, the timescale for a possible collision will, on the average, exceed the time required for any vibrational, rotational or electronic de-excitation. In any case, the rates of many reactions of type (8.6) are not significantly affected by internal excitation of X - as in, for example, the case where X = OH.\textsuperscript{98,380,381} However, it must not be assumed that $E_{T(X)}$ must merely exceed $E_\text{a}$ for reaction (8.6) to occur. The
collision energy $E_{cm}$ will depend upon the relative velocities of $X$ and $H_2$ in a collision, and it is this collision energy which governs the consequences of the collision: for the occurrence of any possible reaction, $E_{cm}$ must exceed $E_a$.

$E_{cm}$ can be calculated from $E_{T(X)}$ by consideration of the collision (8.6) in the centre-of-mass frame of reference (c.m.). If $V$ is the velocity of $X$ relative to $H_2$, then

$$E_{cm} = \frac{1}{2} \mu V^2$$  \hspace{1cm} [8.i]

where $\mu$ is the reduced mass:

$$\mu = \frac{m_X m_{H_2}}{m_X + m_{H_2}}$$  \hspace{1cm} [8.ii].

In keeping with the approximation commonly adopted in the mathematical treatment of trajectories in molecular beam experiments, it is assumed that if $V_{H_2} \ll V_X$, then $V \sim V_X$. By this assumption,

$$E_{cm} = \frac{1}{2} \mu V_X^2$$  \hspace{1cm} [8.iii],

and since $E_{T(X)} = \frac{1}{2} m_X V_X^2$,

$$E_{cm} = \frac{\mu}{m_X} E_{T(X)}$$  \hspace{1cm} [8.iv];

$$E_{cm} = \frac{m_{H_2}}{m_{H_2} + m_X} E_{T(X)}$$  \hspace{1cm} [8.v].

Thus $E_{T(X)}$ must exceed $E_a$ by a factor $F = \frac{m_X + m_{H_2}}{m_{H_2}}$, for reaction (8.6) to have any possibility of occurrence. Because $H_2$ has such a low molecular mass, this factor $F$ is typically large: for example, for $X = OH\cdot$, $F = 9.5$. $OH\cdot$ is one of the lightest fragment radicals for which the hydrogen-abstraction reaction (8.6) is exothermic ($\Delta H_{8.6} = -67$ kJ mol$^{-1}$) and accompanied by a comparatively low activation energy
barrier ($E_a = 17.5$ kJ mol$^{-1}$);$^{32,383}$ thus, for most other such reactions within interstellar clouds, $F$ will be larger than for this reaction. This indicates that, while reactions of type (8.6) may be inhibited by a barrier of only 10 or 20 kJ mol$^{-1}$ (see table 8.1), they will not occur under the conditions described unless $E_T(X)$ exceeds 100 or 200 kJ mol$^{-1}$.

### Table 8.1: Energy parameters for reactions of the type $AH_n + H_2 \rightarrow AH_{n+1} + H$, for species of potential relevance to interstellar cloud chemistry.

<table>
<thead>
<tr>
<th>$AH_n$</th>
<th>$\Delta H$ a</th>
<th>$E_a$ b</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-97.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$^-$</td>
<td>-12.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$</td>
<td>26.2</td>
<td>23.9</td>
<td>384</td>
</tr>
<tr>
<td>CH$_3^-$</td>
<td>2.3</td>
<td>44 ± 2</td>
<td>385-388</td>
</tr>
<tr>
<td>NH$_2^-$</td>
<td>16.6</td>
<td>54</td>
<td>389</td>
</tr>
<tr>
<td>O</td>
<td>-7.8 ± 1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>62.8</td>
<td>17.5</td>
<td>32,383</td>
</tr>
<tr>
<td>Si</td>
<td>-145 ± 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$^-$</td>
<td>-130 ± 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>-132 ± 14</td>
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</tr>
<tr>
<td>SiH$_3^-$</td>
<td>-50 ± 6</td>
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<td>S</td>
<td>-80.3</td>
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<td>SH$^-$</td>
<td>-58.2</td>
<td></td>
<td></td>
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<tr>
<td>C$_2$</td>
<td>49 ± 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$^-$</td>
<td>119 ± 5</td>
<td>5 ± 5</td>
<td>390</td>
</tr>
<tr>
<td>C$_2$H$_3^-$</td>
<td>-4.9 ± 5</td>
<td>21.4</td>
<td>391</td>
</tr>
<tr>
<td>C$_2$H$_5^-$</td>
<td>-16.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN$^-$</td>
<td>82</td>
<td>9.3 ± 1</td>
<td>195,392-394</td>
</tr>
<tr>
<td>HCO$^-$</td>
<td>371.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_3$N$^-$</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes

a. Reaction exothermicity in kJ mol$^{-1}$, using values obtained from reference 184.

b. Activation energy in kJ mol$^{-1}$, using values obtained from the references shown. Activation energies are not listed for those reactions which are endothermic.

c. This quantity has not been determined.
The effect of unreactive collisions, with \( H_2 \) and with \( \text{He} \), should also be considered. If the \( X/H_2 \) collision is considered as one between smooth elastic spheres, then the fraction, \( f \), of translational energy lost from \( X \) per collision is:

\[
\frac{8}{3} \frac{m_X m_{H_2}}{(m_X + m_{H_2})^2} \left( \frac{T_X - T_{H_2}}{T_X} \right)
\]  

\[\text{[8.vi].}\]

\( T_X \) is the effective translational temperature of the fragment \( X \); in most instances, if \( X \) has sufficient translational energy to overcome \( E_a \), then \( T_X \gg T_{H_2} \) (\( T_{H_2} \sim 20 \text{ K} \)), and so the expression can be approximated by

\[
\frac{8}{3} \frac{m_X m_{H_2}}{(m_X + m_{H_2})^2}
\]

\[\text{[8.vii].}\]

In this manner, if a fragment \( X \) is produced by dissociative recombination of \( XY^+ \) and then collides (unreactively) with \( n \) molecules of \( H_2 \), \( E_{T(X)} = (1 - f')^n E_{T(X)}(\text{init.}) \).

For \( X = \text{OH} \), \( f' = 0.251 \): an \( \text{OH} \) radical produced by dissociative recombination will lose one quarter of its translational energy upon each unreactive collision with \( H_2 \) (for collision with \( \text{He} \), \( f' = 0.411 \)). Thus, if \( E_{T(X)} \) is not vastly in excess of that required to overcome \( E_a \), comparatively few unreactive collisions are required to quench \( X \) so as to prevent any subsequent reaction with \( H_2 \). Since reactive collision of \( X \) with \( H_2 \) is not expected to approach unit efficiency, reactions of type (8.6) represent an inefficient source of \( \text{XH} \) - however, if no other source of \( \text{XH} \) exists, such reactions may be important nevertheless.

Having determined the translational threshold for occurrence of reaction (8.6), we must next study the dissociative recombination process (8.7) to determine
whether this threshold can be met by the energy release of such recombination processes. For the dissociative recombination of a thermalised ion $XY^+$ with a thermalised electron (at $T \sim 20$ K), the reactants have negligible translational energy, and so any translational energy residing in the product fragments must result from the exothermicity of reaction (8.7). Since the reactants can, to a good approximation, be considered 'at rest', the product fragments are required by conservation of linear momentum to have zero net linear momentum also: thus, $m_X V_X = -m_Y V_Y$. The translational energy of $X$ can thus be expressed as a function of the total translational energy release:

$$E_{T(\text{total})} = \frac{1}{2} m_X V_X^2 + \frac{1}{2} m_Y V_Y^2 \quad \text{(8.viii)}$$

and since

$$V_Y = -\frac{m_X}{m_Y} V_X \quad \text{(8.ix)}$$

$$E_{T(X)} = \frac{m_Y}{m_X + m_Y} E_{T(\text{total})} \quad \text{(8.x)}$$

The total translational energy release will depend upon the distribution of energy released by recombination:

$$-\Delta H_{8.7} = E_{T(\text{total})} + E_{R'} + E_{V'} + E_{E'} \quad \text{(8.xi)}$$

where $E_{R'}$, $E_{V'}$, and $E_{E'}$ represent the energy released as rotational, vibrational and electronic excitation of the product fragments. Very little is yet known about the distribution of energy in dissociative recombination reactions: theoretical treatments of these reactions$^{52,82}$ suggest that translational excitation of the products accounts for a considerable fraction of the reaction exothermicity. In the extreme case, where there is negligible internal excitation, $-\Delta H_{8.7} = E_{T(\text{total})}$ and thus $E_{T(X)} = -\frac{m_Y}{m_X + m_Y} \Delta H_{8.7}$. In these circumstances the threshold for reaction (8.6) becomes
that is, dissociative recombination processes whose exothermicity does not exceed this threshold cannot produce fragments $X$ with sufficient translational energy to permit the occurrence of reaction (8.6). 

It should be noted, in relation to the above formula for the threshold, that dissociative recombination reactions of the types

$$\text{XH}^+ + e \rightarrow \text{X} + \text{H}\cdot$$  \hspace{1cm} (8.8)

and

$$\text{XH}_2^+ + e \rightarrow \text{X} + \text{H}_2$$  \hspace{1cm} (8.9)

will impart most of the translational energy released to the light $\text{H}\cdot/\text{H}_2$ fragment. Therefore, $E_{\text{T(total)}}$ for such recombinations must be very large to permit the occurrence of a subsequent reaction (8.6) with even a modest activation barrier.

These factors will now be considered more specifically for the interstellar occurrence of reaction (8.6) with $X = \text{OH}\cdot$, that is,

$$\text{OH}\cdot + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}\cdot$$  \hspace{1cm} (8.10).
Section 8.3: Reaction between OH· and H₂, for OH· produced by the dissociative recombination of H₃O⁺.

Very few experimental determinations of dissociative recombination product channels have yet been performed. The reaction

\[
\begin{align*}
\text{H}_3\text{O}^+ & + e^- \rightarrow \text{H}_2\text{O} + \text{H}^- & (8.11a) \\
& \rightarrow \text{OH}^- + \text{H}_2 & (8.11b) \\
& \rightarrow \text{OH}^- + \text{H}^- + \text{H}^- & (8.11c) \\
& \rightarrow \text{O} + \text{H}_2 + \text{H}^- & (8.11d)
\end{align*}
\]

has recently been investigated by Herd et al.⁸⁵ in a FALP apparatus, using laser-induced fluorescence to determine the yield of OH· produced. Channels (8.11b) and (8.11c) account for (65 ± 15%) of H₃O⁺ recombinations: unfortunately, since OH· is the only neutral product yet detected in such experiments, the efficiency of any of these channels cannot be readily assessed. Herd et al contend that channel (8.11b) accounts for most of the OH· produced, in accordance with Bates⁵² who considers that this channel represents a favourable crossing of potentials in the recombination process. Bates also suggests that the H₂ product of this recombination will be vibrationally excited in accordance with the Franck-Condon principle, since the H−H separation in H₃O⁺ is significantly greater than in ground-state H₂. Consideration of the Franck-Condon factors involved indicates that the degree of vibrational excitation of H₂ is likely to be between 2.0 and 3.4 eV: the remainder of the energy released by recombination, which Bates describes as the 'partial exothermicity' of the reaction, is 2.2 to 3.6 eV. Most of
this partial exothermicity must appear as translational energy of the products.\textsuperscript{52} This is in accordance with the experimental results, which indicate that 46\% of all \( \text{H}_3\text{O}^+ \) recombinations (and, therefore, 70\% of recombinations yielding \( \text{OH}^- \)) produce \( \text{OH}^- \) in the ground vibrational state. It is reasonable to assume that the degree of rotational excitation of products is also slight.

If it is assumed that channel (8.11b) is the dominant product channel for recombination of \( \text{H}_3\text{O}^+ \), and that the energy released by neutralisation is partitioned only into \( \text{H}_2 \) vibration and product translation, can the \( \text{OH}^- \) produced by channel (8.11b) react with \( \text{H}_2 \) via reaction (8.10) to produce \( \text{H}_2\text{O} \), under conditions in cold interstellar clouds?

The relevant parameters are

\[
\begin{align*}
\Delta H_{8.11b} & = -552 \text{ kJ mol}^{-1}; \\
E_v' & > 190 \text{ kJ mol}^{-1} \ (\approx 2.0 \text{ eV}), \\
\therefore \quad E_T(\text{Total}) & < 362 \text{ kJ mol}^{-1} .
\end{align*}
\]

\[
\begin{align*}
\text{m}_X & = 17.0 \text{ g mol}^{-1}; \\
\text{m}_Y & = 2.0 \text{ g mol}^{-1}; \\
E_a & = 17.5 \text{ kJ mol}^{-1}.
\end{align*}
\]

Calculation of the threshold for the occurrence of reaction (8.10), according to the expression derived earlier, gives a value of \( E_T(\text{Total}) > 1579 \text{ kJ mol}^{-1} \). This required translational energy release is vastly in excess of the maximum possible energy release. The possibility of additional vibrational, rotational or electronic excitation of \( \text{OH}^- \) during the recombination process (8.11), or \( \text{OH}^- \) production by channel (8.11c), further reduces the total available translational energy, and
therefore OH· produced by reaction (8.11) cannot possibly undergo further reaction with H₂ under the conditions considered here.

Section 8.4: Reaction between OH· and H₂, for OH· produced from dissociative recombination of HOCO⁺.

The reaction

\[
\text{HOCO}^+ + e^{-} \rightarrow \text{OH}^- + \text{CO} \quad [0.34] \quad (8.12a)
\]
\[
\rightarrow \text{H}^- + \text{CO}_2 \quad (8.12b)
\]
\[
\rightarrow \text{H}^- + \text{O} + \text{CO} \quad (8.12c)
\]

\[\Delta H_{8.12a} = -670 \text{ kJ mol}^{-1},\]

has also been studied recently by the FALP-LIF technique.\textsuperscript{84,85} Channel (8.12a) produces two molecular fragments of comparable mass, and thus the threshold for the possibility of reaction (8.10) occurring subsequently for OH· produced by this channel should be lower than in the case of H₃O⁺ recombination described above.

The distribution of energy in reaction (8.12a) is not known, but an analogy may be made with the photodissociation of HONO, which is isoelectronic with HOCO⁺.\textsuperscript{395,396}

\[
\text{HONO} + \text{hv} \rightarrow \text{HONO}(\text{Å}) \rightarrow \text{OH} + \text{NO} \quad (8.13)
\]
\[\Delta H_{8.13} = -123 \text{ kJ mol}^{-1}.\]
The energy distribution of reaction (8.13) has been extensively studied: approximately 46% of the total available energy appears as translational excitation of OH· ($E_{T(OH)} \sim 57 \text{ kJ mol}^{-1}$), implying that virtually three-quarters of the available energy is manifested as recoil energy of the products. Although reaction (8.13) is substantially less exothermic than reaction (8.12a), it is probable that rapid recombination of HOCO$^+$ + e would manifest a similarly large fraction of its exothermicity as recoil energy. The observed distribution of translational and rotational energies in reaction (8.13) is consistent with the impulse model of Tuck,$^{397}$ and by analogy, the energy distribution of reaction (8.12a) can be partially predicted in this manner. Tuck's impulse model considers that the energy released by dissociation acts directly along the axis of the bond undergoing cleavage. By this model,

$$E_{T(OH)} : E_{T(CO)} : E_{R(OH)} : E_{R(CO)} = m_{\text{CO}}m_{\text{OH}} : m_{\text{CO}}m_{\text{OH}} : m_{\text{CO}}m_{\text{OH}} \sin^2 \theta : m_{\text{O}}m_{\text{OH}}m_{\text{O}} \sin^2 \Phi.$$ 

Using $\theta = 119^\circ$ and $\Phi = 174^\circ$ (see table 8.2), the fraction of the available energy channelled into each of these modes is

$$E_{T(OH)} : E_{T(CO)} : E_{R(OH)} : E_{R(CO)} = 0.6008 : 0.3649 : 0.0290 : 0.0053.$$ 

This model does not account for possible vibrational and electronic excitation of the products OH· and CO. Vibrational excitation is expected to be slight (since $r(O-H)$ and $r(C=O)$ in HOCO$^+$ are very close to the ground-state internuclear separations of 0.97 and 1.128 Å, for OH· and CO respectively). This is supported by the observation that 50% of the OH· produced by channel (8.12a) is in the ground vibrational state.$^{84,85}$ Electronic excitation of the CO is not energetically possible, but production of electronically excited OH· ($A^2 \Sigma^+$) can occur. Indeed,
Adams et al have reported the detection of weak optical emissions due to OH· $A^2\Sigma$ → $X^2\Pi$ transitions in a HCO$_2^+$/e$^-$ plasma, but believe that much of the OH· produced is in the ground electronic state ($X^2\Pi$).

If OH· is produced in the ground electronic state ($X^2\Pi$) and if vibrational excitation is considered negligible, $E_{T\text{Total}} = 647$ kJ mol$^{-1}$; for production of OH· ($A^2\Sigma^+$), $E_{T\text{Total}} = 243$ kJ mol$^{-1}$. Can reaction (8.10) occur for OH· so produced?

Using $m_X = 17.0$ g mol$^{-1}$ and $m_Y = 28.0$ g mol$^{-1}$, the threshold for possibility of reaction (8.10) is $E_{T\text{Total}} > 267$ kJ mol$^{-1}$. Therefore, OH· ($X^2\Pi$) produced by channel (8.12a) has ample energy to permit hydrogen-atom abstraction from H$_2$, although it appears that electronically-excited OH· ($A^2\Sigma^+$) lacks just sufficient translational energy to drive reaction (8.10).

### Table 8.2: Calculated geometry of HOCO$^+$.

<table>
<thead>
<tr>
<th>r(H–O) a</th>
<th>r(O=C) a</th>
<th>r(C=O) a</th>
<th>$\theta$ b</th>
<th>$\Phi$ b</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0082</td>
<td>1.2973</td>
<td>1.1542</td>
<td>111.9</td>
<td>171.8</td>
<td>c</td>
</tr>
<tr>
<td>0.987</td>
<td>1.224</td>
<td>1.121</td>
<td>117.2</td>
<td>180.0</td>
<td>d</td>
</tr>
<tr>
<td>1.000</td>
<td>1.246</td>
<td>1.171</td>
<td>127.8</td>
<td>171.6</td>
<td>e</td>
</tr>
<tr>
<td>0.986</td>
<td>1.237</td>
<td>1.135</td>
<td>118.0</td>
<td>174.5</td>
<td>f</td>
</tr>
<tr>
<td>0.9874</td>
<td>1.2161</td>
<td>1.1298</td>
<td>119.34</td>
<td>173.64</td>
<td>g</td>
</tr>
<tr>
<td>0.972</td>
<td>1.220</td>
<td>1.111</td>
<td>119.7</td>
<td>174.0</td>
<td>h</td>
</tr>
</tbody>
</table>

**Notes**

a. Bond length in angstroms.
b. Bond angles in degrees. $\theta$ is the angle $\angle$(HOC), $\Phi$ is the angle $\angle$(OCO).
c. STO-3G calculations, reference 398.
d. SCF/CI calculations, reference 399.
e. RMP2/4-31G calculations, reference 400.
f. CISD+Q calculations, reference 401.
g. Empirically corrected MP2/6-31G(d) calculations, reference 402.
h. MC SCF/6-31G* calculations, reference 403.
Having postulated that reaction (8.10) might occur for OH· (X 2Π) from the dissociative recombination of HOCO+, it becomes desirable to estimate in some manner the efficiency of this process. While a detailed assessment of the reaction efficiency is beyond the scope of this present work, it is certainly possible to gain an approximate value of the efficiency. For OH· (X 2Π) produced by channel (8.12a),

\[ E_{T\text{Total}} = 647 \text{ kJ mol}^{-1} \]

if vibrational excitation is neglected as discussed above;

\[ E_{cm} = 42.4 \text{ kJ mol}^{-1} \]

for the first OH· + H2 collision following dissociative recombination. Schatz\textsuperscript{381} has calculated the reactive cross-section for reaction (8.10) as a function of translational, rotational and vibrational energy. The calculated reactive cross-section for internally cold (v=0, j=0) reactants can be used to determine the efficiency of each collision with H2, if the collision cross-section is known. The hard-sphere estimate of the collision cross-section, \( Q_{\text{tot}} \), for reaction (8.10) is 30 Å\(^2\). This value has been used in table 8.3, which shows the cumulative fraction of OH· (X 2Π) lost to reaction (8.10) after n+1 collisions with H2. These figures show that \( \sim 6\% \) of the OH· (X 2Π) radicals react on the first collision, \( \sim 4\% \) react on the second collision and less than 2% react on the third collision. There is very little additional possibility for reaction after the third collision, since \( E_{cm} \) rapidly drops below \( E_a \) after this.
This calculation demonstrates that approximately 10% of OH· (X 2Π) radicals from HOCO+ recombination should be converted to H₂O by reaction (8.10), under conditions pertaining to cold quiescent interstellar clouds.

