KINETICS AND PHOTOCHEMISTRY
OF TRANSIENT FREE-RADICALS

A THESIS
SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
Doctor of Philosophy in Chemistry

IN THE
University of Canterbury

BY
Roger Francis Meads

University of Canterbury
1992
To my parents

Beverley Ada Meads

and

George Percival Meads

how fortunate I am
The machine does not isolate man from the great problems of nature
but plunges him more deeply into them.

Saint-Exupéry

Let us learn to dream, gentlemen, then perhaps we shall discover the truth;
But let us beware of publishing our dreams abroad before they have been scrutinized
by our vigilant intellect ...
Let us always allow the fruit to hang until it is ripe.
Unripe fruit brings even the grower but little profit;
It damages the health of those who consume it;
It endangers particularly the youth who cannot yet distinguish between ripe and unripe fruit.

Kekulé, 1890
Abstract

We report here several experimental and theoretical studies of free-radicals in the gas phase. Bimolecular rate constants for the reactions

\[
\begin{align*}
\text{BH} + \text{NO} & \rightarrow \text{products} \quad k = 1.26 \pm 0.07 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \\
\text{BH} + \text{C}_2\text{H}_4 & \rightarrow \text{products} \quad k = 1.41 \pm 0.09 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \\
\text{CN} + \text{NH}_3 & \rightarrow \text{HCN} + \text{NH}_2 \quad k = 3.0 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \\
\text{CN} + \text{ND}_3 & \rightarrow \text{DCN} + \text{ND}_2 \quad k = 1.5 \pm 0.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}
\end{align*}
\]

have been measured and upper limits to the rate constants for the reactions

\[
\begin{align*}
\text{BH} + \text{CO} & \rightarrow \text{products} \quad k < 1.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \\
\text{BH} + \text{CH}_4 & \rightarrow \text{products} \quad k < 1.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \\
\text{BH} + \text{C}_2\text{H}_6 & \rightarrow \text{products} \quad k < 9.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \\
\text{BH} + \text{O}_2 & \rightarrow \text{products} \quad k < 1.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}
\end{align*}
\]

have been set. BH (\(1\Sigma^+)\) radicals were generated by excimer-laser photolysis of diborane at 193 nm and detected by time-resolved laser-induced fluorescence. The effects of varying the temperature and the nature of the buffer gas on the reactions of BH with NO and C\(_2\)H\(_4\) have been investigated. CN (\(2\Sigma^+)\) radicals were generated by excimer-laser photolysis of C\(_2\)N\(_2\) at 193 nm and their time evolution was monitored by absorption spectroscopy.

In addition to the rate constant measurements, the products of the reactions of CN with NH\(_3\) and ND\(_3\) have been determined using mass spectrometry and infrared absorption spectroscopy. The methods of \textit{ab initio} molecular orbital theory have been used to determine structures and relative energies of species which could
conceivably be involved in these reactions. The results of all studies have been interpreted in relation to the mechanisms of the reactions concerned.

Prompt emission observed during the 193 nm excimer-laser photolyses of diborane and stannane has been characterised and the identity of the probable emitting species for each band observed has been assigned on the basis of band structure, known thermochemistry and the dependence of band intensity on photolysis laser power. The results obtained have been interpreted in terms of the nature of the photodissociation processes.
Acknowledgements

The successful completion of this work has been aided by the valued contributions of a number of people. First and foremost I would like to thank my family, for their continual support, patience and love.

I am very grateful to my supervisors for their guidance during the course of this work. I would like to thank Professor Leon F. Phillips for his supervision during the past four years and similarly, Dr. Peter W. Harland and Dr. Robert G. A. R. Maclagan for their support and encouragement. Thanks also to Professor Michael P. Hartsborn, Dr. Donald A. House and Dr. Murray J. McEwan.

The contribution made by the technical staff of this department is greatly appreciated. In particular I wish to thank Messrs Peter C. Chadwick, John E. Davis, Alexander M. Fergusson, Russell W. Gillard, David J. MacDonald, Robert M. McGregor, David W. Morrison, Bruce A. Reid, Geoffery Speer, Derek T. Williams, Barrie Wood and John J. York for their advice and assistance.

The friendship, advice and amusement provided by fellow researchers; Dr. John Harrison, Dr. Jayantha Wimalasena, Brett Cameron, David Marsden, Michael Tavendale and Murray Salt is also greatly appreciated.

Roger F. Meads.
March 1, 1992
# TABLE OF CONTENTS

2.3 Reagent Chemicals and Handling Techniques ........................................... 15

2.4 Data Reduction Procedures ........................................................................ 17

3 Kinetics of Reactions of BH with NO, C₂H₄, O₂, CH₄, C₂H₆ and CO ............. 19

  3.1 Introduction ............................................................................................ 19

  3.2 Experimental ........................................................................................... 20

  3.3 Results and Discussion ............................................................................ 23

    3.3.1 BH + NO ......................................................................................... 24

    3.3.2 BH + C₂H₄ .................................................................................... 29

    3.3.3 BH + CH₄, C₂H₆, O₂ and CO ......................................................... 29

  3.4 Conclusions ............................................................................................ 31

4 Photoexcitation of Diborane and Stannane at 193 nm .................................. 33

  4.1 Introduction ............................................................................................ 33

  4.2 Experimental ........................................................................................... 35

  4.3 Results and Discussion ............................................................................ 37

  4.4 Conclusions ............................................................................................ 43

5 Theoretical study of the reaction of CN with NH₃ ........................................ 45

  5.1 Introduction ............................................................................................ 45

  5.2 Principles of *ab initio* molecular orbital theory ..................................... 46

    5.2.1 The potential energy surface ............................................................ 46
# TABLE OF CONTENTS

5.2.2 The Hartree-Fock approximation .............................................. 48
5.2.3 Post Hartree-Fock theory ...................................................... 49
5.2.4 Basis Sets ................................................................. 51
5.3 Details of Calculations .......................................................... 53
5.4 Results and Discussion .......................................................... 53
5.5 Conclusions ................................................................. 67

6 Kinetics of reactions of CN with NH₃ and ND₃ .............................. 68
6.1 Introduction ................................................................. 68
6.2 Experimental ................................................................. 73
6.3 Results and Discussion .......................................................... 76
6.4 Conclusions ................................................................. 82

7 Products of reactions of CN with NH₃ and ND₃ .............................. 84
7.1 Introduction ................................................................. 84
7.2 Experimental ................................................................. 85
7.3 Results and Discussion .......................................................... 87
7.4 Conclusions ................................................................. 92

8 Conclusions ................................................................. 94

Bibliography ................................................................. 100
# List of Tables

1. Dependence of the rate constants of the reactions of BH with NO and C₂H₄ on the nature of the buffer gas. ........................................ 27

2. Thermochemistry of the possible products from the photodissociation of diborane at 193 nm ...................................................... 37

3. Atomic tin lines observed during the 193 nm photolysis of stannane . 42

4. Optimized Hartree-Fock and MP2 geometries ............................... 57

5. Calculated HF//HF, MP4SDQ//HF, MP4SDQ//MP2 and QCISD(T)//MP2 energies and zero-point vibrational energy .................. 59

6. Calculated Hartree-Fock harmonic vibrational frequencies ................ 64

7. Results of previous studies of the reactions of CN-radicals ............. 71

8. Results of previous studies of the reaction of CN with NH₃ ............ 72

9. Room temperature rate constants for the reaction of CN with NH₃ . 80

10. Comparison of experimental and calculated geometries for HCN, HNC and the CHN (TS). ....................................................... 90
List of Figures

1 Experimental configuration for the collection of kinetic data using excimer-laser photolysis/dye-laser-induced fluorescence ........................................ 22

2 Laser-induced fluorescence decay profiles of BH in the presence of NO 24

3 Stern-Volmer plot for the decay of BH in the presence of NO ........ 25

4 Temperature dependences of the reaction of BH with NO and C₂H₄ . 26

5 Emission from excited BH₂ observed during the 193 nm photolysis of diborane ................................................................. 38

6 Emission from excited BH observed during the 193 nm photolysis of diborane ................................................................. 39

7 Expanded view of the emission from excited BH₂ in the region 320 to 345 nm. ................................................................. 40

8 Relative energies of species conceivably involved in the reaction of CN with NH₃ ................................................................. 62

9 Experimental configuration for the collection of kinetic data using excimer-laser photolysis/diode-laser absorption spectroscopy .... 75

10 Transient absorption profiles of CN-radicals in the presence of ND₃ . 77

11 Pseudo first-order decay plots for CN in the presence of ND₃ .... 78
12  Stern-Volmer plot for the reaction of CN with ND₃  . . . . . . . . 79
13  Calculated G-1 energies for the HCN⇌HNC equilibrium  . . . . . 89
Chapter 1

Introduction

The fields of experimental kinetics, spectroscopy and dynamics of small molecules have seen a number of advances in recent years as part of the continuing quest to understand the fundamental interactions of atoms and molecules with each other and with electromagnetic radiation. Gas-phase systems are of particular interest in this regard since the finer details of these elementary processes are not masked by the effects of interference from the matrix which is a complex problem in condensed phases. The use of molecular beam apparatus can extend this ideal further allowing the study of species under essentially collisionless conditions. In a recent series of very elegant experiments, this phenomenon has allowed the characterization of species in transition between reactants and products both for unimolecular photodissociation [1,2] and bimolecular chemical reactions [3,4,5].

Despite these advances, the field of gas-phase kinetics remains as one of the most important and fruitful means of obtaining fundamental information on the rates at which these interactions occur. The realm of the gas-phase kineticist extends to cover both intermolecular and intramolecular processes and includes processes by which atoms and molecules interact with electromagnetic radiation. The results of such studies provide information on the potential-energy surfaces characterizing these interactions and are vital for use in modelling studies of the complex chemistry occurring in many practical chemical systems.
Progress in experimental chemical kinetics has been closely linked to technical innovation. In this regard, the advent of commercially available lasers, of which there are now many types employing gas, liquid and solid-state lasing media [6,7], has provided a major impetus in the development of this, and many other areas of chemistry [8,9]. Lasers possess a number of properties which make them an essential part of most modern kinetics experiments. Foremost among these are the very high photon densities (brightness) and monochromaticity (narrow bandwidth) of lasers and the wide regions of the electromagnetic spectrum that they now cover. In combination with frequency mixing techniques and methods of discrete shifting [10,11], "continuously" tunable, monochromatic, coherent light sources are available at nearly any desired wavelength in the range 150–1100 nm with many other regions extending well into the infra-red and vacuum-ultraviolet [9] also covered.

The application of lasers to the study of chemical kinetics has become the focus for many research groups. High power lasers operating at discrete wavelengths in the ultraviolet and vacuum-ultraviolet regions are ideal sources for the generation of transient species such as atoms, molecules, radicals and ions by laser-photolysis of a stable precursor molecule. Single and multi-photon photolysis can provide the experimentalist with access to a large number of rovibronic states of the photofragments [12]. However, photofragments produced in this manner can often have large excesses of internal energy, which introduces additional problems involving cascading and thermalization. Measurement of the energy distributions of the photolysis products can provide information on the photolysis process [13]. In addition to the characteristics already mentioned, the short pulse-widths and high spatial coherence of these pulsed-laser beams have the major advantage, over other means of production such as pulse-radiolysis or discharge-flow techniques, of being able to produce high concentrations of photofragments in a well defined volume, instantaneously and with comparative cleanliness [14]. Judicious choice of the precursor and reactant molecules with respect to the photolysing wavelength can substantially reduce the co-production of unwanted species which can interfere with the process being studied by competing reaction, quenching or absorption of the analysing laser-light.
This method also allows for a simpler interpretation of the experimental data as opposed to, for example, shock-tube [15] and combustion systems [16,17], where extensive numerical modelling is required to determine the kinetic information for the reactions of interest.

Lasers have also proven to be very powerful tools for the detection of transient species whether produced by laser photolysis or by other means. The most widely used laser based detection technique is laser-induced fluorescence [14] in which fluorescence is excited from one or more rovibronic transition of the species of interest by a pulsed, or more recently continuous-wave, dye-laser. Dye-lasers generally lase in the visible and near ultra-violet regions and are tunable over the fluorescence band of the organic dye being used. The detection of fluorescence excited in this manner has proven to be very sensitive to low molecular concentrations although it has the disadvantage of often being limited by fluorescence quenching, sometimes at relatively low pressures. There is the additional problem that not all species will fluoresce as energy degradation of the laser-excited state by non-radiative means may be more efficient.

Since the initial experiments by Laguna and Baughcum [18], detection of transient species by infra-red diode-laser absorption has become more popular. This method has the advantage that almost all species, with the exception of homonuclear diatomic molecules, will absorb infra-red radiation and the very narrow bandwidth of diode-lasers provides for high chemical selectivity between species produced by the photolysis laser pulse. Being an absorption technique, it can be used to study reactions over a wide range of temperatures and pressures but has the disadvantage of being generally less sensitive than detection by laser-induced fluorescence, since a change in signal needs to be detected as opposed to emission above an essentially zero background. Multiple pass optical arrangements are often used to increase the sensitivity of this method of detection.

In conjunction with experimental studies, recent developments in theoretical methods have an important contribution to make to our understanding of the potential-energy surfaces characterizing chemical processes. The development of ab
initio molecular orbital theory [19,20,21] and the implementation and commercial distribution of software based on these methods, predominantly by Gaussian Inc, has meant that the ability to calculate these potential-energy surfaces is now available to the non-specialist. A recent review provides a useful guide to the concepts and features of many of the currently used methods of ab initio quantum chemistry [22].

Current computational capabilities generally preclude calculation of entire potential-energy surfaces for all but the simplest of systems, since they may span many degrees of freedom. However, by probing the stationary points of the surface which correspond to intermediate and transition state species, much information can be obtained. Knowledge of the relative energies of reactants, products, intermediates and transition states gives good insight into the possible mechanism(s) of a chemical reaction and the relative importance of each, while calculations of the relative energies and/or Morse-type potential curves for the possible electronic states of a molecule have great value in spectroscopic applications.

Other theoretical methods, either statistically based, such as Rice-Ramsperger-Kassel-Marcus theory [23] and Activated-Complex theory [24] or dynamically based, such as Quasi-classical trajectory theory [25,26] can use the results of these ab initio studies to calculate the rates of various processes such as chemical reactions or unimolecular decompositions under experimentally inaccessible conditions. Although there is no substitute for experimental data, theoretical studies are certain to feature prominently as our understanding of chemical reactivity increases.

1.1 Scope of the Present Work

The work described in this thesis consists of five studies, four experimental and one theoretical, involving the reactions of cyanogen (CN) and boron hydride (BH) radicals and the spectroscopy of the products of the photodissociations of diborane (B$_2$H$_6$) and stannane (SnH$_4$). Studies of reactions of free-radicals such as these are
particularly relevant to the chemistry of atmospheric and/or combustion processes as well as being amenable to theoretical treatments due to the relative simplicity of the species involved. The combination of experiment and theory is able to provide a far greater insight into elementary processes such as these than either one alone.

General descriptions of experimental equipment and procedures used are given in chapter 2, with details of specific methodology relevant to individual experiments give in the appropriate chapter. In each of the experimental studies, the radical(s) of interest were produced by laser photolysis of a stable precursor molecule in a flow-system. In the kinetics experiments, the time-evolution of these species was monitored by either laser-induced fluorescence (chapter 3) or absorption spectroscopy (chapter 6). The emissions observed during the multi-photon photolysis of diborane and stannane were characterised and the probable emitting species of each band observed was assigned on the basis of band structure, known thermochemistry and laser power dependences (chapter 4).

In addition to these experimental studies, an \textit{ab initio} molecular orbital theory study of the reaction of CN with NH$_3$ is presented (chapter 5). In conjunction with the kinetic (chapter 6) and product analysis (chapter 7) studies done on this reaction the most likely mechanism of reaction is deduced.

Finally, in chapter 8 some general conclusions about the work presented in the preceding chapters are drawn and areas for possible extension of this work are discussed.
Chapter 2

Experimental

2.1 Introduction

In this chapter the major pieces of equipment used in the experiments discussed herein will be described. Technical specifications and considerations regarding the use of this equipment will be outlined together with data reduction procedures and methods of preparation and purification of reagents used. Specific methodology detailing the use of the equipment is deferred until the experimental section of the appropriate chapter. In all experiments, free-radicals were produced by laser-photolysis of a stable precursor molecule in a flow-system. These radicals were then characterised by either their spectroscopic or kinetic behaviour.

2.2 Apparatus

2.2.1 Excimer Laser

The photolysis light source used was a Lumonics model TE861-T, thyratron-switched, multigas, Excimer Laser. Gas mixtures of argon fluoride (ArF) and krypton
fluoride (KrF) were used to produce output at 193.3 and 248.5 nm respectively. Pulse energies, measured by a Scientech model 364 power/energy meter, were typically 50–70 millijoules. The laser output beam had a rectangular cross-section of approximately $2 \times 1 \text{ cm}^2$ which, for experiments involving the production of either $\text{B}_2\text{H}_6$ or $\text{SnH}_4$ photofragments, was focussed to a point of approximately $2 \times 1 \text{ mm}^2$. In all experiments the effective pulse energy incident upon the radical precursor was less than the maximum energy measured as a result of spatial filtering, due either to apertures or cell design, and scattering of the light by cell windows and optical elements. Knowledge of the absolute laser power was only important in the emission spectroscopy experiments of chapter 4. The high pulse energies and short pulse widths ($\approx 10 \text{ ns}$) of excimer lasers make them well suited to the present experiments.

### 2.2.2 Diode Laser

The probe light source used in the studies of CN-radical reactions was a Laser Analytics Infra-red Diode Laser. The laser diodes were cooled to cryogenic temperatures by a CTI-Cryogenics model 22C Cryodyne, Closed Cycle Helium Refrigerator. The cooled lead-salt diodes lase in many tunable, monochromatic modes. Frequency tuning of the infra-red radiation is achieved by varying either the refrigerator temperature (coarse tuning) or the injection current (fine tuning). Individual modes were selected using a monochromator (Laser Analytics model SP5151) adjacent to the cold-head, which has a grating blazed at ca. 10 microns. The wavelength scale of the monochromator was calibrated using the output of a helium-neon laser. Individual modes could generally be tuned over a range of ca. $1 \text{ cm}^{-1}$ with a maximum continuous-wave power output of ca. 1 mW. The total range covered by a single diode (semi-continuously with many mode-breaks) is approximately 100 cm$^{-1}$. The narrow bandwidth of the diode-laser provides for high chemical selectivity between moieties produced by the photolysis laser pulse and is applicable to the observation of both the decay of reactant species (chapter 6) and the buildup of products (chapter 7).
The diode-laser system also incorporates an internally-coupled, confocal Etalon (Laser Analytics model SP5945) which provides infra-red Fabry-Perot calibration fringes while the laser frequency is scanned, to assist in the determination of the absolute lasing frequency in the manner described by Reich et al. [27]. The etalon has the added feature of being able to be used to lock the laser emission frequency to the etalon path-difference [27,28]. This allows the stabilization of the laser emission frequency, or for varying the laser frequency by scanning the path difference around it's mean value via an internal scanner plate. Alignment of the infra-red beam through the etalon and reaction cells was done using the collimated output of a visible helium-neon laser on a co-linear path to the diode-laser beam.

2.2.3 Dye Laser

The probe light source used in the studies of BH-radical reactions was an AVCO model C5000/4000 Nitrogen Pumped Dye Laser. The thyratron-switched nitrogen laser produces 10 ns, 1 mJ pulses at 337.1 nm which are coupled onto a flowing-dye cassette. To produce output at 433.4 nm needed for these experiments, the dye Stilbene 420 (Exciton Chemical Company) was used. Tuning of the output wavelength over the dye's fluorescence band is accomplished via a gear box attached to the diffraction-grating drive. The dye-laser output pulses had typical energies of a few microjoules and a bandwidth of less than 0.1 nm (fwhm) when the laser was properly tuned. Spectral profiles were measured using a McPherson model 218, 0.3 m monochromator.

2.2.4 Detection Systems

In the experiments described here, three different types of detector were used: namely infra-red detectors, photomultipliers and a quadrupole mass spectrometer.
Infra-red detectors

The intensity of the infra-red diode-laser beam was monitored using Judson J15D14-M204-S01M-60 liquid-nitrogen cooled, mercury-cadmium-telluride detectors. Peak response is at ca. 11 microns falling to 60% at 4 microns. Detector output was amplified by a matched Judson PA-100 pre-amplifier (55 dB gain). Cable lengths between the detector and pre-amplifier were shielded and kept as short as possible to minimize the possibility of pick-up.

Photomultipliers

Prompt emission and laser-induced fluorescence was detected using either an EMI 9813QA, bi-alkali cathode, high-gain photomultiplier (peak response at ca. 360 nm) or an EMI 9558QB, tri-alkali cathode, red sensitive photomultiplier (peak response at ca. 400 nm). Both the photomultipliers and their pre-amplifiers were housed in a cylinder of μ-metal as a shield against electromagnetic noise.

Mass Spectrometer

A Spectramass Dataquad Quadrupole Mass Spectrometer was used for mass analysis of gaseous samples. Gaseous ions were detected using a secondary-electron multiplier. The quadrupole was pumped to pressures of ca. $10^{-8}$ torr by a Varian VHS-4 diffusion pump backed by a Welch Duo-Seal model 1376 mechanical pump. Analysis was done at pressures ranging from $10^{-7}$ to $10^{-5}$ torr as measured by an ion-gauge adjacent to the quadrupole. The diffusion pump and quadrupole are separated by a large liquid-nitrogen cold trap to prevent contamination of samples with diffusion pump oil fragments.
2.2.5 Monochromators

Three monochromators were used during the course of the experiments described here: namely a McPherson model 218, 0.3 m monochromator, a Jarrell-Ash 0.75 m Czerny-Turner monochromator and a Laser Analytics model SP5151 monochromator, used for mode selection of the diode-laser output, which has been described previously. Both the McPherson and the Jarrell-Ash monochromators were used to resolve the emission spectra described in chapter 4 and the McPherson monochromator was also used for a variety of other functions which included determining spectral profiles of the dye-laser and tuning of the dye-laser to the desired wavelength. Three different interchangeable gratings were used in the McPherson monochromator, all of which have 1200 grooves/mm, blazed at 500, 300 and 150 nm while the grating used in the Jarrell-Ash monochromator was blazed at 300 nm. The wavelength scales of the both these monochromators were calibrated using the emission of a mercury Pen-Ray lamp.

2.2.6 Reaction Cells

General considerations relevant to the design of the photolysis cells used in the laser-induced fluorescence (chapter 3) and the laser absorption (chapter 6) experiments will be discussed here. Additional details pertinent to the individual cells will be given in the experimental section of the appropriate chapter. The object of this section is to illustrate the differing criteria borne in mind during the design and construction of the two cells.

The cell used for the laser-induced fluorescence experiments was designed with respect to two major criteria; namely the need for temperature control and the need to minimize the effects of stray light. Temperature control was achieved by constructing the sidearms of the cell from a double layer of glass tubing and circulating a variety a liquids between the layers. The temperature of the liquids used was thermostatically controlled in a reservoir and circulated by an in-line pump. Insulation
of the cell with several layers of Cayo-wool allowed experiments in the temperature range 250-350K to be carried out.

A number of approaches were used to suppress stray light. Room light was eliminated by painting the cell with several layers of black paint. The effects of broad-band fluorescence excited from the Suprasil windows (most likely caused by defects, impurities and non-linear processes within the quartz) were minimized by the use of long sidearms on the cell, as the observed fluorescence intensity decreased with distance from the photomultiplier. Scattering of the photolysis and probe laser-light by the optics and the windows was also a problem. Angling the windows from perpendicular to the optical axis and using appropriate combinations of Corning glass filters to give a narrow bandpass in the region of interest helped minimize this and the effects of the window fluorescence. Despite these measures, it was necessary to wait 50 µs after the photolysis laser pulse before collecting data. This period also served to ensure that all species were thermalized and equilibrated with the cell wall temperature.

The cell used for the diode-laser absorption experiments was designed with one major consideration in mind: the need to maximize the length of the path along which the photolysis and probe laser beams overlapped. While overlap between the photolysis and probe laser beams was also necessary for the laser-induced fluorescence experiments, the decrease in sensitivity of laser absorption compared to laser-induced fluorescence made it especially necessary to maximize the overlap path length in these experiments.

Cell windows of calcium fluoride were used to enable the probe (infra-red) laser beam to be introduced co-linearly into the volume swept out by the photolysis (ultra-violet) laser beam. This proved to be far superior to introducing the two laser beams through different windows (each transparent to only one or other of the laser beams), which resulted in the probe laser beam being unable to pass through the entire length of the volume swept out by the photolysis laser beam in the cell. The number of passes attainable through this volume was a compromise between the need to have the excimer laser close to the cell and the (external) mirrors in
front of it as far back as possible to facilitate more reflections, and the diameter of the \( \text{CaF}_2 \) windows available limiting spatial resolution. The length of the cell was limited by the size of the annealing oven in the departmental glassblowing workshop to ca. 1.2 metres.

Both cells were evacuated by a Welch duo-seal model 1397 rotary pump backing a Heraeus R150 Roots blower. The pumps were separated from the cell and reagent manifold by a large liquid-nitrogen cold-trap which served the dual purpose of removing corrosive gases before passage through the pump and preventing contamination of the cell with pump oil. The actual pumping speed was controlled by a throttling valve situated immediately before the cold-trap.

Both cells were constructed of Schott-Duran glass in the glassblowing workshop of this department. Cell pressure was monitored via a B19 ground-glass joint by a MKS type 222CA 0-10 torr Baratron and, in the case of the CN experiments, also by a Texas Instruments model 144 quartz-spiral gauge. The reference vacuum for this instrument was provided by a two-stage glass diffusion-pump. All joints were lubricated with Apiezon N or H grade vacuum grease.

### 2.2.7 Reagent Manifold

Preparation and control of gas mixtures for laser photolysis was done in a glass vacuum-manifold. Incorporated in this were glass-bulbs and a variety of cold-traps for the purification and storage of reagent gases together with metered lines for the buffer, reactant and radical precursor constituents of each gas mixture. There was some flexibility in the system via interconnections between the lines so that, for example buffer could also be channeled through the radical precursor line and into a saturator which was used to admit vapor from solid ICN into the cell on the stream of buffer gas.

Gas flows were measured by Tylan model FM360 mass flow-meters, calibrated by standard bubble-tube techniques, and regulated by either Whitey (for flows less than
50 sccm) or Edwards needle-valves in conjunction with glass stop-cocks (J. Young Scientific Glassware Limited). The requirements of the experiment being undertaken dictated which of the available flow-meters, from a range having capacities 10, 50, 200 and 500 sccm, were used on which line. All the flow-meters used had calibration factors (actual flow/indicated flow) which were linear over their entire range. The flow-meters were connected to a Tylan model RO20A readout box which gave the flow in standard cubic centimetres per second (sccm) directly.

The pressure in any of the lines could be measured by a MKS 0-1000 torr, type 315BH-1000 capacitance manometer, controlled by a type MKS type 170M controller. The reference vacuum for this instrument was provided by an Edwards 1" diffusion pump. The manifold was constructed of Schott-Duran glass so that modifications, of which there were many, could be done cheaply and with relative ease. The ultimate geometry of the manifold was dependent on the experiment being undertaken.

Diborane and stannane were prepared in a separate vacuum line housed remotely from the main laboratory. Both manifolds were leak tested regularly using a tesla-coil and by monitoring the pressure in the manifold as a function of time when the pumps were blocked off. All vacuum pumps, including the diffusion pump, were separated from the manifold by large liquid-nitrogen cold-traps.

2.2.8 Microcomputers and Software

Experiments in which data was acquired using the Boxcar Integrator were controlled using a Digital Equipment Corporation (DEC) LSI 11/23 minicomputer via a DEC AXV-11C A/D-D/A interface, incorporating sixteen 12-bit analogue-to-digital input channels and two 12-bit digital-to-analogue output channels. This system has twin floppy-disk drives for data storage. The DEC system controlled experimental parameters such as the boxcar gate delay (as a fraction of the preset timebase), the sampling rate and the number of points taken before collecting and storing the data for later analysis. All programs for the collection of data using the boxcar,
both kinetic and spectroscopic, and subsequent analysis of this data were written by Professor L. F. Phillips.

Experiments in which data was acquired using the LeCroy transient recorder were controlled using the LeCroy Waveform Catalyst software run on an IBM-clone 80386DX (with 80387 math co-processor) personal computer. In the configuration used for our experiments the LeCroy system essentially functioned as a 32 MHz dual-channel, digital oscilloscope. Data transfer between the computer and transient recorder was via a GPIB interface (LeCroy 8901A, PC IEEE-488 AT-GPIB (16-bit) interface card). Data was stored on the computer’s hard-disk and analysed using software written by the author.

2.2.9 Instrumentation

Oscilloscope

Many diagnostic procedures throughout the course of these experiments were performed using a Tektronix model 7904, 500 MHz oscilloscope. This instrument is capable of being used with a variety of amplifying and timebase modules which provide a wide range of display options. Those modules most commonly used were a 7A26 dual-trace amplifier, a 7A22 differential amplifier, a 7B85 delaying timebase and a 7B80 timebase. The oscilloscope was routinely used for checking timing aspects of each piece of equipment as well as their timing relationships to other equipment relative to a trigger pulse. It was also used for signal monitoring especially when maximizing the signal-to-noise ratio with respect to experimental parameters.

Boxcar Integrator

The main data acquisition device used for the BH-radical kinetic experiments and the emission studies was a Princeton Applied Research (PAR) model 160 Boxcar Integrator. This instrument was used for gating and averaging the signal relative to
a trigger pulse, either directly or as a slave to a minicomputer. Further aspects of the boxcar's pulse generation capabilities will be outlined in chapter 3. All boxcar parameters were optimised to ensure that the maximum signal-to-noise ratio was obtained and care was taken to ensure that the time-constants, inherent in the boxcar's operation, did not distort the signal in any way.

**Transient Recorder**

The main data acquisition device used for the CN-radical kinetic experiments was a LeCroy transient recorder. This instrument consists of two LeCroy TR8837F transient digitizers whose input and timing pulses are provided by a LeCroy 6103 dual-channel amplifier/attenuator all situated in a LeCroy 8013A Camac crate. All modules were programmable via the LeCroy Waveform Catalyst software and have the capability to run in autosequence mode, which was used in our experiments to increase the signal-to-noise ratio while the diode-laser frequency was being scanned to locate the transient absorption. The transient digitizers were configured to allow a portion of the pretrigger region (the time immediately before the CN radicals are produced) of the trace to be collected for the determination of $I_0$ (intensity at $t = 0$) values needed for data reduction procedures.

**2.3 Reagent Chemicals and Handling Techniques**

The reagent chemicals used during the course of these experiments may be divided into three categories according to the purpose they served. These are buffer/carrier gases, reactant gases and radical precursors.

Helium (New Zealand Industrial Gases Scientific or Instrument grades, nominal purity > 99.99%), argon (NZIG Welding grade, np > 99.99%), nitrogen (NZIG oxygen-free grade, np > 99.995%) and sulphur hexafluoride (Air Products Instrument grade, np > 99.99%) were used as buffer and/or carrier gases. Helium, argon
and nitrogen were purified by passage over reduced BASF BTS catalyst heated to 150°C followed by passage through a silica-gel cold-trap (liquid-nitrogen cooled for helium and dry-ice/ethanol cooled for argon and nitrogen). Sulphur hexafluoride was used without further purification.

Ethane dinitrile ($\text{C}_2\text{N}_2$, Matheson Gas Products, np > 99.99%), iodine cyanide (ICN), stannane and diborane were used as radical precursors. $\text{C}_2\text{N}_2$ was purified by trap-to-trap distillation and freeze-pump-thaw cycles. ICN was prepared using the method outlined in Organic Syntheses, Volume 4 [29] and purified using the recrystallization methods suggested. Diborane was prepared using the methods of Jeffers [30] and of Freeguard and Long [31]. Purification of samples prepared by either method was done via trap-to-trap distillation and by freeze-pump-thaw cycles. Despite these measures diborane prepared by the method of Jeffers proved unsuitable for the borane emission spectroscopy experiments (see chapter 4) due to contamination with SnH$_4$. Stannane was prepared using the method of Schaeffer and Emilius [32] and used without further purification.

Nitric oxide (Matheson Gas Products CP grade, np > 99.2%), nitrogen dioxide, ammonia (Christchurch Gas, Coal and Coke Co, np > 99.9%), oxygen (Matheson Gas Products UHP grade, np > 99.99%), methane (NZIG UHP grade, np > 99.97%), ethane (Matheson Gas Products CP grade, np > 99%), ethene (NZIG CP grade, np > 99.5%), carbon monoxide (Matheson Gas Products CP grade, np > 99.5%) and $d_3$-ammonia (ND$_3$) were used as reactant gases. Nitric oxide was purified by passage through a silica-gel dry-ice/ethanol cooled cold-trap ($-78^\circ$C). Ammonia was purified by trap-to-trap distillation and by freeze-pump-thaw cycles over anhydrous potassium hydroxide. Nitrogen dioxide was synthesised by mixing excess oxygen with nitric oxide in a 10-ℓ bulb. The reaction mixture was purified by freeze-pump-thaw cycles with a pure sample being indicated by the lack of any blue-green colouration in the frozen (white) solid. $d_3$-Ammonia was synthesised by reaction of D$_2$O with MgN$_3$ in a vacuum system. The product gas mixture was purified by distillation into a 5-ℓ bulb followed by freeze-pump-thaw cycles. The purity of our sample was checked using mass spectrometry which showed no evidence
for the presence of contaminants. The remaining gases were used without further purification.

2.4 Data Reduction Procedures

Brief details regarding the determination of bimolecular rate coefficients from experimental data are given here. Further details, pertinent to individual experiments, are given in the experimental section of the appropriate chapter.

The concentrations (number densities) of the constituents of each gas mixture were calculated from their partial pressures and the temperature at which the experiment was conducted. Partial pressures were determined from the indicated flow-rates, corrected with pre-determined flow-meter calibration factors (actual flow/indicated flow) and heat capacity correction factors supplied by the flow-meter manufacturer, and total pressure. In the case of ND₃ the heat capacity correction factor was calculated using the manufacturer's formulae and data taken from the JANAF thermochemical tables [33].

The data collected in the BH-radical kinetics experiments, in the form of laser-induced fluorescence intensities vs. time, were corrected for background signal (measured with the dye-laser blocked) and then converted to ln(I) vs. time format. The pseudo first-order decay constant $k'$, is determined from the slope of a plot of these values. These constants were determined for all the reactant (NO, C₂H₄, etc) concentrations for which experimental data had been collected. The bimolecular rate constant is obtained from the slope of a plot of $k'$ vs. [reactant]. The degree of accuracy of the rate constants obtained was reflected by the 95% confidence intervals calculated from a Student-t test of the linear least-squares fit.

The data collected in the CN-radical kinetics experiments was in the form of infra-red intensities vs. time. The value of $I₀$ was determined from the pre-trigger portion of the data and the post-trigger data was then converted to ln($\frac{I}{I₀}$) vs. time format. The pseudo first-order decay constant $k'$, is determined from the slope of
a plot of these values. Once these values had been determined the rest of the data reduction procedure was identical to that carried out in the BH-radical experiments.
Chapter 3

Kinetics of Reactions of BH with NO, C$_2$H$_4$, O$_2$, CH$_4$, C$_2$H$_6$ and CO

3.1 Introduction

The combustion chemistry of boron has long been of interest due to the potential of elemental boron and boron-containing systems as high energy fuels. On a volumetric basis, the theoretical energy release from elemental boron exceeds that available from conventional liquid-hydrocarbon fuels or aluminium-based fuels by factors of three and two [34] respectively. This has stimulated a great deal of interest in the enhancement of liquid-hydrocarbon fuel combustion via the use of boron-hydrocarbon slurry suspensions. Practical difficulties encountered due to the inhibiting effect of the buildup of boron oxide coatings on unburned boron particles, preventing complete oxidation of boron to B$_2$O$_3$, has meant that the full potential of such systems is yet to be realised.

Similarly, there has also been considerable interest in the combustion of boranes, due to their high energy release, wide limits of flammability and small quenching
diameters [35] and a number of studies of borane oxidation have been undertaken. From a study of the reactions of oxygen and nitrogen atoms with diborane and borane carbonyl, Anderson and Bauer [36] concluded that to account for the energetics of the observed products, the reaction pathway must involve hydrogen abstraction from the initial adduct to form BH and BH₂. Further work by Jeffers and Bauer [37] confirmed that only the reactions

\[ \text{BH} + \text{O} \rightarrow \text{BO}^* + \text{H} \]
\[ \text{BH}_2 + \text{O} \rightarrow \text{BO}^* + \text{H}_2 \]

were exoergic enough to produce BO in the electronically excited states observed as well as verifying the presence of BH from the detection of BH \( \tilde{A} \rightarrow \tilde{X} \) emission. Subsequent to these studies Borchardt et al. [38] have proposed a detailed mechanism for the oxidation of diborane in which reactions involving boron hydrides play an important part in the overall reaction scheme.

Despite their potential importance, very little is known about the rates of fundamental processes involving boron hydride radicals. At the time this work was done, no previous measurements of the kinetics of BH reactions had been made. Pasternak et al. [39] had reported room-temperature rate constants for the reactions of BH₃ with CO, NO and C₂H₄ and upper limits to the rate constants for reactions with O₂ and H₂O. Since this work, Rice et al. [40] have reported measurements of the room-temperature rate coefficients of BH reactions and more recently Garland et al. [41] have reported a similar study including measurements made at elevated temperatures. A theoretical and experimental study of the association reaction of BH with D₂ has also been reported [42]. All other studies of the reactions of boranes have been conducted in the same laboratory.

3.2 Experimental

Boron hydride (BH) radicals were produced by the 193.3 nm photolysis of diborane (B₂H₆) using the focussed output of an ArF excimer laser. The laser was operated at
Chapter 3. Kinetics of Reactions of BH with NO, C₂H₄, O₂, CH₄, C₂H₆ and CO₂

a frequency of ca. 17 Hz and produced pulses with energies of 50–70 mJ, as measured by a Scientech model 364 power/energy meter. The laser repetition frequency was chosen so that the pumping speed on the reaction cell was sufficient for the contents of the cell to be swept out between pulses. The low pulse energies combined with the small absorption cross-section of diborane at 193 nm (ca. $4.4 \times 10^{-20}$ cm² [43]) ensured that pseudo first-order conditions were maintained in all experiments with [Reactant] $\gg$ [BH].

The reaction cell used in these experiments (see section 2.2.6) essentially consisted of a six-way glass cross comprising two long (30 cm) side-arms, a pump-out port, two B34 tapered ground-glass sockets, used to provide optical access to the viewing region for the photomultiplier and the monochromator, and a B19 tapered ground-glass socket used to allow pressure and temperature monitoring. This arrangement of the photomultiplier and monochromator eliminated the need for the use of collection optics. Suprasil-quartz windows were attached to the end of the side-arms with epoxy resin. The reactant gas mixture was introduced from both ends of the cell to minimize dead space. Some buildup of photolysis products on the windows did occur, predominantly on the window through which the photolysis laser beam entered, however the high photon flux of the photolysis laser beam acted as an efficient cleaner of the area of the window through which it passed. A diagram of this cell can be found on page 110 of reference [44].

BH-radicals were monitored by laser-induced fluorescence, excited in the $Q_{00}$ branch of the $\tilde{A} \rightarrow \tilde{X}$ transition at 433.4nm [45], with an AVCO C5000/4000 nitrogen-pumped dye-laser using Stilbene-420 dye. The laser-induced fluorescence was detected at right angles to the plane of the photolysis and probe-laser beams, through Corning 7–69 and 3–73 glass filters with a combined bandpass of 410–490 nm (peak transmission 37% at 430 nm), by an EMI 9813QA photomultiplier. The photomultiplier output was amplified and taken to a computer controlled PAR model 160 Boxcar Integrator.

The experimental setup is shown in figure 1. A 10 volt TTL pulse produced by
Chapter 3. Kinetics of Reactions of BH with NO, C₄H₄, O₂, CH₄, C₂H₆ and CO₂

Figure 1: Experimental configuration for the collection of kinetic data using excimer-laser photolysis/dye-laser-induced fluorescence

A variable frequency, square-wave generator simultaneously triggers the photolysis laser and the boxcar integrator, initiating the timebase ramp. The decay of laser-induced fluorescence from BH-radicals is measured by varying the delay between the photolysis and probe lasers in the following way. The boxcar integrator has the facility to produce a 5V output pulse essentially synchronous with the opening of the input gate and this is used to trigger the probe laser. With the gate delay, as a fraction of the timebase, varied under the external control of a microcomputer, the laser-induced fluorescence decay profile can be measured. Additional flexibility in the timing system was provided by the addition of a variable delay between the
opening of the gate and the probe laser being triggered. Both the timing system and the input gate were optimised to maximize the signal-to-noise ratio.

Cell pressure was measured using a MKS model 222CA 0-10 torr Baratron. The range of pressures we could use were limited by fluorescence quenching at greater than approximately 2.5 torr and signals being too small to be accurately measured at pressure less than ca. 0.3 torr. For this reason we chose to investigate the effect of pressure on the reaction by varying the nature of the buffer gas rather than the total pressure. The temperature of the gas stream was measured by a calibrated copper-constantan thermocouple situated just below the viewing region. Flow rates of reactant molecules were measured with calibrated Tylan mass flow-meters and controlled with needle valves. Reactant partial pressures were calculated from the measured flow rates and total pressure. The purity, handling and preparation of gases used in this experiment have been discussed previously in section 2.3.

### 3.3 Results and Discussion

Typical pseudo first-order decay plots for BH in the presence of varying concentrations of NO are shown in figure 2. Signals from the first 60 microseconds of each decay are not included in the plots due to a significant background arising mainly from window fluorescence in this time period. The linearity of plots obtained confirms that BH was being removed by first-order processes. The bimolecular rate coefficient is obtained from the slope of a plot of the first-order rate constants as a function of the NO concentration (figure 3). The results we obtain show that the rates at which BH reacts with NO and \( C_2H_4 \) are both fast and exhibit a negative dependence on temperature, as illustrated in figure 4. The error bars in figure 4 represent the 95% confidence intervals obtained from a Students-t test of the linear least-squares fit. Removal of the rate constants at the lowest temperature measured, which have large 95% confidence intervals, does not significantly affect the slopes of these plots.
3.3.1 BH + NO

We measure the rate constant for the room-temperature reaction of BH with NO to be \((1.26 \pm 0.07) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\), in 0.5–2.0 torr of He. This is in good agreement with the later determinations of Rice et al. \([40]\) \(((1.35 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1})\)

\(^1\)Previously reported rate constants from this study \([46,44]\) differ slightly from those presented here due to a small error made in previous data reduction procedures
and Garland et al. [41] ((9.4 ± 0.9) × 10^{-11} cm^3 s^{-1}). Garland et al's. measurements, made in the temperature range 298–600K, confirm the negative temperature dependence we observe. Their results were fitted to the Arrhenius expression\(^2\)
\[
k(T) = 4.5 \pm 0.8 \exp\left(\frac{2.0 \pm 0.6}{RT}\right) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}.
\]
Rice et al's. measurements show the rate constant is independent of pressure in the range 5–100 torr of He. This result appears to contradict the dependence of the rate constant on the nature of the buffer gas we find in our study, where an increase in the collision efficiency of the buffer gas appears to decrease the rate of reaction (table 1).

\(^2\)Throughout this thesis \(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\).
Chapter 3. Kinetics of Reactions of BH with NO, C\textsubscript{2}H\textsubscript{4}, O\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and CO

Figure 4: Temperature dependences of the reactions of BH with NO (triangles) and C\textsubscript{2}H\textsubscript{4} (circles)

We attribute this dependence to depletion of NO in the viewing region by a radical chain reaction involving diborane photolysis products as well as other species such as NH, N and O atoms. The observed rate is then dependent on the rate of diffusion of NO into the viewing region and as a result would exhibit the observed dependence on the buffer gas. Due to the limitations of our system and the small single-photon absorption cross section of diborane at 193 nm, we were unable to have more than a ten-fold excess of NO over the precursor B\textsubscript{2}H\textsubscript{6} in order to obtain measurable signals over the timebase used whereas Rice et al's. measurements were performed with at least a 100-fold excess of NO over borane carbonyl precursor. Any
Chapter 3. Kinetics of Reactions of BH with NO, C₂H₄, O₂, CH₄, C₂H₆ and CO₂

Table 1: Dependence of the rate constants of the reactions of BH with NO and C₂H₄ on the nature of the buffer gas.