Section 8.5: Discussion.

The possible formation of H₂O by reaction (8.10) is astrophysically significant. Millar et al.⁴⁰⁴ have modelled the consequences of changing p, the fraction of H₃O⁺ recombinations which produce OH·. They find that if p = 0, then H₂O becomes the predominant oxygen-containing species (with the exception of CO); however, if p > 0.1, then O₂ predominates over H₂O owing to the rapidity of reaction (8.4), between OH· and O. Experimentally, p = 0.65 ± 0.15.⁸⁵ This suggests that O₂ will have a higher abundance than H₂O, and H₂O is in fact observed to be localised in small regions of dense clouds whereas the ion H₃O⁺ is widespread.⁴⁰⁵

Table 8.3: Calculated cumulative efficiency of reaction (8.10), for OH· (X 2Π) from dissociative recombination of HOCO⁺.

<table>
<thead>
<tr>
<th>n</th>
<th>Ecm</th>
<th>Qₙ</th>
<th>Pₙ</th>
<th>Pr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42.4</td>
<td>1.7</td>
<td>0.06</td>
<td>0.94</td>
</tr>
<tr>
<td>1</td>
<td>31.8</td>
<td>1.1</td>
<td>0.09</td>
<td>0.91</td>
</tr>
<tr>
<td>2</td>
<td>23.8</td>
<td>0.6</td>
<td>0.11</td>
<td>0.89</td>
</tr>
<tr>
<td>3</td>
<td>17.8</td>
<td>&lt;0.1</td>
<td>0.11</td>
<td>0.89</td>
</tr>
<tr>
<td>4</td>
<td>13.3</td>
<td>0</td>
<td>0.11</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Notes
a. Number of collisions (with H₂) elapsed since the dissociative recombination event.
b. Centre-of-mass collision energy, in kJ mol⁻¹.
c. Calculated reaction cross section, in Å², from reference 381.
d. Cumulative fraction of OH· radicals lost through reaction (8.10), calculated from Qₙ using a hard-sphere collision cross-section Qₙₕ = 30 Å².
e. Fraction of OH· radicals remaining.
Nevertheless, the dissociative recombination of HOCO$^+$ should produce OH· with ample energy to drive reaction (8.10). This suggests a further connection between the abundances of the oxygen-containing species. If reaction (8.3), involving CO$_2$ formation from OH· and CO, has negligible activation energy then this reaction will compete with reaction (8.4) as a primary destruction mechanism for (cold) OH·. If the CO abundance significantly exceeds that of atomic oxygen, reaction (8.3) may dominate over reaction (8.4): $n$(CO)/$n$(O) will depend upon the overall C/O abundance ratio within the cloud (a parameter which is uncertain), the local density and the cloud age (bimolecular reactions will remove O more efficiently than CO). In dense regions especially, CO is likely to have a higher abundance than O, favouring CO$_2$ formation via reaction (8.3). Protonation of CO$_2$, followed by dissociative recombination, should yield OH· capable of H$_2$O formation as shown here, and this may help account for the observation of H$_2$O within denser regions of clouds.$^{405}$

The H$_3$O$^+$ and HOCO$^+$ abundances within Sgr B2 (the only interstellar source for which abundances of both ions have been reported) are similar: $n$(H$_3$O$^+)$ \sim 10^{-9}$ $n$(H$_2$)$^{406}$ and $n$(HOCO$^+)$ > 10^{-10}$ $n$(H$_2$)$^{407}$. The results of Herd et al$^{85}$ indicate that [34 ± 8]% of HOCO$^+$ recombinations produce OH·. The estimation reported here suggests that, in the absence of electronic excitation of the OH· product, \sim 10% of these radicals can produce H$_2$O via reaction (8.10), leading to an effective branching ratio of \sim 3% efficiency of H$_2$O formation by HOCO$^+$ recombination. A maximum of [35 ± 15]% of H$_3$O$^+$ recombinations may yield H$_2$O - although Herd et al$^{85}$ indicate that the H$_3$O$^+$ recombinations not yielding OH· may very likely produce O + H$_2$ + H· by predissociation of vibrationally excited OH· ($A$ $^2\Sigma^+$). Since the abundances of the HOCO$^+$ and H$_3$O$^+$ ions are comparable, and since the
calculated efficiency of H$_2$O formation from HOCO$^+$ recombination is so low (~3%), dissociative recombination of HOCO$^+$ is unlikely to have a major effect on the production of H$_2$O in the interstellar environment unless H$_3$O$^+$ recombination is also a very inefficient source of H$_2$O.

A possible experiment to test the production of H$_2$O from HOCO$^+$ dissociative recombination would be one analogous to the FALP-LIF experiments of Smith and co-workers, but employing H$_2$ as a buffer gas in the place of helium. The rate for reaction (8.10) is comparatively insensitive to the rotational and vibrational state of OH$^+$, so an apparent reduction in the product channel (8.12a), in excess of that expected for OH$^+$ + H$_2$ at room temperature, would indicate the rapid occurrence of this reaction due either to translational or to electronic excitation. An additional test would be to see whether the fraction of H$_3$O$^+$ recombination channels yielding OH$^+$, in a similar experiment with H$_2$ buffer gas, was similarly reduced: as described above, OH$^+$ produced from reactions (8.11b) and (8.11c) should lack sufficient translational excitation to allow reaction (8.10) to proceed rapidly.

It is of some interest to note the parallel which exists between the occurrence of reaction (8.10) under the conditions described here, and the conditions within shocked regions of diffuse interstellar clouds. The present scenario describes the reaction of translationally excited, internally cold OH$^+$ with cold H$_2$. Within shocked diffuse clouds the same reactants are expected to be translationally hot (as a result of the shock, for which an effective temperature $T \sim 2000$ K $\rightarrow 5000$ K may be appropriate) but internally cooled: OH$^+$, since it possesses a large dipole moment, will radiate away any vibrational or rotational energy, and H$_2$ will
radiate vibrational or rotational energy by electric quadrupole transitions, and diffuse clouds are usually of sufficient transparency to render re-absorption unlikely. In effect, therefore, the only difference between the occurrence of reaction (8.10) within dense clouds (following dissociative recombination of the OH· precursor) and within shocked diffuse clouds is in the translational energy of the hydrogen molecule. Both scenarios suggest analogy with molecular beam techniques, in which reactants are supersonically cooled with respect to vibration and rotation: it seems likely that such beam experiments could help verify the efficiencies of the reactions concerned.

The application of this hypothesis of translationally-driven interstellar reactions, to other products of dissociative recombination reactions, is uncertain. Observed interstellar ions are typically small - HOCO+ is the largest yet observed, on the basis of molecular weight - and the possibility exists that neutral-neutral processes may be more important than ion-molecule reactions in determining the abundances of larger molecules such as cyanopolyynes. Activation barriers for many radical-H₂ reactions of possible interstellar significance are undetermined or uncertain. In addition, too little is known concerning the product distributions of other dissociative recombination reactions of interstellar relevance. Further experimental work is required to at least establish which theories are able to satisfactorily account for the products observed. For these reasons, discussions concerning the subsequent reactivity of recombination products of other large ions seem unproductive.
CHAPTER 9.

A COMPARISON OF THE REACTIVITIES OF UNSATURATED, LINEAR $C_4H_n^+$, $C_3H_nN^+$, AND $C_3H_nO^+$ IONS.

Section 9.1: Introduction.

Giles et al\textsuperscript{226} have determined that, as a general rule for the ions $C_nH_m^+$ ($n = 4 \rightarrow 6; m = 0 \rightarrow 6$), only those ions having $m \leq 1$ react with $H_2$. Similarly, ions with $m \leq 1$ were observed to be more reactive with CO than their more highly hydrogenated counterparts. Bohme et al\textsuperscript{355} have explored the reactivity of $C_n^+$ ($n = 1 \rightarrow 6$) and $C_nH^+$ ($n = 2 \rightarrow 5$) with CO, and observe a similar pattern of reactivity. The reactions of $C_n^+$ ($n = 3 \rightarrow 19$) with $D_2$ and $O_2$ have been studied by McElvany et al\textsuperscript{364} who observed that $C_nD_2^+$ did not react further with $D_2$. These authors have interpreted their observations via a model involving linear carbon-chain ions $:C=\left(C=O\right)_{n}X: C^+$ which have carbene character at the terminal C atoms.

H-atom abstraction from $H_2$ is calculated to be exothermic only for reaction at these termini, since this does not involve disruption of the cumulene-type bonding of the carbon chain. Similarly, association with CO is more efficient if
the ion concerned features such carbene moieties, since these lone pairs can add
directly to the CO molecule.

Bohme and co-workers\textsuperscript{245,271,329-331,408} have also explored the reactivity of the ions
C\textsubscript{3}H\textsuperscript{+}, C\textsubscript{2}N\textsuperscript{+} and C\textsubscript{4}N\textsuperscript{+}: many reactions of these ions can be accounted for by their
carbene character. Bohme's results are applicable to ions of the type C\textsubscript{n}N\textsuperscript{+}
(where n is even) or C\textsubscript{n}H\textsuperscript{+} (where n is odd), since for these ions resonance forms
can be drawn which illustrate the partial localisation of the cationic charge upon
the terminal (carbene) carbon atom: for example,

\[ \text{\textsuperscript{+}C}-(\text{C\equiv C})_x-\text{C\equiv N}: \text{and} \text{\textsuperscript{+}C}-(\text{C\equiv C})_x-\text{C\equiv C-H}. \]

Bohme et al have not considered ions such as C\textsubscript{3}N\textsuperscript{+} to be potential carbene
cations: such ions have no possible resonance structure featuring a positive
charge upon the carbene carbon. However, Parent\textsuperscript{269,270} has performed MNDO
calculations upon several C\textsubscript{n}N\textsuperscript{+} (n = 4 \rightarrow 8) ions: these calculations indicate that
all these ions have some carbene character. Parent's studies\textsuperscript{269,270} also include
experimental results for the reactions of these C\textsubscript{n}N\textsuperscript{+} ions with methane: some
product channels in these reactions are attributed to the presence of carbene
character. This suggests that the absence of charge upon the terminal carbon
atom is not, in itself, an impediment to carbene reactivity in ion-molecule
reactions.

In the studies described in chapters 4, 6, and 7, similar patterns of reactivity were
observed for C\textsubscript{3}H\textsubscript{n}N\textsuperscript{+} and C\textsubscript{3}H\textsubscript{n}O\textsuperscript{+} ions. This chapter thus describes a
comparison between the reactivities of these types of ions.
Section 9.2: Discussion.

Rate coefficients for reactions of the ions concerned with H$_2$, CO, C$_2$H$_2$ and HCN are summarised in table 9.1: these neutrals have been selected since results for the series C$_4$H$_n^+$ (n = 0 → 4) are available, whereas reactions of these ions with other neutrals have not, in general, been studied. (The units used in this table are $10^{-10}$ cm$^3$ mole$^{-1}$ s$^{-1}$ rather than $10^{-9}$ cm$^3$ mole$^{-1}$ s$^{-1}$, to amplify differences in reactivity.)

Table 9.1: A comparison of C$_4$H$_n^+$, C$_3$H$_n$N$^+$ and C$_3$H$_n$O$^+$ reactivities.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>H$_2^a$</th>
<th>CO$^a$</th>
<th>C$_2$H$_2^a$</th>
<th>HCN$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_4^+$</td>
<td>0.96$^{bc}$</td>
<td>4.5$^b*$</td>
<td>15$^d$</td>
<td>28$^d$</td>
</tr>
<tr>
<td>C$_4$H$^+$</td>
<td>1.5$^b$</td>
<td>4.7$^b*$</td>
<td>15$^d$</td>
<td>17$^d$</td>
</tr>
<tr>
<td>C$_4$H$_2^+$</td>
<td>&lt;0.005$^b$</td>
<td>0.32$^b*$</td>
<td>1.4$^d$</td>
<td>&lt;$0.2^d$</td>
</tr>
<tr>
<td>C$_4$H$_3^+$</td>
<td>&lt;0.005$^b$</td>
<td>0.013$^b*$</td>
<td>2.4$^d$</td>
<td>&lt;$0.5^d$</td>
</tr>
<tr>
<td>C$_4$H$_4^+$</td>
<td>&lt;0.005$^b$</td>
<td>&lt;0.005$^b$</td>
<td>1.2$^d$</td>
<td>&lt;$0.3^d$</td>
</tr>
<tr>
<td>C$_3$N$^+$</td>
<td>8.1</td>
<td>5.4$^*$</td>
<td>10.2</td>
<td>22</td>
</tr>
<tr>
<td>C$_3$HN$^+$</td>
<td>0.012</td>
<td>0.56$^*$</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>C$_3$H$_2$N$^+$</td>
<td>&lt;0.005</td>
<td>&lt;0.01</td>
<td>&lt;0.1</td>
<td>0.6$^*$</td>
</tr>
<tr>
<td>C$_3$H$_3$N$^+$</td>
<td>0.01</td>
<td>0.07$^*$</td>
<td>9.3</td>
<td>1.9</td>
</tr>
<tr>
<td>C$_3$H$_4$N$^+$</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.1</td>
<td>0.34$^*$</td>
</tr>
<tr>
<td>C$_3$O$^+$</td>
<td>8.0</td>
<td>0.72$^*$</td>
<td>10.8</td>
<td>29</td>
</tr>
<tr>
<td>C$_3$HO$^+$</td>
<td>&lt;0.005</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.04$^*$</td>
</tr>
<tr>
<td>C$_3$H$_2$O$^+$</td>
<td>&lt;0.005</td>
<td>&lt;0.01</td>
<td>4.3</td>
<td>1.9$^*$</td>
</tr>
<tr>
<td>C$_3$H$_3$O$^+$</td>
<td>&lt;0.005</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.02$^*$</td>
</tr>
</tbody>
</table>

Notes

a. Rate coefficient in units of $10^{-10}$ cm$^3$ mole$^{-1}$ s$^{-1}$. An asterisk indicates that the only reactive channel observed is association.
b. Reference 226.
c. at 300 K; $k = 4.1 \times 10^{-10}$ cm$^3$ mole$^{-1}$ s$^{-1}$ at 80K.
d. Reference 225.
General trends evident in these data are:

(i). Ions lacking terminal carbon atoms do not react rapidly with H₂.
(ii). Ions lacking terminal carbon atoms do not undergo efficient association with CO.
(iii). The radical cations C₃HN⁺, C₃H₃N⁺ and C₃H₂O⁺ are substantially more reactive than the non-radical cations C₃H₂N⁺, C₃H₄N⁺, C₃HO⁺ and C₃H₃O⁺.
(iv). For the C₄Hⁿ⁺ ions, radical cations are no more reactive than non-radical cations.

H-atom abstraction is predicted to be exothermic for the reactions of HC₃N⁺, C₃H₃N⁺ and C₃H₂O⁺; however, these reactions occur very slowly at room temperature. The failure of the reaction

\[
\text{C₃H₂O⁺ + H₂} \rightarrow \text{C₃H₃O⁺ + H·} \quad (9.1)
\]

\[\Delta H_{9,1} = -8 \text{ kJ mol}^{-1}\]

to proceed at a measurable rate may indicate that this reaction is endothermic: alternatively, in keeping with the low reactivity of HC₃N⁺ and C₃H₃N⁺ with H₂, reaction (9.1) may just be slow. An exothermic reaction may be slow due to an activation energy barrier (accompanied by a positive temperature dependence) or the formation of a weakly-bound collision complex which has a shorter lifetime than the time required for reaction to occur (often diagnosed by a negative temperature dependence: the reaction between C₄⁺ and H₂ appears to involve such a mechanism). A study of the variation of the rate of reaction (9.1) with
temperature, or with effective centre-of-mass energy, might indicate which of these factors is at work in this reaction.

The resonance forms most likely to contribute to the electronic structures of the ions $\text{C}_3\text{H}_n\text{N}^+$ and $\text{C}_3\text{H}_n\text{O}^+$ are shown in figures 9.1 and 9.2. These figures indicate that, as with the carbon cluster ions and their reaction products, only the terminal carbon atoms in these ions can possess significant carbene character, and only those ions with terminal carbon atoms have any resonance forms in which carbene character is evident (with the exception of $\text{HC}_3\text{O}^+$, for which one carbene form seems plausible). Other ions can be drawn in such a way that carbene character is present - for example, $\text{HC}_3\text{N}^+$ can be drawn as the structures $\text{H}^+\text{C}^+\text{C}==\text{N}:$ and $\text{H}^+\text{C}^-\text{C}==\text{N}$, but these forms are not expected to

---

**Figure 9.1:** Resonance forms of the ions $\text{C}_3\text{H}_n\text{N}^+$ ($n = 0 \rightarrow 4$).

- ($n = 0$) $\text{C}^+\text{C}==\text{N}$: $\leftrightarrow$ $\text{C}^+\text{C}==\text{N}+$ $\leftrightarrow$ $\text{C}^==\text{C}==\text{N}$
- ($n = 1$) $\text{H}^+\text{C}^==\text{C}==\text{N}^-$ $\leftrightarrow$ $\text{H}^+\text{C}^==\text{C}^==\text{N}^+$ $\leftrightarrow$ $\text{H}^+\text{C}==\text{C}==\text{N}^-$
- ($n = 2$) $\text{H}^+\text{C}==\text{C}==\text{N}^-$ $\leftrightarrow$ $\text{H}^+\text{C}==\text{C}==\text{N}^+$
- ($n = 3$) $\text{H}_2\text{C}==\text{C}==\text{N}^-$ $\leftrightarrow$ $\text{H}_2\text{C}==\text{C}==\text{N}^+$ $\leftrightarrow$ $\text{H}_2\text{C}==\text{C}==\text{N}^-$
- ($n = 4$) $\text{H}_2\text{C}==\text{C}==\text{N}^-$ $\leftrightarrow$ $\text{H}_2\text{C}==\text{C}==\text{N}^+$ $\leftrightarrow$ $\text{H}_2\text{C}==\text{C}==\text{N}^-$
contribute significantly to the character of the ion under thermal conditions, since they require the excitation of two \( \pi \) electrons into a non-bonding orbital. This is expensive in terms of energy requirements, and de-excitation is likely to be facile since the positive charge in these forms is localised on the neighbouring C atom, inviting the re-formation of the missing \( \pi \) bond:

\[
\begin{align*}
\text{H-} & \ddagger \text{C-} \underset{\ddagger}{\text{C}}=\text{C=N}; \quad \rightarrow \quad \text{H-} \ddagger \text{C}=\ddagger \text{C}=\text{C=N}; \quad (9.2a) \\
\text{H-} & \ddagger \text{C}=\ddagger \text{C}=\text{N}; \quad \rightarrow \quad \text{H-} \ddagger \text{C}=\text{C}=\ddagger \text{C}=\text{N}; \quad (9.2b).
\end{align*}
\]

Figure 9.2: Resonance forms of the ions \( \text{C}_3\text{H}_n\text{O}^+ \) (\( n = 0 \rightarrow 3 \)).

\[
\begin{align*}
(n = 0) \quad & \text{C}=\text{C}-\ddagger \text{C}=\ddagger \text{O}^+ \quad \leftrightarrow \quad \ddagger \text{C}=\text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad :\ddagger \text{C}-\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
\leftrightarrow \quad & :\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad :\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad :\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
\leftrightarrow \quad & :\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad :\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
(n = 1) \quad & \text{H-} \ddagger \text{C}=\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H-} \ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H-} \ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
\leftrightarrow \quad & \text{H-} \ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
(n = 2) \quad & \text{H}_2\text{C}=\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H}_2\text{C}=\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H}_2\text{C}=\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
\leftrightarrow \quad & \text{H}_2\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H}_2\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H}_2\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
\leftrightarrow \quad & \text{H}_2\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O}; \\
(n = 3) \quad & \text{H}_2\text{C}=\text{CH}-\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H}_2\text{C}=\text{CH}-\ddagger \text{C}=\ddagger \text{O}; \quad \leftrightarrow \quad \text{H}_2\ddagger \text{C}=\ddagger \text{C}=\ddagger \text{O};
\end{align*}
\]
In addition to those structures shown in figure 9.1, the diradical resonance forms $\cdot\text{C}≡\text{C}≡\text{N}·$, $\cdot\text{C}≡\text{C}≡\text{C}≡\text{N}·$ and $\cdot\text{C}≡\text{C}≡\text{N}·$ may also contribute to the reactivity of the C$_3$N$^+$ ion: Harland and Maclagan$^{259}$ have calculated that the lowest-lying triplet state of CCCN$^+$ is only 4 kJ mol$^{-1}$ above the ground (singlet) state, although this energy difference neglects the effect of vibrational and rotational internal energy. When vibrational and rotational effects are considered, the triplet state is 28 kJ mol$^{-1}$ above the singlet state at 298K.$^{259}$

In table 9.1, only the ions with terminal C atoms react rapidly with H$_2$. The reactivity of the C$_3$H$_n$N$^+$ and C$_3$H$_n$O$^+$ ions with H$_2$ can thus be rationalised as occurring most efficiently via a mechanism of carbene insertion into the H-H bond: such a mechanism also accounts for the observed trends in hydrocarbon ion reactivity with H$_2$.$^{226,364}$ Similarly, the trend in C$_3$H$_n$N$^+$/C$_3$H$_n$O$^+$ reactivity with CO can be explained by a carbene model: carbene addition to CO is seen to occur efficiently according to the results in table 9.1. An alternative and more mechanistic viewpoint is that the ions having carbene character form more stable and hence longer-lived 'tight' collision complexes with CO, increasing the probability of collisional stabilisation before complex fragmentation can occur.