<table>
<thead>
<tr>
<th>Buffer</th>
<th>$k_{BH+NO}$</th>
<th>$k_{BH+C₂H₄}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.26 ± 0.07 × 10⁻¹⁰</td>
<td>1.41 ± 0.09 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Ar</td>
<td>9.5 ± 0.6 × 10⁻¹¹</td>
<td>1.39 ± 0.09 × 10⁻¹⁰</td>
</tr>
<tr>
<td>N₂</td>
<td>9 ± 1 × 10⁻¹¹</td>
<td>1.71 ± 0.09 × 10⁻¹⁰</td>
</tr>
<tr>
<td>SF₆</td>
<td>6 ± 2 × 10⁻¹¹</td>
<td>1.33 ± 0.05 × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

Table 1: Dependence of the rate constants of the reactions of BH with NO and C₂H₄ on the nature of the buffer gas.

effects due to NO depletion in the manner we suspect would be more noticeable in our system. The observed lifetime of BH in our system in the absence of NO, is considerably less than that reported by Rice et al. which provides support for the existence of the radical chain reaction we propose.

Harrison and Maclagan [47] have reported an *ab initio* molecular orbital theory study of this reaction in which they have calculated the MP4SDQ/6-31G*/HF/6-31G* energies of species conceivably involved. Their results indicate that there are four spin-allowed, exothermic product channel possible in this reaction.

\[
\begin{align*}
\text{BH} + \text{NO} & \rightarrow [\text{HBNO}]^\dagger \\
& \rightarrow \text{HNB} + \text{O} \quad \Delta E = -7.2 \text{ kJ mol}^{-1} \\
& \rightarrow \text{HBNO} \quad \Delta E = -299.0 \text{ kJ mol}^{-1} \\
& \rightarrow [\text{HBON}]^\dagger \\
& \rightarrow \text{BO} + \text{NH} \quad \Delta E = -193.5 \text{ kJ mol}^{-1} \\
& \rightarrow \text{HBO} + \text{N} (^2\text{D}) \quad \Delta E = -136.9 \text{ kJ mol}^{-1}
\end{align*}
\]

Reaction to form HNB + O involves a hydrogen shift in the intermediate HBNO complex. Harrison and Maclagan suggest that, by analogy to the HBN=HNB rearrangement which has a substantial barrier, that the barrier to the H migration would close this barely exothermic product channel. Stabilization of the HBNO adduct is also unlikely to be occurring since Rice et al. did not observe any dependence of the rate on total pressure which would be expected if this were the case. Harrison and Maclagan report the barrier to a hydrogen shift in the HBON adduct to be 75.2 kJ mol⁻¹ above the cis isomer at 0K. This barrier is thus 57.2 kJ mol⁻¹ below
Chapter 3. Kinetics of Reactions of BH with NO, C$_2$H$_4$, O$_2$, CH$_4$, C$_2$H$_6$ and CO$_2$

the energy of the reactants so that formation of BO and NH via this channel or fragmentation to form HBO and N(2D) are the most likely product channels in this reaction.

Although the actual products of reaction have not, as yet, been determined, Kawashima et al. [48,49] have observed the HBO species spectroscopically, in the $\nu_1$, $\nu_2$, $2\nu_2$ and $\nu_3$ vibrational states during their studies of ac-discharges in B$_2$H$_6$/O$_2$ and B$_2$H$_6$/NO mixtures using infra-red diode-laser absorption.

Phillips [46] has calculated the dynamical capture rate of BH and NO to form the HBON adduct over the centrifugal barrier of a dipole-dipole potential. The results of these calculations show the capture rate to be essentially temperature independent over the range 200-400K and slightly greater than or equal to the observed rate of reaction. Inclusion of a factor for the rates of rearrangement and dissociation of the intermediate gives calculated reaction rates slightly less than or equal to the observed rates and exhibiting a small negative temperature dependence. The observed data generally lies between the two extremes and so therefore it would seem that this model adequately accounts for both the observed rate of reaction and temperature dependence. Phillips notes the following points regarding the application of this model to the BH/NO system. Although the factor for barrier crossings is statistical, the dynamical lifetime of the HBON complex (time taken for successive barrier crossings) must be used since a shorter lifetime, as calculated statistically, is not physically possible. Even though the dynamical lifetime is used, it is only of the order of 1 picosecond and there would seem barely enough time to allow statistical redistribution of energy from the newly formed B-O bond. Secondly the overall rate constants, with such a small system, are very strongly dependent on the nature of the activated complex assumed for the process of dissociation back to reactants. He concludes that a larger system would more thoroughly explore the capabilities of this model.
3.3.2 BH + C₂H₄

We measure the rate constant for the room-temperature reaction of BH with C₂H₄ to be \((1.41 \pm 0.09) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\) at pressures near 1 torr. This is in good agreement with value reported by Rice et al. \(((1.17 \pm 0.04) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1})\), at 11 and 50 torr total pressure, and reasonable agreement with the value of Garland et al. \(((9.5 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1})\). Garland et al., whose measurements span the temperature range 298–600K, confirm that the rate exhibits a negative temperature dependence and were able to fit their data to the expression \(k(T) = 4.0 \pm 0.7 \exp \left( \frac{21\pm0.6}{RT} \right) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}\). All workers observe the reaction to be independent of pressure.

Subsequently Rice et al. have suggested that the reaction proceeds via addition of BH to the carbon-carbon double bond analogous to the isoelectronic reaction of C\(^{13}\text{D}\) atoms with C₂H₄, in which labelling studies indicate that addition to the double bond is the major reaction channel [50]. In the related reaction of BH with 2,3-dimethyl-2-butene, Rice et al. measure the rate constant to be \((1.9\pm0.1) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\). This enhancement in the rate constant was attributed by these workers to be due to the increase in electron donating ability of the methyl substituents over hydrogen and also implies that the major mechanism of the reactions of BH with double-bond containing species is addition, since in this case, other processes such as insertion or abstraction are essentially blocked.

3.3.3 BH + CH₄, C₂H₆, O₂ and CO

We have set upper limits \((k + 95\% \text{ confidence intervals})\) to the rate constants for the room temperature reactions of BH with CH₄, C₂H₆, O₂ and CO. Strong chemiluminescence transmitted through the Corning filters, decaying on the timescales we collected data, prevented us from measuring the rate at which BH reacts with NO₂ and from using N₂O as a buffer gas. Chemiluminescence was also a problem with the BH + O₂ reaction but the intensity was not such that it prevented us from
measuring the BH laser-induced fluorescence decays. The emissions are probably
due to the formation of BO* and BO₂* by reaction of B(2P) atoms formed in our
system (see chapter 4) with the oxygen-containing species [51,52,53].

**BH + O₂**

Our upper limit for the room-temperature reaction of BH with O₂ \((k < 1.3 \times 10^{-13}
\text{ cm}^3 \text{s}^{-1})\) is consistent with the rate constant of Rice et al. \((8 \pm 1 \times 10^{-13}
\text{ cm}^3 \text{s}^{-1})\) and the temperature dependant data of Garland et al. \(k(T) = 4.9 \pm 0.6 \exp\left(-\frac{1094.0}{RT}\right) \times
10^{-11} \text{ cm}^3 \text{s}^{-1}\). These workers find the reaction to be independent of pressure in
the range 10–50 torr. Exothermic pathways possible in this reaction are

\[
\begin{align*}
\text{BH} + \text{O}_2 & \longrightarrow \text{HBO} + \text{O} \quad \Delta H = -488 \text{ kJ mol}^{-1} \\
& \longrightarrow \text{BOH} + \text{O} \quad \Delta H = -274 \text{ kJ mol}^{-1} \\
& \longrightarrow \text{BO} + \text{OH} \quad \Delta H = -402 \text{ kJ mol}^{-1} \\
& \longrightarrow \text{BO}_2 + \text{H} \quad \Delta H = -502 \text{ kJ mol}^{-1} \\
& \longrightarrow \text{HOBO} \quad \Delta H = -996 \text{ kJ mol}^{-1}
\end{align*}
\]

In their modelling study of diborane/O₂ flames, Shaub and Lin [54] assumed the
dominant reaction pathway produces BO and OH and estimated the rate constant
to be \(6 \times 10^{-14} \text{ cm}^3 \text{s}^{-1}\). Since it was the intention of these workers to model the
combustion features qualitatively, the higher value measured would not significantly
affect any conclusions they formed.

**BH + CO**

Rice et al. find the reaction of BH with CO to be pressure dependent using He
\((k = (3.9 \pm 0.3) \times 10^{-13} \text{ (10 torr)}, \ (5.8 \pm 0.2) \times 10^{-12} \text{ (404 torr}) \text{ cm}^3 \text{s}^{-1})\), CF₄ and
SF₆ as buffer gases. Our upper limit \((k < 1.1 \times 10^{-11} \text{ cm}^3 \text{s}^{-1})\), measured in 1
torr of He, is effectively an extrapolation of their data. They assume the reaction
proceeds through a HBCO complex which is stabilized by collisions with the bath
gas. However, to attain agreement between the TST-RRKM type model they use
and their data for BH and BH$_3$ reactions with CO, which show relatively similar pressure dependences, they had to assume a B–C bond strength approximately twice that in BH$_3$CO for this complex. This would suggest that their model provides an inadequate description of this reaction.

BH + CH$_4$ and C$_2$H$_6$

Our upper limits for the reactions of BH with CH$_4$ and C$_2$H$_6$ are $k < 1.6 \times 10^{-12}$ and $k < 9.1 \times 10^{-13}$ cm$^3$ s$^{-1}$ respectively. Both upper limits are likely to be inflated by the presence of C$_2$H$_4$ as an impurity, especially the upper limit set for C$_2$H$_6$. Obtaining sufficiently pure samples of C$_2$H$_6$ was a problem also mentioned by other workers.

3.4 Conclusions

We have measured rate constants for the reactions of BH with NO and C$_2$H$_4$ and set upper limits to the rate constants for the reactions of BH with O$_2$, C$_2$H$_6$, CH$_4$ and CO. BH was produced by laser photolysis of B$_2$H$_6$ and detected by time resolved laser-induced fluorescence. The results obtained were

\[
\begin{align*}
    \text{BH + NO} & \quad k = 1.26 \pm 0.07 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \\
    \text{BH + C}_2\text{H}_4 & \quad k = 1.41 \pm 0.09 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \\
    \text{BH + CH}_4 & \quad k < 1.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \\
    \text{BH + C}_2\text{H}_6 & \quad k < 9.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \\
    \text{BH + O}_2 & \quad k < 1.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \\
    \text{BH + CO} & \quad k < 1.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}
\end{align*}
\]

at room temperature. The reactions of BH with NO and C$_2$H$_4$ have been found to exhibit negative temperature dependences over the range 260–350K. The reaction of BH with NO also exhibits a dependence on the nature of the buffer gas used.
All measurements are in good agreement with the later measurements of Rice et al. [40] and Garland et al. [41]. In each case the results obtained have been interpreted in terms of the likely mechanism and products of reaction.

This work has been previously reported [46].
Chapter 4

Photoexcitation of Diborane and Stannane at 193 nm

4.1 Introduction

Laser Photolysis is a commonly used technique for generating gas phase free-radicals in order to study their kinetics and spectroscopy. Since the high power ultra-violet lasers used for photolysis generally deliver more energy to the radical-precursor than is needed for dissociation, analysis of prompt emission from excited photofragments can yield information about the energetics and dynamics of the fragmentation process. Work of this kind has been done to obtain information about the various photodissociation mechanisms of H$_2$O and ICN at 248 nm [55], acrylonitrile and acrolein at 193 nm [56,57] and ammonia and hydrazine at 193 nm [58,59,60,61]. Differences in selection rules governing transitions between states of differing geometry in absorption and emission, means that laser photolysis has considerable potential for generating new spectra.

The aim of this work was to characterize the emissions observed during the 193 nm photolyses of diborane and stannane in terms of the identity of the emitting species and the gross nature of the photodissociation processes by which they
are produced. The interest in the photodecomposition of stannane arose due to the presence of this molecule as an impurity in the initial samples of diborane we prepared by reaction of NaBH$_4$ with anhydrous SnCl$_2$ [30].

The ultra-violet photochemistry of diborane has not been extensively investigated. The ultra-violet absorption spectrum of diborane has been reported by Blum and Herzberg [62] and by Price [63] and shows two maxima, at approximately 155 and 180 nm. In the first reported investigation of the photochemical decomposition of diborane, Hirata and Gunning [64] used Hg ($^3$P$_1$) atoms to photosensitize the process at 253.7 nm and concluded that products they observed were consistent with

$$B_2H_6 + h\nu \rightarrow B_2H_5 + H$$

being the primary photochemical step. Further studies of the diborane photolysis by Bufalini and Todd [65] and by Kreye and Marcus [66], both using the 184.9 nm emission of a mercury-lamp, also found that their data, primarily comprising time-dependent pressure changes and product analyses, was consistent with the initial formation of B$_2$H$_5$ and H. Postulation of the formation of BH$_3$ in these experiments was necessary to explain the production of B$_5$H$_{11}$ although the quantum yield for the production of BH$_3$ was thought to be a order of magnitude less than that for the production of B$_2$H$_5$ + H. Consistently, but again without any direct evidence, Clark and Anderson [67] proposed a method for the photochemical purification of silane contaminated with species including diborane, using an ArF excimer-laser at 193 nm, and discussed the findings in terms of the photolysis initially producing B$_2$H$_5$ + H.

Direct evidence as to the identity of the primary photolysis products was first provided by the work of Irion and Kompa. From the results of a study of the photo-induced reaction of B$_2$H$_6$ with D$_2$, they concluded that the observed kinetics and isotopically exchanged products were consistent with BH$_3$ being a chain-carrier [43]. They postulated that the polymer and higher borane products observed in previous studies did implicate the presence of B$_2$H$_5$, but that B$_2$H$_5$ was formed by reaction of the secondary photolysis products of BH$_3$, notably BH$_2$ and BH, with
BH$_3$ and not from the photolysis of B$_2$H$_6$. The continuous-wave photolysis sources used in the previous experiments would have photolyzed any BH$_3$ formed before it could be detected whereas the pulsed photolysis source used in Irion and Kompa's experiments did not.

Further experiments by these workers provided additional evidence for the production of BH$_3$ in the photolysis step. By adding PF$_3$ to the photolysis mixture, they were able to trap the BH$_3$ as it was produced in the form of a BH$_3$•PF$_3$ complex. Quantitative infra-red spectroscopy of this complex enabled them to determine the quantum yield for the production of BH$_3$, from the 193 nm photolysis of diborane, to be $2.00 \pm 0.25$ [68]. This work also confirmed their former postulate of BH$_3$ as a chain carrier in the 193 nm photo-induced B$_2$H$_6$/D$_2$ exchange.

The amount of spectroscopic information known about either BH$_3$ or BH$_2$ is limited. The infra-red diode-laser absorption study of Kawaguchi et al. [69] is the only observation of the gas-phase spectrum of BH$_3$. These workers used kinetic-spectroscopy and discharge-modulation to detect lines belonging to a Q-branch series of the $\nu_2$ band. Similarly, the only spectrum of BH$_2$ reported is the $\tilde{A} \rightarrow \tilde{X}$ transition between 600 and 840 nm observed by Herzberg and Johns [70] in their flash-photolysis studies. By comparison, extensive spectra of the BH radical have been observed and many electronic states of BH have been characterised [45,71].

To date, it would seem that there is virtually nothing is known about the photochemistry of stannane at 193 nm. The vacuum ultra-violet absorption spectrum of stannane has been reported by Fernandez et al. [72] but these workers observed no notable absorption above 160 nm making our work the first reported above this wavelength.

4.2 Experimental

Samples of diborane and stannane (see section 2.3) were prepared according to the methods of Freeguard and Long [31] and Schaeffer and Emilius [32] respectively and
were photolysed using the output of an ArF excimer-laser at 193.3 nm. Typical pulse energies, measured by a Scientech model 364 power/energy meter, corresponded to fluences of 35 mJ cm$^{-2}$ unfocussed and 3 J cm$^{-2}$ at most, when focussed.

Emission spectra were observed in the first and second orders of a McPherson model 218 0.3 m monochromator and a Jarrell-Ash 0.75 m Czerny-Turner monochromator and detected by either a EMI 9558QB or an EMI 9813QA photomultiplier. Combinations of Corning glass filters were used to select the wavelength region of interest as well as to prevent interference from higher-order spectra. The two monochromators were optically-coupled to different photolysis cells; the McPherson to the photolysis cell described in chapter 3, adjacent to the photolysis region and the Jarrell-Ash to a smaller, 15 cm long glass cell with the optics reconfigured so that the focussed 193 nm radiation traversed the cell in a direction parallel to the monochromator entrance slit. With either arrangement, the emission was so weak that the best resolution attainable corresponded to a triangular slit function of ca. 0.08 nm.

The photomultiplier output was amplified and taken to a PAR model 160 Boxcar Integrator before being digitized and stored on a DEC LSI 11/23 minicomputer. Emission lifetime measurements were made by digitizing the photomultiplier output using a LeCroy 32MHz transient recorder controlled by an IBM-clone personal computer. Discharge spectra were obtained by flowing diborane or diborane-rare-gas mixtures through either a microwave or weak tesla discharge. In these experiments the photomultiplier output was detected by a high-speed Keithley model 417 picocommometer and displayed on a chart-recorder.

Diborane and stannane were flowed slowly through the cells at pressures less than ca. 25 millitorr. All emissions observed were prompt, and only detected on a sub-microsecond timescale. All spectra shown here are uncorrected for the wavelength response of the photomultiplier/monochromator combination.
4.3 Results and Discussion

<table>
<thead>
<tr>
<th>Process</th>
<th>Number of Photons</th>
<th>Products</th>
<th>Excess energy (kJ mol(^{-1}))</th>
<th>Emission maximum (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2BH(_3)</td>
<td>454 ± 33</td>
<td>263 ± 18</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>BH(_3) + BH(_2) + H</td>
<td>25 ± 8</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>BH(_3) + BH(_2) + H</td>
<td>644 ± 33</td>
<td>186 ± 9</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>BH(_3) + BH + 2H</td>
<td>296 ± 33</td>
<td>404 ± 44</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>BH(_3) + B + 3H</td>
<td>-35 ± 42</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>2BH(_2) + 2H</td>
<td>218 ± 33</td>
<td>550 ± 83</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>BH(_3) + B + 3H</td>
<td>584 ± 42</td>
<td>205 ± 14</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>BH(_2) + BH + 3H</td>
<td>488 ± 33</td>
<td>245 ± 17</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>BH(_2) + B + 4H</td>
<td>157 ± 42</td>
<td>760 ± 200</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>2BH + 4H</td>
<td>140 ± 33</td>
<td>850 ± 200</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>BH + B + 5H</td>
<td>428 ± 42</td>
<td>280 ± 27</td>
</tr>
</tbody>
</table>

Table 2: Thermochemistry of the possible products from the photodissociation of diborane at 193 nm

Table 2 summarizes the thermochemistry associated with the photodissociation of diborane by 1 to 4 photons at 193 nm. Heats of formation were taken from the JANAF thermochemical tables [73] for B\(_2\)H\(_6\), BH, B and H, from Pople et al. [74] for BH\(_2\) and from Page et al. [75] for BH\(_3\). Process involving the elimination of H\(_2\) might also have been included but they are not required to account for the present observations.

The emission we observe from the photolysis of diborane comprises three distinct regions: atomic boron(I) lines at 249.7 nm and 208.9 nm with intensity proportional to the laser power ca. cubed; a structured region between 320 and 390 nm attributed to two bands of BH\(_2^+\), with intensity proportional to the square of the laser power (figure 5); the BH \(\tilde{A}^1\Pi \rightarrow \tilde{X}^1\Sigma\) transition [45] between 420 and 450 nm also with intensity proportional to the square of the laser power (figure 6). The power dependences given were generally found to be within 10% of their stated integral values.
Chapter 4. Photoexcitation of Diborane and Stannane at 193 nm

Figure 5: Emission from excited BH$_2$ observed during the 193 nm photolysis of diborane
Figure 6: Emission from excited BH observed during the 193 nm photolysis of diborane.
Figure 7: Expanded view of the emission from excited BH$_2$ in the region 320 to 345 nm. The line at 326.3 nm is from Sn(I).
and there was no appreciable variation of band shape with laser intensity.

The band lying between 320 and 345 nm, shown in figure 7, exhibits evident K-structure with peak separations averaging 52 cm\(^{-1}\) on the blue side of the apparent band origin at 334 cm\(^{-1}\) and 42 cm\(^{-1}\) on the red side. These separations, which correspond to approximately 2(\(A'\)–\(B'\)) of a prolate near-symmetric top, seem reasonable for BH\(_2\) (\(A'' = 41.6\) cm\(^{-1}\), \(B'' \approx C'' \approx 6.6\) cm\(^{-1}\)) but not for BH\(_3\) (\(A'' = B'' = 8\) cm\(^{-1}\), \(C'' = 4\) cm\(^{-1}\)). This band has a dependence on laser power that is consistent with the production of excited BH\(_2\) by process 3 of table 2. Phillips [76] has simulated this band as a perpendicular transition of a near symmetric top. He found it necessary to use an extremely non-Boltzmann distribution over the initial rotational levels, restricting \(J'\) to the range 12–32 with a rotational temperature of 1250K in this \(J'\) range. The results qualitatively predict the band shape and sub-band spacings. The narrow spectral range of this band suggests that the geometries of the upper and lower states are quite similar.

The band lying between 360 and 390 nm also has an intensity proportional to the square of the laser power and on this basis it is also assigned to BH\(_2\). This band has some sharp features at approximately 368 and 373 nm and like the band between 320 and 345 nm, the narrow spectral range of this band implies that the electronic transition does not involve a large change in geometry.