Ions with carbene character may react with HCN and with C$_2$H$_2$ via C-H bond insertion or via carbene addition to the C≡C or C≡N groups. Either mechanism permits the formation of a cyclic reactive intermediate. Such an intermediate has been invoked by Bohme$^{29,271,329}$ to explain the observed products from reactions of the carbene ions C$_3$H$^+$ and C$_4$N$^+$ with the neutrals CH$_4$, NH$_3$, H$_2$O and H$_2$S, and the formation of a cyclic reactive intermediate may explain the loss of CO in several reactions of C$_3$O$^+$. C$_3$O$^+$ also has parallels with the reactivity of
C$_3$H$^+$ and C$_4$N$^+$ (see figure 9.3) since product channels common to reaction with
CH$_4$, NH$_3$ and H$_2$O differ from those seen in the reactions with HCN and C$_2$H$_2$. In
common with the C$_3$H$^+$ and C$_4$N$^+$ reactions depicted in figure 9.3, the reactions
of C$_3$O$^+$ are better described by a mechanism involving carbene X–H bond
insertion than by a scheme involving addition to the C≡X group. The loss of CO
as the dominant product channel of the reactions with HCN and C$_2$H$_2$ is more
conveniently explained by formation of the cyclic intermediate

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{X}
\end{array}
\quad (X = \text{C$_2$H, CN})
\]

resulting from C–H bond insertion than by formation of the structure

\[
\begin{array}{c}
\text{H} \\
\text{O=}_C\text{C=}_C\text{Y} \\
\text{Y}
\end{array}
\quad (Y = \text{CH, N})
\]

which would result from carbene attack at the triple bond: loss of CO from the
latter structure would give a cyclic product ion

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{Y}
\end{array}
\quad (Y = \text{CH, N})
\]

as the initial product. The heats of formation of these cyclic ions are not known:
they are likely to have considerably higher $\Delta$H$_f$ than the linear ions HCCCH$^+$
and HCCCN$^+$, and thus it is quite possible that the production of the above cyclic
product ions is endothermic in these reactions.
Figure 9.3: A comparison of the reactivity of $C_3O^+$ with the carbene cations $C_3H^+$ and $C_4N^+$. The reactions shown do not completely describe the reactivity of these cations: reaction types shown are, rather, those which are most effectively described in terms of a carbene $\sigma$ bond insertion mechanism.

(a). Reaction channels observed for reaction of $C_3H^+$, $C_4N^+$ ($R = H, CN$) with the neutral $H-X$.\textsuperscript{271,329-331}

\[ R-\overset{+}{C}=C=H + H-X \quad \rightarrow \quad R-\overset{+}{C}=C=H_X \]

(i). $X = CH_3, NH_2, OH, SH.$
\[ \rightarrow \quad H-C=C=R + :CX^+ \]

(ii). $X = CN, C_2H, C_4N; (X = H, R = H)$
\[ \rightarrow \quad R-\overset{+}{C}=C=C_X \]

(iii). ($R = CN$). $X = H, CH_3, C_2H, C_4H, NH_2, SH.$
\[ \rightarrow \quad X-C=C=C+: + H-R \]

(b). Reaction channels observed for reaction of $C_3O^+$ with the neutral $H-X$.

\[ O=C-C=C^+ + H-X \quad \rightarrow \quad O=C-C=C_X \]

(i). $X = H, CH_3, NH_2, OH.$
\[ \rightarrow \quad O=C=C=CH^+ + X \]

(ii). $X = C_2H, NH_2.$
\[ \rightarrow \quad O=C-C=C^+ \]

(iii). $X = C_2H, CN.$
\[ \rightarrow \quad X-C=C=H^+ + CO \]
The reaction products from C$_3$N$^+$ can also be explained in terms of carbene reaction mechanisms. The most commonly observed product channels with neutrals of the type H–X are H-atom abstraction (seen with X = H, CH$_3$, OH, CN), X-group abstraction (seen with X = CH$_3$, C$_2$H, OH) and adduct formation (seen with X = H, C$_2$H, CN, and with the neutrals N$_2$, CO and C$_2$N$_2$). Carbene H–X insertion followed by X loss can adequately account for production of HCCCN$^+$ in several reactions (the formation of this isomer is assumed: no other C$_3$HN$^+$ isomers have been reported in the literature). Alternatively, a simple one-step abstraction mechanism can account for HCCCN$^+$ production. O-atom abstraction in the reactions with O$_2$ and CO$_2$ can satisfactorily be attributed to carbene reactivity

\[
\text{N}=\text{C}^+\text{C}=\text{C}^+ + \text{O}=\text{X} \rightarrow \text{N}=\text{C}^+\text{C}=\text{O}^+ + :\text{X} \quad (9.3);
\]

similarly, such double-bond formation might also account for the adduct formation observed with the normally unreactive neutral N$_2$:

\[
\text{N}=\text{C}^+\text{C}=\text{C}^+ + :\text{N}=\text{N}^+ \rightarrow \text{N}=\text{C}^+\text{C}=\text{N}^+=\text{N}^+ \quad (9.4).
\]

Several canonical forms of this possible structure for the adduct ion can be drawn. The formation of HCNH$^+$ in the reactions with H$_2$O and NH$_3$ cannot easily be explained by a mechanism involving carbene insertion or addition reactions, without the occurrence of substantial rearrangement within the collision complex. These reactions might more satisfactorily be interpreted in terms of nitrene reactivity (a nitrene is a univalent nitrogen with four nonbonding electrons), although a degree of rearrangement is still required.
However, the canonical forms of C$_3$N$^+$ displayed in figure 9.1 suggest that C$_3$N$^+$ does not possess significant classical nitrene character.

HCN and C$_2$H$_2$ are more reactive neutrals than H$_2$ or CO (as is evident from the large rates observed for their reactions with many ions),$^{182}$ so it is reasonable that ions without carbene character may also undergo reasonably rapid reaction with these neutrals. Table 9.1 indicates that reactions of C$_3$H$_n$N/O$^+$ ions with HCN and C$_2$H$_2$ are reasonably rapid ($k > 1.0 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$) if the ions possess terminal C atoms, or are radicals. Ions which do not fulfil either of these criteria are not observed to react significantly with C$_2$H$_2$ or with HCN, although a slow association channel may be evident. This pattern of reactivity is not reflected in the reactions of C$_4$H$_n^+$ with these neutrals, however: in these reactions only the ions featuring terminal C atoms are observed to react rapidly with HCN, and rates for reaction with C$_2$H$_2$ are also substantially lower for $n \geq 2$ than for $n = 0$ or 1. A possible explanation for this difference is that the reactions of these hydrocarbon ions with C$_2$H$_2$ and HCN have only been studied using the ICR technique, and thus channels which require a degree of rearrangement would be expected to occur with reduced efficiency under conditions which are less conducive to the formation of reasonably long-lived collision complexes. A SIFT study of these reactions would hopefully resolve this issue.

Finally, the observation that the most reactive polyatomic carbon-containing ions are highly unsaturated linear ions with terminal C atoms seems very relevant to the chemical evolution of cold interstellar clouds. The abundance of highly unsaturated linear molecules in these clouds, the relative scarcity of double bonds as opposed to alternating single and triple bonds, and the complete
absence of branched-chain compounds are all observational constraints which suggest that the production of highly unsaturated compounds is somehow kinetically favoured (although it should be noted that observations of interstellar molecules are biased towards the detection of linear, unsaturated species since these have the simplest rotational spectra): the rather sketchy exploration of ion reactivity in this chapter supports the notion that ion-molecule reactions can account for the higher efficiency of production of these very unsaturated compounds.
CHAPTER 10.
A SUMMARY.

Section 10.1: Overall conclusions.

Thermochemical values determined in the present work are summarised in table 10.1.

The proton affinities of $C_2N_2$ and $C_4H_2$ were determined by measurement of the reaction rates for proton transfer between bases of similar PA (CH$_3$Cl and C$_2$H$_4$ with C$_2$N$_2$, and BrCN and CH$_3$NO$_2$ with C$_4$H$_2$). The value of PA($C_2N_2$) (674 kJ mol$^{-1}$) thus obtained is in very good agreement with previous determinations, but our value of PA($C_4H_2$) (741 kJ mol$^{-1}$, which is supported by several other studies) is in serious disagreement with the accepted literature value of this quantity.

Studies of the reactivity of the CCN$^+$ and CNC$^+$ isomers, produced by a variety of techniques, have established that the higher-energy CCN$^+$ isomer is more reactive with a variety of neutral reagents. This finding is in keeping with the study of $C_2N^+$ reactivity performed independently by Bohme et al.$^{245}$ The isomeric ratio CCN$^+$:CNC$^+$ (~1:4), for $C_2N^+$ produced by electron impact ionisation upon each of several source gases within the SIFT ion source, is very close to the calculated ratio of rovibrational states for CCN$^+$:CNC$^+$ at the saddle-point energy (using parameters calculated by DeFrees and MacLean$^{241}$): this close
similarity in values is explained in terms of the competition between unimolecular rearrangement (isomerisation) and bimolecular collisional deexcitation of the C$_2$N$^+$ ions. At low pressures, the rate of isomerisation is fast compared to the rate of quenching and so the observed isomeric ratio should adhere closely to the density-of-states ratio at the saddle-point energy. For C$_2$N$^+$

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Comments</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA(CH$_3$Cl)</td>
<td>673 ± 4 kJ mol$^{-1}$</td>
<td>referenced to PA(C$_2$H$_4$)</td>
<td>3</td>
</tr>
<tr>
<td>PA(C$_2$N$_2$)</td>
<td>674 ± 4 kJ mol$^{-1}$</td>
<td>referenced to PA(C$_2$H$_4$)</td>
<td>3</td>
</tr>
<tr>
<td>PA(BrCN)</td>
<td>747 ± 4 kJ mol$^{-1}$</td>
<td>referenced to PA(CH$_3$NO$_2$)</td>
<td>3</td>
</tr>
<tr>
<td>PA(C$_2$H$_2$)</td>
<td>741 ± 6 kJ mol$^{-1}$</td>
<td>referenced to PA(CH$_3$NO$_2$)</td>
<td>3</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_2$O)</td>
<td>≤ 661 kJ mol$^{-1}$</td>
<td>from reaction CCCN$^+$ + H$_2$O</td>
<td>4</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$NO$^+$)</td>
<td>≤ 1567 kJ mol$^{-1}$</td>
<td>from reaction CCCN$^+$ + CO$_2$</td>
<td>4</td>
</tr>
<tr>
<td>$\Delta$H$_2$(HNC$^+$)</td>
<td>≤ 1373 kJ mol$^{-1}$</td>
<td>from HCN$^+$ + CO $\rightarrow$ HNC$^+$ + CO</td>
<td>5</td>
</tr>
<tr>
<td>PA(CN)</td>
<td>≥ 595 kJ mol$^{-1}$</td>
<td>from HCN$^+$ + CO $\rightarrow$ HNC$^+$ + CO</td>
<td>5</td>
</tr>
<tr>
<td>$\Delta$H$_2$(HNCN$^+$)</td>
<td>≤ 471 kJ mol$^{-1}$</td>
<td>from reaction HNC$^+$ + N$_2$O</td>
<td>5</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_5$H$_2$N$^+$)</td>
<td>≤ 1247 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_3$N$^+$ + C$_2$H$_2$</td>
<td>6</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$H$_2$N$^+$)</td>
<td>≤ 561 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_3$N$^+$ + NH$_3$</td>
<td>6</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_5$H$_4$N$^+$)</td>
<td>≤ 1177 kJ mol$^{-1}$</td>
<td>from reaction HCN$^+$ + CH$_2$CHCN</td>
<td>6</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_5$O$^+$)</td>
<td>≥ 1252 kJ mol$^{-1}$</td>
<td>from reaction C$_5$O$^+$ + H$_2$O</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$HO)</td>
<td>≤ 299 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_2$O$^+$ + NH$_3$</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$HO$^+$)</td>
<td>≤ 1268 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_2$O$^+$ + C$_2$H$_2$</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$O$^+$)</td>
<td>≤ 1203 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_2$O$^+$ + C$_2$H$_2$</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$HO$^+$)</td>
<td>≤ 985 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_2$O$^+$ + C$_2$H$_2$</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$HO$^+$)</td>
<td>≤ 1203 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_2$O$^+$ + C$_2$H$_2$</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$H$_2$O$^+$)</td>
<td>≤ 1012 kJ mol$^{-1}$</td>
<td>from reaction C$_3$H$_2$O$^+$ + CH$_3$CH</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta$H$_2$(C$_3$O$_2$$^+$)</td>
<td>≤ 709 kJ mol$^{-1}$</td>
<td>from reaction C$_3$O$_2$$^+$ + CH$_4$</td>
<td>7</td>
</tr>
<tr>
<td>PA(C$_3$O$_2$)</td>
<td>≥ 727 kJ mol$^{-1}$</td>
<td>from reaction C$_3$O$_2$$^+$ + CH$_4$</td>
<td>7</td>
</tr>
</tbody>
</table>

Notes

a. assuming a ± 2 kJ mol$^{-1}$ uncertainty in PA(CH$_3$NO$_2$).
b. NCCCO$^+$ is the most probable structure of this ion.
c. HCCCCCNH$^+$ is the structure ascribed to this ion.
d. The structure of this species is not known.
e. CCCO$^+$ is the most probable structure of this ion.
f. HCCCO$^+$ is the structure ascribed to this species.
g. CCCCO$^+$ is the structure ascribed to this ion.
h. HCCCCCO$^+$ is the structure ascribed to this ion.
i. OCCCCOH$^+$ is the structure ascribed to this ion.
produced by the reaction of C+ with C2N2, ~10% of the C2N+ produced is the higher-energy isomer. Production of CCN+ from ground-state C+ is endothermic, but can be accounted for if some fraction of the C+ undergoing reaction is metastably excited.

In contrast to the observation that the higher-energy isomer of C2N+ is the more reactive form, extensive studies of C3N+ reactivity have established that the lowest-energy isomer (CCCN+) is substantially more reactive than a higher-energy form (which we believe to be a cyclic isomer, in accordance with the theoretical and experimental study by Harland and Maclagan). The most abundant form of C3N+ (which accounts for at least 90% of the C3N+ ion signal formed by electron impact upon HC3N or upon C4N2) is seen to react much more rapidly with several neutral reagents than does a less abundant isomer. The most abundant isomer is CCCN+ since this is the ion structure most likely to arise from electron impact upon HCCCN or NCCCCN. This isomer is the lowest-energy form of C3N+ according to Maclagan's calculations and according also to the observation that the predominant C3N+ ion formed by several chemical ionisation reactions (within the flow tube) has identical reactivity to CCCN+: the C3N+ product of these chemical ionisation reactions is not constrained to have the CCCN+ structure, and the fact that this isomer predominates for C3N+ formed in this fashion indicates that CCCN+ is the lowest-energy isomer. The lack of reactivity of c-C3N+ is not completely understood, but indicates that there may be substantial activation energy barriers inhibiting many reactions of this ion.
CHN$^+$ produced by electron impact ionisation upon HCN produces HCN$^+$ and HNC$^+$ in a ratio of approximately 3:1. Many previous theoretical and experimental studies have demonstrated that HCN$^+$ is the higher-energy isomer: our studies of CHN$^+$ reactivity unearthed two reactions in which HCN$^+$ was converted to HNC$^+$, which we explain by a mechanism involving forth-and-back proton transfer. Isomerisation of HCN$^+$ to HNC$^+$ in this manner is expected to be the dominant product channel for all bimolecular reactions HCN$^+$ + X for which \( 518 < \text{PA}(X) < 595 \text{ kJ mol}^{-1} \), these limits representing the values for \( \text{PA(CN)} \) and \( \text{PA(CN)} \) respectively.

Isomerism was investigated in the CH$_2$N$^+$ system, but was not detected. The absence of any evidence of the higher-energy isomer, CNH$_2^+$, demonstrates either that none of the diagnostic reactions employed in this study succeed in distinguishing CNH$_2^+$ from HCNH$^+$, or that none of the ion generation techniques produce substantial amounts of CH$_2$N$^+$ in the CNH$_2^+$ form. An explanation for the possible failure of some diagnostic reactions is that they serve to isomerise CNH$_2^+$ to HCNH$^+$, by a forth-and-back mechanism such as was used to explain the isomerisation of HCN$^+$ to HNC$^+$. Further studies on this system will be required to resolve these issues.

Reactions of HCN$^+$ with CF$_4$, and HCNH$^+$ with CCl$_4$, exhibit product channels in apparent conflict with literature values for the heats of formation of reactants and products in these systems.$^{184}$ These observations can be rationalised (i) by the assumption that the literature values for the heats of formation of CF$_3^+$ and of CCl$_3^+$ are in error, (ii) by the assumption that these two reactions may represent 'entropy-driven' processes - that is, they are endothermic but exergonic,
or (iii) by the assumption that weakly-bound van der Waal's complexes are formed in these reactions, rather than the ionic and neutral products assigned in the present work. Further studies are required to determine which of these cases applies to each of these reactions.

The ions C\textsubscript{3}H\textsubscript{3}N\textsuperscript{+} and C\textsubscript{3}H\textsubscript{4}N\textsuperscript{+} derived from acrylonitrile were seen to have an interesting and varied ion-molecule chemistry in the laboratory. An equally varied chemistry in interstellar clouds is expected providing that both species are unreactive with H\textsubscript{2} as suggested by our SIFT studies: if this is so, then their reactions with trace cloud components will be of significance to models of interstellar chemistry.

Ion-molecule reactions of acrylonitrile were seen to produce HC\textsubscript{3}NH\textsuperscript{+} and HC\textsubscript{5}NH\textsuperscript{+}, suggesting at least a tenuous link between the cloud chemistry of acrylonitrile and that of the cyanopolyynes. In this regard, several reactions of HC\textsubscript{3}N\textsuperscript{+} and HC\textsubscript{3}NH\textsuperscript{+} were also studied, with some parallels evident between the reactivity of HC\textsubscript{3}N\textsuperscript{+} and C\textsubscript{3}H\textsubscript{3}N\textsuperscript{+}, and between HC\textsubscript{3}NH\textsuperscript{+} and C\textsubscript{3}H\textsubscript{4}N\textsuperscript{+}. Production of protonated cyclopropenyldiene in several reactions is also of interest for ion-molecule models of cloud chemistry.