The observed BH \(\bar{\Lambda} \rightarrow \bar{X}\) emission band lying between 420 and 450 nm has a power dependence consistent with production of BH (\(\bar{\Lambda}\)) via process 4 of table 2. This band exhibits a markedly non-Boltzmann distribution indicating that dissociation to form BH\(^*\) was rapid. Comparison with theoretical spectra indicates that the emitting population is both rotationally and vibrationally excited with rotational and vibrational temperatures of ca. 2750K. As noted by Johns et al. [45], the \(\bar{\Lambda} \rightarrow \bar{X}\) emission breaks off at \(J' = 26\) of the (0,0) band and the (3,3) band is absent from the observed spectrum.

At high laser fluences, two atomic boron(I) transitions, \(^2\)S \(\rightarrow\) \(^2\)P (249.7 nm) and \(^2\)D \(\rightarrow\) \(^2\)P (208.9 nm), were observed. The production of \(^2\)D or \(^2\)S boron atoms
from diborane can result from the absorption of a single 193 nm photon by BH (\( \tilde{A} \)) or excited BH (\( \tilde{X} \)) or from multiphoton absorption by larger BH\(_n\) fragments. The observed power dependence is consistent with production of boron atoms via process 7 of table 2.

The BH\(_2\) \( \tilde{A} \rightarrow \tilde{X} \) bands [70] were not observed following laser excitation but were a prominent feature of microwave discharge spectra obtained. The low detection sensitivity above 700 nm in the laser excitation experiments means that there were possibly bands in this region we did not detect. We measure a value for the BH \( \tilde{A} \rightarrow \tilde{X}, Q_{00} \) emission lifetime of 540 ns which is considerably longer than the literature value of 125 ± 5 ns [77,78] and implies that the \( v' = 0 \) level was being repopulated by cascade processes. No emission was observed from the photolysis of diborane at 248 nm, which was attributed to the negligible single-photon absorption coefficient of diborane at this wavelength.

<table>
<thead>
<tr>
<th>( J'' )</th>
<th>( J' )</th>
<th>Wavelength (nm)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ( (^3P_0) )</td>
<td>1 ( (^1P_1) )</td>
<td>254.73</td>
<td>( \approx 1 )</td>
</tr>
<tr>
<td>0 ( (^3P_0) )</td>
<td>1 ( (^3P_1) )</td>
<td>286.42</td>
<td>35</td>
</tr>
<tr>
<td>1 ( (^3P_1) )</td>
<td>1 ( (^1P_1) )</td>
<td>266.20</td>
<td>0</td>
</tr>
<tr>
<td>1 ( (^3P_1) )</td>
<td>2 ( (^3P_2) )</td>
<td>270.73</td>
<td>8</td>
</tr>
<tr>
<td>1 ( (^3P_1) )</td>
<td>1 ( (^3P_1) )</td>
<td>301.00</td>
<td>33</td>
</tr>
<tr>
<td>1 ( (^3P_1) )</td>
<td>0 ( (^3P_0) )</td>
<td>303.50</td>
<td>100</td>
</tr>
<tr>
<td>2 ( (^3P_2) )</td>
<td>1 ( (^1P_1) )</td>
<td>279.10</td>
<td>0</td>
</tr>
<tr>
<td>2 ( (^3P_2) )</td>
<td>2 ( (^3P_2) )</td>
<td>284.08</td>
<td>23</td>
</tr>
<tr>
<td>2 ( (^3P_2) )</td>
<td>1 ( (^3P_1) )</td>
<td>317.60</td>
<td>86</td>
</tr>
<tr>
<td>2 ( (^1D_2) )</td>
<td>1 ( (^1P_1) )</td>
<td>326.33</td>
<td>20</td>
</tr>
<tr>
<td>2 ( (^1D_2) )</td>
<td>2 ( (^3P_2) )</td>
<td>333.16</td>
<td>( \approx 10 )</td>
</tr>
<tr>
<td>2 ( (^1D_2) )</td>
<td>1 ( (^3P_1) )</td>
<td>380.21</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3: Atomic tin lines observed during the 193 nm photolysis of stannane

The atomic tin lines observed during the 193 nm photolysis of stannane are listed in table 3. The intensity of these lines is linearly proportional to the photolysis laser
power which implies they result from the absorption of a single 193 nm photon. Since the energy of the highest populated Sn(I) state is 39257.1 cm\(^{-1}\), this leaves only 150 kJ mol\(^{-1}\) available for the dissociation of SnH\(_4\) to products which must include gas-phase atomic tin.

By taking the enthalpy of formation of SnH\(_4\)(g) at 0K to be 174.8 kJ mol\(^{-1}\) [79], we are forced to rule out the process

\[
\text{SnH}_4(g) + h\nu \rightarrow \text{Sn}(g) + 4\text{H}(g)
\]

as a primary excitation step since \(\Delta H_0^\circ\) for this process is 991 kJ mol\(^{-1}\) for the production of ground state Sn(g). This would require more energy than is available from a single 193 nm photon. However for the process

\[
\text{SnH}_4(g) + h\nu \rightarrow \text{Sn}(g) + 2\text{H}_2(g)
\]

we find \(\Delta H_0^\circ = 127.2\) kJ mol\(^{-1}\) which permits the unusual photoexcitation step

\[
\text{SnH}_4(g) + h\nu_{193} \rightarrow \text{Sn}(g)(^{1}\text{P}_1) + 2\text{H}_2(g)
\]

The same energy limitations require that photodissociation to give Sn(\(^3\)P) follows a similar process. Similar primary processes involving the elimination of a single hydrogen molecule have been previously proposed for the photolysis of CH\(_4\) at 123.6 nm and [80], and silane at 147 nm [81]. The low intensities of the tin lines we observe suggest that photodissociation via process 1 may only be a minor primary channel relative to

\[
\text{SnH}_4(g) + h\nu_{193} \rightarrow \text{SnH}_2(g) + \text{H}_2(g)
\]

Further work is warranted to show the presence of H\(_2\) and to determine whether SnH\(_2\) also forms from the photodissociation process.

### 4.4 Conclusions

Emission observed during the 193.3 nm photolyses of stannane and diborane have been characterised and the identity of the probable emitter has been assigned, in each
case, on the basis of photolysis-laser power dependences, known thermochemistry and band structure.

The emissions observed during the photolysis of diborane, together with the probable emitter, were

- 320–390 nm \( \text{BH}_2^* \) (two bands)
- 420–450 nm \( \text{BH} \ \bar{A}^1\Pi \rightarrow \bar{X}^1\Sigma \)
- 208.9, 249.7 nm Boron(I) atoms

The emissions attributed to \( \text{BH}_2^* \) are new transitions.

The emissions observed during the photolysis of stannane were all assigned to known electronic transitions of atomic Sn(I).

In both cases the results obtained have been interpreted in terms of the nature of the respective photodissociation processes.

This work has been previously reported [76,82].
Chapter 5

Theoretical study of the reaction of CN with NH$_3$

5.1 Introduction

During the past decade, the rate at which CN-radicals react with other radicals, atoms and molecules has become of interest to an increasing number of experimental research groups (see chapter 6), for a variety of reasons. Despite these efforts, only a few theoretical studies of these systems have been reported. In conjunction with experiments, theoretical studies of the type we present here, are useful for elucidation of the mechanism(s) by which the reaction proceeds and of the likely product channels open to reactants. The results of such studies, providing information on the form and relative energetics of the potential energy surface over which the reaction occurs, can then be used in dynamical or statistical type calculations to enable prediction of the rate coefficients under experimentally inaccessible reaction conditions.

Previous ab initio studies have been reported for the reactions of CN with H$_2$ [83] and CN with HCl [84]. Rate coefficients for the reaction of CN with H$_2$ have been calculated using these ab initio results in a transition-state theory approach [85] and by using reduced-dimensionality reaction probabilities [86]. There have
been no reported theoretical studies of the reaction of CN with NH$_3$.

The aims of this study were to determine the mechanism by which CN reacts with NH$_3$ and the likely products of reaction in conjunction with the experimental studies reported in chapters 6 and 7. The mechanism of reaction in particular, is not well understood. This reaction has been shown experimentally to exhibit the characteristics normally associated with radical-radical reactions [87]. This is unexpected since the reaction of CN with NH$_3$ is between a radical and a neutral molecule.

Discussion of the implications of the \textit{ab initio} results we present in relation to the experimentally determined kinetic properties and products of reaction is deferred to chapters 6 and 7 respectively. Only the characteristics and properties expected to be displayed by each possible reaction channel will be discussed here.

\section{5.2 Principles of \textit{ab initio} molecular orbital theory\textsuperscript{1}}

\subsection{5.2.1 The potential energy surface}

The course of a chemical reaction is governed by the form of the potential energy surface $U(q)$, over which it occurs. The potential energy surface represents the dependence of the total potential energy ($U$) of the system on the co-ordinates ($q$) of the constituent nuclei. For a system of $N$ nuclei, the potential energy surface is a function of $3N-6$ ($3N-5$ for linear systems) independent variables and is therefore a surface in a space of $3N-6$ dimensions.

To determine the form of the potential energy surface it is necessary to solve the non-relativistic time-independent Schrödinger wave equation

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

\textsuperscript{1}The content of this section is based primarily on the excellent texts by Szabo and Ostlund [19], Levine [20] and Hehre \textit{et al.} [21].
where $\mathcal{H}$ is the Hamiltonian for a system of $N$ nuclei and $n$ electrons, at a number of points for each of the $3N-6$ variables. For all but the smallest systems, this is currently impractical. Usually only the important features of the potential energy surface are determined such as stationary points (points where the gradient, the first derivative of $U$ with respect $q_i$, is zero). Stationary points may be characterised by the eigenvalues of the force constant (second derivative of $U$ with respect $q_i$) matrix or Hessian, as either intermediates or transition states. Intermediates are local minima which have all real eigenvalues while transition states are saddle points (first order saddle points, convex in one dimension) and have one negative eigenvalue. Knowledge of the relative energies of reactants, products, intermediates and transition states gives good insight into the possible reaction mechanism(s) and the relative importance of each.

Within the framework of the Born-Oppenheimer approximation, in which by virtue of their much smaller mass, the electrons can be considered as moving in a field of fixed nuclei, terms in the Hamiltonian corresponding to kinetic energy of the nuclei and the repulsion between the nuclei, can be ignored and considered constant respectively. Hence the Hamiltonian (in atomic units) reduces to

$$
\mathcal{H} = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{r_{ij}}
$$

(2)

where $Z_A$ is the atomic number of nucleus $A$ and the Laplacian $\nabla_i^2$ involves differentiation with respect to the co-ordinates of the $i$th electron. The first term in equation 2 is the operator for the kinetic energy of the electrons; the second term represents coulomb attraction between the nuclei and electrons and the third term represents repulsion between the electrons. The Hamiltonian of this form is termed the electronic Hamiltonian and solution of the Schrödinger wave equation

$$
\mathcal{H}_{\text{elec}} \Psi = \mathcal{E}_{\text{elec}} \Psi
$$

(3)

yields the electronic energy of the system. The total energy of the system for fixed nuclei is obtained by addition of the constant term representing nuclear repulsion.

$$
\mathcal{E}_{\text{total}} = \mathcal{E}_{\text{elec}} + \sum_{A=1}^{N} \sum_{B>A}^{N} \frac{Z_A Z_B}{R_{AB}}
$$
where $R_{AB}$ is the distance between nuclei $A$ and $B$. Solution of equation 3 is achieved by allocating each electron to its own spin orbital and combining these into an N-electron wavefunction. Spin orbitals have dependence on both spatial and spin co-ordinates. A Slater determinant is used to give a wavefunction which is an antisymmetrised product of the spin orbitals in order to obey the antisymmetry or Pauli Exclusion principle. For a closed-shell N-electron system

$$\Psi(x_1, x_2, \ldots, x_N) = (N!)^{-\frac{1}{2}} \begin{vmatrix}
\chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_k(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_k(x_2) \\
\vdots & \vdots & \cdots & \vdots \\
\chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_k(x_N)
\end{vmatrix}$$

where $x_i$ represent the space and spin co-ordinates of electron $i$. Slater determinants correlate the motions of electrons with the same spin while the motion of electrons with opposite spin are uncorrelated. If a single Slater determinant is used as the approximation to the true wavefunction then this is called the Hartree-Fock approximation.

### 5.2.2 The Hartree-Fock approximation

The simplest wave function that can be used to describe the ground state of a closed-shell N-electron system is a single Slater determinant. The best wavefunction is determined variationally to give the lowest energy, which is an upper bound to the true energy of the system. Minimization of the energy with respect to the choice of the spin orbitals leads to the Hartree-Fock equations

$$f|\chi_a\rangle = \epsilon_a|\chi_a\rangle$$

where $\epsilon_a$ is the energy of spin orbital $\chi_a$ and $f$ is the Fock operator which represents the sum of a core Hamiltonian operator and the Hartree-Fock potential. The Hartree-Fock potential is the average potential experienced by an electron due to the presence of the other electrons and hence depends on the spin orbitals of the other electrons. The Hartree-Fock equations are thus non-linear and must be solved
iteratively. This is done using the Self-Consistent-Field procedure in which the spin orbitals are varied until those used to construct the Fock operator are also its eigenfunctions. The Hartree-Fock equations are reduced to a set of matrix equations by expansion of the spin orbitals in a set of basis functions to allow their solution for molecular species

\[ \chi_i(r) = \sum_{\mu=1}^{k} C_{\mu} \phi_{\mu}(r) \]

for \( k \) basis functions.

The ground state wavefunction \( \Psi_0 \) corresponds to filling the \( N \) lowest energy spin orbitals with the \( N \)-electrons. The ground state energy is thus given by

\[ \mathcal{E}_0 = \langle \Psi_0 | H | \Psi_0 \rangle \]

Hartree Fock calculations are usually classified as either restricted or unrestricted depending on whether or not orbitals of different spin are constrained to having the same spatial form. Unrestricted determinants generally produce lower energies than restricted determinants but they are contaminated by spin states of higher multiplicity (that is, they are not eigenfunctions of the total spin operator).

The lowest energy attainable using the Hartree-Fock approximation is achieved by using a complete (infinite) basis set and is termed the Hartree-Fock limit. For the sake of computational manageability a finite basis set must be used so that energies higher than the Hartree-Fock limit generally result.

### 5.2.3 Post Hartree-Fock theory

The major assumptions inherent in the Hartree-Fock approximation limit its accuracy, so that even the energy attained at the Hartree-Fock limit represents an upper bound to the true energy of the system. It can be shown that the exact wavefunction for the ground and excited states of an \( N \)-electron system can be written as a linear combination of all possible \( N \)-electron Slater determinants formed from a complete
set of spin orbitals. The variational determination of the wavefunction in this manner is called configuration interaction (CI) as each determinant represents a unique electron configuration. Determinants are referred to as N-tuply excited, relative to the ground state configuration, corresponding to the promotion of N-electrons from the occupied spin orbitals to the unoccupied spin orbitals. The lowest energy eigenvalue of the Hamiltonian is the exact ground state energy of the system within the Born-Oppenheimer approximation. The difference between the exact energy $E$ and the Hartree-Fock limit energy is called the correlation energy

$$E_{\text{corr}} = E - E_{HF}$$

since motion of electrons of opposite spin are uncorrelated in the Hartree-Fock approach.

An alternative multideterminantal approach to the calculation of correlation energy is to use perturbation theory. In this approach the correlation energy is calculated by including correlation effects as a perturbation $\mathcal{V}$ on the reference determinant $\mathcal{H}_0$.

$$\mathcal{H}\ket{\Psi} = (\mathcal{H}_0 + \lambda \mathcal{V}) \ket{\Psi} = E \ket{\Psi}$$

The exact ground-state energy $E$ and wavefunction $\Psi$ can then be expanded as an infinite series of the form

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \cdots$$
$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots$$

The energy and wavefunction are formulated by setting $\lambda = 1$ and truncating the series to various orders. The Hartree-Fock Hamiltonian is chosen as $\mathcal{H}_0$ as we are interested in obtaining a perturbation expansion of the correlation energy. This choice of Hamiltonian is known as Møller-Plesset perturbation theory and in this case the perturbation is the difference between the true interelectronic repulsion and the Hartree-Fock average interelectronic potential. Møller-Plesset perturbation theory is referred to by the highest order energy term allowed so that truncation

---

$^2$The Hartree-Fock energy represents the sum of the zeroeth and first order terms.
after third order is termed MP3. For computational manageability, terms higher than fourth order are seldom included.

Second and higher order terms in the expansion contain matrix elements of the perturbation operator involving excited determinants. In the Hamiltonian matrix, elements involving the ground state with singly-excited determinants vanish due to Brillouin’s theorem while matrix elements involving the ground state with triply and higher order excited determinants vanish because the Hamiltonian contains only one and two electron terms. The result is that only doubly-excited determinants contribute to MP2 and MP3 energies while MP4 energies also have contributions from singly, triply and quadruply-excited determinants since they have non-zero matrix elements with doubly-excited determinants. MP4 calculations have the additional terminology indicating the excitations that are included so that an MP4SD calculation includes only contributions from singly and doubly-excited determinants. Triply-excited determinants are the hardest to handle computationally and consequently are sometimes excluded.

5.2.4 Basis Sets

The most commonly used basis functions for the expansion of spin orbitals are Slater functions and Gaussian functions

\[ \phi_{\text{Slater}} (\zeta, r) = N (\zeta) S \exp^{-\zeta r} \]
\[ \phi_{\text{Gaussian}} (\alpha, r) = N (\alpha) G \exp^{-\alpha r^2} \]

where \( N \) is a normalization factor, \( \alpha \) and \( \zeta \) are Gaussian and Slater exponents respectively, and \( r \) is the distance from the centre of the function. \( G \) and \( S \) specify the type (s, p, d, ...) of Gaussian or Slater function as a dependence on the cartesian co-ordinates x, y and z. Slater functions better represent atomic orbitals than do Gaussian functions, mainly due to the failure of Gaussian functions to give the desired cusp at the origin and so require fewer terms for a representation of comparable quality. Gaussian functions however provide for more efficient evaluation of
integrals and can be evaluated explicitly without recourse to numerical integration, which increases accuracy. By use of a basis set in which each basis function is a fixed linear-combination (contraction) of Gaussian functions (primitives), approximation of functions with the desired qualities can be attained while retaining rapid integral evaluation.

The simplest basis set is one which comprises the number of functions required to accommodate all of the electrons of the atom while maintaining overall spherical symmetry and is called a minimal basis set. Minimal basis sets are useful for calculations on large molecules where large amounts of computation must be done but can only be used for the prediction of chemical properties in a qualitative manner. The most commonly used minimal basis set is the STO-3G basis set in which three primitive Gaussians are contracted for each basis function to approximate a Slater type orbital.

The minimal basis set may be improved by using two basis functions for each minimal basis function. The resulting double-zeta basis set is capable of allowing for anisotropic effects within the molecule. A further improvement is achieved by using a split-valence basis set in which the valence region of the molecule is represented by two basis functions. The chemical properties of a molecule are generally dominated by valence shell electrons. Use of a split valence basis set in which the valence region is separated into inner and outer regions, described by separate basis functions, allows for greater flexibility in the optimization of the molecular orbitals and so a better description of these properties.

Allowance for the effects of anisotropic charge distribution experienced by an atom in a molecule can be accounted for by the addition of polarization functions to the basis set, generally as a set of d-type functions for non-hydrogen atoms and p-type functions for hydrogen. It has been empirically determined that addition of d-functions to heavy atoms is more important than adding p-functions to hydrogen. The basis set used in this study, the 6-31G* is an example of a split-valence basis set with a set of d-type polarization functions on the non-hydrogen atoms. A good description of the inner shell electrons by the basis set is also important, since
although inner shell electrons generally contribute little to the chemical properties of the molecule, they do contribute to the electronic energy. The criterion of energy minimization may otherwise cause valence functions to be borrowed by the inner shell to lower the electronic energy, to the detriment of the representation of the valence shell and thus the description of the bonding and molecular properties of the molecule.

5.3 Details of Calculations

The geometries of species conceivably involved in the reaction of CN with NH$_3$ were optimised at the HF and, in certain cases, the MP2 levels of theory. Harmonic vibrational frequencies, MP4SDQ and QCISD(T) energies were calculated using these geometries. All calculations were done with a 6-31G* basis set using either Gaussian82 [88] or Gaussian90 [89].

5.4 Results and Discussion

The geometries of species conceivably involved in the reaction of CN with NH$_3$, optimized at the HF/6-31G* level of theory, are summarized in table 4, over the following four pages, in standard Z-matrix format. The rows of values in {braces} are MP2 geometries. In tables defining multiple structures, $Z_n$ refers to the ordering of atoms for that structure while distances and angles should be read from the first line before the second line for each species.