Studies on the reactivity of the ions C\textsubscript{3}H\textsubscript{n}O\textsuperscript{+} (n=1 to 3), undertaken as part of an investigation into the interstellar chemistry of ions related to C\textsubscript{3}O and HC\textsubscript{3}HO, indicated that these three ions are remarkably unreactive with the most abundant interstellar molecules. This observation supports the notion that dissociative recombination of these ions should provide an efficient source of tricarbon monoxide and propynal within dense interstellar clouds.
The rôle of translationally excited OH· (produced by dissociative recombination of H3O+ and HOCO+) within dense interstellar clouds was evaluated, with results which can be extended to reactions of any translationally excited radicals within cold clouds. This translational energy is very inefficient in promoting chemical processes within cold interstellar clouds, because the chemically interesting fragments (i.e., those heavier than H· or H2) of dissociative recombination reactions possess little of the total translational energy released by recombination. In addition, the centre-of-mass collision energy for collision of such a fragment with a cold H2 molecule is very much less than the fragment's translational energy, and this collision energy is not likely to exceed the activation energy barrier for a radical-H2 reaction. In consequence, the translational energy released by recombination of most positive ions is able only to be thermalised by collision. Possible exceptions to this rule are when the dissociative recombination yields two molecular fragments of comparable mass - for example, the production of OH· + CO from HOCO+ + e. The dissociative recombination of HOCO+ should thus have an effect on the production of H2O in cold clouds, although this effect is likely to be slight when compared to the dominant H2O production processes.

Reactions of the ions C3HnN+ (n = 0 - 4) and C3HnO+ (n = 0 - 3) were compared to the reactions of C4Hn+ (n = 0 -4) with H2, CO, C2H2 and HCN. These studies showed that ions containing bare terminal carbon atoms were substantially more reactive than ions lacking bare terminal carbon atoms, in keeping with a model explaining such differences in reactivity by the presence of carbene character in ions featuring bare terminal C atoms. For the ion series C3HnN+ and C3HnO+,
radical ions were also found to be more reactive than non-radical ions, although this pattern of reactivity was not apparent in the reported reactions of \( \text{C}_4\text{H}_n^+ \).

**Section 10.2: Suggestions for further work.**

Modifications to the Canterbury SIFT in the near future should allow further exploration of many facets of the present work.

The first such modification, the inclusion of a drift region in the SIFT, will permit a more detailed study of energetics of several types of processes. Drift experiments could determine the barriers to isomerisation for the isomeric systems \( \text{C}_2\text{N}^+ \), \( \text{C}_3\text{N}^+ \) and \( \text{CHN}^+ \). Acceleration of the reactant ions by application of a voltage gradient should result in the internal partitioning of energy in the reactant ions sufficient to overcome such isomerisation barriers; two thresholds should be apparent. The first threshold arises when the higher-energy isomer possesses sufficient internal energy to isomerise, resulting in severe depletion of this higher-energy isomer; the second threshold arises when the lower-energy isomer has sufficient energy to isomerise, resulting in the production of an equilibrium in which the isomeric ratio reflects the density-of-states ratio at this barrier height. Care with such experiments would be necessary to ensure that the titration reaction used to identify the isomeric ratio is able to distinguish between the drift-accelerated isomers, whose reactivity will differ from that exhibited by the thermalised isomers.
Another application of the drift technique which should prove useful is in the examination of H-atom abstraction reactions from $\text{H}_2$. Brown et al.\textsuperscript{41} have postulated that such reactions are inhibited by a slight barrier, and many such reactions reported in the present work are observed to occur slowly if at all despite their exothermicity. An exploration of the energetic factors involved would help in the modelling of such reactions as they relate to the chemical evolution of interstellar clouds. Of the reactant ions studied in the present work, c-C$_3$N$^+$, HC$_3$N$^+$, HC$_3$NH$^+$, C$_3$H$_3$N$^+$, C$_3$HO$^+$, C$_3$H$_2$O$^+$, C$_3$H$_3$O$^+$, C$_3$O$_2^+$ and C$_4$N$_2^+$ were found to react very slowly (if at all) with $\text{H}_2$ at room temperature. A study of these reactions in a SIFDT apparatus is recommended. A study of these reactions at varying temperatures, especially below 300 K, should also prove helpful in examining the possible reactivity of these ions under interstellar conditions. The addition of a variable-temperature jacket, permitting the study of reactions over the temperature range 80 K - 550 K, is planned for the Canterbury SIFT.

Further examinations of the isomeric systems CCCN$^+$ / c-C$_3$N$^+$ and HCNH$^+$/CNH$_2^+$ are also recommended. It is desirable to find a source gas giving a sufficiently pure signal of c-C$_3$N$^+$ to permit determination of the product channels for reactions of this ion: as suggested in chapter 4, a cyclic compound such as azetidine may be a suitable source gas. Additional studies of the CH$_2$N$^+$ system may reveal the reactivity of the proposed interstellar ion CNH$_2^+$. Efforts in this direction should involve the study of further CH$_2$N$^+$ generating methods and diagnostic reactions.
SIFT study of the reactions of C₄Hₙ⁺ (n = 0 - 4) with HCN and C₂H₂ is relevant to the comparison of C₄Hₙ⁺, C₃HₙN⁺ and C₃HₙO⁺ reactivity outlined in chapter 9. These C₄Hₙ⁺ reactions have only been studied using the ICR technique and thus product channels involving association, or rearrangement of partially stabilised collision complexes, might not have been apparent in these ICR studies.

Recent reports suggest that radical-molecule processes are a major source of interstellar nitriles such as acrylonitrile, but further work is necessary on such reactions to determine whether they do indeed lack activation energy barriers. Similarly, further experimental investigations, and refinement of theoretical treatments of such processes as dissociative recombination and radiative association, will reduce current uncertainties concerning the relationship between CH₂CHCN and the C₃HₙN⁺ ions which can be generated from acrylonitrile.

Some preliminary efforts to study ion-atom reactions (of X⁺ with H⁺, O, N⁺ and ultimately C) were made during the present work, using a microwave discharge to dissociate reactant molecules. The results of these studies were inconclusive and are therefore not presented here, but further studies of such ion-atom reactions would be of great significance in the modelling of interstellar chemistry, especially since neutrals such as H⁺, O and C are expected to be relatively abundant within interstellar clouds. In particular, the reaction

\[
\text{H}_3^+ + \text{C} \rightarrow \text{CH}^+ + \text{H}_2 \quad (10.1)
\]

\[\Delta H_{10.1} = -101 \text{ kJ mol}^{-1}\]
is very important in models of interstellar chemistry, since C is about as abundant as CO within some cloud regions. This reaction, which is presumed to occur rapidly, is a major loss process for H$_3^+$ and an important step in the synthesis of the methyl ion CH$_3^+$: an experimental study of this reaction would be very valuable.

Studies of reactions of many ions with O would also be useful, since atomic oxygen is thought to be responsible for the destruction of several reactive species within interstellar clouds and as such may limit the developing molecular complexity.

A refinement of the dissociative technique employed for ion-atom reactions would also allow study of ion-radical reactions of interest in interstellar cloud modelling: the reactions of ions with radicals such as CN·, OH·, CH$_3$· and C$_2$H· have not been studied experimentally.

A study of the reaction of H$_2$ with OH· produced from dissociative recombination of HOCO$^+$ would assist in testing the hypothesis, presented in chapter 8, that such reactions may be of relevance to interstellar chemistry. Such verification is likely to be difficult, however, in view of the low efficiency predicted for the production of H$_2$O by reaction following HOCO$^+$ recombination, and SIFT studies are not likely to be of much assistance in this endeavour. Experiments using a FALP-LIF apparatus may be more helpful in this respect, as discussed in chapter 8.
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APPENDIX.

Computer programs.

Program "HELLO"

10 REM ** HELLO **
40 CD$ = CHR$ (13) + CHR$ (4)
50 PRINT CHR$ (4); "PR#3"
55 TEXT
60 HOME: PRINT: VTAB (10): HTAB (10): PRINT "ENSURE YOUR PROGRAM DISC IS IN DRIVE 1"
70 HTAB (10): PRINT "AND YOUR DATA DISC IN DRIVE 2 BEFORE PROCEEDING"
80 PRINT: PRINT: HTAB (10): PRINT "(Press any key when ready)");: GET K1$
90 PRINT CD$; "RUN OPTIONS,D1"
Program "OPTIONS"

10    REM ** PROGRAM OPTIONS **
20    DIM OPST$ (10)
30    CD$ = CHR$ (13) + CHR$ (4)
40    TEXT
50    PRINT CHR$ (4); "PR#3"
90    OPST$(1) = "COLLATE DATA INTO DATA FILE": REM to be replaced by automatic data collection option.
92    OPST$(2) = "RESET THE CURRENT FILENAMES"
94    OPST$(3) = "CALCULATE A RATE CONSTANT"
96    OPST$(4) = "CALCULATE TWO OR MORE RATE CONSTANTS"
98    OPST$(5) = "DISPLAY A PRODUCT RATIO"
100   OPST$(6) = "EXAMINE OR EDIT A FILE"
102   OPST$(7) = "MONITOR PRESSURE"
120   NC% = 8
125   OPST$(NC%) = "QUIT"
130   HOME: PRINT "MAKE A CHOICE:"; PRINT "---- - ------": PRINT
140   FOR I = 1 TO NC%
150   HTAB (10): PRINT ";"; OPST$(I); PRINT
160   NEXT
170   PRINT : PRINT "Enter an option (1-"; NC%; "); ";
180   GET K$: OP% = ASC (K$) - 48: IF OP% < 1 OR OP% > NC% GOTO 180
190   PRINT OP%; ". "; OPST$(OP%)
200   PRINT "Sure about that? (Y/N): ";
201   GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 201
203   PRINT KS$: IF KS$ = "N" GOTO 130
205   HOME
210   IF OP% = 1 THEN PRINT CD$; "RUN MEANFLOWS,D1"
220   IF OP% = 2 THEN PRINT CD$; "RUN SETFILES,D1"
230   IF OP% = 3 THEN PRINT CD$; "RUN RASCAL,D1"
240   IF OP% = 4 THEN PRINT CD$; "RUN MULE,D1"
250   IF OP% = 5 THEN PRINT CD$; "RUN PROD RAT,D1"
260   IF OP% = 6 THEN PRINT CD$; "RUN STUDYFILES,D1"
270   IF OP% = 7 THEN PRINT CD$; "RUN PRESSMONITOR,D1"
490   PRINT
500   END
Program "MEANFLOWS"

100 GOSUB 1000
110 REM initialise program
200 GOSUB 2000
210 REM average flow measurements
300 GOSUB 3000
310 REM input ion counts
400 GOSUB 4000
410 REM write file
500 PRINT CD$; "RUN OPTIONS,D1"
600 END

1000 REM * INITIALISE PROGRAM *
1010 CD$ = CHR$(13) + CHR$(4)
1020 DIM FM(400): DIM X(40): DIM Y(40,6)
1030 TF% = 0: CF% = 1
1035 BLANK$ = " "
1040 PRINT CHR$(4); "PR#3"
1050 INPUT "ENTER RUN NUMBER ? (1-30): "; RN$: NM$ = "FLOWFILE" + RN$
1060 PRINT CD$; "OPEN "; NM$; ";D2"
1070 PRINT CD$; "READ "; NM$
1080 INPUT NF%
1090 FOR I = 1 TO NF%
1100 INPUT FM(I)
1110 NEXT
1120 PRINT CD$; "CLOSE "; NM$
1130 FOR I = 1 TO 40
1140 X(I) = 0
1150 FOR J = 1 TO 6
1160 Y(I,J) = 0
1170 NEXT
1180 NEXT
1260 L$ = "L": M$ = "M": S$ = "S"
1270 HOME: PRINT "VOLUME SCALE FACTORS:": PRINT "-------- ---- -------": PRINT :
1300 INPUT "Smallest volume? (cm^3): "; SV
1310 INPUT "Largest volume? (cm^3) <0 to quit>: "; LV: IF LV < SV THEN L$ = "S"
1320 IF L$ = "S" THEN M$ = "S"
1330 IF M$ = "M" THEN INPUT "Medium volume? (cm^3) <0 to quit>: "; MV: IF MV < SV THEN M$ = "S"
1340 IF L$ = "L" THEN LS = LV / SV
1350 IF M$ = "M" THEN MS = MV / SV
1360 PRINT : PRINT : PRINT
1400 IF L$ = "L" THEN PRINT "Large vol. scale factor = "; INT (1000 * LS + 0.5) / 1000
1410 IF M$ = "M" THEN PRINT "Medium vol. scale factor = "; INT (1000 * MS + 0.5) / 1000
1420 PRINT : PRINT "Any changes? (Y/N): ";
1430 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 1430
1440 PRINT KS$: IF KS$ = "Y" GOTO 1260
1500 RETURN

2000 REM * AVERAGE THE FLOW MEASUREMENTS *
2010 TF% = TF% + 1: HM% = 0: PF = 0
2020 HOME: PRINT "Flow ": TF%: ": PRINT "--------": PRINT
2030 FOR J = 1 TO (17 - HM%)
IF CF% + J > NF% GOTO 2060
VTAB (6 + HM% + J): PRINT CF% + J", "FM(CF% + J)
NEXT
VTAB (HM% + 3): PRINT HM% + 3", "FM(CF%)": POKE 1403,40: PRINT "Include this? (Y/N): ";
GET KS$: IF KS$ < "Y" AND KS$ < "N" GOTO 2010
PRINT KS$: IF KS$ = "Y" THEN HM% = HM% + 1:PF = PF + FM(CF%)
CF% = CF% + 1
VTAB (HM% + 3): PRINT "More measurements for this flow? (Y/N): ";
GET KS$: IF KS$ < "Y" AND KS$ < "N" GOTO 2150
PRINT KS$: IF KS$ = "Y" THEN HM% = HM% + 1:PF = PF + FM(CF%)
FOR X = (HM% + 6) TO 23
VTAB (X): PRINT BLANK$;BLANK$
NEXT
IF KS$ = "L" THEN PF = PF * LS
IF KS$ = "M" THEN PF = PF * MS
IF PF < 1E - 05 THEN X(TF%) = 0: GOTO 2200
X(TF%) = PF / HM%:LX% = 3 - INT ( LOG (X(TF%)) / LOG (10))
X(TF%) = INT (X(TF%) * (10 ^ LX%) + 0.5) / (10 ^ LX%)
PRINT : PRINT "This flow value is ",X(TF%)
PRINT: PRINT "More flows yet? (Y/N): ";
GET KS$: IF KS$ < "Y" AND KS$ < "N" GOTO 2410
PRINT KS$: IF KS$ = "Y" GOTO 2010
RETURN
3000 REM * INPUT ION SIGNALS *
PT$ = TF%
3020 HOME: PRINT "INPUT ION SIGNALS: ": PRINT "----- -- -----": PRINT
3030 PRINT "How many ion masses? (1-6): ";
3040 GET KS$:MAX = ASC (KS$) - 48: IF MAX < 1 OR MAX > 6 GOTO 3040
3050 PRINT KS$
3060 FOR I = 1 TO MAX
3070 HOME: PRINT "$ION #";I;":": PRINT "$------": PRINT
3080 FOR I = 1 TO PTS
3090 PRINT I; ";";INT (X(I) * 10000 + 0.5) / 10000: POKE 1403,25
3100 INPUT "Count? ";Y(I,J)
3110 NEXT
3120 NEXT
3500 RETURN
4000 REM * WRITE DATA FILE *
4010 HOME: PRINT "WRITE DATA FILE: ": PRINT "----- ---- ----": PRINT
4020 INPUT "Filename? <NONE to quit> ";SF$: IF SF$ = "N" OR SF$ = "NONE" THEN RETURN
4030 PRINT : PRINT "Writing data file ";SF$;" now ...
4040 PRINT CD$:"OPEN ";SF$","D2"
4050 PRINT CD$:"WRITE ";SF$"
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4070 PRINT MAX
4080 FOR I = 1 TO PTS
4090 FOR J = 1 TO MAX
4100 PRINT Y(I,J)
4110 PRINT X(I)
4120 NEXT
4130 NEXT
4140 PRINT CD$;"CLOSE ";SF$
4150 PRINT CD$;"OPEN FILENAMES,D2"
4160 PRINT CD$;"READ FILENAMES"
4170 INPUT DF$; INPUT FF$
4180 PRINT CD$;"CLOSE FILENAMES"
4200 PRINT CD$;"OPEN FILENAMES,D2"
4210 PRINT CD$;"WRITE FILENAMES"
4220 PRINT SF$
4230 PRINT FF$
4240 PRINT CD$;"CLOSE FILENAMES"
4300 PRINT CD$;"DELETE ";NM$","D2"
4500 RETURN
Program "SETFILES"

10 REM ** PROGRAM SETFILES **
20 CD$ = CHR$(13) + CHR$(4)
30 PRINT CHR$(4);"PR#3"
40 PRINT CD$;"OPEN FILENAMES,D2"
50 PRINT CD$;"READ FILENAMES"
60 INPUT DF$
70 INPUT FF$
80 PRINT CD$;"CLOSE FILENAMES"
90 TEXT : HOME : PRINT
100 VTAB (5): PRINT "THE CURRENT DATA FILENAME IS ";DF$
110 PRINT : PRINT "NEW DATA FILENAME ?": INPUT "(L' to leave unchanged): ";ND$
120 IF ND$ < > "L" THEN DF$ = ND$
130 VTAB (13): PRINT "THE CURRENT FORMAT FILENAME IS ";FF$
140 PRINT : PRINT "NEW FORMAT FILENAME ?": INPUT "(L' to leave unchanged):";NF$
150 IF NF$ < > "L" THEN FF$ = NF$
160 VTAB (21): PRINT "DATA FILE = ";DF$: PRINT "FORMAT FILE = ";FF$
170 PRINT : PRINT "ANY CHANGES? (Y/N): ";
180 GET NC$: IF NC$ < > "Y" AND NC$ < > "N" GOTO 180
190 PRINT NC$
200 IF NC$ = "Y" GOTO 90
210 HOME
300 PRINT CD$;"OPEN FILENAMES,D2"
305 PRINT CD$;"WRITE FILENAMES"
310 PRINT DF$
320 PRINT FF$
330 PRINT CD$;"CLOSE FILENAMES"
350 PRINT CD$;"RUN OPTIONS,D1"
360 END
Program "RASCAL"

10 REM ** PROGRAM RASCAL **
11 REM Last change in calibration: 3rd July 1989
15 PRINT CHR$(4);"BRUN LOMEM:"; & LOMEM: = 2048
20 DIM XP(25),YP(25,6),RCNC(25),Y(25)
26 DIM TS$(6)
30 CD$::=CHR$(13)+CHR$(4)
35 CC$ = CHR$(9)
60 FOR I = 1 TO ll:TY%(1) = 1: NEXT
70 TY%(2) = 2:TY%(8) = 2:TY%(10) = 2:TY%(11) = 2
75 PRINT CD$;"OPEN FILENAMES,D2": PRINT CC$;"READ FILENAMES": INPUT DF$:
80 INPUT FF$:
95 RF$ = "N":RC$ = "N"
97 PRINT CHR$(4);"PR#3"
100 GO SUB 1000
110 REM display menu
200 IF OP% = 1 THEN GOSUB 2000
210 REM read data/format files
300 IF OP% = 2 THEN GOSUB 3000
310 REM display / adjust data file
400 IF OP% = 3 THEN GOSUB 4000
410 REM display / adjust rate variables
500 IF OP% = 4 THEN GOSUB 5000
510 REM calculate rate coefficient
600 IF OP% = 5 THEN GOSUB 6000
610 REM draw log graph
700 IF OP% < > 6 GOTO 100
800 PRINT CD$;"RUN OPTIONS,D1"
1000 REM options menu
1015 TS$(1) = "Load data / format files":TS$(2) = "Display / edit data in memory":TS$(3) = "Display / adjust rate variables":TS$(4) = "Calculate rate constant":TS$(5) = "Display graph":TS$(6) = "Quit"
1020 PRINT "RATE CALCULATION:"; PRINT "--------": PRINT "Make a choice":; PRINT "------": PRINT FOR I = 1 TO 6: PRINT POKE 1403,10: PRINT "(";I;")",; TS$(I): NEXT: PRINT PRINT "WHICH OPTION ? (1-6): ";
1030 GET KS$:OP% = ASC (KS$) - 48: IF OP% < 1 OR OP% > 6 GOTO 1030
1040 PRINT OP%: PRINT ; PRINT OP%;": ";TS$(OP%): FOR I = 1 TO 6:TS$(I) = "": NEXT: RETURN
2000 REM load data file
2010 RC$ = "N": HOME: PRINT "READ DATA / RATE VARIABLE FILES:"; PRINT "---- --- ---- --- ------- ----": PRINT : VTAB 7: PRINT "CURRENT DATA FILENAME IS: ";DF$:
3000 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" THEN 2020
3010 PRINT KS$: IF KS$ = "Y" THEN PRINT : INPUT "NEW FILENAME ?... ";DF$
3040 PRINT : PRINT "READING YOUR DATA FILE ";DF$; NOW ".;YU% = 0
3060 FOR I = 1 TO PTS:Y(I) = 0: IF YP(I,1) > = 1.0 THEN Y(I) = LOG (YP(I,1))
3070 NEXT
**READ RATE VARIABLES FILE ALSO?** (Y/N): ";

**READ RATE VARIABLES FILENAME IS** ";FF$: PRINT: PRINT
"CHANGE THIS?** (Y/N): ";

**GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 2110
**PRINT KS$: IF KS$ = "N" THEN RETURN

**PRINT "CURRENT RATE VARIABLES FILENAME IS" ";FF$: PRINT: PRINT
"PLEASE ENTER A NEW FILENAME: \n...”;FF$: PRINT CD$:"OPEN ";FF$; D2”; PRINT CD$; "READ ";FF$: FOR I = 1 TO 11: INPUT RV$(I); QV(I) = VAL (RV$(I))

**2180 NEXT: PRINT CD$; "CLOSE ";FF$: HOME : RF$ := "Y": RETURN
**3000 REM examine I edit data file
**3005 HD$ = "EXAMINE DATA FILE": UD$ = "-------- ---- ---- ----
**3010 GOSUB 3600: PRINT: PRINT "WHICH OPTION? (0-5): ";
**3020 PRINT WO%: PRINT: PRINT "(Press any key to proceed)

**WHICH OPTION?** (0-5): ";

**GET KS$: WO% = ASC (KS$) - 48: IF WO% < 0 OR WO% > 5 THEN 3020
**3035 PRINT WO%: PRINT: PRINT "(Press any key to proceed)

**IF WO% = 1 AND MAX < = 1 THEN 3020: REM don't need to choose ion signal if only one ion monitored

**3035 PRINT WO%: IF WO% = 0 THEN RETURN
**3040 ON WO% COSUB 3100, 3200, 3300, 3400, 3500
**3090 RETURN
**3100 REM choose ion signal for rate calculation
**3110 HD$ = "SELECT ION SIGNAL FOR RATE CALCULATION": UD$ = "-------- ---- ---- ----
**3120 GET KS$: YU% = ASC (KS$) - 48: IF YU% < 1 OR YU% > MAX GOTO 3120
**3130 PRINT YU%: PRINT: PRINT "(Press any key to proceed)

**GET KS$; WO% = ASC (KS$) - 48: IF WO% < 0 OR WO% > 5 THEN 3030
**3090 RETURN
**3100 REM examine I edit data file
**3110 HD$ = "EXAMINE DATA FILE": UD$ = "-------- ---- ---- ----": GOSUB 3600: PRINT: PRINT "WHICH OPTION? (0-5): ";
**3120 GET KS$: YU% = ASC (KS$) - 48: IF YU% < 1 OR YU% > MAX GOTO 3120
**3130 PRINT YU%: PRINT: PRINT "(Press any key to proceed)

**PRINT "EDIT DATA POINT": UD$ = "-------- ---- ---- ----": GOSUB 3600: PRINT: PRINT "WHICH POINT? (0 - ";PTS;") \n...": INPUT "<0 = esc> \n...": WP: IF WP > PTS OR WP < 0 THEN RETURN

**PRINT "EDIT DATA POINT": UD$ = "-------- ---- ---- ----": GOSUB 3600: PRINT: PRINT "CHANGE X ? <"; XP(WP): > (Y/N): ";
**3220 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 3230
**3240 PRINT KS$: IF KS$ = "Y" THEN INPUT "Enter new value <-1 to escape>: \n...": XP(WP) = X
**3250 FOR J = 1 TO MAX: PRINT: PRINT "CHANGE Y": J: "; YP(WP, J): > (Y/N): ";
**3260 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 3260
**3270 PRINT KS$: IF KS$ = "Y" THEN INPUT "Enter new value <-1 to escape>: \n...": Y: IF Y > - 0.0001 THEN YP(WP, J) = Y
**3280 NEXT : RETURN

**PRINT "EDIT DATA POINT": UD$ = "-------- ---- ---- ----": GOSUB 3600: PRINT: PRINT "WHICH POINT? (0 - ";PTS;") \n...": INPUT "<0 = esc> \n...": WP: IF WP > PTS OR WP < 1 THEN RETURN

**FOR WP = 0 TO PTS - 1: XP(I) = XP(I + 1); Y(I) = Y(I + 1): FOR J = 1 TO MAX: YP(I, J) = YP(I + 1, J): NEXT : NEXT : PTS = PTS - 1: GOTO 3310
HOME: PRINT HD$: PRINT UD$: PRINT "X": FOR J = 1 TO MAX: POKE 1403,(10 * (J + 1)): PRINT "Y":: NEXT: PRINT FOR I = ST TO FI:QX = 2 - INT ((LOG (I) / LOG (10)) + 0.0001): POKE 1403,QX: PRINT I": ",YP(I);: NEXT: IF FI > = PTS THEN RETURN

HOME: PRINT "INITIALISE RATE VARIABLES:"; PRINT "--------- ---- ---------": PRINT FOR I = 1 TO 11:KS$ = CHR$(I + 64): PRINT KS$": ",VS$(I); ";RS$(I);: POKE 1403,40: INPUT ": ";VS$(I);QV$I = VAL (RS$(I)): NEXT

HOME: PRINT "EDIT RATE VARIABLES:"; PRINT "---- ---- ---- ----": PRINT FOR I = 1 TO 11:KS$ = CHR$(I + 64): PRINT KS$": ",VS$(I);: POKE 1403,22: PRINT " = ";RS$(I): NEXT: PRINT ": RETURN : REM display rate variables
5000 REM set up log graph
5010 TEXT : HOME
5020 IF PTS < 1 THEN PRINT ; VTAB (11) ; HTAB (25) ; PRINT "PLEASE LOAD A DATA FILE !" ; HTAB (25) ; PRINT "(Press any key ... )" ; GET KS$ : RETURN
5030 PRINT "DRAW LOG GRAPH:" ; PRINT "---- ---- ----" ; PRINT
5040 MX = 0 : MY = 0 : MN = 20
5050 FOR I = 1 TO PTS
5060 IF MX < XP(I) THEN MX = XP(I)
5070 IF Y(I) < 0 GOTO 5100
5080 IF MY < YQ) THEN MY = Y(I)
5090 IF MN > Y(I) THEN MN = Y(I)
5100 NEXT
5110 XS = 240 / MX
5120 YS = 160 / (MY - MN)
5300 GOSUB 9000
5310 REM draw graph
5400 PRINT ; VTAB (12) ; POKE 1403, 30 ; PRINT "LOAD SOME DATA ! ! !" ; POKE 1403, 30 ; PRINT "(Press any key ... )" ; GET KS$ : RETURN
5410 GET KS$ ; IF KS$ < > "Y" AND KS$ < > "N" GOTO 5410
5420 PRINT KS$
5430 IF KS$ = "N" GOTO 5500
5440 PRINT CD$ ; "PR#1"
5450 PRINT CHR$ (9) ; "G2"
5490 PRINT CD$ ; "PR#3"
5500 RETURN
6000 REM calculate rate constant
6010 HOME
6015 IF PTS < 1 THEN PRINT ; VTAB (12) ; POKE 1403, 30 ; PRINT "LOAD SOME DATA ! ! !" ; POKE 1403, 30 ; PRINT "(Press any key ... )" ; GET KS$ : RETURN
6020 IF RF$ = "N" THEN PRINT ; VTAB (12) ; POKE 1403, 25 ; PRINT "INITIALISE RATE VARIABLES ! ! !" ; POKE 1403, 25 ; PRINT "(Press any key ... )" ; GET KS$ : RETURN
6025 RC$ = "Y" ; IF YU% = 0 THEN YU% = 1
6030 PRINT "RATE COEFFICIENT CALCULATION:" ; PRINT "---- --------- ---------"
6050 GOSUB 7000 : REM initialise constants & physical parameters
6060 GOSUB 7200 : REM determine ion velocity IVEL
6070 GOSUB 7400 : REM determine SLOPE (d ln[ion]/d [react. neutral]) by least-squares analysis
6080 GOSUB 7600 : REM determine correction factor CTWO to compensate for off-axis ion diffusion
6090 GOSUB 7700 : REM determine effective reaction distance ZEFF
6095 K = - (SLOPE * IVEL) / (CTWO * ZEFF)
6100 GOSUB 8000 : REM determine correction for non-uniform velocity profile
6105 GOSUB 8200 : REM determine axial diffusion correction
6150 GOSUB 8600 : REM package results for printout
6400 GOSUB 8800 : REM display & print results
6500 RETURN
7000 REM initialise constants & parameters
7010 PI = 3.1415926 : TUBERAD = 3.66 : Z(1) = 70.9 ; Z(2) = 42.9 ; VELCRR = 4.0 / 3.0 ; ZERO = 2.405
7020 RU% = INT (QV(1) + 0.5) ; DAY$ = RV$(2) ; PO% = INT (QV(3) + 0.5) ; NVOL = QV(4) ; TGAS = QV(5) + 273.16 ; PBUFF = QV(6)
7030 TYFLOW = QV(7) ; TITLE$ = RV$(8) ; IMASS = QV(9) ; CARRIER$ = RV$(10) ; COMMENTS$ = RV$(11)
7040 IF COMMENTS$ < > "" THEN COMMENTS$ = "(" + COMMENTS$ + ")"
IF CARRIERS < > "H2" AND CARRIERS < > "N2" AND CARRIERS < > "AR" THEN CARRIERS = "HE"

RETURN

REM DETERMINE ION VELOCITY VION

IF CARRIERS = "H2" THEN G1AS = 8.75E - 05:GMASS = 2.0159:POL = 0.79:FLLOWCRR = 8.4:F2LOWCRR = 0.2968
IF CARRIERS = "HE" THEN G1AS = 1.94E - 04:GMASS = 4.0026:POL = 0.199:FLLOWCRR = 11.7:F2LOWCRR = 0.4353
IF CARRIERS = "N2" THEN G1AS = 1.76E - 04:GMASS = 28.014:POL = 1.76:FLLOWCRR = 9.703:F2LOWCRR = 1.0 / 1.754
IF CARRIERS = "AR" THEN G1AS = 2.217E - 04:GMASS = 39.948:POL = 1.60:FLLOWCRR = 9.703:F2LOWCRR = 1.44 / 1.754

QBUFF = FLLOWCRR + (TFLLOWCRR)

VBUFF = (QBUFF / (PI - TUBERAD)) * (760 / PBUFF) * (TGAS / 273.16)

IVEL = VELCRR ...

SLOPE = (W3 / W1) - 10

SIG = SQR (C) / SQR (PTS * MIC)

Z1 = - Z1 / SLOPE

Z2 = Z2 / IINTERCEPT

RETURN

REM determine CTWO

RMOB = (13.876 / SQR (POL)) * SQR ((IMASS + GMASS) / (IMASS * GMASS))

DFFCO = (RMOB * 0.02354) * (760 / PBUFF) * (TGAS / 273.16)

CTWO = 1 - 2* ((DFFCO * JZERO / (TUBERAD * IVEL)) ^ 2) + 6* ((DFFCO * JZERO / (TUBERAD * IVEL)) ^ 4)

RETURN

REM determine ZEFF

ZEFF = Z(PO%) - (0.0 * PBUFF)

RETURN
354

8000 REM NON-UNIFORM VELOCITY CORRECTION
8010 W = 2 / (1 + (5.52 * YMFP / (PBUFF * TUBERAD)))
8020 BEE = 1 + (2.76 * YMFP / (PBUFF * TUBERAD))
8030 ELL = (0.25 - BEE) * (0.1 - 0.6 * BEE) - ((0.15 - 0.75 * BEE)^2)
8040 EMM = 1.6 * BEE - 0.4
8050 ENN = 0.025 - 0.075 * BEE
8060 GAMMA = (-1 / (2 * ELL)) * (ENN - ((2 * EMM * ENN + 6.4 * ELL) / (2 * SQR (EMM * 
ENN - 32 * ELL))))
8070 NUNVELCO = W * GAMMA
8080 K1 = K * NUNVELCO
8090 RETURN
8100 REM AXIAL DIFFUSION
8110 DLTA = (1 / (2 * ELL)) * (EMM - SQR (EMM - EMM - 32.0 * ELL))
8120 L2AMBDA = DLTA / (W * TUBERAD) + GAMMA / W * BMEAN
8130 EPSIL = L2AMBDA / DFFCO / DFFCO / IVEL
8140 AXDFCO = 1 / (1 - EPSIL)
8150 K2 = K / AXDFCO
8160 K2 = K / 0.8186: REM Correction factor (3/7/89)
8170 RETURN
8180 REM package results for printout
8190 K2 = K / 1E15
8200 EK% = -15
8210 K2 = K / 10:EK% = EK% + 1: IF K2 > 10 GOTO 8630
8220 S1 = INT (S1 / (K2 / 1E10) * 10000 + 0.5) / 10000:K2 = INT (K2 / 1000 + 0.5) / 1000
8230 I2 = INT (I2 / 1INTERCEPT * 10000 + 0.5) / 1000:1INTERCEPT = INT (1INTERCEPT * 1000 + 0.5) / 10
8240 I4 = INT ((EXP (1INTERCEPT - I2) - EXP (1INTERCEPT)) * 10 + 0.5) / 10
8250 I4 = ABS (I4)
8260 HOME: PRINT "DO YOU WANT A PRINTOUT? (Y/N): ";
8270 GET PT$: IF PT$ < > "Y" AND PT$ < > "N" GOTO 8825
8280 PRINT PT$: IF PT$ = "N" GOTO 8990
8290 HOME: PRINT CHR$(4);"PR#1": PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT
8300 "-------------------------------------------
8310 PRINT TITLE$;"m/z = ";IMASS
8320 PRINT "Date: ";DAY$;"Run ";RU%;"Data file ";DF$; PRINT COMMENTS$
8330 PRINT "T = ";INT (TGAS * 10 + 0.5) / 10; "K = ";INT (PBUFF * 10000 + 0.5) / 1000;Torrs of 
"CARRIER$; (Tylan flow = ";INT (TYFLOW + 0.5);")
8340 PRINT "Portal ";PO%;"Neutral vol = ";INT (10 * NVOL + 0.5) / 10; "cm^3"
8350 PRINT "Corrected reaction distance = ";INT (ZEFF * 10 + 0.5) / 10; "cm"
8360 PRINT "Neutral flow | Ion signal": PRINT " (torr/s) | ": PRINT "---------

8370 FOR I = 1 TO PTS
8380 PRINT "; HTAB (4); PRINT XP(I); HTAB (16); PRINT "; ";YP(I,YU%)
8390 NEXT
8400 PRINT: PRINT: PRINT: PRINT "k = ";K: PRINT "k (carr) = (";K2;" / - "S1;")E;EK%;"cm^3
8410 molecule^-1 s^-1": PRINT
PRINT "Intercept = ";I1; +/- ";I2;" In. counts": PRINT " = ";I3;" +/- ";I4;" ion counts"
PRINT: PRINT CHR$(4);"PR#3"
RETURN
REM graphics
PRINT CHR$(17);"e0"
HGR2: HCOLOR=3
HPLOT 20,3 TO 20,165 TO 262,165: HPLOT 18,5 TO 22,5: HPLOT 260,163 TO 260,167
FOR I = 1 TO PTS: YC = 165 - INT (YS * (Y(I) - MN) + 0.5): XC = 20 + INT (XS * XP(I) + 0.5)
HPLOT XC,YC - 2 TO XC,YC + 2: HPLOT XC - 2,YC TO XC + 2,YC: NEXT: REM setup coordinates of points
IF RC$ < > "Y" THEN GET KS$: PRINT KS$: TEXT: PRINT CHR$(4);"PR#3": RETURN
REM setup calculated decay curve
XM = RCNC(1): FOR I = 1 TO PTS: IF RCNC(I) > XM THEN XM = RCNC(I)
NEXT
FOR I = 1 TO 48: DB = I * XM / 48.0: DA = I1INTERCEPT + SLOPE * DB: CD = 165 - INT (YS *
(DA - MN) + 0.5)
XV = 20 + (5 * I): IF CD > 4 AND CD < 166 THEN HPLOT XV,CD
NEXT
GET KS$: PRINT KS$: TEXT: PRINT CHR$(4);"PR#3"
RETURN
Program "MULE"

1 REM ** PROGRAM MULE **
2 PRINT CHR$ (4);"PR#3"
3 PRINT CHR$ (4);"BRUN LOMEM:"; & LOMEM: 16384
4 CD$ = CHR$ (13) + CHR$ (4)
6 CCS = CHR$ (9)
7 POKE 7,0: POKE 8,0
8 GOSUB 9000: REM input default filenames
13 DIM AX(50),AY(50),AZ(65): DIM B(50),C(50),D(50),T(50): DIM A(20),S(20),V(20),X(20),Y(20),P(21,20)
17 HGR: HCOLOR= 1:X = 0:Y = 0: TEXT :XAXIS = 270:YAXIS = 180:BASE = 2
20 HOME: GOSUB 900: REM input data
25 GOSUB 1200: REM calculation of weights
30 HOME: GOSUB 1250: REM input of trial values
35 GOSUB 1600: REM loading of initial simplex points
40 GOSUB 1800: REM calculation of initial simplex values
45 GOSUB 2000: REM set expansion & contraction parameters
50 GOSUB 2200: REM find highest & lowest points and simplex centroid
55 GOSUB 2400: REM iteration to improve simplex
60 GOSUB 2800: REM check if minimum reached: if so, produce output; otherwise repeat iteration
65 IF C3 = 0 GOTO 50
70 GOSUB 3000
75 IF K$ = "D" GOTO 20
80 IF K$ = "T" GOTO 30
900 REM INPUT OF DATA
901 JP = 0
910 HOME: PRINT "MULE: MULTIPLE EXPONENTIAL FITTING": PRINT "---- -------- ---- --------": PRINT: PRINT "LOAD DATA FILE:";
920 PRINT "CURRENT DATA FILENAME IS ";DF$:
925 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" THEN 925
930 PRINT KS$:
935 IF KS$ = "T" GOTO 940
936 IF KS$ = "NONE" GOTO 1028
937 IF KS$ < > "N" THEN DF$ = KS$
940 PRINT : PRINT "ENTER NEW FILENAME (N=leave unchanged/NONE=escape): ";KS$
945 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" THEN 945
950 PRINT KS$:
955 IF KS$ = "N" THEN 910
960 HOME: PRINT : VTAB (12): POKE 1403,20: PRINT "READING FILE ";DF$; " NOW ..."
1000 PRINT CD$;"OPEN ";DF$; ",D2"
1007 PRINT CD$;"READ ";DF$
1008 INPUT L
1009 INPUT M
1010 FOR A = 1 TO L
1011 INPUT C(A): INPUT T(A)
1015 NEXT
1016 PRINT CD$;"CLOSE"
1018 GOSUB 18000: GOTO 1065
1028 I = 0
1029 I = I + 1
1030 INPUT "FLOW(TORR/S) ? ";T(I)
IF \text{T(I)} < 0 THEN \text{L} = I - 1; GOSUB 18000; \text{DF} = \text{''H''}; HOME; GOTO 1065