To ensure that these tables are interpreted correctly, let us consider the structure of the transition-state species TS$_4$ as an example. The Z-matrix defining the structure of this species has an ordering of atoms listed under $Z_1$; $Z_2$–$Z_5$ should be ignored in this case. The bond distances and angles are then read from the table first line before second line for each group of parameters. In this case the HF values
are: \( r_1 = 1.18, \ r_2 = 1.44, \ r_3 = 1.34, \ r_4 = 1.00, \ r_5 = 1.00;\ \zeta_1 = 121.7, \ \zeta_2 = 67.5,\ \zeta_3 = 115.9, \ \zeta_4 = 116.9;\) \( \) and \( \phi_1 = 180.0, \ \phi_2 = 187.9, \ \phi_3 = -23.3, \ \phi_4 = 196.9 \) For this species an MP2 geometry has been calculated. The MP2 values are: \( r_1 = 1.18,\ \ r_2 = 1.44, \ r_3 = 1.34, \ r_4 = 1.02, \ r_5 = 1.01;\ \zeta_1 = 121.4, \ \zeta_2 = 78.0, \ \zeta_3 = 116.5,\ \zeta_4 = 117.1;\) \( \) and \( \phi_1 = 180.0, \ \phi_2 = 172.1, \ \phi_3 = -23.2, \ \phi_4 = 196.2.\)

Transition state species are labelled TS\(_x\), while intermediates, reactants and products are labelled according to their connectivity of atoms. TS\(_9\) and TS\(_{10}\) are most likely torsional transition states of the intermediate species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Geometry ( r_x(\text{Å}), \zeta_x, \phi_x ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>( r_{CN} ) 1.16 {1.13} | ( )</td>
</tr>
<tr>
<td>NH</td>
<td>( r_{NH} ) 1.02 | ( )</td>
</tr>
<tr>
<td>N(_2)</td>
<td>( r_{NN} ) 1.08 | ( )</td>
</tr>
<tr>
<td>CH(_2) (( ^3B_1))</td>
<td>( r_{CH} ) 1.07 ( \zeta_{HCH} ) 130.8 | ( )</td>
</tr>
<tr>
<td>CH(_2) (( ^1A_1))</td>
<td>( r_{CH} ) 1.10 ( \zeta_{HCH} ) 103.3 | ( )</td>
</tr>
<tr>
<td>NH(_2)</td>
<td>( r_{NH} ) 1.01 ( \zeta_{HNH} ) 104.4 | ( )</td>
</tr>
<tr>
<td>N(_2)H</td>
<td>( r_{NN} ) 1.18 ( r_{NH} ) 1.03 ( \zeta_{NNH} ) 113.0 | ( )</td>
</tr>
<tr>
<td>HCN</td>
<td>( r_{CH} ) 1.06 ( r_{CN} ) 1.13 ( \zeta_{HCN} ) 180.0 | ( )</td>
</tr>
<tr>
<td>HNC</td>
<td>( r_{HN} ) 0.99 ( r_{NC} ) 1.15 ( \zeta_{HNC} ) 180.0 | ( )</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>( r_{CH} ) 1.07 ( \zeta_{HCH} ) 120.0 ( \phi_{HCHH} ) 180.0 | ( )</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>( r_{NH} ) 1.00 ( \zeta_{HNH} ) 107.2 ( \phi_{HNHH} ) 114.8 | ( ) {1.02 106.4 113.1} | ( )</td>
</tr>
<tr>
<td>H(_2)CN</td>
<td>( r_{HC} ) 1.08 ( r_{CN} ) 1.26 ( \zeta_{HCN} ) 120.8 | ( )</td>
</tr>
<tr>
<td>( \phi_{HCNH} ) 180.0 | ( )</td>
<td></td>
</tr>
<tr>
<td>cis HCNH</td>
<td>( r_{HC} ) 1.08 ( r_{CN} ) 1.23 ( r_{NH} ) 1.01 | ( )</td>
</tr>
<tr>
<td>( \zeta_{HCN} ) 133.8 ( \zeta_{CNH} ) 115.2 ( \phi_{HCNH} ) 0.0 | ( )</td>
<td></td>
</tr>
<tr>
<td>trans HCNH</td>
<td>( r_{HC} ) 1.08 ( r_{CN} ) 1.23 ( r_{NH} ) 1.01 | ( )</td>
</tr>
<tr>
<td>( \zeta_{HCN} ) 126.9 ( \zeta_{CNH} ) 114.5 ( \phi_{HCNH} ) 180.0 | ( )</td>
<td></td>
</tr>
</tbody>
</table>
### Chapter 5. Theoretical study of the reaction of CN with NH₃

#### Table

<table>
<thead>
<tr>
<th>$Z_1$</th>
<th>$Z_2$</th>
<th>$Z_3$</th>
<th>$Z_4$</th>
<th>$Z_5$</th>
<th>$r_x$</th>
<th>$L_x$</th>
<th>$\phi_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>N</td>
<td>N</td>
<td>H</td>
<td>H</td>
<td>1</td>
<td>$r_1$</td>
<td>90.0</td>
</tr>
<tr>
<td>N</td>
<td>X</td>
<td>X</td>
<td>C</td>
<td>N</td>
<td>1</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>2</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>C</td>
<td>N</td>
<td>2</td>
<td>$r_2$</td>
<td>4</td>
</tr>
<tr>
<td>N</td>
<td>C</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>1</td>
<td>$r_3$</td>
<td>3</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>6</td>
<td>$r_4$</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>6</td>
<td>$r_5$</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>$Z_x$</th>
<th>$r_1, r_2, r_3, r_4, r_5$ (Å)</th>
<th>$L_1, L_2, L_3, L_4$ (deg)</th>
<th>$\phi_1, \phi_2, \phi_3, \phi_4$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHNHNC</td>
<td>4</td>
<td>1.00 1.15 2.00</td>
<td>90.2 90.6</td>
<td>180.0 180.0</td>
</tr>
<tr>
<td>HHNHCN</td>
<td>5</td>
<td>1.01 1.01</td>
<td>127.0 127.0</td>
<td>91.0 91.0</td>
</tr>
<tr>
<td>cis</td>
<td>1</td>
<td>1.23 1.01 1.36</td>
<td>26.6 47.2</td>
<td>187.7 177.5</td>
</tr>
<tr>
<td>H₂NCNH</td>
<td>1</td>
<td>1.00 1.00</td>
<td>116.6 117.4</td>
<td>192.4 27.0</td>
</tr>
<tr>
<td>trans</td>
<td>1</td>
<td>1.24 1.00 1.35</td>
<td>25.2 139.7</td>
<td>184.3 187.5</td>
</tr>
<tr>
<td>H₂NCNH</td>
<td>1</td>
<td>1.00 1.00</td>
<td>116.6 117.2</td>
<td>185.6 31.9</td>
</tr>
<tr>
<td>TS₂</td>
<td>4</td>
<td>1.56 1.17 1.07</td>
<td>151.8 140.5</td>
<td>180.0 180.0</td>
</tr>
<tr>
<td>TS₃</td>
<td>5</td>
<td>1.01 1.01</td>
<td>115.9 115.9</td>
<td>110.4 110.4</td>
</tr>
<tr>
<td>TS₄</td>
<td>1</td>
<td>1.18 1.44 1.34</td>
<td>121.7 67.5</td>
<td>180.0 187.9</td>
</tr>
<tr>
<td>TS₅</td>
<td>1</td>
<td>1.00 1.00</td>
<td>115.9 116.9</td>
<td>-23.3 196.9</td>
</tr>
<tr>
<td>TS₆</td>
<td>1</td>
<td>1.19 1.00 1.91</td>
<td>107.4 109.6</td>
<td>132.9 234.5</td>
</tr>
<tr>
<td>TS₇</td>
<td>1</td>
<td>1.07 1.01</td>
<td>99.4 99.5</td>
<td>228.4 25.0</td>
</tr>
<tr>
<td>TS₈</td>
<td>1</td>
<td>1.19 1.99</td>
<td>100.8 111.6</td>
<td>157.1 232.3</td>
</tr>
<tr>
<td>TS₉</td>
<td>1</td>
<td>1.03 1.03</td>
<td>95.8 96.0</td>
<td>230.7 26.0</td>
</tr>
<tr>
<td>TS₁₀</td>
<td>1</td>
<td>1.24 1.02 1.31</td>
<td>25.5 92.2</td>
<td>182.9 180.1</td>
</tr>
<tr>
<td>TS₁₀</td>
<td>2</td>
<td>1.28 1.01 1.24</td>
<td>162.5 81.9</td>
<td>180.0 180.0</td>
</tr>
<tr>
<td>TS₁₀</td>
<td>3</td>
<td>1.24 1.08 1.44</td>
<td>36.5 150.5</td>
<td>180.0 180.0</td>
</tr>
</tbody>
</table>

### Notes
- $Z_i$ represent atomic positions.
- $r_x$, $L_x$, and $\phi_x$ are distances, angles, and dihedral angles, respectively.
- The table lists various species and their geometric properties associated with the reaction of CN with NH₃.
# Chapter 5. Theoretical study of the reaction of CN with NH₃

## Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>Z₁, Z₂</th>
<th>r₁, r₂, r₃, r₄, r₅ (Å)</th>
<th>L₁, L₂, L₃, L₄ (deg)</th>
<th>φ₁, φ₂, φ₃ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂NHCN</td>
<td>1</td>
<td>1.26 1.08 1.38</td>
<td>119.0 125.5</td>
<td>176.9 -33.7 193.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00 1.00 1.00</td>
<td>115.0 114.6</td>
<td></td>
</tr>
<tr>
<td>TS₇</td>
<td>1</td>
<td>1.17 1.83 1.35</td>
<td>102.9 98.9</td>
<td>177.4 -24.8 200.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00 1.00 1.00</td>
<td>114.0 115.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>{1.17 1.63 1.36}</td>
<td>102.8 97.7</td>
<td>176.9 -25.8 201.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.01 1.01 1.00</td>
<td>112.8 115.5</td>
<td></td>
</tr>
<tr>
<td>TS₈</td>
<td>1</td>
<td>1.18 1.06 1.96</td>
<td>111.8 147.3</td>
<td>180.0 126.8 -126.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.01 1.01 1.00</td>
<td>98.9 98.9</td>
<td></td>
</tr>
<tr>
<td>H₂NHNC</td>
<td>2</td>
<td>1.29 1.00 1.42</td>
<td>122.7 125.7</td>
<td>180.0 121.9 121.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00 1.00 1.00</td>
<td>107.9 107.9</td>
<td></td>
</tr>
</tbody>
</table>

## Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>Z₁, Z₂</th>
<th>r₁, r₂, r₃, r₄, r₅ (Å)</th>
<th>L₁, L₂, L₃, L₄ (deg)</th>
<th>φ₁, φ₂, φ₃ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂NHCN</td>
<td>1</td>
<td>1.26 1.08 1.38</td>
<td>119.0 125.5</td>
<td>176.9 -33.7 193.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00 1.00 1.00</td>
<td>115.0 114.6</td>
<td></td>
</tr>
<tr>
<td>TS₇</td>
<td>1</td>
<td>1.17 1.83 1.35</td>
<td>102.9 98.9</td>
<td>177.4 -24.8 200.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00 1.00 1.00</td>
<td>114.0 115.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>{1.17 1.63 1.36}</td>
<td>102.8 97.7</td>
<td>176.9 -25.8 201.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.01 1.01 1.00</td>
<td>112.8 115.5</td>
<td></td>
</tr>
<tr>
<td>TS₈</td>
<td>1</td>
<td>1.18 1.06 1.96</td>
<td>111.8 147.3</td>
<td>180.0 126.8 -126.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.01 1.01 1.00</td>
<td>98.9 98.9</td>
<td></td>
</tr>
<tr>
<td>H₂NHNC</td>
<td>2</td>
<td>1.29 1.00 1.42</td>
<td>122.7 125.7</td>
<td>180.0 121.9 121.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00 1.00 1.00</td>
<td>107.9 107.9</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 5. Theoretical study of the reaction of CN with NH$_3$

<table>
<thead>
<tr>
<th>$Z_1$</th>
<th>$Z_2$</th>
<th>$Z_3$</th>
<th>$r_x$</th>
<th>$\angle_x$</th>
<th>$\phi_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>N</td>
<td>C</td>
<td>1</td>
<td>$r_1$</td>
<td>$\angle_1$</td>
</tr>
<tr>
<td>N</td>
<td>C</td>
<td>N</td>
<td>1</td>
<td>$r_2$</td>
<td>$\angle_2$</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>X</td>
<td>3</td>
<td>$r_3$</td>
<td>$\angle_3$</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>3</td>
<td>$r_4$</td>
<td>$\angle_4$</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>3</td>
<td>$r_5$</td>
<td>$\angle_5$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>$Z_x$</th>
<th>$r_{1,2,3,4,5}$ (\AA)</th>
<th>$\angle_{1,2,3,4}$ (deg)</th>
<th>$\phi_{1,2,3}$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$NCN</td>
<td>1</td>
<td>1.16 2.35 1.00</td>
<td>180.0 109.8</td>
<td>0.0 120.0 -120.0</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>109.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.45</td>
<td>105.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>105.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>122.1</td>
<td>-0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>113.6</td>
<td>-113.6</td>
<td></td>
</tr>
<tr>
<td>TS$_1$</td>
<td>1</td>
<td>1.18 1.49 1.08</td>
<td>118.3 108.9</td>
<td>0.0 120.8 -120.8</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>108.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$N$_2$</td>
<td>2</td>
<td>1.14 1.34 1.00</td>
<td>178.2 90.0</td>
<td>0.0 113.6 -113.6</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>114.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HCN$_2$H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>H</td>
</tr>
</tbody>
</table>

Table 4: Optimized Hartree-Fock and MP2 geometries
### Chapter 5. Theoretical study of the reaction of CN with NH₃

<table>
<thead>
<tr>
<th>Species</th>
<th>(-\text{HF/\text{HF}})</th>
<th>(-\text{MP4SDQ/\text{HF}})</th>
<th>(-\text{MP4SDQ/\text{MP2}})</th>
<th>ZPVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H})</td>
<td>0.49823</td>
<td>0.49823</td>
<td></td>
<td>0.49823</td>
</tr>
<tr>
<td>((^3\Sigma))NH</td>
<td>54.95943</td>
<td>55.07668</td>
<td></td>
<td>21.1</td>
</tr>
<tr>
<td>((^1\Sigma_g))N₂</td>
<td>108.94395</td>
<td>109.25323</td>
<td></td>
<td>16.5</td>
</tr>
<tr>
<td>((^2B₁))N₂H</td>
<td>55.55770</td>
<td>55.70801</td>
<td></td>
<td>54.0</td>
</tr>
<tr>
<td>((^2A'))N₂H</td>
<td>109.42540</td>
<td>109.72814</td>
<td></td>
<td>37.0</td>
</tr>
<tr>
<td>((^2B_2))H₂CN</td>
<td>93.43231</td>
<td>93.69658</td>
<td></td>
<td>70.1</td>
</tr>
<tr>
<td>((^2A'))cisHCNH</td>
<td>93.39296</td>
<td>93.66992</td>
<td></td>
<td>70.8</td>
</tr>
<tr>
<td>((^2A'))transH CNH</td>
<td>93.39875</td>
<td>93.67926</td>
<td></td>
<td>72.6</td>
</tr>
<tr>
<td>((^3B_1))CH₂</td>
<td>38.92150</td>
<td>39.01990</td>
<td></td>
<td>48.4</td>
</tr>
<tr>
<td>((^1A_1))CH₂</td>
<td>38.87237</td>
<td>38.99199</td>
<td></td>
<td>47.2</td>
</tr>
<tr>
<td>(\text{NH₃})</td>
<td>56.18436</td>
<td>56.36828</td>
<td></td>
<td>97.2</td>
</tr>
<tr>
<td>({^2A})CH₃</td>
<td>39.55899</td>
<td>39.68759</td>
<td></td>
<td>81.3</td>
</tr>
<tr>
<td>((^2\Sigma))CN</td>
<td>92.20483</td>
<td>92.45165</td>
<td></td>
<td>11.9</td>
</tr>
<tr>
<td>((^1\Sigma))HNC</td>
<td>92.85533</td>
<td>93.13711</td>
<td></td>
<td>44.8</td>
</tr>
<tr>
<td>((^1\Sigma))HCN</td>
<td>92.87520</td>
<td>93.15973</td>
<td></td>
<td>47.2</td>
</tr>
<tr>
<td>(\text{NH₃+CN})</td>
<td>148.38919</td>
<td>148.81993</td>
<td></td>
<td>109.1</td>
</tr>
<tr>
<td>({^3\Sigma})H₂NCN</td>
<td>147.90866</td>
<td>148.36089</td>
<td></td>
<td>97.2</td>
</tr>
<tr>
<td>(\text{CH₃N₂})</td>
<td>148.46201</td>
<td>148.90581</td>
<td></td>
<td>121.8</td>
</tr>
<tr>
<td>(\text{HNCHNH})</td>
<td>148.46452</td>
<td>148.89329</td>
<td></td>
<td>124.1</td>
</tr>
<tr>
<td>(\text{HN₂CH₂})</td>
<td>148.40203</td>
<td>148.83625</td>
<td></td>
<td>128.2</td>
</tr>
<tr>
<td>(\text{HCN₂H₂})</td>
<td>148.33630</td>
<td>148.79398</td>
<td></td>
<td>127.1</td>
</tr>
<tr>
<td>(\text{H₂NHCN})</td>
<td>148.36843</td>
<td>148.80955</td>
<td></td>
<td>128.1</td>
</tr>
<tr>
<td>(\text{H₃N CN})</td>
<td>148.39970</td>
<td>148.84083</td>
<td></td>
<td>115.8</td>
</tr>
<tr>
<td>({^3\Sigma})H₂NCN</td>
<td>148.42681</td>
<td>148.86105</td>
<td></td>
<td>108.1</td>
</tr>
<tr>
<td>(\text{cisH₂NCN})</td>
<td>148.43537</td>
<td>148.88253</td>
<td></td>
<td>123.8</td>
</tr>
<tr>
<td>(\text{HHNHNC})</td>
<td>148.44280</td>
<td>148.88263</td>
<td></td>
<td>108.3</td>
</tr>
<tr>
<td>(\text{H₂NH CN})</td>
<td>148.46726</td>
<td>148.90307</td>
<td></td>
<td>125.9</td>
</tr>
<tr>
<td>(\text{transH₂NCN})</td>
<td>148.44412</td>
<td>148.89416</td>
<td></td>
<td>125.8</td>
</tr>
</tbody>
</table>
Chapter 5. Theoretical study of the reaction of CN with NH$_3$

<table>
<thead>
<tr>
<th>Species</th>
<th>$-\text{HF}//$HF</th>
<th>$-\text{MP4SDQ}//$HF</th>
<th>$-\text{MP4SDQ}//$MP2</th>
<th>ZPVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS$_1$</td>
<td>148.33274</td>
<td>148.80557</td>
<td></td>
<td>104.8</td>
</tr>
<tr>
<td>TS$_2$</td>
<td>148.36319</td>
<td>148.81372</td>
<td></td>
<td>107.1</td>
</tr>
<tr>
<td>TS$_3$</td>
<td>148.37265</td>
<td>148.82743</td>
<td></td>
<td>101.6</td>
</tr>
<tr>
<td>TS$_4$</td>
<td>148.38240</td>
<td>148.83249</td>
<td>148.83462</td>
<td>99.1</td>
</tr>
<tr>
<td>TS$_5$</td>
<td>148.38825</td>
<td>148.83593</td>
<td>148.83660</td>
<td>112.0</td>
</tr>
<tr>
<td>TS$_6$</td>
<td>148.40229</td>
<td>148.85436</td>
<td></td>
<td>117.8</td>
</tr>
<tr>
<td>TS$_7$</td>
<td>148.39037</td>
<td>148.83878</td>
<td>148.83928</td>
<td>100.3</td>
</tr>
<tr>
<td>(2A')</td>
<td>148.41344</td>
<td>148.85192</td>
<td></td>
<td>110.0</td>
</tr>
<tr>
<td>TS$_8$</td>
<td>148.38204</td>
<td>148.83354</td>
<td></td>
<td>115.6</td>
</tr>
<tr>
<td>TS$_{10}$</td>
<td>148.37786</td>
<td>148.82571</td>
<td></td>
<td>121.2</td>
</tr>
</tbody>
</table>

Table 5: Calculated HF//HF, MP4SDQ//HF, MP4SDQ//MP2 and QCISD(T)//MP2 (in braces) energies (hartree$^3$) and zero-point vibrational energy (kJ mol$^{-1}$)

As can be seen from table 4, a number of the calculated geometries contain stretched bonds. It has been noted that fourth-order unrestricted Møller-Plesset energies, which include contributions from triple substitutions show poor results for geometries of this kind due to slow convergence of the unrestricted Møller-Plesset series [90]. Overestimation of the effects of triple substitutions in the MP4 energy has also been noted to occur for unsaturated radicals, such as cyano, and in some molecules which contain multiple bonds [91,92]. As a result of this we have only calculated MP4 energies at the MP4SDQ level rather than at the MP4SDTQ level.

For species which warranted higher level calculations, QCISD(T)//MP2 energies were calculated. The QCISD(T) method [93] is known to give energies close to the full-CI results, particularly for geometries close to equilibrium, however since the relative computational time for a QCISD(T) energy calculation is several days compared to several hours for an MP4SDQ energy calculation, QCISD(T) energies were only calculated for species corresponding to important features of the potential

$^3$1 Hartree = 2625.502 kJ mol$^{-1}$
energy surface. Energies other than the MP4SDQ//HF will be referred to specifically in the text. All energies are uncorrected for zero-point vibrational energy unless otherwise stated.

The HF/6-31G*//HF/6-31G*, MP4SDQ/6-31G*//HF/6-31G* and zero-point vibrational energies of these species are given in table 5 together with MP4SDQ/6-31G*//MP2/6-31G* and QCISD(T)/6-31G*//MP2/6-31G* energies for species for which they were calculated. The important points to notice from this table are that the MP4SDQ//HF energy of CN is lower than the MP4SDQ//MP2 energy and that the transition-state species TS$_3$ has a relative energy above the energy of the reactants at the HF//HF level but below the energy of the reactants at the MP4SDQ//HF level. The relative energetics of TS$_3$ will be further discussed later. The apparent discrepancy in the CN energies indicates that the partial inclusion of correlation energy in the optimization (MP2 level) does not represent the correlation effects in this species very well. As a result of this, the energies quoted relative to reactants at the MP4SDQ//MP2 level probably overestimate the true energy differences slightly. The MP4SDQ//MP4SDQ energy of this species is only ca. 1 kJ mol$^{-1}$ below the MP4SDQ//HF energy indicating this overestimation at the MP4SDQ//MP2 level will be small.