INPUT "ION COUNT \text{? };C(I)

PRINT; GOTO 1029

RETURN

REM CALCULATION OF WEIGHTS
FOR I = 1 TO L; \text{B(I)} = 100 / \text{D(I)}; NEXT; RETURN

HOME; \text{NF} = 0; PRINT
PRINT
PRINT "INPUT OF TRIAL VALUES:"
PRINT \\
"PRE-EXP(AD AS THE PRE-EXPONENTIAL FACTOR OF DECAY \#i"
PRINT
PRINT "SLOPE(Ki) AS THE RATE COEFF. (cm3/molec.s) OF DECAY \#i"
PRINT
PRINT "STEP OF Ai & Ki AS A PERCENTAGE 1-25%; ie ENTER A VALUE IN THE RANGE 1-10"; PRINT
PRINT "ENTER INTERCEPT AS 0 TO FINISH INPUT OF TRIAL RATE VARIABLES"
PRINT
PRINT ;PE = 1; \text{P(J)} = -1
\text{I} = I + 2; PRINT "ENTER TRIAL VALUES FOR DECAY \#";PE; PRINT
INPUT "PRE-EXP(Ai) \text{?} ; \text{A(I)}; IF \text{A(I)} = 0 GOTO 1452
\text{INPUT "SLOPE(Ki) \text{?} ; \text{A(I + 1)}; INPUT "STEP OF Ai \text{?} ; \text{S(I)}; INPUT "STEP OF Ki \text{?} ; \text{S(I + 1)}"
PRINT ;PE = PE + 1; GOTO 1425
PRINT ;INPUT "TORR/S TO MOLEC.S/CM3 CONVERSION VALUE \text{?} ; \text{CV}
\text{M} = I; \text{N} = I - 1; GOSUB 7000; GOSUB 8000; \text{L1} = L - N; IF \text{L1} < = 0 THEN PRINT "INSUFFICIENT DATA POINTS!!"; PRINT
RETURN
GOSUB 6200; RETURN; REM loading of initial simplex points
REM CALCULATION OF INITIAL SIMPLEX VALUES
FOR I = 1 TO \text{M}; \text{V(I)} = \text{\"1 + A1\" ...} \text{X(O)} - (\text{\"A1 \" P(J1, I)) NEXT
GOSUB 5600; GOSUB 5200; \text{Y1} = \text{X1}; IF \text{Y1} > \text{Y(K1)} GOTO 2485
GOSUB 5800; \text{Y(J1)} = \text{Y2}; GOTO 2650
\text{J2} = 0
FOR I = 1 TO \text{M}; IF I < \text{J1 AND Y1 < = Y(I)} THEN \text{J2} = \text{J2 + 1
2500 NEXT
2510 IF J2 = 0 GOTO 2540
2520 GOSUB 5600: GOSUB 5800: Y(J1) = Y1: GOTO 2560
2540 IF Y1 = Y(J1) THEN GOSUB 5600: GOSUB 5800: Y(J1) = Y1: GOTO 2560
2550 FOR I = 1 TO N: A(I) = (B1 * P(I1,J1)) + ((1 - B1) * X(I)): NEXT
2560 GOSUB 5200: Y1 = X1: IF Y1 = Y(J1) THEN GOSUB 5800: Y(J1) = Y1: GOTO 2650
2605 FOR I = 1 TO N: A(I) = P(K1,1): NEXT
2610 FOR I = 1 TO M
2620 FOR J = 1 TO N: P(I,J) = (P(I,J) + A(m/2): NEXT
2630 NEXT
2640 GOSUB 1800
2650 RETURN
2800 REM CHECK IF MINIMUM REACHED
2810 Y1 = Y(K1): GOSUB 5500: GOSUB 20000: NF = NF + 2: IF C1 < 1 THEN Y5 = Y1: K8 = 0: Y4 = Y1: C3 = 0: GOTO 2950
2820 IF (R2 > R1) OR (R2 > R1) THEN C3 = 1: GOTO 2950
2830 IF C1 > 100 THEN C3 = 2: GOTO 2950
2840 IF ABS (Y5 - Y1) > 0.01 THEN K8 = 0: Y5 = Y1: GOTO 2950
2945 Y5 = Y1
2950 IF C3 = 1 THEN INPUT "END OF ITERATION. PRESS RETURN FOR OUTPUT MENU": A$
2951 IF C3 = 2 THEN INPUT "TOO MANY ITERATIONS. PRESS RETURN FOR OUTPUT MENU": A$
2952 IF C3 = 3 THEN INPUT "CHANGE DURING LAST ITERATION TOO SMALL. PRESS RETURN FOR OUTPUT MENU": A$
2960 RETURN
3000 REM OUTPUT OF RESULTS
3005 GOTO 3097
3010 GOSUB 2200: VTAB (9 + N): IF C3 > 1 THEN PRINT "ITERATION SUCCESSFUL"
3020 GOSUB 2200: VTAB (9 + N): IF C3 > 1 OR C3 < 3 THEN PRINT "ITERATION SUCCESSFUL": GOTO 3079
3030 PRINT "ITERATION UNSUCCESSFUL": PRINT : PRINT : IF C3 = 2 THEN PRINT "TOO MANY ITERATIONS REQUIRED"
3040 IF C3 = 3 THEN PRINT "CHANGE DURING LAST ITERATION TOO SMALL"
3050 IF C3 = 4 THEN PRINT "ZERO VALUE MISMATCH"
3060 IF C3 > 4 THEN PRINT "REASON FOR FAILURE UNKNOWN"
3079 A$ = C1 - 1: PRINT "NO. OF ITERATIONS = ";A$: PRINT "IMPROVED FROM INITIAL FIT OF ";Y4: IF ZQ = 1 THEN GOTO 3144
3097 GOSUB 9999: HOME: IF SS = 2 THEN GOSUB 13000
3100 IF SS = 1 THEN GOSUB 12000
3102 IF SS < 3 GOTO 3097
3104 GOTO 3247
3105 PRINT "ITERATED VALUES": PRINT "-------- -------": PRINT : PRINT :EP = 0
3120 VTAB (4): PRINT "DECAY | PRE-EXP FACTOR | SLOPE": PRINT " | (ION COUNTS) | (CM3/MOLEC.S)": PRINT "-------- |---------- |----------": PRINT :ZQ = 1: GOTO 3010
3144 PRINT "THESE VALUES GIVE A FIT OF ";Y(K1): GOSUB 11000: IF PZ = 1 THEN HOME: GOTO 3105
GOTO 3097
HOME
PRINT "DATA TABLE;": PRINT "----- -----": PRINT "FLOW FITTED CTS EXPTLCTS WEIGHT": PRINT "-------------------------------------": JG = 0
FOR J = 1 TO L: GOSUB 5400: A = 5: JG = JG + (Z - C(J)) * (Z - C(J)): VTAB (A + J): POKE 1403,0: PRINT T(J);: POKE 1403,9: PRINT Z(J);: POKE 1403,15: PRINT "C(J);: POKE 1403,29: PRINT "D(J);: NEXT
PRINT: PRINT: PRINT "FLOW IN TORRIS RMS(diff) = SQR (JG / L): PRINT: PRINT: GOSUB 11000: IF PZ = 1 GOTO 3170
GOTO 3097
HOME: INPUT "ERROR!! PRESS RETURN": A$
PRINT: PRINT: PRINT "SURE ABOUT THAT? (Y IN): "
GET KS$: OP% = ASC (KS$) - 48: IF OP% < 1 OR OP% > 4 GOTO 3255
PRINT OP%: PRINT: PRINT "SURE ABOUT THAT? (Y IN): "
GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 3265
PRINT KS$: IF KS$ = "N" GOTO 3247
IF OP% = 1 GOTO 3097
IF OP% = 2 THEN K$ = 'T": RETURN
IF OP% = 3 THEN K$ = "D": RETURN
IF OP% = 4 THEN PRINT CD$; "RUN OPTIONS,D1"
REM calculation of simplex value
X1 = 0
FOR J = 1 TO L: GOSUB 5400: X1 = X1 + (Z - C(J)) * (Z - C(J)) * B(J): NEXT
X1 = SQR (X1 / L): RETURN
REM calculation of function
Z = 0
FOR K = 1 TO N STEP 2: Z = Z + (A(K) * EXP (A(K + 1) * T(J))): NEXT
RETURN
REM calculation of function
Z = 0
FOR K = 1 TO N STEP 2: Z = Z + (A(K) * EXP (A(K + 1) * T(J))): NEXT
RETURN
REM RMS
Z5 = 0: X4 = 0: X6 = 0
FOR K = 1 TO L: Z5 = Z5 + A(K): NEXT
FOR F = 1 TO N STEP 2: Z5 = Z5 + P(K1,F) * EXP (T(K) * P(K1,F + 1)): NEXT
X6 = X6 + C(K) * C(K): X4 = X4 + (Z5 - C(K)) * (Z5 - C(K)): NEXT
R1 = SQR (X4 / L): R2 = SQR (SQR (X6 / L)): RETURN
FOR I = 1 TO N: A(I) = V(I): NEXT: RETURN: REM rearrangement of curve fitting parameters
FOR I = 1 TO N: P(I,J) = A(I): NEXT: RETURN: REM insertion into simplex of new values
PRINT "*** DATAFILE "; DF$; "***": PRINT: RETURN
J1 = 0: IF I < 1 THEN J1 = 1: IF I - 5 > 0 THEN J1 = 5 - J1
RETURN: REM random no. generator for simplex loading
XL = 0: REM sum Ai
FOR K = 1 TO N: P(I,J) = A(I): NEXT: RETURN: REM loading of ordered initial simplex
FOR I = 1 TO M: REM loading of ordered initial simplex
NEXT
NEXT: RETURN
FOR A = 1 TO L: IF T(A) = 0 THEN XG = A: REM find C(I) at zero flow
NEXT: RETURN
FOR I = 1 TO M: REM loading of random initial simplex
FOR J = 1 TO N: GOSUB 6000: P(I,J) = A(J) + (J1 * S(J)): NEXT
6420 NEXT : RETURN
6500 GOSUB 6300: GOSUB 6100: XF = ABS(C(XG) - XL) * 2 / N: REM improve Ai
6510 FOR K = 1 TO N STEP 2: A(K) = A(K) - XF: IF (C(XG) - XL) > I - 2 / N: REM improve Ai
6520 NEXT : RETURN
6699 HOME
6700 PRINT "DATAFILE NAME:"; DF$: PRINT "-------- ____";
6710 PRINT "INITIAL TRIAL VALUES": PRINT "-------- ------ -------": PRINT "DECAY 1 PRE-EXP FACTOR 1 SLOPE": PRINT "______ 1 __________ 1 __________": PRINT "1 VALUE 1 STEP 1 VALUE 1 STEP";
6720 FOR I = 1 TO N STEP 2: EP = I: IF JNT (K - K / 2) = K / 2 THEN T = 25
6730 K = (K + 3) / 2: IF K > N / 2 GOTO 7200
6740 RETURN
6750 PRINT : PRINT "DISPLAY AND/OR EDIT TRIAL VALUES? (Y/N): "; ; REM edit trial values
6760 IF A$ < "Y" AND A$ < "N" GOTO 760
6770 PRINT "CONVERSION VALUE OR WHICH DECAY? (1-"; N / 2; ");
6780 GET KS$: TG% = ASC(KS$) - 48: IF TG% < 0 OR TG% > 4 GOTO 780
6790 PRINT "WHICH VALUE? <0 to quit> (0-4): ",
6800 IF TG% = 0 GOTO 7040
6810 IF TG% = 1 THEN INPUT "PRE-EXP Ai ?"; A(P)
6820 IF TG% = 2 THEN INPUT "SLOPE Ki ?"; A(P + 1)
6830 IF TG% = 3 THEN INPUT "STEP OF Ai ?"; S(P)
6840 IF TG% = 4 THEN INPUT "STEP OF Ki ?"; S(P + 1)
6850 GOTO 7300
6860 PRINT : PRINT "CONVERSION VALUE = "; CV: PRINT : INPUT "CHANGE TO 
 CV: GOTO 7030
FOR I = 1 TO N STEP 2: E(I) = S(I); E(I + 1) = S(I + 1); W(I) = A(I); W(I + 1) = A(I + 1); NEXT: RETURN
FOR I = 1 TO N STEP 2: PRINT A(I + 1) = A(I + 1) * CV; S(I + 1) = S(I + 1) * A(I + 1) / 100; S(I) = S(I) * A(I) / 100; NEXT: RETURN
PRINT CD$; "OPEN FILENAMES.D2": PRINT CD$; "READ FILENAMES": INPUT DFS: PRINT CD$; "CLOSE FILENAMES": RETURN
IF PZ = 1 THEN PRINT CHR$ (4); "PR#1": PRINT CHR$ (9); "8S": PRINT CHR$ (4); "PR#3": LK = 2; PZ = 2: RETURN
PRINT: PRINT: PRINT "DUMP OUTPUT ? (Y/N) ";
GET KS$: IF KS$ < > "Y" AND KS$ < > "N" THEN LK = 2; PZ = 2: RETURN
PRINT KS$: IF KS$ = "N" THEN LK = 2; PZ = 2: RETURN
PRINT "No | Flow | Ion Signal | Weighting | PRINT" | (Torr/s) | (Observed) | (Calculated) |": PRINT "________|___________|___________|
12050 JG = 0
12070 IF PU$ < > "Y" AND (6 + J) > 2 THEN PU$ = "Y": PRINT CHR$ (4); "PR#1": PRINT CHR$ (9); "8S"
12080 NEXT
12085 PRINT: PRINT "SQR(RMS(experimental)) = ", R2: PRINT "RMS(weighted difference) = ", Y(K1)
12090 IF PU$ < > "Y" THEN PU$ = "Y": PRINT CHR$ (4); "PR#1": PRINT CHR$ (9); "8S"
12100 PRINT
12200 HOME: IF PTS$ < > "Y" THEN PRINT: VTAB (7)
12210 FOR A = 1 TO N STEP 2: PRINT "DECAY "; INT (A + 1.5) / 2; ": PRINT "-- --": PRINT : PRINT "Intercept = "; A(A); (initially ";W(A); , step "S(A); "): PRINT "Slope = "; A(A + 1) / CV; ": (initially ";W(A + 1); , step "S(A + 1); "): PRINT : NEXT
12220 IF PTS$ = "Y" GOTO 12300
12230 PRINT: PRINT "DO YOU WANT A PRINTOUT ? (Y/N) ";
12240 GET PTS$: IF PTS$ < > "Y" AND PTS$ < > "N" GOTO 12240
12250 PRINT PTS$: IF PTS$ = "Y" GOTO 12200
12280 IF PTS = "Y" THEN PRINT CHR$ (4); "PR#3"
12400 HOME
12990 RETURN
13000 REM GRAPHICS* 
13005 GD$ = "N"
13010 TEXT: HOME: PRINT
13015 LC% = OP% 
13020 VTab (5): POKE 1403,15: PRINT "GRAPHICS": VTab (6): POKE 1403,15: PRINT "-- --"
VTAB (10): POKE 1403,15: PRINT "(1). GRAPH USING INITIAL TRIAL VALUES, FULL AXIS RANGE."
VTAB (12): POKE 1403,15: PRINT "(2). GRAPH USING INITIAL TRIAL VALUES, HIGHER RESOLUTION."
VTAB (14): POKE 1403,15: PRINT "(3). GRAPH USING ITERATED VALUES, FULL AXIS RANGE."
VTAB (16): POKE 1403,15: PRINT "(4). GRAPH USING ITERATED VALUES, HIGHER RESOLUTION."
VTAB (18): POKE 1403,15: PRINT "(5). DUMP GRAPH ON PRINTER."
VTAB (20): POKE 1403,15: PRINT "(6). OUTPUT MENU."

GET KS$: OP% = ASC (KS$) - 48: IF OP% < 1 OR OP% > 6 GOTO 13090
PRINT KS$: IF OP% = 6 THEN RETURN

IF OP% = 5 GOTO 14000: REM dump graph
HOME: PRINT
HV = 1: LV = 0: IF OP% < 2 AND OP% > 4 GOTO 13240

VTAB (5): PRINT "ENTER THE UPPER AND LOWER BOUNDS OF THE X-AXIS (between 0 & 1)"
VTAB (10): INPUT "UPPER BOUND OF AXIS ? (0-1):"; HV
IF HV < 0 OR HV > 1 GOTO 13140
VTAB (12): INPUT "LOWER BOUND OF AXIS ? (0-1):"; LV
IF LV < 0 OR LV > 1 GOTO 13160
HOME: PRINT

POKE 1403,25: PRINT .. CALCULATING ..": POKE 1403,25: PRINT "*
FOR K = 1 TO N STEP 2
WA(K) = A(K): WA(K + 1) = A(K + 1): IF OP% = 1 OR OP% = 2 THEN WA(K) = W(K): WA(K + 1) = W(K + 1) * CV
NEXT
KH = T(1): KL = T(1)
FOR A = 2 TO L
IF KH < T(A) THEN KH = T(A)
IF KL > T(A) THEN KL = T(A)
NEXT
KH = (KH - KL) * HV: KL = (KH - KL) * LV: MH = 0: ML = 0
FOR J = 1 TO N STEP 2
MH = MH + WA(J) * EXP (WA(J + 1) * KL): ML = ML + WA(J) * EXP (WA(J + 1) * KH)
NEXT
FOR A = 1 TO L
IF T(A) < KL OR T(A) > KH GOTO 13420
IF MH < C(A) THEN MH = C(A)
IF ML > C(A) THEN ML = C(A)
NEXT
FL = KH - KL: CL = LOG (MH) - LOG (ML)
FOR A = 1 TO L
KJ = (LOG (C(A)) - LOG (MH)) * 154 / CL
AY(A) = 1 + ABS (INT (KJ)): AX(A) = 10 + ABS (INT (T(A) * 250 / FL))
NEXT
PF = 0
FOR K = 10 TO 260 STEP 4
BY = 0: XZ = (K - 10) * FL / 250
FOR I = 1 TO N STEP 2
PO = EXP(X*WA(I + 1)); AP = WA(I) * PO; BY = BY + AP

NEXT

ZZ = LOG(MH) - LOG(BY); PF = PF + 1; AZ(PF) = 1 + INT(ZZ * 154 / CL)

NEXT

IF (AX(I) + 1 < 9) OR (AX(I) - 1 > 261) OR (AY(I) + 1 < 1) OR (AY(I) - 1 > 156) GOTO 13600

HPLOT AX(I) - 1,AY(I) - 1 TO AX(I) + 1,AY(I) + 1 TO AX(I) + 1,AY(I) - 1 TO AX(I) - 1,AY(I) - 1; HPLOT AX(I),AY(I)

NEXT

PF = 0

FOR J = 10 TO 260 STEP 4

PF = PF + 1: X = J; Y = AZ(PF)

IF (Y < 155) AND (Y > 1) THEN HPLOT X,Y

NEXT

IF OP% = 2 OR OP% = 4 THEN PRINT: VTAB(22): PRINT "GRAPH FROM ";LV; " TO ";RV; " OF X-AXIS RANGE"

VF$("Y"): GOTO 13010

REM dump graph

IF CD$ <"Y" THEN PRINT: PRINT "NO GRAPH TO DUMP!": GET KS$: PRINT KS$: GOTO 13010

PRINT CD$;"PR#1"

IF LC% = 1 OR LC% = 2 THEN PRINT "GRAPH OF INITIAL VALUES": PRINT "----- ----- ---- ---- ---- ----"

IF LC% = 3 OR LC% = 4 THEN PRINT "GRAPH OF ITERATED VALUES": PRINT "---------- ---- ---- ---- ---- ---- ---- ----"

PRINT: IF LC% = 2 OR LC% = 4 THEN PRINT "from ";LV; " to ";RV; " of x-axis range."

INPUT "EDITING REQUIRED? (Y/N) ";A$

IF A$ = "N" THEN GOTO 18130

INPUT "WHICH POINT? ";DH

IF (DH < 1) OR (DH > L) THEN GOTO 18000

INPUT "FLOW(TORR/S)? ";T(DH)

INPUT "ION COUNTS ";C(DH)

INPUT "WEIGHTING ";D(DH)

GOTO 18001
18130 HOME : RETURN
20000 REM ITN OUTPUT
20010 IF NF > 1 THEN GOTO 20060
20015 HOME
20020 PRINT "SQR(RMS(exptl))=";R2
20030 VTAB (3): PRINT "ITN."
20031 ZY = 0:YZ = 0
20035 FOR K = 1 TO N STEP 2
20036 YZ = YZ + 1
20040 VTAB (3): POKE 1403,10 + ZY: PRINT "DECAY ";YZ
20050 ZY = ZY + 20
20055 NEXT K
20060 VTAB (1): POKE 1403,35: PRINT "RMS(wtd.diff.) =";Y(K1)
20070 VTAB (4 + NF): PRINT C1
20075 ZY = 0
20076 FOR I = 1 TO N STEP 2
20080 VTAB (5 + NF): POKE 1403,10 + ZY: PRINT P(K1,I + 1) / CV
20085 VTAB (4 + NF): POKE 1403,10 + ZY: PRINT P(K1,I)
20086 ZY = ZY + 20
20087 NEXT I
20090 IF NF = 16 THEN NF = - 2
20100 RETURN
Program "PROD RAT"

10 REM ** PROGRAM PROD RAT **
20 DIM XP(25),YP(25,6),X(25),Y(25,6)
25 DIM TS$(4),ES$(5),SH$(6),TT(25)
30 CD$ = CHR$(13) + CHR$(4)
35 CC$ = CHR$(9)
40 TS$(1) = "Load data file":TS$(2) = "Select from data in memory":TS$(3) = "Display product ratio graph":TS$(4) = "Quit"
50 ES$(0) = "Quit":ES$(1) = "Select ion signals for product distribution":ES$(2) = "Edit a data point":ES$(3) = "Delete a row of data":ES$(4) = "Add a data point":ES$(5) = "Delete a column of data"
75 PRINT CD$;"OPEN FILENAMES,D2": PRINT CD$;"READ FILENAMES": INPUT DF$:
95 RF$ = "N":RC$ = "N"
97 PRINT CHR$(4);"PR#3"
100 GOSUB 1000
110 REM display menu
200 IF OP% = 1 THEN GOSUB 2000
210 REM read data file
300 IF OP% = 2 THEN GOSUB 3000
310 REM display / adjust data file
400 IF OP% = 3 THEN GOSUB 4000
410 REM draw graph
500 IF OP% < 4 GOTO 100
600 PRINT CD$;"RUN OPTIONS,D1"
1000 REM options menu
1010 TEXT:
1020 PRINT "PRODUCT RATIO": PRINT "-------- -----": PRINT ; MAKE A CHOICE": PRINT "-------- -----": PRINT ; FOR I = 1 TO 4: PRINT : POKE 1403,10: PRINT "(",J, ").";
1030 GETKS$:OP% = ASC (KS$) - 48: IF OP% < 1 OR OP% > 4 GOTO 1030
1040 PRINT OP%: RETURN
2000 REM load data file
2010 HOME: PRINT "READ DATA FILE": PRINT "-------- -----": PRINT ; VTAB 10: PRINT ; CURRENT DATA FILENAME IS; ":DF$; PRINT ; PRINT "CHANGE THIS ? (Y/N)";
2020 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" THEN 2020
2030 PRINT KS$: IF KS$ = "Y" THEN PRINT ; INPUT "NEW FILENAME ? ... ";DF$
2040 PRINT ; PRINT "READING YOUR DATA FILE \".DF$\": NOW ... \".YU% = 0
2050 PRINT CD$;"OPEN \".DF$\",D2": PRINT CD$;"READ \".DF$; INPUT PTS: INPUT MAX: FOR I = 1 TO PTS: FOR J = 1 TO MAX: INPUT YP(I,J): INPUT XP(I): NEXT: NEXT:
2060 PRINT CD$;CLOSE \".DF$
2070 FOR J = 1 TO MAX:SH$(J) = "Y":MD(J) = 1: NEXT : GOSUB 6000
2070 RF$ = "Y"
2500 RETURN
3000 REM examine/edit data file
3005 IF RF$ < > "Y" THEN RETURN
3005 HD$ = "EXAMINE DATA FILE":UD$ = "-------- -----"
3010 GOSUB 3600: REM display data file
3020 PRINT ; FOR I = 0 TO 5: POKE 1403,10: PRINT "(",I, ").";ES$(I): NEXT : PRINT ; PRINT "WHICH OPTION ? (0-5)\":"
3030 GET KS$:WO% = ASC (KS$) - 48: IF WO% < 0 OR WO% > 5 THEN 3030
3035 PRINT WO%: IF WO% = 0 THEN GOSUB 6000: RETURN
3040 ON WO% GOSUB 3100,3200,3300,3400,3500
3045 GOTO 3000
3050 RETURN
3100 REM choose ion signal for rate calculation
3110  **HD$ = "SELECT PRODUCT IONS TO BE INCLUDED:"; UD$ = "----- ----- ----- ----- -----"; GOSUB 3600: PRINT
3115  FOR I = 1 TO 6: MD(I) = 1: NEXT
3120  **NP = 0: FOR J = 1 TO MAX: PRINT "Include Y";J;? (Y/N); ";
3125  **GET SHS(I): IF SHS(I) < > "Y" AND SHS(I) < > "N" GOTO 3130
3130  **IF SHS(I) = "Y" THEN NP = NP + 1
3135  **PRINT SHS(I): IF SHS(I) = "N" THEN PRINT: GOTO 3170
3140  **PRINT "Mass disc. factor? <default=1> ";
3145  IF SH$(J) = "Y" AND KS$ < > "N" GOTO 3150
3150  **GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 3150
3155  **PRINT KS$: IF KS$ < > "Y" THEN INPUT "Enter mass discrimination factor <1 - 9.9>: "; MD(J)
3160  NEXT
3170  **GET KS$: RETURN
3175  **REM Edit data point
3180  **HD$ = "EDIT DATA POINT:"; UD$ = "----- ----- ----- ----- -----": GOSUB 3600: PRINT: PRINT "Which point? (0 - ";PTS;") "; INPUT "<0 = esc>":; WP: IF WP > PTS OR WP < = 0 THEN RETURN
3185  **PRINT": PRINT "Change X ? <";XP(WP);"> (Y/N); ";
3190  **GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 3230
3195  **PRINT KS$: IF KS$ = "Y" THEN INPUT "Enter new value <1 to escape>: ";X: IF X > - 0.0001 THEN XP(WP) = X
3200  **FOR J = 1 TO MAX: PRINT "Change Y";J;? <";YP(WP,J);"> (Y/N); ";
3205  **GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 3260
3210  **PRINT KS$: IF KS$ = "Y" THEN INPUT "Enter new value <1 to escape>: ";Y: IF Y > - 0.0001 THEN YP(WP,J) = Y
3215  NEXT: RETURN
3220  **REM delete a data point
3225  **HD$ = "DELETE DATA POINT:"; UD$ = "----- ----- ----- ----- -----": GOSUB 3600: PRINT: PRINT "Which point? (0 - ";PTS;") "; INPUT "<0 = esc>":; WP: IF WP > PTS OR WP < = 1 THEN RETURN
3230  **FOR I = WP TO PTS - 1: XP(I) = XP(I + 1): FOR J = 1 TO MAX: YP(I,J) = YP(I + 1,J): NEXT: NEXT: WP = PTS - 1: GOTO 3310
3235  **REM add a data point
3240  **HD$ = "ADD A DATA POINT:"; UD$ = "----- ----- ----- ----- -----": GOSUB 3600: PRINT: PRINT "Enter X-value <1 to escape>: ";X: IF X < - 0.0001 THEN RETURN
3245  **PTS = PTS + 1: IF PTS > 25 THEN PRINT: PRINT "FILE EXCEEDS MAX. ALLOWABLE SIZE !!": PRINT "(Press any key to continue)";
3250  **GET KS$:PTS = 25: GOTO 3500
3255  **XP(PTS) = X: PRINT: FOR J = 1 TO MAX: PRINT "Enter Y";J;?:YP(PTS,J):= YP(J + 1,J): NEXT: GOTO 3410
3260  **IF MAX < = 1 THEN RETURN: REM delete a column of data
3265  **HD$ = "DELETE A COLUMN OF DATA:"; UD$ = "----- ----- ----- ----- -----": GOSUB 3600: PRINT: PRINT "Which column data ? (Y = 0 to ";MAX;": INPUT "$) <0 = esc>":; WC$: PRINT: PRINT "Sure about that? (Y/N): ";
3270  **GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 3520
3275  **PRINT KS$: IF KS$ = "N" GOTO 3510
3280  **IF WC$ < = 0 OR WC$ > MAX THEN RETURN
3285  **MAX = MAX - 1: FOR J = WC$: TO MAX: SHS(J) = SHS(J + 1): FOR I = 1 TO PTS: YP(I,J) = YP(I + 1,J): NEXT: NEXT: RETURN
3290  **REM list data file contents
3295  ST = 1:FI = PTS: IF FI > 15 THEN FI = 15
3300  **HOME: PRINT HD$: PRINT UD$: PRINT: PRINT " X": FOR J = 1 TO MAX: POKE 1403,(10 * (J + 1)): PRINT "Y";J;= NEXT: PRINT: FOR I = ST TO FI;FX = 2 - INT ((LOG (I) / LOG (10)) + 0.0001): POKE 1403,FX; PRINT "I:";";XP(I);
3305  **FOR J = 1 TO MAX: POKE 1403,(10 * (J + 1)): PRINT YP(J);: NEXT: PRINT: NEXT: IF FI > = PTS THEN RETURN
3310  FI = PTS:ST = FI - 15: GET KS$: GOTO 3610
4000 REM draw graph
4005 IF RF$ < > "Y" THEN RETURN
4010 HOME: PRINT CHR$(17);"eO"; HGR2: HCOLOR= 3
4020 HPLOT 30,4 TO 30,165 TO 271,165: FOR I = 5 TO 157 STEP 8: HPLOT 28,1 TO 30,165: NEXT
4030 FOR I = 1 TO PTS: FOR J = 1 TO MAX: IF SH$(J) = "Y" THEN ON J GOSUB 4200,4220,4240,4260,4280,4300
4040 NEXT : NEXT
4050 GET KS$: PRINT KS$: TEXT: PRINT CHR$(4);"PR#3"
4100 PRINT: VTAB (11): PRINT "Dump graph on printer? (Y/N): ";
4110 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 4110
4120 PRINT KS$: IF KS$ = "N" THEN RETURN
4130 PRINT CD$;"PR#1": PRINT CHR$(9);"G2": PRINT CD$;"PR#3": RETURN
4200 HPLOT X(I) - 2,Y(I,J) TO X(I) + 2,Y(I,J): RETURN
4210 HPLOT X(I) - 1,Y(I,J) TO X(I) + 1,Y(I,J): HPLOT X(I),Y(I,J) - 2 TO X(I),Y(I,J) + 2: RETURN
4220 HPLOT X(I) - 2,Y(I,J) - 1 TO X(I) + 1,Y(I,J) + 1: HPLOT X(I),Y(I,J) + 1 TO X(I),Y(I,J) - 1: HPLOT X(I),Y(I,J) + 2 TO X(I) - 1,Y(I,J) + 2: RETURN
4230 HPLOT X(I) - 1,Y(I,J) - 1 TO X(I) + 1,Y(I,J) + 1: HPLOT X(I) + 1,Y(I,J) TO X(I) - 1,Y(I,J): HPLOT X(I) + 2,Y(I,J) TO X(I),Y(I,J) + 2: RETURN
4240 NEXT: IF XP(I) > MX THEN MX = XP(I)
4250 REM calculate % of ion signal at each flow
4260 MX = 0
4270 FOR I = 1 TO PTS; TT(I) = 0: FOR J = 1 TO MAX: IF SH$(J) = "Y" THEN TT(I) = TT(I) + YP(I,J) * MD(J)
4280 NEXT : IF TT(I) < 1 THEN TT(I) = 1
4290 FOR J = 1 TO MAX: IF SH$(J) < > "Y" GOTO 6040
4300 Y(I,J) = 165 - INT (160 * YP(I,J) * MD(J)) / TT(I) + 0.5)
4310 NEXT: IF XP(I) > MX THEN MX = XP(I)
4320 NEXT
4330 FOR I = 1 TO PTS: X(I) = 30 + INT (240.0 * XP(I) / MX + 0.5): NEXT
4340 RETURN
Program "STUDYFILES"