The thermochemistry of the possible products channels from this reaction are summarized below where it can be seen that there are four exoergic sets of products. The quoted energies include a scaled (see below) correction for zero-point vibrational energy. The relative energies of species on pathways to exoergic products, with the exception of N$_2$ + CH$_3$, are plotted in figure 8. The energies plotted in this figure are uncorrected for zero-point vibrational energy.

\[
\begin{align*}
\text{NH}_3 + \text{CN} &\rightarrow \text{N}_2\text{H} + \text{CH}_2 (^{1}\text{A}_1) & \Delta E &= 239.9 \text{ kJ mol}^{-1} \\
&\rightarrow \text{N}_2\text{H} + \text{CH}_2 (^{3}\text{B}_1) & \Delta E &= 167.7 \text{ kJ mol}^{-1} \\
&\rightarrow \text{NH} + \text{cis} \text{ HCNH} & \Delta E &= 177.2 \text{ kJ mol}^{-1} \\
&\rightarrow \text{NH} + \text{trans} \text{ HCNH} & \Delta E &= 154.3 \text{ kJ mol}^{-1} \\
&\rightarrow \text{NH} + \text{H}_2\text{CN} & \Delta E &= 106.6 \text{ kJ mol}^{-1}
\end{align*}
\]
Chapter 5. Theoretical study of the reaction of CN with NH₃

---

\[ \text{NH}_2 + \text{HNC} \quad \Delta E = -75.4 \text{ kJ mol}^{-1} \]
\[ \text{H}_2\text{N} \text{CN} + \text{H} \quad \Delta E = -125.3 \text{ kJ mol}^{-1} \]
\[ \text{NH}_2 + \text{HCN} \quad \Delta E = -162.4 \text{ kJ mol}^{-1} \]
\[ \text{N}_2 + \text{CH}_3 \quad \Delta E = -327.5 \text{ kJ mol}^{-1} \]

Additional calculations done on the reactants NH₃ and CN and the products NH₂, HNC and HCN following the G-1 procedure⁴ show some important results. The first is that at this level of theory, which has been shown to give energies close to experimentally determined ones [94], the exoergicities of reaction to form NH₂ + HNC and NH₂ + HCN are reduced to 26.4 and 88.0 kJ mol⁻¹ respectively. Secondly, a significant contribution to the G-1 energy (ca. 0.05 hartree) arises from the inclusion of higher polarization functions (2df) in the basis set. This suggest that a larger basis set, which includes higher polarization functions on the non-hydrogen atoms, would improve the accuracy of the results obtained for all species. Such a basis set would stabilize species with stretched bonds more than other species. Higher level optimizations for all species would also increase accuracy, however higher level calculations using bigger basis sets for such a large system as this, would place impractical demands on both computer CPU time and disk-storage space.

The harmonic vibrational frequencies calculated for all species are given in table 6. In an extensive study, DeFrees and McLean [95] have shown that calculated HF/6-31G* vibrational frequencies generally overestimate the corresponding experimentally determined anharmonic ones by ca. 12%. These workers conclude that the application of an empirical scaling factor of 0.89 results in a mean error of only 49 cm⁻¹. The vibrational frequencies and zero-point vibrational energies quoted are unscaled.

Reaction of CN with NH₃ can result in the initial formation of four possible complexes depending on their relative orientations. Of these, we were able to optimize structures for those resulting from orientation of the C or N end of CN toward the

---

⁴These calculations were done as part of a study of the HNC=HCN equilibrium in conjunction with the experimental determination of the products of reaction in chapter 7.
Chapter 5. Theoretical study of the reaction of CN with NH₃

Figure 8: Relative energies of species conceivably involved in the reaction of CN with NH₃.

\[ E_{\text{UMP4SDQ/ HF}} \text{ (kJ mol}^{-1} \text{)} \]
### Chapter 5. Theoretical study of the reaction of CN with NH₃

<table>
<thead>
<tr>
<th>Species</th>
<th>Harmonic Vibrational Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>σ 1982</td>
</tr>
<tr>
<td>NH</td>
<td>σ 3528</td>
</tr>
<tr>
<td>N₂</td>
<td>σ₉ 2758</td>
</tr>
<tr>
<td>CH₂ (³B₁)</td>
<td>A₁ 1238 A₁ 3327 B₂ 3527</td>
</tr>
<tr>
<td>CH₂ (¹A₁)</td>
<td>A₁ 1567 A₁ 3151 B₂ 3177</td>
</tr>
<tr>
<td>NH₂</td>
<td>A₁ 1710 A₁ 3606 B₂ 3707</td>
</tr>
<tr>
<td>N₂H</td>
<td>A' 1264 A' 1661 A' 3276</td>
</tr>
<tr>
<td>HCN</td>
<td>π 889 σ 2438 σ 3679</td>
</tr>
<tr>
<td>HNC</td>
<td>π 541 σ 2309 σ 4094</td>
</tr>
<tr>
<td>CH₃</td>
<td>A'' 307 E' 1540 A' 3285 E' 3461</td>
</tr>
<tr>
<td>NH₃</td>
<td>A₁ 1208 E 1849 A₁ 3690 E 3823</td>
</tr>
<tr>
<td>H₂CN</td>
<td>B₁ 1033 B₂ 1073 A₁ 1436 A₁ 1639 A₁ 3234 B₂ 3319</td>
</tr>
<tr>
<td>cis HCNH</td>
<td>A' 1013 A'' 1063 A' 1267 A' 1664 A' 3250 A' 3582</td>
</tr>
<tr>
<td>trans HCNH</td>
<td>A' 1033 A'' 1100 A' 1332 A' 1701 A' 3295 A' 3678</td>
</tr>
<tr>
<td>H₃NCH</td>
<td>E 66 182 E 369 E 1170 E 1827 2056</td>
</tr>
<tr>
<td>trans H₂NCNH</td>
<td>375 495 540 755 1092 1185</td>
</tr>
<tr>
<td>HHNHNC</td>
<td>1397 1788 1933 3771 3776 3922</td>
</tr>
<tr>
<td>HHNHCN</td>
<td>120 131 197 275 390 867</td>
</tr>
<tr>
<td>HHNHCN</td>
<td>871 1706 2314 3643 3744 3818</td>
</tr>
<tr>
<td>HHNHCN</td>
<td>107 120 155 252 365 1021</td>
</tr>
<tr>
<td>H₂NCNH</td>
<td>1022 1708 2422 3560 3634 3734</td>
</tr>
<tr>
<td>H₂NCNH</td>
<td>461 532 691 1159 1324 1805</td>
</tr>
<tr>
<td>H₂NCN</td>
<td>2603 3788 3891</td>
</tr>
<tr>
<td>cis H₂NCNH</td>
<td>334 480 534 780 1044 1153</td>
</tr>
<tr>
<td>H₂NHCN</td>
<td>1344 1801 1965 3598 3764 3904</td>
</tr>
<tr>
<td>HCN₂H₂</td>
<td>376 555 694 977 1154 1298</td>
</tr>
<tr>
<td>H₂NHCN</td>
<td>1416 1766 1825 3293 3789 3898</td>
</tr>
<tr>
<td>H₂NHCN</td>
<td>667 841 948 1016 1106 1141</td>
</tr>
<tr>
<td>H₂NHNC</td>
<td>1255 1589 1826 3200 3764 3888</td>
</tr>
<tr>
<td>H₂NHNC</td>
<td>154 560 701 1010 1232 1440</td>
</tr>
<tr>
<td>CH₃N₂</td>
<td>1509 1624 1849 3734 3768 3830</td>
</tr>
<tr>
<td>CH₃N₂</td>
<td>180 505 912 1147 1243 1543</td>
</tr>
<tr>
<td>HNCHNH</td>
<td>1622 1628 1690 3235 3328 3330</td>
</tr>
<tr>
<td>HNCHNH</td>
<td>611 656 848 1077 1197 1234</td>
</tr>
<tr>
<td>HNCHNH</td>
<td>1299 1510 1592 3329 3685 3715</td>
</tr>
</tbody>
</table>
Species Harmonic Vibrational Frequencies (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Species</th>
<th>HN$_2$CH$_2$</th>
<th>TS$_1$</th>
<th>TS$_2$</th>
<th>TS$_3$</th>
<th>TS$_4$</th>
<th>TS$_5$</th>
<th>TS$_6$</th>
<th>TS$_7$</th>
<th>TS$_8$</th>
<th>TS$_9$</th>
<th>BS$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS$_4$</td>
<td>856 194 525 670 1111 1300</td>
<td>1210 1816 2077 3407 3727 3822</td>
<td>1048 279 528 535 617 667</td>
<td>1130 1297 1808 2206 3793 3906</td>
<td>697 132 333 727 867 902</td>
<td>975 1723 1798 3540 3651 3754</td>
<td>576 371 406 1073 1116 1247</td>
<td>1339 1662 1899 3206 3282 3681</td>
<td>446 462 809 965 1189 1241</td>
<td>856 169 309 561 689 777</td>
<td>1408 1573 1796 3355 3685 3787</td>
</tr>
</tbody>
</table>

Table 6: Calculated Hartree-Fock harmonic vibrational frequencies

H (H$_3$) end of NH$_3$ (H$_2$NHCN and H$_2$NHNC respectively) and from orientation of the C end of CN toward the N end of NH$_3$ (H$_3$NCN). The formation of H$_3$NCN and H$_2$NHNC would be favoured by dipole-dipole forces. We were unable to optimize a structure resulting from collision with the N end of CN oriented towards the N end of NH$_3$. Our closest approximation to this structure has a energy only 4 kJ mol$^{-1}$ below the energy of the reactants and 4.5 kJ mol$^{-1}$ higher in energy than the reactants with the inclusion of zero-point vibrational energies. A normal co-ordinate analysis of this structure shows that it possesses two imaginary vibrations meaning it is neither an intermediate or transition-state species. All other collision complexes optimized are stable relative to the energy of the reactants.
The formation of the $\text{H}_2\text{NHNC}$ intermediate proceeds over a barrier lying 16 kJ mol$^{-1}$ higher in energy than the reactants. As a result of this barrier, the rate constant for reaction via this pathway would be expected to exhibit a positive temperature dependence. The $\text{H}_2\text{NHNC}$ intermediate has a geometry essentially consisting of an $\text{NH}_2$ and a HNC molecule connected by a long bond which suggests that this pathway is a direct H-abstraction mechanism. At the Hartree-Fock level of theory, formation of the $\text{H}_2\text{NHCN}$ complex proceeds over a barrier lying 43.4 kJ mol$^{-1}$ higher in energy than the reactants and like $\text{H}_2\text{NHNC}$, this species has a geometry essentially consisting of an $\text{NH}_2$ and a HCN molecule connected by a long bond suggesting a H-abstraction mechanism. Inclusion of correlation energy lowers the energy of this species to below that of the reactants however all attempts to optimize this structure at the MP2 level failed. The reasons for this are unclear, but preliminary indications from the MP2 optimizations suggest that the MP2 geometry would be significantly different from the HF geometry. Therefore the accuracy of the MP4SDQ//HF energies is questionable and we believe the Hartree-Fock energy better represents the relative energetics of this species than does the MP4SDQ energy. Both of these species have barrierless pathways to products $\text{HNC} + \text{NH}_2$ and $\text{HCN} + \text{NH}_2$ respectively.

The $\text{H}_3\text{NCN}$ intermediate has no barriers to formation and has possible pathways involving dissociation of a H atom or 1,3 migration of a H atom available to it. Our results show that the barrier to H dissociation, to form $\text{H}_2\text{NCN}$ and H, lies 37.7 kJ mol$^{-1}$ above the energy of the reactants. The rate constant for reaction via this mechanism would therefore be expected to display a positive dependence on temperature, that is increase as the temperature is increased. The barrier to migration of H from N to $\text{N}'$ proceeds over a barrier 21.9 kJ mol$^{-1}$ above the energy of the $\text{H}_3\text{NCN}$ intermediate and 33.0 kJ mol$^{-1}$ below the energy of the reactants. At the MP4SDQ//MP2 and QCISD(T)//MP2 levels of theory this barrier lies 23.7 and 33.5 kJ mol$^{-1}$ above the energy of the $\text{H}_3\text{NCN}$ intermediate and 37.7 and 9.3 kJ mol$^{-1}$ below the energy of the reactants respectively. The true energetics of this barrier is likely to be better represented by the QCISD(T) energy than the MP4SDQ energies.
A secondary barrier of this form on the potential-energy surface is the origin of a reaction rate constant displaying a negative dependance on temperature. As the temperature is raised the number of states with sufficient energy to redissociate to reactants increases relative to the number of states with sufficient energy for H-migration. The effect of this is that the apparent rate of disappearance of reactants decreases as the temperature is raised.

Following H-migration, the cis-form of the H₂NCNH intermediate has pathways involving isomerism to the trans-form or dissociation to products NH₂ and HNC available to it. This intermediate is very asymmetric indicating that considerable contortion of the molecular skeleton occurred during the H-transfer process. Our results show the barrier to dissociation to products is 48.4 kJ mol⁻¹ higher in energy than the barrier to isomerism. From the trans H₂NCNH intermediate, further rearrangement involving migration of the same H atom from N' to C leads to the products NH₂ and HCN. The results of the G-1 calculations mentioned earlier, which showed that the exoergicities of reaction to form NH₂ and HCN or NH₂ and HNC to be considerably less than those calculated at the MP4SDQ//HF level, suggest that more extensive calculations, at higher levels of theory and with bigger basis sets, may show the pathway to formation of NH₂ + HNC to be less favoured than the pathway to formation of NH₂ + HCN.

Reaction via this mechanisms would be expected to proceed at a rate controlled by the relative rates of passage across the secondary barrier and on to products and of dissociation back to reactants. The form of this potential energy surface is similar to that thought to be characteristic of a radical-radical association reaction where the collision complex rearranges via a four-centre transition state to yield products [96]. This is a somewhat surprising similarity since this is a reaction between a radical and a neutral molecule.
5.5 Conclusions

The methods of \textit{ab initio} molecular orbital theory have been used to calculate the structures and relative energies of species conceivably involved in the reaction of CN with NH$_3$. Geometries of these species were optimised at the Hartree-Fock and levels of theory with energies calculated at the MP4SDQ//HIF, MP4SDQ//MP2 and QCISD(T)//MP2 levels.

The results show that there are four energy allowed sets of reaction products possible; namely NH$_2$ + HNC, H$_2$NCN + H, NH$_2$ + HCN and N$_2$ + CH$_3$ in order of increasing exoergicity. Complete mechanistic pathways to all sets of products, with the exception of N$_2$ + CH$_3$, have been found. Initial collision complexes on the pathways to the formation of all other sets of exoergic products are all stable relative to the energy of the reactants.

Barriers to reaction lying on the pathways to formation of HNC + NH$_2$ and HCN + NH$_2$ \textit{via} direct H-abstraction mechanisms, and H$_2$NCN + H means that the rate constants for reaction \textit{via} these pathways would be expected to display positive temperature dependences. A \textit{secondary} barrier to reaction lying on a separate pathway to the formation of NH$_2$ + HCN and/or HNC indicates that the rate constant for reaction \textit{via} this mechanism would display a negative temperature dependence.

The accuracy and limitations of the methods used in relation to the results obtained has been discussed.

A paper based on this work is in preparation [97].
Chapter 6

Kinetics of reactions of CN with NH$_3$ and ND$_3$

6.1 Introduction

The cyanogen radical (CN) is known to be an important species in a wide range of chemical systems. It is one of the most abundant and widely distributed of interstellar molecules, its electronic and rotational emissions having been observed with high spatial resolution over a large number of interstellar regions, originating from numerous astronomical sources $[98,99,100]$ including stars, cometary coma and dust and molecular clouds. It is thought to be an important intermediate in processes controlling the nitrogen balance in planetary atmospheres $[101]$ and interstellar clouds $[102]$. Electronic and vibrational CN emissions have also been of interest due to the possibility of laser action. Gain coefficients and quenching behaviours of emissions from excited CN molecules have been measured $[103]$ to determine the viability of development of a CN chemical-laser.

CN-radicals are commonly observed transient species in flames $[104,105]$ and are thought to play an important part in processes controlling the production of the pollutant NO from hydrocarbon flames $[106]$ and from flames doped with nitrogen
Chapter 6. Kinetics of reactions of CN with NH₃ and ND₃

compounds [107]. Studies have demonstrated that although the organically bound fuel-N is initially converted to HCN, the large increase in production of NO observed from hydrocarbon flames doped with nitrogenous fuels [108] has a rate determining step consistent with the reaction [107,109]

\[
CN + OH \rightarrow NCO + H
\]

To understand the complex chemistry occurring in many practical chemical systems such as these, computer modelling is necessary. In order for these models to be accurate, knowledge of the rate coefficients of many component reactions over wide ranges of reaction conditions are required. Such information is vital if these models are to be used predictively, as done by Herbst and Klemperer [110] to predict the observed correlation [111] between the abundances of CN and CO in interstellar clouds. Towards this end, a number of studies of the rate of reactions of cyanogen radicals with species known to be present and thought to be important in such systems have been undertaken (table 7).

The data in these tables represents work done in the area of CN-radical kinetics during the past decade. The rate coefficient listed is either a generally agreed upon value or an intermediate value where a spread of rate constants have been reported. Where possible results showing the dependence of the rate constant on temperature and/or vibrational excitation of CN are quoted. The temperature range and data listed are taken from the first reference cited. Of all the studies undertaken, the reactions of CN with O₂ [87,113,117,123,124,125,128,135,136,138,139,140,141] and H₂ [86,113,114,117,118,123,124,139,141] have received the most attention. Both reactions have been studied over wide temperature ranges extending down to temperatures found in warm interstellar clouds in the case of CN + O₂. The now well established room-temperature rate constant for this reaction has been used as a benchmark value in many studies.

In this study we report room temperature rate coefficients for the reactions of CN-radicals with NH₃ and ND₃. To date, four previous measurements of the rate
6. Kinetics of reactions of CN with NH₃ and ND₃

<table>
<thead>
<tr>
<th>Species</th>
<th>Temp (K)</th>
<th>Rate coefficient (cm³ s⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>99-716</td>
<td>$2.49 \pm 0.02 \left( \frac{T}{298} \right)^{-0.5\pm0.015} \times 10^{-11}$</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td>294-716</td>
<td>$1.86 \pm 0.08 \exp \left( \frac{-1340\pm20}{RT} \right) \times 10^{-11}$</td>
<td>[87]</td>
</tr>
<tr>
<td>H₂</td>
<td>295-768</td>
<td>$2.4 \pm 0.7 \left( \frac{T}{298} \right)^{1.6\pm0.2} \exp \left( \frac{-790\pm20}{T} \right) \times 10^{-12}$</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.42 \pm 0.38 \left( \frac{T}{298} \right)^{2.8\pm0.6} \exp \left( \frac{-790\pm20}{T} \right) \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>D₂</td>
<td>295-768</td>
<td>$0.79 \pm 0.15 \left( \frac{T}{298} \right)^{1.1\pm0.3} \exp \left( \frac{-1930\pm140}{T} \right) \times 10^{-12}$</td>
<td>[113,114,86]</td>
</tr>
<tr>
<td>CH₃C₂H</td>
<td>294</td>
<td>$2.1 \pm 0.5 \times 10^{-10}$</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.3 \pm 0.5 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>294</td>
<td>$1.6 \pm 0.2 \times 10^{-10}$</td>
<td>[115]</td>
</tr>
<tr>
<td>C(CH₃)₄</td>
<td>294</td>
<td>$1.1 \pm 0.1 \times 10^{-10}$</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.1 \pm 0.1 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>C₇H₁₆</td>
<td>294</td>
<td>$2.3 \pm 0.2 \times 10^{-10}$</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.6 \pm 0.3 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>CH₃OH</td>
<td>294</td>
<td>$1.2 \pm 0.2 \times 10^{-10}$</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.3 \pm 0.2 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>C₂F₃H</td>
<td>294</td>
<td>$4.2 \pm 0.3 \times 10^{-11}$</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.6 \pm 0.3 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>C₂F₄</td>
<td>294</td>
<td>$2.5 \pm 0.3 \times 10^{-11}$</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.6 \pm 0.3 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>295-764</td>
<td>$0.78 \pm 0.17 \exp \left( \frac{-18900\pm800}{RT} \right) \times 10^{-11}$</td>
<td>[116,117,118]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.58 \pm 0.06 \exp \left( \frac{-15800\pm400}{RT} \right) \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>HBr</td>
<td>295-764</td>
<td>$2.0 \pm 0.4 \exp \left( \frac{-7700\pm700}{RT} \right) \times 10^{-11}$</td>
<td>[116,117,118]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.4 \pm 0.3 \exp \left( \frac{-8300\pm400}{RT} \right) \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>HI</td>
<td>295-764</td>
<td>$6.1 \pm 0.6 \exp \left( \frac{300\pm500}{RT} \right) \times 10^{-11}$</td>
<td>[116,117,118]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7.2 \pm 0.2 \exp \left( \frac{200\pm100}{RT} \right) \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>295</td>
<td>$1.42 \pm 0.01 \times 10^{-12}$</td>
<td>[87,119,120]</td>
</tr>
<tr>
<td></td>
<td>294-716</td>
<td>$4.95 \pm 0.2 \exp \left( \frac{1090\pm220}{RT} \right) \times 10^{-11}$</td>
<td>[87,119,120]</td>
</tr>
<tr>
<td>Species</td>
<td>Temp (K)</td>
<td>Rate Coefficient (cm³ s⁻¹)</td>
<td>Ref</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>----------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>CH₄</td>
<td>292-1488</td>
<td>$(1 \pm 2)T^{2.64\pm0.24} \exp\left(\frac{220\pm150}{T}\right) \times 10^{-19}$</td>
<td>[119–123, 112, 113]</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>294-700</td>
<td>$3.49 \pm 0.26 \exp\left(\frac{571\pm13}{T}\right) \times 10^{-11}$</td>
<td>[126,123,115]</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>294-700</td>
<td>$4.72 \pm 0.25 \exp\left(\frac{509\pm20}{T}\right) \times 10^{-11}$</td>
<td>[126,123,115]</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>294-984</td>
<td>$(3.7 \pm 0.2)T^{2.7\pm0.2} \exp\left(\frac{810\pm80}{T}\right) \times 10^{-19}$</td>
<td>[122,121,123,127,115]</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>rt</td>
<td>$2.3 \pm 0.3 \times 10^{-10}$</td>
<td>[123]</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>292-1270</td>
<td>$(2 \pm 3)T^{1.22\pm0.2} \exp\left(\frac{400\pm150}{T}\right) \times 10^{-14}$</td>
<td>[121,122,127,115]</td>
</tr>
<tr>
<td>Cl₂</td>
<td>rt</td>
<td>$6.0 \pm 0.3 \times 10^{-12}$</td>
<td>[128]</td>
</tr>
<tr>
<td>F₂</td>
<td>rt</td>
<td>$6.4 \pm 0.8 \times 10^{-14}$</td>
<td>[128]</td>
</tr>
<tr>
<td>HCN</td>
<td>296-578</td>
<td>$10^{-11.41\pm0.15} \times \exp\left(\frac{-670\pm100}{T}\right)$</td>
<td>[129]</td>
</tr>
<tr>
<td>BrCN</td>
<td>296-578</td>
<td>$10^{-10.7\pm0.4} \times \exp\left(\frac{-1340\pm330}{T}\right)$</td>
<td>[129]</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>296-578</td>
<td>$10^{-10.19\pm0.10} \times \exp\left(\frac{-1140\pm70}{T}\right)$</td>
<td>[129]</td>
</tr>
<tr>
<td>HC₂CN</td>
<td>rt</td>
<td>$1.70 \pm 0.08 \times 10^{-11}$</td>
<td>[130]</td>
</tr>
<tr>
<td>H₂O</td>
<td>518-1027</td>
<td>$1.33 \pm 0.13 \exp\left(\frac{-31200\pm600}{RT}\right) \times 10^{-11}$</td>
<td>[131,132]</td>
</tr>
<tr>
<td>NO₂</td>
<td>297-740</td>
<td>$10^{-10.40\pm0.12} \times \exp\left(\frac{-186\pm33}{T}\right)$</td>
<td>[119]</td>
</tr>
<tr>
<td>N₂O</td>
<td>300-740</td>
<td>$10^{-11.8\pm0.4} \times \exp\left(\frac{-3560\pm181}{T}\right)$</td>
<td>[133]</td>
</tr>
<tr>
<td>CO₂</td>
<td>2510-3510</td>
<td>$6.6 \exp\left(\frac{-19200}{T}\right) \times 10^{-10}$</td>
<td>[134,135]</td>
</tr>
<tr>
<td>N</td>
<td>300</td>
<td>$1.00 \pm 0.13 \times 10^{-10}$</td>
<td>[136,134]</td>
</tr>
<tr>
<td>O</td>
<td>2510-3510</td>
<td>$1.03 \exp\left(\frac{-1000}{T}\right) \times 10^{-11}$</td>
<td>[134,137,138]</td>
</tr>
</tbody>
</table>