10 REM ** PROGRAM STUDYFILES **
20 DIM XP(40): DIM YP(40,6): DIM RC$(20)
25 DIM VNS$(12): DIM RGS(12): DIM TY(12): DIM VQ(12)
30 CD$ = CHR$(13) + CHR$(4)
40 TS$(1) = "LOAD A DATA FILE"
42 TS$(2) = "LOAD A FORMAT FILE"
44 TS$(3) = "DISPLAY FILE CONTENTS"
46 TS$(4) = "EDIT FILE CONTENTS"
48 TS$(5) = "SAVE A FILE"
50 TS$(6) = "RETURN TO MAIN MENU"
51 TS$(7) = "QUIT"
55 NC% = 7
60 GOSUB 9000
61 REM get default filenames
65 FOR I = 1 TO 12: TY(I) = 1: NEXT
70 TY(2) = 2: TY(8) = 2: TY(10) = 3: TY(11) = 2
80 FTS$(1) = "N": FTS$(2) = "N": FTS$(3) = "N": MF$ = "N"
85 VNS$(1) = "Run number": VNS$(2) = "Date": VNS$(3) = "Portal no.": VNS$(4) = "Neutral vol."
86 RGS$(1) = "(1 - 30)": RGS$(2) = "": RGS$(3) = "(1 - 2)": RGS$(4) = "(100 - 900)"
90 VNS$(5) = "T (degrees C)": VNS$(6) = "Tube pressure": VNS$(7) = "Tylan flow value": VNS$(8) = "Reaction title"
91 RGS$(5) = "(0 - 50)": RGS$(6) = "(0.1 - 1.0)": RGS$(7) = "(1 - 400)": RGS$(8) = ""
95 VNS$(9) = "Ion mass (amu)": VNS$(10) = "Carrier gas": VNS$(11) = "Comments"
96 RGS$(9) = "(1 - 50)": RGS$(10) = "(H2/HE/N2/AR)": RGS$(11) = ""
98 DS$(0) = "Escape": DS$(1) = "Edit a data point": DS$(2) = "Delete a row of data": DS$(3) = "Add a data point": DS$(4) = "Delete a column of data"
100 GOSUB 1000
110 REM get option desired
120 REM
200 IF OP% = 1 THEN GOSUB 2000
210 REM load data file
220 REM
300 IF OP% = 2 THEN GOSUB 3000
310 REM load format file
320 REM
600 IF OP% = 3 THEN GOSUB 6000
610 REM examine file contents
620 REM
700 IF OP% = 4 THEN GOSUB 7000
710 REM edit file contents
720 REM
800 IF OP% = 5 THEN GOSUB 8000
810 REM save file
900 IF OP% = 6 THEN PRINT CD$; "RUN OPTIONS,D1"
910 REM return to main menu
950 IF OP% < > NC% GOTO 100
990 END
1000 REM options menu
1010 HOME
1020 PRINT "STUDY FILES": PRINT "----- -----": PRINT "Make a choice": PRINT "----- - -----":
PRINT
1030 FOR I = 1 TO NC%
1040 HTAB(10): PRINT "(";I; "): TS$(I)
1045 PRINT
1050 NEXT
PRINT "WHICH OPTION? (1-";NC%;"): ";
GET OS$: OP% = ASC (OS$) - 48: IF OP% < 1 OR OP% > NC% GOTO 1070
PRINT OP%: PRINT ";TS$(OP%)
RETURN
REM load data file
HOME: PRINT "LOAD DATA FILE:"; PRINT ";"; DFS$ 
PRINT "Current data filename is "; DFS$ 
PRINT: PRINT "Change this? (Y/N): "; KS$ = STR$ (INKEY$)
IF KS$ < > "Y" AND KS$ < > "N" GOTO 2040
PRINT KS$: IF KS$ = "N" THEN 2060
PRINT "New filename? (N=no change I NONE=don't read): "; NF$ = SPACE$(INKEY$)
IF NF$ = "" OR NF$ = "NONE" THEN RETURN
IF NF$ < > "N" THEN DFS$ = NF$ 
PRINT: PRINT "READING FILE "; DFS$; " NOW ..." 
PRINT CD$; "OPEN "; DFS$; ";D2"
PRINT CD$; "READ "; DFS$ 
INPUT PTS 
FOR I = 1 TO PTS 
FOR J = 1 TO MAX 
INPUT YP(I,J); XP(I) 
NEXT 
NEXT 
PRINT CD$; "CLOSE "; DFS$ 
FT$(1) = "Y" 
IF FT$(2) = "Y" THEN MF$ = "Y"
RETURN
REM read format file
HOME: PRINT "READ RATE VARIABLES FILE:"; PRINT " ---- ---- ---- ----": PRINT 
VTAB (7): PRINT "Current filename is "; FF$ 
PRINT: PRINT "Change this? (Y/N): "; KS$ = STR$ (INKEY$)
IF KS$ < > "Y" AND KS$ < > "N" GOTO 3040
PRINT KS$: IF KS$ = "N" GOTO 3100
PRINT "New filename? (N=no change I NONE=don't read): "; NF$ = SPACE$(INKEY$)
IF NF$ = "" OR NF$ = "NONE" THEN RETURN
IF NF$ < > "N" THEN FF$ = NF$ 
PRINT: PRINT "READING FILE "; FF$; " NOW ...": PRINT 
PRINT CD$; "OPEN "; FF$; ";D2"
PRINT CD$; "READ "; FF$ 
FOR I = 1 TO 11 
INPUT RC$(I); VQ(I) = VAL (RC$(I)) 
NEXT 
PRINT CD$; "CLOSE "; FF$ 
FT$(2) = "Y" 
IF FT$(1) = "Y" THEN MF$ = "Y"
RETURN
REM examine file contents
HOME : PRINT "DISPLAY A FILE:"; PRINT " ---- ---- ----": PRINT 
FOR I = 1 TO 2 
IF FT$(I) = "Y" THEN TF% = I 
NEXT 
GOTO 6130 
PRINT "Data or format file? (D/F): "; 
GET KS$: IF KS$ < > "D" AND KS$ < > "F" GOTO 6105
IF KS$ = "D" THEN TF% = 1 
IF KS$ = "F" THEN TF% = 2
IF FS$(TF%) < > "Y" THEN 6110
PRINT KS$
IF TF% = 1 THEN HD$ = "DATA FILE " + DF$:UL$ = "---- ----"
IF TF% = 2 THEN HD$ = "FORMAT FILE " + FF$:UL$ = "---- ----"
ON TF% GOSUB 6200,6400
GET KS$ GOSUB 6200,6400
RETURN
REM display data file
ST = 1:FI = PTS: IF FI > 15 THEN FI = 15
HOME : PRINT HD$: PRINT UL$: PRINT
PRINT " X"
FOR J = 1 TO MAX: POKE 1403,(10 * (J + 1)): PRINT " Y";: NEXT
PRINT
PRINT
FOR I = ST TO FI
QX = 2 - INT (LOG (1) / LOG (10)): POKE 1403,QX: PRINT I", "XP(I);
FOR J = 1 TO MAX
POKE 1403,(10 * (J + 1)): PRINT YP(I,J);:
NEXT
PRINT
NEXT
IF PI > = PTS THEN 6350
ST = ST + 15:FI = PT$ THEN FI = PTS:ST = PTS - 15
GET KS$: GOTO 6210
RETURN
REM display rate vbles file
FOR I = 1 TO 11
I$ = CHR$(I + 64)
PRINT "; I$;"); POKE 1403,30: PRINT "; RC$(I)
NEXT
PRINT RC$(I)
NEXT
RETURN
REM edit file
HOME : PRINT "EDIT A FILE:": PRINT ".---- - ----": PRINT
IF TF% = 1 OR TF% = 2 OR TF% = 3 GOTO 7050
IF MF$ = "Y" GOTO 7040
FOR I = 1 TO 3
FOR IF PTS(I) = "Y" THEN TF% = I
NEXT
NEXT
GOTO 7050
IF TF% < 1 THEN HOME : PRINT : VTAB (11): POKE 1403,30: PRINT "LOAD A FILE FIRST!": PRINT "(Press any key to continue)": GET KS$: RETURN
PRINT "Data or format file? (D/F): ";
GET KS$: IF KS$ < > "D" AND KS$ < > "F" GOTO 7041
PRINT KS$
IF KS$ = "F" THEN TF% = 2
IF KS$ = "D" THEN TF% = 1
IF PTS(TF%) < > "Y" GOTO 7041
ON TF% GOSUB 7100,7400
RETURN
REM edit data file
HOME : PRINT "EDIT DATA FILE " + DF$:UL$ = "---- ----"
GOSUB 6200: REM display data file
PRINT
FOR I = 1 TO 4: POKE 1403,10: PRINT I;", ";DS$(I): NEXT
PRINT PRINT " WHICH OPTION? (0-4): "; WO$ = ASC (KS$) - 48: IF WO$ < 0 OR WO$ > 4 THEN 7140
PRINT KS$: IF WO$ = 0 THEN RETURN
7160 ON WO% GOSUB 7200,7260,7300,7360
7170 GOTO 7110
7180 RETURN
7200 REM edit data point
7210 HD$ = "EDIT DATA POINT";UL$ = "- - - - - -"; GOSUB 6200: REM display data file
7215 PRINT : PRINT "Which point? (0-";PTS;") "; INPUT "(0=esc): ";WP
7220 IF WP > PTS OR WP < 0 THEN RETURN
7225 REM display file
7228 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" THEN 7228
7230 PRINT KS$: IF KS$ = "Y" THEN INPUT "Enter new value (-1 to escape): ";X
7235 FOR J = 1 TO MAX
7238 PRINT: PRINT "Change X";J; "? "; XP(WP,J): INPUT " (YIN): "; YP(WP,J)
7240 GET KS$: IF KS$ = "N" THEN RETURN
7242 PRINT: PRINT "Change Y";J; "? "; YP(WP,J): INPUT " (YIN): "; YP(WP,J)
7245 NEXT
7250 RETURN
7260 REM delete data point
7265 HD$ = "DELETE DATA POINT";UL$ = "- - - - - -"; GOSUB 6200: REM display data file
7270 PRINT : PRINT "Which point? (0-";PTS;") "; INPUT "(0=esc): ";WP
7275 IF WP > PTS OR WP < 1 THEN 7298
7280 FOR I = WP TO PTS - 1
7282 XP(I) = XP(I + 1)
7285 FOR J = 1 TO MAX
7288 YP(I,J) = YP(I + 1,J)
7290 NEXT
7292 NEXT
7295 PTS = PTS - 1
7296 GOTO 7265
7298 RETURN
7300 REM add a data point
7305 HD$ = "ADD A DATA POINT";UL$ = "- - - - - -"; GOSUB 6200: REM display data file
7310 PRINT : PRINT "Enter x-value (-1 to escape): ";X
7315 IF X = 0 THEN PTS = PTS + 1: IF PTS > 40 THEN PRINT : PRINT "FILE EXCEEDS MAX. ALLOWABLE SIZE!"; PRINT "(Press any key to continue ) "; GET KS$:PTS = 40: RETURN
7318 IF X < 0 THEN 7355
7320 XP(PTS) = X
7325 FOR J = 1 TO MAX
7330 PRINT "Enter Y";J; " : "; YP(PTS,J)
7335 NEXT
7335 RETURN
7360 REM delete a column of data
7365 HD$ = "DELETE A COLUMN OF DATA";UL$ = "- - - - - -"; GOSUB 6200: REM display data file
7370 PRINT "Which data column? (Y= 0 to ";MAX;") (0=esc): "; W
7375 GET KS$: WC% = ASC (KS$) - 48: IF WC% < 0 OR WC% > MAX THEN 7375
7380 PRINT KS$: IF WC% = 0 THEN RETURN
7382 PRINT : PRINT "Sure about that? (Y/N): "; W
7385 GET KS$: IF KS$ < > "Y" AND KS$ < > "N" THEN 7385
7388 PRINT KS$: IF KS$ = "N" THEN RETURN
7389 MAX = MAX - 1: IF MAX < 1 THEN MAX = 1: RETURN
7390 FOR J = WC% TO MAX
7392 YP(I,J) = YP(I,J + 1)
7393 NEXT
7394 NEXT
7395 RETURN
REM edit rate variables file
HD$ = "EDIT FORMAT FILE:"; UL$ = "----- -------"
GOSUB 6400: REM display file
PRINT: PRINT "EDIT WHICH ENTRY ?(A-K) (N = escape): ";
GET WO$: WP% == ASC (WO$) - 64: IF WP% < 1 OR (WP% > 11 AND WO$ < > "N")
GOTO 7440
PRINT WO$: IF WO$ == "N" THEN RETURN
ON TY(WP%) GOSUB 7500, 7560, 7620
GOTO 7410
RETURN
REM edit numerical entries
PRINT: PRINT WO$; "."; VN$(WP%); RG$(WP%)
PRINT "Current value == "; VQ(WP%)
PRINT: INPUT "New value? (-999 to leave unchanged): "; NV
IF NV > -999 THEN VQ(WP%) == NV: RC$(WP%) == STR$(VQ(WP%))
RETURN
REM edit character-type entries
PRINT: PRINT WO$; "."; VN$(WP%); RG$(WP%)
PRINT "Current value == "; RC$(WP%)
PRINT: INPUT "New value? (N to leave unchanged): "; NV$
IF NV$ <> "Nil" THEN RC$(WP%) = NV$
RETURN
REM edit carrier gas value
PRINT: PRINT WO$; "."; VN$(WP%); RG$(WP%)
PRINT "Current value == "; RC$(WP%)
PRINT: INPUT "New value? (blank to leave unchanged): "; NV$
IF NV$ == "HE" OR NV$ == "ID" OR NV$ == "N2" OR NV$ == "AR" THEN RC$(WP%) = NV$
RETURN
REM save a file
HOME: PRINT "SAVE A FILE:"; PRINT "---- ---- "; PRINT
IF MP$ == "Y" GOTO 8040
FOR I == 1 TO 3
IF FT$(I) == "Y" THEN SP% == 1
NEXT
PRINT KS$:
IF KS$ == "N" THEN RETURN
PRINT: PRINT "WRITING FILE "; DF$; " NOW ...
PRINT CD$; "OPEN "; DF$; ";D2"
ON TF% GOSUB 8100, 8400
RETURN
REM save data file
HD$ = "SAVE DATA FILE:"; UL$ = "---- -------"
GOSUB 6200: REM show file contents
PRINT: PRINT "CURRENT FILENAME IS "; DP$
INPUT "ENTER NEW FILENAME ('N' to use current name): "; KS$
IF KS$ < > "N" THEN DP$ = KS$
PRINT: PRINT "PROCEED ? (Y/N): ";
GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 8170
PRINT KS$: IF KS$ == "N" THEN RETURN
HOME: PRINT: VTAB (11): POKE 1403, 25: PRINT "WRITING FILE "; DP$; " NOW ...
PRINT CD$; "OPEN "; DP$; ";D2"
PRINT CD$; "WRITE "; DP$
PRINT PTS
PRINT MAX
FOR I = 1 TO PTS
FOR J = 1 TO MAX
PRINT YPI(J): PRINT XP(I)
NEXT
NEXT
PRINT CD$;"CLOSE ";DFS$
RETURN
REM save rate vbles file
HD$ = "SAVE RATE VARIABLES FILE":UL$ = "---- ---- ---- ----"
GOSUB 6400: REM show file contents
INPUT "ENTER NEW FILENAME (N' to use current name): ";KS$
IF KS$ < > "N" THEN FFS$ = KS$
PRINT "PROCEED ? (Y/N): ";
GET KS$: IF KS$ < > "Y" AND KS$ < > "N" GOTO 8470
PRINT CD$;"OPEN ";FF$;,D2"
FOR I = 1 TO 11
PRINT RC$(I)
NEXT
PRINT CD$;"CLOSE ";FF$;
RETURN
REM get default filenames
PRINT CD$;"OPEN FILENAMES,D2"
PRINT CD$;"READ FILENAMES"
INPUT DFS$
INPUT FFS$
PRINT CD$;"CLOSE FILENAMES"
RETURN
Program "PRESSMONITOR"

10 PRINT CHR$ (4) "PR#3"
20 LOMEM: 32768
30 DIM IN$(20)
40 DIM SEL(20,2)
50 DIM SL(100,2)
55 DIM FM(400)
60 LS = 120
70 LA = 25
80 CD$ = CHR$ (13) + CHR$ (4)
120 PRINT CD$ "LOADATTENT"
130 PRINT CD$ "LOADTEMP1"
140 PRINT CD$ "LOADCONVERT"
150 PRINT CD$ "LOADMADMMAIN"
170 PRINT CD$ "LOADTEMP2"
280 HOME
290 Z = 0: D = 0: REM : TO ALLOW SETTING UP STEP
295 DZ = 0
300 NF% = 0: XU% = 0
340 HOME: PRINT "MONITOR NEUTRAL REACTANT FLOW": PRINT "------- ------- -------- ---": PRINT "" IN$(1) = "3"
350 AD = 2
360 S = 3: SS = "DELAY(20=1SEC)" : RG$ = "1:256": GOSUB 760: DD = VO
370 PRINT
380 POKE 25040, AD: POKE 25042, DD
390 S = 9: SS = "CHANNEL NO" : RG$ = "0:7": GOSUB 760: CH = VO
400 TT = 0
410 PRINT
420 CH = CH + (IT * 16)
430 POKE 25060, CH
440 AGAIN = 1
450 PRINT
460 HGAIN = 1
470 PRINT
474 POKE 31232, 0
475 POKE 31233, 0
476 POKE 31235, 0
477 POKE 31234, 0
480 CALL 24576: REM AD SAMPLE
505 XH = PEEK (31232)
507 XL = PEEK (31233)
510 XH = (XH * 256) + XL
520 SH = PEEK (31234)
530 SL = PEEK (31235)
540 SH = (SH * 256) + SL
550 BH = PEEK (29408 + TT * 2)
560 BL = PEEK (29408 + TT * 2 + 1)
565 V1H = PEEK (25051)
567 V2L = PEEK (25050)
570 BH = BH * 256 + BL
580 P1T = (XH * BH) / (HGAIN * AGAIN)
582 P2T = (SH * BH) / (HGAIN * AGAIN)
584 P1T = P1T / 8141
586 P2T = P2T / 8141
590 SLOPE = (P2T - P1T) / (DD * .05)
610 CH = PEEK (25039)
375

380 IF KX$ = "Y" GOTO 710
385 TEXT: HOME: PRINT CHR$(4)"PR#1"
390 PRINT SLOPE
395 PRINT CHR$(4)"PR#3"
400 IF KX$ = "N" GOTO 1220
405 FM(NF%) = SLOPE
410 AUT = 0:
415 GOTO 290
420 GOTO 340
425 PRINT S$i"(';RG$i")<"iIN$(S)i">": GOSUB 1020:0K
430 IF A > 0 THEN IN$(S) = A$:
435 GOTO 800
440 A = LEN (IN$(S»: IF A = 0 GOTO 980
445 FOR I = 1 TO A: IF MID$ (IN$(S),I,1) = "," THEN B = I + 1:1
450 NEXT
455 IF S = 4 OR 5 GOTO 990
460 R$ = ":":R = 0: FOR J = 1 TO L
465 IF R$ = ":":R = 0: FOR J = 1 TO L
470 IF MID$ (RG$,J,1) = "," THEN R$ = R$ + MID$ (RG$,J,1): IF J < L GOTO 970
475 IF VAL (R$) = 0 AND ASC (R$) < > 48 GOTO 930
480 IF R = 0 THEN VO = VAL (IN$(S)): IF VO < VAL (R$) GOTO 950
485 PRINT VO
490 IF R = 1 THEN IF VO > VAL (R$) GOTO 950
495 IF R = 2 THEN V1 = VAL (MID$(IN$(S),B)):
500 IF V1 < VAL (R$) GOTO 950
505 IF R = 3 THEN IF V1 > VAL (R$) GOTO 950
510 R = R + 1:OK = 1:R$ = "": GOTO 970
515 IF IN$(S) < > R$ THEN R$ = "": GOTO 970
520 OK = 1: GOTO 960
525 OK = 0
530 J = L
535 PRINT R$: NEXT
540 IF OK = 0 THEN PRINT CHR$(7)"INVALID ENTRY;CHECK (RANGE)"
545 AUT = 0: GOTO 760
550 VO = VAL (IN$(S)): RETURN
555 IF B THEN BS$ = LEFT$(IN$(S),B - 2): RETURN
560 BS$ = IN$(S): RETURN
565 A = 0:B = 0:A$ = "": IF AUT = 1 AND S < LS AND PEEK (-16384) < 128 THEN PRINT :
570 RETURN
575 ALT = 0
585 GET CS$C = ASC (CS$): IF C > 31 GOTO 1200
590 IF C < > 8 GOTO 1120
595 IF A = 0 GOTO 1020
600 PRINT CS$;" ";CS$;A = A - 1
605 IF A > 0 THEN A$ = LEFT$(A$,A)
610 IF A < 1 GOTO 1020
615 GOTO 1050
620 GOTO 1150
625 IF C = 13 THEN PRINT : RETURN
630 IF C = 27 AND ES THEN GOSUB 11000:
635 AUT = 1: POP : POP : GOTO 110
640 IF C = 1 THEN AUT = 1: LS = 50: DTET = 1: GOTO 1020
645 IF C = 4 THEN PRINT : PRINT CS$;A$: POP : GOTO 760
1160 IF C = 7 THEN GOSUB 730 GOTO 1050
1170 IF C = 20 THEN GOSUB 840 GOTO 1050
1180 IF C = 19 THEN GOSUB 840
1190 IF C = 24 THEN PRINT CHR$(92): GOTO 1020
1200 IF C = 44 AND B = 0 THEN B = A + 2
1210 PRINT C$;A = A + 1:A$ = A$ + C$: GOTO 1050
1220 PRINT CD$;"RUN OPTIONS,D1"
1450 HOME: INPUT "ENTER RUN NUMBER ? (1-30): ";RN$
1460 NM$ = "FLOWFILE" + RN$
1500 PRINT CD$;"OPEN ";NM$;",D2"
1510 PRINT CD$;"WRITE ";NM$
1520 PRINT NF%
1530 FOR I = 1 TO NF%
1540 PRINT FM(I)
1550 NEXT
1560 PRINT CD$;"CLOSE ";NM$
1570 PRINT CD$;"RUN OPTIONS,D1"
Program "COLLIRAT"

10 REM ** PROGRAM COLLIRAT **
15 REM This program calculates the collision rate coefficient for an
20 REM ion-molecule reaction, based on Su & Chesnavich's method
25 REM (involving parametrization of collision rate by trajectory
40 CD$ = CHR$(13) + CHR$(4)
50 PRINT CHR$(4): "PR#3"
100 GOSUB 1000
110 REM initialise program
120 REM ----------------------
300 GOSUB 3000
310 REM input variables
320 REM ---------------------
400 GOSUB 4000
410 REM perform calculation
420 REM ---------------------
500 GOSUB 5000
510 REM display results
520 REM ---------------------
600 IF NG$ = "Y" GOTO 300
700 END
990 REM ---------------------
1000 REM initialise program
1010 GA = 1.6605E-24: REM grams per amu
1020 QI = 4.80298E-10: REM ionic charge in esu
1030 KB = 1.38062E-16: REM Boltzmann's const. in erg/K
1040 PI = 3.1415927
1500 RETURN
1990 REM ---------------------
3000 REM input variables
3010 HOME: PRINT "INPUT VARIABLES:"; PRINT "----- ---------": PRINT
3020 INPUT "Reaction title ? : ";RT$
3030 PRINT; INPUT "Mass of ion ? (in amu): ";MI
3040 INPUT "Mass of neutral ? (in amu): ";MN
3050 RAM = MI * MN / (MI + MN)
3060 PRINT "Reduced mass = "; INT(RAM * 100 +0.5)/100; "amu"
3070 PRINT "Polarizability of neutral ? (in cm3): ";PN
3080 PRINT "Dipole moment (in esu cm) <NB 1 Debye = 1E-18 esu cm>: "
3090 PRINT "Permanent dipole moment of neutral ? (in esu cm): ";DM
3100 PRINT "Temperature ? (in degrees C): ";TC
3110 PRINT: PRINT: PRINT " Any changes? (Y/N) : ";
3120 GET KS$: IF KS$ <> "Y" AND KS$ <> "N" GOTO 3120
3130 PRINT KS$: IF KS$ = "Y" GOTO 3010
3500 RETURN
3990 REM ---------------------
4000 REM perform calculation
4010 RGM = RAM * GA: REM convert reduced mass to grams
4015 TK = TC + 273.2
4020 KL = 2 * PI * QI * (PN / RGM) ^ 0.5
4030 X = DM / (((KB * TK) ^ 0.5) * (PN ^ 0.5))
4040 K1CAP = 0.4767 * X + 0.6200
4050 IF X <= 2 THEN K1CAP = ((X + 0.5090) ^ 2) / 10.526 + 0.9754
4060 KC = K1CAP * KL
4500 RETURN
4990 REM ---------------------
REM display results
IF PT$ = "Y" THEN PRINT CHR$(4);"PR#1"
HOME
PRINT "ION-MOLECULE COLLISION RATE CALCULATION:"; PRINT "--- --------- ---
PRINT
PRINT RT$
PRINT: PRINT "Calculated collision rate k(c) = ";KC
PRINT: PRINT "Collision efficiency K(cap) = ";K1CAP
PRINT "Capture rate k(L) = ";KL
PRINT: PRINT
PRINT "Reduced mass = "; INT(100 * RAM + 0.5) / 100; "amu"
PRINT "Polarizability of neutral = ";PN; "cm^3"
PRINT "Permanent dipole moment of neutral = ";DM; "esu cm"
PRINT "Temperature = "; INT(100 * TK + 0.5) / 100; "K"
IF PT$ = "Y" GOTO 5200
PRINT: PRINT "Do you want a printout? (Y/N): ";
GET PT$: IF PT$ <> "Y" AND PT$ <> "N" GOTO 5170
PRINT PT$: IF PT$ = "Y" GOTO 5210
IF PT$ = "Y" THEN PRINT CHR$(4);"PR#3"
PRINT: PRINT: PRINT "More calculations? (Y/N): ";
GET NG$: IF NG$ <> "Y" AND NG$ <> "N" GOTO 5220
PRINT NG$
RETURN
ERRATA:

The following amendments should be made to the text:

p. 10, 5 lines from bottom. "frequencies" should read "rates".

p. 20, 7 lines from bottom. "is commonly" should read "can be"; reference 60 quoted on this line should be replaced by reference 61.

p. 30, equation (1.ix). "k = ln ..." should read "k = - ln ..."

p. 63, line 2. "poymerisation" should read "polymerisation".

p. 70, line 8. "-0.705" should read "0.705"

p. 71, line 2. "-6.448" should read "6.448"

p. 74, table 3.2, note 'c'. "rate coefficient, using" should read "rate coefficient, in units of 10^-9 cm^3 molec^-1 s^-1, using". The same amendment should be made to note 'c' in tables 4.2 (p.100), 5.2 (p. 142), 6.1 (p. 201) and 7.3 (p. 242).

p. 98, table 4.1. This table has two notes 'b'. The second of these should be changed to 'c'; likewise, the existing note 'c' should be changed to 'd', etc.

p. 107, table 4.5. "geometries", in the title of this table, should read "properties".

p. 117, table 4.7. The printed value of k_2 for reaction with C_2H_2, ">0.06", should read ">0.6".

p. 147, equation (5.iii). "[CF+]" should read "[CF_3+]".

p. 206, 4 lines from bottom. "HC_3N+" should be indented appropriately.

p. 213, line 5. "C_2H_2N+" should read "C_2H_2N++".

p. 218, line 14. "was" should read "is".

p. 234, 3 lines from bottom. "though" should read "thought".

p. 245, line 13. "from from" should read "from".

p. 248, reaction (7.16). "H_2" should read "e ".

p. 255, line 4. "C_4N++" should read "C_4N+".