Table 7: Results of previous studies of the reaction of CN-radicals. For species which have two entries in the table, the upper entry represents CN ($v'' = 0$) and the lower entry represents CN ($v'' = 1$). T is the temperature at which the measurements were made. ‘rt’ indicates room temperature. The gas constant $R = 8.314$ J K⁻¹ mol⁻¹. All rate coefficients listed are expressed in ‘per molecule’ units, that is, cm³ s⁻¹ implies cm³ molecule⁻¹ s⁻¹.
Chapter 6. Kinetics of reactions of CN with NH$_3$ and ND$_3$

<table>
<thead>
<tr>
<th>Year</th>
<th>$v''$</th>
<th>Temp (K)</th>
<th>Rate Coefficient (cm$^3$ s$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1968</td>
<td>-</td>
<td>687</td>
<td>$8.8 \pm 5.0 \times 10^{-12}$</td>
<td>[142]</td>
</tr>
<tr>
<td>1972</td>
<td>0</td>
<td>300</td>
<td>$2.1 \times 10^{-11}$</td>
<td>[143]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>$2.5 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>300</td>
<td>$3.8 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>375</td>
<td>$1.8 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>375</td>
<td>$2.3 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>-</td>
<td>295</td>
<td>$2.5 \pm 0.5 \times 10^{-11}$</td>
<td>[117]</td>
</tr>
<tr>
<td>1988</td>
<td>0</td>
<td>294-716</td>
<td>$1.52 \pm 0.23 \exp \left( \frac{-1500 \pm 600}{RT} \right) \times 10^{-11}$</td>
<td>[87]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
<td>$1.55 \pm 0.15 \exp \left( \frac{-2600 \pm 400}{RT} \right) \times 10^{-11}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 8: Results of previous studies of the reaction of CN with NH$_3$

constant for the reaction CN with NH$_3$ have been reported but no measurements of the rate constant for the reaction of CN with ND$_3$. The reaction of CN with NH$_3$ was first studied by Boden and Thrush [142] in 1968. They generated CN-radicals by reaction of C$_2$N$_2$ with O atoms at 687K and monitored their time evolution by absorption spectroscopy. The analysing light for these measurements was generated by a microwave discharge in a mixture of Ar, N$_2$ and CH$_4$ which emitted CN $^3B\rightarrow^1X$ radiation. The rate coefficient they obtained, along with those reported by subsequent workers are shown in table 8.

Bullock et al. [143] extended this work four years later, including a study of the dependences of the rate constant on temperature and on vibrational excitation of CN. They produced CN-radicals by pulse-radiolysis of dilute mixtures of C$_2$N$_2$ and NH$_3$ in argon and monitored the decay of CN in the $v'' = 0, 2$ and 4 vibrational levels by absorption spectroscopy, using a high-pressure xenon-lamp, at 300 and 375K. They found that the rate coefficient exhibited a negative dependence on temperature and a positive dependence on vibrational excitation of CN. The rate constant they determined from extrapolation of their data to 687K essentially shows
agreement with that determined by Boden and Thrush at this temperature. More recently, de Juan et al. [117] and Sims and Smith [87] have studied this reaction using laser-photolysis and laser-induced fluorescence to generate and monitor CN respectively. The results obtained by Sims and Smith, which span a wide temperature range, provide support for the negative temperature dependence and positive dependence on vibrational excitation of CN of the rate coefficient found by Bullock et al., although they report a room-temperature rate constant somewhat higher than that of previous workers.

All previous studies of the reaction of cyanogen with ammonia make use of the well known CN $\text{B} \rightarrow \text{X}$ electronic system, in either absorption or emission to monitor the CN decay. In this study we monitor the CN concentration via the $(1,0)$ vibrational band of the ground electronic state.

### 6.2 Experimental

Cyanogen radicals were produced by 193.3 nm photolysis of $\text{C}_2\text{N}_2$ in mixtures of $\text{C}_2\text{N}_2$, He and either NH$_3$ or ND$_3$, by the unfocussed output of an ArF excimer-laser. The excimer-laser was operated at a frequency of ca. 10 Hz and produced pulses with energies of approximately 50 mJ, as measured by a Scientech model 364 power/energy meter. The low pulse energies combined with the small absorption cross-section of $\text{C}_2\text{N}_2$ at 193 nm (ca. $1.1 \times 10^{-19}$ cm$^2$ [114]) ensured that pseudo first-order conditions were maintained throughout all experiments with [NH$_3$] or [ND$_3$] $\gg$ [CN].

The photolysis cell used for these experiments (see section 2.2.6) consisted essentially of a length of 50 mm internal-diameter glass tubing approximately 1200 millimetres long, with ground-glass flanges at either end onto which calcium fluoride windows were attached. Calcium fluoride was chosen because of its high optical transparency from the vacuum-ultraviolet through to infra-red wavelengths, allowing both photolysis and probe laser beams to introduced to the cell co-linearly.
The excimer-laser and diode-laser beams enter from opposite ends of the cell and the diode-laser beam makes four passes diagonally through the entire length of the volume swept out by the excimer-laser beam. The reaction gas mixture flows into the cell from the end where the excimer-laser beam enters. Additional buffer gas flows into the cell through four ports around each window designed to reduce the deposition of CN-polymer on them.

The intensity of the diode-laser beam was monitored by focussing it into a Judson liquid-nitrogen cooled, mercury-cadmium-telluride detector with a KRS-5 lens. The detector output was amplified by a matched Judson PA-100 pre-amplifier and taken to the transient recorder or the oscilloscope. Cyanogen rovibrational line positions were calculated using the spectroscopic constants of Cerny et al. [144] and were in excellent agreement with those observed by Davies and Hamilton [145]. The diode-laser was tuned to the P(10) (v = 0 → 1) line of the ground (X2Σ+) electronic state at ca. 2003.06254 cm⁻¹. The absolute frequency was determined by calibration with known CO line positions [146] interpolated by the fringes of the etalon.

The experimental setup is shown in figure 9. A 10-volt pulse produced by a variable frequency, square-wave generator simultaneously triggers the photolysis laser and the transient recorder. The transient recorder is configured to allow the collection of data from the pre-trigger region, so that the value of I₀ (intensity at t = 0) may be determined, as well as from the post-trigger region in which the transient CN absorption decays. The number of points digitized per pulse and the sampling rate of the recorder were selected so that the entire decay of the absorption of CN-radicals was recorded and the experimental repetition rate was kept as high as possible. Typically the decays of CN-radicals from 500 photolysis laser pulses were averaged. Decreasing the repetition rate increases the data collection time of an experiment and exacerbates problems associated with the diode-laser frequency drifting due to instability in the refrigerator temperature. This problem was minimized by checking to ensure the diode-laser was centered on the CN rovibrational line before each measurement was taken. The excimer laser, the diode laser and the transient digitizer are all triggered from separate opto-isolated circuits to reduce
Figure 9: Experimental configuration for the collection of kinetic data using excimer-laser photolysis/diode-laser absorption spectroscopy

Flow rates of reagent molecules were measured with calibrated Tylan mass flowmeters and controlled with needle valves. Cell pressure, typically around 2 torr, was measured using a MKS model 122AA 0-10 torr Baratron. Reactant partial pressures were calculated from the measured flow rates and total pressure. All experiments were conducted at room temperature (296 ± 2) K. The purity, handling and preparation of gases used in this experiment has been discussed previously in section 2.3.
6.3 Results and Discussion

In our reaction system CN radicals can be removed by reaction with NH₃, the radical precursor C₂N₂, the reaction products HCN and NH₂ (see chapter 7), NH₃ photolysis products NH₂ and H and other CN-radicals, or via diffusion out of the active volume¹.

Since \([\text{NH}_3] \gg [\text{NH}_2], [\text{NH}], [\text{H}], [\text{HCN}]\) and [CN] the rate of removal of CN-radicals with time may be expressed as

\[
\frac{-d[\text{CN}]}{dt} = k_{\text{diff}}[\text{CN}] + k_{\text{C}_2\text{N}_2}[\text{CN}][\text{C}_2\text{N}_2] + k_{\text{NH}_3}[\text{CN}][\text{NH}_3]
\]  

(4)

Solution of this equation and imposing the boundary condition that at \(t = 0\), [CN] = [CN]₀ yields

\[
[\text{CN}] = [\text{CN}]_0 \exp(-k't)
\]  

(5)

where \(k' = k_{\text{diff}} + k_{\text{C}_2\text{N}_2}[\text{C}_2\text{N}_2] + k_{\text{NH}_3}[\text{NH}_3]\). Combining this with the Beer-Lambert law yields an expression relating the experimentally observed absorption intensity as a function of time, to the concentration of CN-radicals.

\[
\ln \left( \ln \left( \frac{I_n}{I_t} \right) \right) = \ln (\epsilon[\text{CN}]_0) - k't
\]  

(6)

Figure 10 shows time-resolved plots of the transient absorption of CN in the presence of two differing concentrations of ND₃. Both curves are the results obtained from averaging over 500 photolysis laser pulses. The pseudo-first-order decay constant is obtained from the slope of a plot of the natural logarithm of absorption versus time (equation 6) as shown in figure 11. The first 50 microseconds of each decay were not included in the fitting procedure, to ensure any residual effects of pickup from the excimer-laser discharge are eliminated. The linearity of plots obtained confirms that CN was being removed by first-order processes. The bimolecular rate coefficient \(k\), is obtained from the slope of a plot of the pseudo first-order rate constants as a function of the reactant concentration (figure 12).

¹The active volume in this context is the volume of the cell swept out by the excimer-laser beam.
The intercept of figure 12 represents the sum of the rates of removal of CN by all processes other than reaction with NH$_3$ (or ND$_3$) including reaction with C$_2$N$_2$. At the partial pressures of C$_2$N$_2$ used, the contribution to the intercept from reaction with C$_2$N$_2$ [147] is small. The negative intercept we obtain is almost certainly due to overestimation of the actual NH$_3$ concentration in the active volume. NH$_3$ is depleted in the active volume by photolysis at 193 nm [148] and as a result of this the concentrations we calculate (see section 2.3) will slightly overestimate the actual concentration of NH$_3$ in the region where CN-radicals are produced. The

---

\[ \text{The intercept is in fact statistically zero.} \]
Chapter 6. Kinetics of reactions of CN with NH₃ and ND₃

Figure 11: Pseudo first-order decay plots for CN in the presence of ND₃. The data from figure 10 was used to create these plots.

Effect of this will be that the data points in our Stern-Volmer plot (figure 12) will be shifted in the [reactant] co-ordinate toward more positive values, hence our negative intercept. The single-photon absorption cross-section of NH₃ is $4.5 \times 10^{-18}$ cm² [149] so that together with the slow reactant flow-rates we employ, significant NH₃ depletion may occur. Since [NH₃] is at least in a 500-fold excess of [CN], NH₃ photolysis would not affect our pseudo first-order reaction conditions or the decay constants we obtain. Similar arguments apply to the reaction of CN with ND₃ although depletion by photolysis will occur to lesser extent since ND₃ has a smaller
Chapter 6. Kinetics of reactions of CN with NH₃ and ND₃

Figure 12: Stern-Volmer plot for the reaction of CN with ND₃

single-photon absorption coefficient\(^3\) at 193 nm.

Photolysis of C₂N₂ at 193 nm has been shown to produce CN-radicals in both the \(v'' = 0\) and \(v'' = 1\) vibrational levels of the ground electronic state [151,152] with rotational temperatures of around 900K. Measurements of the relative population of each state indicate that between 13 [151] and 26% [152] of CN-radicals are produced in the \(v'' = 1\) level. Population of higher vibrational levels was not observed. Although rotational equilibration to 300K has been shown to be rapid [124], and

\(^3\)Although to date the single-photon absorption coefficient of ND₃ at 193 nm has not been measured, studies such as the jet-cooled spectra obtained by Vaida et al. [150] indicate that a smaller value is likely.
would occur in the time we wait before fitting decays, vibrational relaxation occurs on a longer timescale. The major pathways for deactivation of CN (v'' = 1) are via energy transfer to C₂N₂ and by reaction with NH₃. Vibrational energy transfer to NH₃ is unlikely to be important due to a large difference in the vibrational frequencies of CN and NH₃. Energy transfer to C₂N₂ [124], repopulating the v'' = 0 level should only be competitive with reaction with NH₃ [87] at low NH₃ concentrations. Systematic removal of data points corresponding to low NH₃ concentrations does not affect the rate coefficient we obtain beyond the errors we quote. Therefore it would seem that the small fraction of CN-radicals formed in the v'' = 1 vibrational state are not effecting our analysis of CN (v'' = 0) radicals to a discernable degree and that the rate constant we report is a good measure of the rate at which CN (X 2Σ⁺, v'' = 0) radicals react with NH₃.

The results obtained, together with the room-temperature rate coefficients obtained by other workers are shown in table 9. The quoted uncertainty for our results represents the 95% confidence level obtained from a Students-t test of the linear-least-squares fit.

Our results are in excellent agreement with recent study of Sims and Smith [87] and are also in good agreement with the earlier study of de Juan et al. [117] from the same laboratory.
Chapter 6. Kinetics of reactions of CN with NH$_3$ and ND$_3$

The results of the experimental studies of this reaction show that it displays characteristics normally associated with radical-radical reactions [153]; those being the rate of reaction is close to the collisional rate and displays a negative dependence on temperature. Despite the kinetic data available, the mechanism by which CN reacts with NH$_3$ is unclear. As Sims and Smith [87] point out, this reaction has a rate constant several orders of magnitude faster than the reaction of CN with other H-atom containing small molecules such as H$_2$ and CH$_4$ where the H–X bond strength is less than in NH$_3$. Experimental evidence to date indicates that the reactions of CN with H$_2$ and CH$_4$ proceed via a direct H-abstraction type mechanism [123], so it seems unlikely that reaction with NH$_3$ does also. In addition to this, \textit{ab initio} theoretical studies of the reactions of CN with H$_2$ [83] and NH$_3$ (see chapter 5) show that there are barriers of 16–40 kJ mol$^{-1}$ on the pathways to products via direct H-abstraction mechanisms. The rate coefficients for reaction via these mechanisms would be expected to display positive temperature dependences as observed for reaction with H$_2$ [113] but not for reaction with NH$_3$. Therefore it would seem that CN does not react with NH$_3$ via a direct H-abstraction type mechanism as the barrier on the pathway to products is inconsistent with both the observed fast rate and negative temperature dependence. Similar reasoning would suggest that reaction of CN with NH$_3$ to form H$_2$NCN + H via the mechanism presented in chapter 5 would also be inconsistent with the observed experimental data since this pathway also has a barrier to reaction.

Recent theoretical investigations into the origin of the negative temperature dependence [153,154] indicate that the fate of such reactions may be determined by long-range intermolecular forces such as dipole and quadrupole interactions. Dynamical calculations of the rate of capture over a dipole-dipole potential by Phillips [97] show the capture rate to be \textit{ca}. 7$\times$ greater than the measured rate of reaction. This implies that there is a secondary barrier on the reaction pathway.

The results of the \textit{ab initio} molecular orbital theory study presented in chapter 5 show that there is another possible pathway for reaction in which dipole-dipole forces orient CN and NH$_3$ to form the H$_3$NCN intermediate. Reaction to products
from this intermediate proceeds over a secondary barrier lying 33.5 kJ mol\(^{-1}\) higher in energy than the intermediate but 9.3 kJ mol\(^{-1}\) lower than the energy of the reactants at the QCISD(T)//MP2 level of theory. A secondary barrier of this form would explain the negative temperature dependence and be consistent with fast rate of reaction observed and the results of Phillips. As the temperature is raised the number of states with sufficient energy to redissociate to reactants increases relative to the number of states with sufficient energy for H-migration. The effect of this is that the apparent rate of disappearance of CN decreases as the temperature is raised.

Additional calculations by Phillips, with the inclusion of a statistically based factor for the probability of crossing the secondary barrier gives calculated rates of reactions in good agreement with experimental values. The experimental (2.0) and calculated magnitudes of the kinetic isotope effect \((\frac{k_H}{k_D})\) are also in agreement. Phillips notes that excellent agreement between the experimental and calculated rate of reaction and magnitude of the kinetic isotope effect can be obtained with a small adjustment to the height of this secondary barrier. His results suggest that the height of this barrier is bounded by the MP4SDQ//MP2 and QCISD(T)//MP2 energies. For reasons discussed in chapter 5 regarding the slow convergence of the unrestricted Møller-Plesset series and the limitations of the basis set used, this seems a reasonable conclusion.

This pathway is therefore the most likely mechanism of reaction of CN with NH\(_3\) and ND\(_3\). The observed products of reaction and the relationship to the conclusions drawn about the mechanism of reaction here will be discussed in chapter 7.

### 6.4 Conclusions

We have measured rate constants for the room temperature reactions of CN with NH\(_3\) and ND\(_3\). CN-radicals were produced by laser photolysis of C\(_2\)N\(_2\) at 193 nm and their time evolution was monitored by infra-red absorption spectroscopy. The
results obtained were

\[ \text{CN} + \text{NH}_3 \quad k = 3.0 \pm 0.4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1} \]
\[ \text{CN} + \text{ND}_3 \quad k = 1.5 \pm 0.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1} \]

All measurements are in good agreement with the results of previous workers.

Comparison of the results obtained with the results of other experimental and theoretical studies of the reaction of CN with NH\(_3\), indicates that the reaction proceeds initially to a dipole-dipole favoured intermediate (H\(_3\)NCN) which subsequently rearranges over a secondary barrier and dissociates to give products.

A paper based on this work is in preparation [97].
Chapter 7

Products of reactions of CN with NH₃ and ND₃

7.1 Introduction

Complete characterization of a reaction requires that, in addition to kinetic studies, the products of reaction be determined. Since reactions involving free radicals may have more than one set of possible products, determination of the products that form and how the overall rate of reaction is partitioned between different product channels (branching ratio) is important. Although the likely products of reaction can often be determined on thermodynamic grounds, other forces, such as those controlling favourable orientation of reactants for collision or rearrangement and dissociation of any intermediate complexes formed, can often supercede thermodynamic considerations. Product determination can therefore provide fundamental information on the relative heights of barriers in the possible reaction channels, and the importance of other forces in determining which products form.

Of the many reactions of CN-radicals that have been studied, the products of reaction have been determined for only a few of these. Balla et al. observed the kinetic buildup of HCN from the reactions of CN with H₂ [114], CH₄ and C₂H₆ [121].
The rate constant they determined for the growth of HCN from the reaction of CN with H$_2$ was essentially the same as that they obtained for the disappearance of CN indicating that HCN and H are the sole products of reaction.

The NCO radical has been observed as a product of the reaction of CN with O$_2$ by many workers [140,155,156]. CO was also observed as a product of this reaction by Schmatjko and Wolfrum [157], who used a CO laser for time-resolved absorption measurements. From the observed vibrational distribution of CO they concluded that the reaction of CN with O$_2$ proceeds according to

$$\text{CN} + \text{O}_2 \rightarrow \text{CO}(v') + \text{NO} \quad (6 \pm 2)\%$$
$$\rightarrow \text{NCO} + \text{O} \quad (94 \pm 2)\%$$

In a similar manner they determined that the reaction of CN with O proceeds according to

$$\text{CN} + \text{O} \rightarrow \text{CO} + \text{N}(^4\text{S}) \quad (20 \pm 10)\%$$
$$\rightarrow \text{CO} + \text{N}(^2\text{D}) \quad (80 \pm 10)\%$$

Products of the reactions of CN with OCS and N atoms have also determined. Addison et al. [158] observed the spectrum of SCN from the reaction of CN with OCS and Kley et al. [159] observed C atoms from the reaction of CN with N atoms using vacuum-ultra-violet absorption spectroscopy.

Prior to this work, the products of the reaction of CN with NH$_3$ had only been partially characterized. Bullock et al. [143] observed the appearance of NH$_2$(0,0,0) radicals from the pulse-radiolysis of C$_2$N$_2$ in the presence of NH$_3$. The rate constant the obtained for the growth of NH$_2$ was consistent with that they obtained for CN removal. The identity of the product(s) forming in addition to NH$_2$ remained to be determined.

### 7.2 Experimental

CN-radicals were produced by 248.5 nm photolysis of ICN in mixtures of ICN, NH$_3$ and Helium, using the unfocussed output of a KrF excimer laser. ICN rather
than C₂N₂ was used as the CN-radical source in these experiments to prevent NH₃ photolysis, which occurs at 193 nm. The reaction of photolysis products with CN radicals or C₂N₂ could have given rise to signals which may have been attributed to products of the reaction of CN with NH₃. Of particular concern would have been the reactions of H atoms. The photolysis cell and experimental setup for the observation of transient reaction profiles associated with the photolysis-laser pulse have been described in chapter 6. In this study we searched for the buildup of products after the photolysis-laser pulse rather than the decay of CN-radicals.

Mass analysis of samples of the reaction mixture was done using a Spectromass Dataquad quadrupole mass-spectrometer. Samples were taken from the pumpout port of the cell through a needle-valve. The quadrupole was pumped to pressures of ca. 10⁻⁸ torr by a Varian VHS-4 diffusion pump backed by a Welch Duo-Seal model 1376 mechanical pump. Analysis was done at pressures typically ranging from 5 × 10⁻⁶ to 5 × 10⁻⁵ torr as measured by an ion-gauge adjacent to the quadrupole. The diffusion pump and quadrupole are separated by a large liquid-nitrogen cold trap to prevent contamination of samples with diffusion pump oil fragments.

Infra-red diode laser spectra of static mixtures were obtained in a Scintrex model WC-2 1.5 metre White cell. The infra-red beam traversed a path length ca. 75 metres through the cell and was focussed upon its exit by a KRS-5 lens into a Judson liquid-nitrogen cooled, mercury-cadmium-telluride detector. The detector output was amplified by a matched Judson PA-100 pre-amplifier and displayed on the oscilloscope. The absolute frequency was determined using the known line positions [146] of either N₂O (ND₂, H₂NCN) or CO(HCN, HNC) reference gases interpolated by the fringes of the etalon.

Cell pressures were measured using either a MKS model 122AA 0–10 torr Baratron or a Texas Instruments model 144 quartz-spiral gauge. Pressures in the photolysis cell were typically 2–3 torr for flowing mixtures and 90–100 torr for static mixtures. Flow rates of reagent molecules were measured with calibrated Tylan mass flow-meters. All experiments were conducted at room temperature (296 ± 2)K. The purity, handling and preparation of reagent materials used in this experiment have
been discussed in section 2.3.

*Ab initio* molecular orbital theory energy calculations on the HCN/HNC equilibrium were performed using Gaussian90 [89].

### 7.3 Results and Discussion

The results of the *ab initio* molecular orbital theory calculations presented in chapter 5 indicate that there are four exoergic product channels in this reaction. These channels are summarized below. Energies quoted were calculated at the MP4SDQ//HF level of theory.

\[
\begin{align*}
\text{NH}_3 + \text{CN} & \rightarrow \text{NH}_2 + \text{HNC} \quad \Delta E = -75.4 \text{ kJ mol}^{-1} \\
& \rightarrow \text{H}_2\text{NCN} + \text{H} \quad \Delta E = -125.3 \text{ kJ mol}^{-1} \\
& \rightarrow \text{NH}_2 + \text{HCN} \quad \Delta E = -162.4 \text{ kJ mol}^{-1} \\
& \rightarrow \text{N}_2 + \text{CH}_3 \quad \Delta E = -327.5 \text{ kJ mol}^{-1}
\end{align*}
\]

It was shown that the production of H\textsubscript{2}NCN + H proceeds over a barrier lying 37.7 kJ mol\textsuperscript{-1} above the energy of the reactants and therefore the formation of these products would be inconsistent with the experimentally observed fast reaction rate and negative dependence of the rate coefficient on temperature. The absence of a complete pathway to the formation of N\textsubscript{2} and CH\textsubscript{3} lead us to believe that these products were also unlikely to form although their possible production was not discounted entirely. The major problem with this reaction pathway was the inability to optimize a structure responsible for the formation of an N-N bond. Two complete mechanisms to the formation of both NH\textsubscript{2} and HNC and NH\textsubscript{2} and HCN were found, therefore these sets of products were thought to be the most likely reaction products at room temperature.

We mass-analysed samples taken from a flowing mixture of ICN, NH\textsubscript{3} and He while it was being irradiated at 248 nm and compared the resulting mass-spectra with those obtained with the laser off. The results showed a 15–25% increase in
Chapter 7. Products of reactions of CN with NH₃ and ND₃

signal at $m/e = 27$ when the excimer laser was incident upon the sample. Since only stable species are likely to survive the passage from where they are sampled to the quadrupole, the signal increase was assigned to the production of either HCN or HNC. Distinction between isomeric forms with the same mass-to-charge ratio is not possible using a quadrupole mass-spectrometer. No evidence for signal increases beyond that which occurred in background samples was found at $m/e = 28$ (N₂), or $m/e = 42$ and $m/e = 43$ (H₂NCN and H₂NCN/H⁺), or at any other mass below $m/e = 43$ (CN₂H₃⁺).

In order to determine whether HCN, HNC or both species were being produced by the reaction, the diode-laser was tuned to the P(9)(0,0,0 → 0,0,1) line of HCN at 2069.52008 cm⁻¹ [160], then the R(8)(0,0,0 → 0,0,1) line of HNC at 2050.06122 cm⁻¹ [161] and attempts were made to observe the kinetic buildup of these species after the photolysis-light pulse. However the infra-red line strengths of these molecules at these wavelengths were found to be too weak to enable their detection at the levels produced from a single pulse. To overcome this problem, static mixtures of reactants were irradiated at 248 nm for 30–45 minutes to increase the concentrations of products to measurable levels. To increase sensitivity further, the irradiated sample was transferred to the longer path-length White cell. Analysis of the resulting spectra showed the presence of the P(9) and P(15) lines of HCN at 2069.52008 cm⁻¹ and 2050.42112 cm⁻¹ respectively with percentage absorptions in excess of 20 × greater than background levels. No evidence for HNC was found in the region of the R(8) and R(15) lines at 2050.06122 cm⁻¹ and 2069.15057 cm⁻¹ respectively.

We performed additional ab initio molecular orbital theory calculations, following the G-1 procedure outlined by Pople et al. [94], to determine whether there was sufficient energy available from the reaction for HNC, should it form, to isomerize to HCN in the time before analysis. The results, plotted in figure 13 show that HNC lies 61.6 kJ mol⁻¹ above HCN and the HNC/HCN isomerism transition-state (CHN (TS)) lies 186.1 kJ mol⁻¹ above HCN. This means that the energy available from the reaction of CN with NH₃ to either set of products is less than half that required for isomerism of either HCN or HNC.
There have been few experimental determinations of the relative energies of HCN and HNC and only one "experimental" study of the magnitude of the activation barrier. The most recent study of the HCN/HNC energies by Pau and Hehre [162],

determined the HNC isomer to lie 61.9 ± 8.0 kJ mol⁻¹ above the HCN isomer using Ion-Cyclotron Double-Resonance spectroscopy. This is in excellent agreement with our ab initio value. Our calculated geometries are also in good agreement with those determined experimentally [163,164] (table 10), and this is indicative of the degree of accuracy we might expect from our calculations in the transition region.
Recently Lee and Rendell [165] have reported an extensive ab initio study of the structure and energetics of the HCN\textendash{}HNC transition-state. Their calculations, done using a coupled-cluster (CCSD(T)) method with very large basis sets show the CHN (TS) to lie 186.6 ± 4 kJ mol$^{-1}$ above the HCN isomer. Their results are in good agreement with our findings. For reasons Lee and Rendell discuss [165], it would seem that the only "experimental" determination of the transition-state energy [166] is too low and that the ab initio values better represent the relative energy of this species.

From these results it would appear that should HNC form as a product of the reaction of CN with NH$_3$, there is insufficient energy available for it to isomerize to HCN. Since we do not observe HNC in our spectroscopic study we conclude that it is not a reaction product at room temperature.

In addition to the detection of HCN as a product of reaction, ND$_2$ radicals were detected in the regime of line positions calculated from energy levels determined by Meunchausen et al. [167], at approximately 1179.7 cm$^{-1}$. The assignment of the observed transient absorption to a line of ND$_2$ was done by photolysing a sample of pure ND$_3$ at 193 nm and observing a transient absorption at the same frequency.
NH was eliminated as the possible absorber as the frequency of the NH stretch is some 900 cm\(^{-1}\) higher in energy. The percentage absorption due to ND\(_2\) produced by photolysing C\(_2\)N\(_2\) or ICN in the presence of ND\(_3\) was at least twice that due to ND\(_3\) photolysis alone with identical ND\(_3\) concentrations. The absorption buildup also occurred over a much longer timescale than that from the ND\(_3\) photolysis which exhibited instantaneous production at a maximum concentration level. This indicates that ND\(_2\) was being produced both from the photolysis of ND\(_3\) and from the reaction of CN with ND\(_3\). The intensity of the signal due to the kinetic buildup of ND\(_2\) was, however, too weak for a rate coefficient to be determined from it.

The observation of ND\(_2\) as a reaction product is in agreement with the work of Bullock et al. [143] who observed the formation of NH\(_2\)(0,0,0) radicals in their pulse-radiolysis study of the reaction. The rate constant they obtained was in good agreement with that they obtained for the disappearance of CN(0,0) radicals although reduced response of their detection equipment resulted in higher experimental errors. In our study ND\(_2\) rather than NH\(_2\) was investigated simply because of the availability of a laser-diode covering the required spectral region.

The observation of these products is consistent with the conclusions drawn about the mechanism of reaction in the previous chapter. Phillips [97] has calculated the relative rates of passage across the barriers to formation of HCN + NH\(_2\) and HNC + NH\(_2\) (see chapter 5). His results show that the observed rate constant and kinetic isotope effect are both consistent with the proposed mechanism leading to the products NH\(_2\) and HCN. The form of the potential-energy surface governing reaction via this mechanism would indicate that both HCN + NH\(_2\) and HNC + NH\(_2\) should be products of reaction, especially at elevated temperatures. The experimental observation of only one set of products suggests that other forces, rather than just the relative energetics of the potential-energy surface, may be controlling product formation. However, as mentioned in chapter 5, more extensive \textit{ab initio} calculations may show the pathway to the formation of NH\(_2\) + HNC to be energetically less favoured than the pathway to the formation of NH\(_2\) + HCN, at room temperature. Further work is warranted to determine whether the production of NH\(_2\) and HNC
occurs at higher reaction temperatures.

As mentioned previously, we found no evidence for the presence of N\textsubscript{2} in our mass spectra above background levels. However the background signal at \( \frac{m}{e} = 28 \) was higher than that at other mass-to-charge ratios of interest hence a small change in signal would have been harder to detect. We would have liked to have been able to probe for the presence of CH\textsubscript{3} radicals by infra-red kinetic spectroscopy, as this has been shown to be a sensitive method for CH\textsubscript{3} detection. However we were unable to do so as we did not have a laser-diode which covered the desired spectral region. Therefore we cannot rule out the presence of N\textsubscript{2} and CH\textsubscript{3} resulting from a minor reaction channel, but the results of the theoretical study presented in chapter 5 leads us to conclude that formation of these products would not be expected.

Similarly, no evidence was found for the presence of H\textsubscript{2}NCN in our mass spectra beyond background levels. We did a spectroscopic search, similar to that outlined for HCN and HNC, for the presence of this species in the regime of the intense CN-stretch at \( \text{ca.} 2250 \text{ cm}^{-1} \) [168]. We found no evidence for the presence of this species in our reaction mixtures. As mentioned in chapter 6, this formation of this species would involve reaction via a mechanism which has a barrier to reaction so would be inconsistent with the observed negative temperature dependence and fast rate of reaction.

### 7.4 Conclusions

The products of the reactions of CN with NH\textsubscript{3} and ND\textsubscript{3} have been determined using mass spectrometry and infra-red absorption spectroscopy. CN-radicals were produced by excimer-laser photolysis of ICN at 248 nm in both flowing and static mixtures also containing NH\textsubscript{3} or ND\textsubscript{3} and He.

The results obtained indicate than NH(D)\textsubscript{2} and H(D)CN are the sole products of these reactions at room temperature. No evidence was found for the production
of any other species from these reactions. The observation of NH(D)$_2$ as a reaction product is consistent with the results of previous workers.

*Ab initio* quantum chemical calculations on the HCN$\rightleftharpoons$HNC isomerization show that there is insufficient energy available from the reaction for either species to isomerize to the other supporting the accuracy of long timescale observations of HCN.

The results obtained have been discussed in terms of the conclusions drawn about the mechanism of reaction in the previous chapter and shown to be consistent with them. Further work is warranted to determine whether the production of NH$_2$ + HNC occurs in competition with production of NH$_2$ + HCN at elevated temperatures.

A paper based on this work is in preparation [97].
Chapter 8

Conclusions

The principal aim of this work was to study the reactions of cyanogen (CN) and boron hydride (BH) free radicals in the gas phase. The reactions of these species are particularly relevant to the chemistry of atmospheric and/or combustion systems. Observations made during the course of these kinetic studies and the existence of unresolved questions arising from studies of previous workers, led us to perform additional studies to characterize the emission observed during the photolyses of diborane and stannane, and to determine the products and mechanism of the reactions of CN with NH$_3$ and ND$_3$ using both experimental and theoretical methods. In this chapter, we will briefly summarize the results obtained and conclusions drawn from this work and suggest some areas in which this work may be extended.

A study of the kinetics of reactions of BH-radicals has provided the first measurements of bimolecular rate coefficients for the reactions of BH with NO and C$_2$H$_4$. The results obtained at room temperature were

$$\text{BH} + \text{NO} \rightarrow \text{products} \quad k = 1.26 \pm 0.07 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$\text{BH} + \text{C}_2\text{H}_4 \rightarrow \text{products} \quad k = 1.41 \pm 0.09 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

BH ($^1\Sigma$) radicals were generated by excimer-laser photolysis of diborane at 193 nm and monitored by time-resolved laser-induced fluorescence. The effects of varying the temperature in the range 260–350 K and the nature of the buffer gas on the
rate constants for these reactions has been investigated. In addition to these measurements, upper limits to the reactions of BH with O₂, C₂H₆, CH₄ and CO have been set. In each case, the results obtained have been interpreted in terms of the mechanism of reaction.

For the reaction of BH with NO, the observed rate of reaction and negative dependence of the rate coefficient on temperature have been shown to be consistent with the reaction being controlled by the rate of capture over a dipole-dipole potential. Comparison with the results of an ab initio study of this reaction indicates that the most likely products of reaction are HBO + N(²D) and/or BO + NH, although the presence of either of these sets of products has yet to be determined experimentally.

Boron containing combustion systems remain a poorly understood area of chemistry despite the evidence suggesting that they possess considerable potential as high energy fuels. There is considerable scope for further work on the reactions of boron hydrides and other small boron containing molecules, such as boron oxides and oxyhydrides, which are thought to be present in such systems. Detailed knowledge of many elementary reactions of these species is required if modelling of these combustion systems is to be successful. One of the main reasons for the lack of kinetic data on these species is that very little is known about the spectroscopy of these molecules. This makes detection and concentration monitoring using spectroscopic techniques, which are the most commonly used methods of detection in kinetic studies, impossible. Since both the HBO [48,49] and BH₂ [70] radicals have been observed spectroscopically, these species would seem good candidates for kinetic studies in the immediate future. Our results have also demonstrated that the 193 nm photolysis of diborane could be used as a source of BH₂ radicals.

Emission observed during the course of this work, from the 193 nm photolysis of diborane, led us to a study of the photodissociation of this species. These emissions were analysed and the identity of the probable emitter of each band observed was assigned on the basis of the dependence of band intensity on photolysis laser power, known thermochemistry and band structure. The emissions were assigned to two
news transitions of BH$_2$ as well as known transitions of BH ($\tilde{A}$$\rightarrow$$\tilde{X}$) and atomic boron(I). The production of BH and BH$_2$ was shown to arise from the absorption of two 193 nm photons while the production of excited B atoms results from the absorption of three 193 nm photons. Differences in selection rules governing transitions between states of differing geometry in absorption and emission, means that laser photolysis has considerable potential for generating new spectra. A higher resolution study of the emissions observed during the 193 nm photolysis of diborane is warranted. A similar study of the photodissociation of B$_2$D$_6$ would also prove useful to help confirm our assignments of new bands of BH$_2$ as well as to elucidate the spectroscopic nature of the emitting state.

Unexpected emissions observed during the course of this work, due the presence of stannane as an impurity in the diborane, led to a similar study of the photodissociation of this species. All emissions observed from the 193 nm photolysis of stannane were assigned to known atomic tin(I) transitions and were shown to arise from the absorption of a single 193 nm photon. The energy of the highest populated Sn(I) state observed relative to the energy available from a single 193 nm photon, implied that the photodissociation must proceed via the process

$$\text{SnH}_4(\text{g}) + h\nu_{193} \rightarrow \text{Sn}(\text{g}) + 2\text{H}_2(\text{g})$$

(7)

although the low intensities of the emissions observed suggested that this may only be a minor channel relative to

$$\text{SnH}_4(\text{g}) + h\nu_{193} \rightarrow \text{SnH}_2(\text{g}) + \text{H}_2(\text{g})$$

There is scope for further work on the photodissociation of stannane to determine the presence of H$_2$ and whether SnH$_2$ also forms.

A study of the kinetics of reactions of CN-radicals has provided the first measurement of the room temperature rate coefficient for the reaction of CN with ND$_3$, as well as a re-evaluation of the room temperature rate constant for the reaction of CN with NH$_3$. The results obtained were

$$\text{CN} + \text{ND}_3 \rightarrow \text{ND}_2 + \text{DCN} \quad k = 1.5 \pm 0.3 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$$

$$\text{CN} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{HCN} \quad k = 3.0 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$$
CN (2Σ+) radicals were generated by excimer-laser photolysis of C2N2 at 193 nm and their time evolution was monitored by infra-red absorption spectroscopy. Prior to this work the reactions of CN with NH3 and ND3 were not well understood. Unresolved questions remaining from previous studies of the CN + NH3 reaction motivated us to perform additional studies to determine the reaction products and mechanism.

By using the techniques of mass spectrometry and infra-red absorption spectroscopy, the products of reaction were found to be NH(D)2 and H(D)CN at room temperature. *Ab initio* calculations, performed at the state-of-the-art G-1 level of theory, confirmed, that should HNC be forming as a product of reaction, there was insufficient energy available from the reaction for it to isomerize to HCN in the time before analysis.

To determine the mechanism of reaction, a further *ab initio* study was undertaken to calculate the structures and relative energies of species conceivably involved. The results obtained indicated that there were two possible mechanisms by which CN and NH3 could react to form NH2 and HCN. The results of all the kinetic studies done on this reaction show that the rate of reaction is fast and that the rate coefficient exhibits a negative dependence on temperature. Only one of the calculated mechanisms was shown to be consistent with these properties; a pathway in which reaction proceeds *via* a dipole-dipole favoured intermediate (H3NCN) which subsequently rearranges over a secondary barrier and dissociates to give products.

This mechanism, however, would predict that both NH2 + HCN and NH2 + HNC should be products of reaction, especially at elevated temperatures. This suggested that either product formation was being controlled by forces other than the relative energetics of the potential energy surface or that there were some limitations to the accuracy attainable from the *ab initio* calculations performed in this region of the potential energy surface. The results of the state-of-the-art level calculations done on the HCN=HNC equilibrium, which included calculations on the reactants and products of this reaction, indicated that the relative energetics of this region of the potential energy surface may change if higher level optimizations and energy
calculations with larger basis sets were performed, and favour the formation of NH$_2$ + HCN over NH$_2$ + HNC. There remains scope for such higher level calculations to be done on the regions of the potential energy surface which determine the relative favourability of these reaction channels as well as to more accurately determine the height of the secondary barrier. Together with the use of higher levels of theory in both the optimization of geometries and calculation of relative energies, use of improved basis sets which include d and f-type polarization functions and s and p-type diffuse functions would provide more quantitative results.

The limitations of the methods of *ab initio* molecular orbital theory with respect to accuracy of results attainable have been reported for many systems, and methods for overcoming and allowing for these limitations are being devised. From the results reported here, it is clear that calculations at the highest levels of theory using large basis sets are desirable if *quantitative* results are to be obtained. However, for *large* systems such as these, such calculations would place impractical demands on both computer CPU time and disk storage space. Developments in computer architecture will increase the viability of such calculations in the future. Currently calculations with carefully selected basis sets and with moderate inclusion of correlation effects, as was done in our study, are the most practical. Although there is no substitute for experimental data, this work has demonstrated that there is valuable information to be obtained from theoretical calculations.

The results of all studies of the reactions of CN with NH$_3$ and ND$_3$ were shown to be consistent with the reaction being controlled by the rates of capture over a dipole-dipole potential and of subsequent rearrangement and dissociation of the intermediate over a secondary barrier. This provides support for the theories suggesting that the fate of reactions exhibiting kinetic properties such as these, being determined by long range intermolecular forces. This is especially true for reactions such as BH with NO which lack any significant barriers on the reaction pathway.

The work done on these reactions could be extended in a number of areas. Studies to determine the effects of temperature on the rate constant for the reaction of CN with ND$_3$ and of rotational excitation of CN on the rate constants for both reactions
would provide valuable information. The results of such studies would also be useful for comparison to those calculated by statistically and dynamically based reaction rate theories. The fast rate of rotational equilibration of CN would mean that the latter of these two studies would need to be done at low pressures and possibly using the more sensitive laser-induced fluorescence method for detection of CN.

There also remains scope for more work to be done to determine whether HNC forms as a product of the reaction of CN with NH$_3$. Experimental techniques which associate the production of HNC with the photolysis laser pulse, such as infra-red kinetic spectroscopy, would be desirable since long timescale detection techniques are not completely conclusive due to the reactive nature of HNC. Our attempts to observe HNC and HCN using this technique suggest that detection of HNC in the region of the N–H stretch would be likely to be more sensitive than detection in the region of the N–C stretch. Resonance Enhanced Multi-Photon Ionization, which could distinguish between HCN and HNC on the basis of their differing ionization thresholds, would also be a suitable technique for this study. A study to determine if CH$_3$ radicals form as a reaction product could also be done. Infra-red absorption spectroscopy has been shown to be sensitive to the detection of this species and so infra-red kinetic spectroscopy would be an ideal technique for such an investigation.

In terms of the aims of this work, we have extended the understanding of the chemistry of the reactions of the gas phase free-radicals CN and BH, as well as the photochemistry of diborane and stannane. Despite the advances made in experimental physical chemistry, this work has demonstrated that the study of reactive species remains a major undertaking.
Bibliography


