REACTIONS OF EXCITED NITROGEN MOLECULES.

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by

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An attempt to isolate excited nitrogen molecules from the reaction of active nitrogen with iodine proved unsuccessful. The rate constant of the bimolecular reaction between nitrogen atoms and iodine cyanide was found to be $3.5 \times 10^{-14}$ cm$^3$ molecules$^{-1}$ sec$^{-1}$, with probably a small temperature coefficient. A mechanism has been proposed for the excitation of the CN emission arising from the reaction of active nitrogen with the cyanogen halides.
I would like to thank Prof. L.F. Phillips for his encouragement and support during the course of this work.
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Previous reviews on the general field of the reactions and properties of active nitrogen have been given by Jennings and Linnett, Mannella, and Brocklehurst and Jennings. Although the reactions of active nitrogen have been studied for over fifty years, it is only in the last fifteen years that the identities of the main reactive species have been confirmed and the kinetics of its reactions determined. Tanaka et al., from a study of the ultraviolet absorption of active nitrogen, found that the majority of nitrogen atoms present were in the ground state, with less than 0.2% of the atoms in excited energy levels.

The present theory for the afterglow emission from active nitrogen, which has been outlined by Bayes and Kistiakowsky, involves the formation of a number of short-lived excited nitrogen molecules. Although known to be present, these species have rarely been thought to play an important part in the reactions of active nitrogen because of their low steady-state concentrations. In certain cases, their existence has been invoked to account for certain kinetic features of reactions and excitations of reactant molecules.

A number of electronically excited states of nitrogen are metastable, with lifetimes of up to several seconds. The best known of these metastable molecules is the A state of nitrogen which is formed in active nitrogen as a result of the termolecular recombination of nitrogen atoms, with an estimated steady-state concentration of up to one sixth of the nitrogen atom concentration. Recently, Dagan has shown that
the concentration of metastable molecules in active nitrogen was between $4 \times 10^9$ and $2 \times 10^{12}$ molecules cm$^{-3}$ for his reaction system; a concentration at least three orders of magnitude less than that estimated previously. This confirmed predictions by Young$^9$ and Wray$^{10}$ that the A state nitrogen molecules, and probably a number of other excited states of nitrogen, were deactivated by reaction with nitrogen atoms. Thus, it is unlikely that electronically excited nitrogen molecules formed in the nitrogen afterglow are as important in active nitrogen reactions as had originally been thought.

Vibrationally excited nitrogen molecules are known to be formed in discharges producing active nitrogen with concentrations about the same order as that of the nitrogen atoms$^{11}$, but the majority of these vibrationally excited molecules are in the vibrational level $v = 1$ and so are unlikely to influence most reactions to any extent. Molecules excited to vibrational levels up to $v = 29$, corresponding to energies exceeding 160 keals per mole, have been observed in minor amounts$^{12}$ and the deactivation reaction proposed by Young$^{9}$ would help to maintain the concentration of these highly vibrationally excited molecules to a reasonably constant level for a long time after the discharge. Since the steady-state concentration of A state nitrogen molecules was originally thought to be up to one sixth of the nitrogen atom concentration$^7$, it is unlikely that the concentration of highly vibrationally excited molecules would exceed this, and it is probably considerably less.

In Part I of this thesis, the reaction of active nitrogen with
iodine was investigated. This reaction was believed to have excited nitrogen molecules as an intermediate energy carrier, but an attempt to isolate them proved unsuccessful due, as shown by later workers, to their low concentration.

Work by Young and others, indicated that the concentration of excited nitrogen molecules in active nitrogen was very low which cast doubt on many reaction mechanisms that had used these species. One reaction that had often been cited as involving excited nitrogen molecules was that leading to the excitation of CN emission when active nitrogen was reacted with organic compounds. In Part II of this thesis, an investigation was made of one of the simplest of these reactions; the reaction of active nitrogen with the cyanogen halides. A mechanism is derived for this reaction that does not rely on excited nitrogen molecules as the main reactive species.
PART I. THE REACTION OF ACTIVE NITROGEN WITH IODINE.

INTRODUCTION.

The reaction of active nitrogen with iodine has been under investigation for over fifty years and is, perhaps, notable for having aroused suspicions in the minds of both early and recent investigators, that a simple mechanism involving nitrogen atoms as the sole reactive species, could not explain all the properties of the reaction.

Strutt and Fowler (1912)\(^{16}\) found that the reaction of active nitrogen with iodine gave a bright blue glow which consisted of a number of bands of molecular iodine extending from the visible, down to about 2300 Å, with the most prominent bands at 3430 Å. These bands were the same as those developed in the vacuum tube spectrum of iodine, but with different relative intensities. The atomic iodine line at 2062 Å was also detected.

Strutt (1913)\(^{17}\) attempted to detect the formation of nitrides in the reaction system by freezing out the products in liquid air, dissolving in potash, and testing for the presence of ammonia. There was no evidence of the formation of any stable nitride detectable by this method.

Newman (1922)\(^{18}\) activated nitrogen by exposing it to α-rays. Although he assumed that he had formed Strutt's active nitrogen, he gave insufficient data to enable this conclusion to be verified. Amongst other reactions, he activated the nitrogen in a static
system containing crystals of iodine. The pressure of the nitrogen in the reaction vessel decreased slightly, and he interpreted this as evidence of compound formation. He was unable to detect the presence of any nitride of iodine by conventional analytical means (the details of the method of analysis were not given).

Wendt (1922) suggested in a letter to "Nature", that attempts by Strutt and Newman to detect nitride formation would not be expected to be successful. Any binary compounds formed between nitrogen and iodine would be, from a consideration of relative electronegativities, nitrogen iodides and not iodine nitrides. Thus, the hydrolysis of these binary compounds would not give ammonia or ammonium salts. Wendt had not made any experimental tests to support this supposition.

Newman, in an accompanying reply to Wendt's letter, conceded to this interpretation, and cited the adsorption of nitrogen as evidence that compound formation had taken place.

During this period, a considerable amount of discussion had been taking place between various groups of workers on the energy and nature of active nitrogen. Some workers thought that active nitrogen was predominantly atomic in nature, while others opted for excited nitrogen molecules as the reactive species present. In this latter group were Willey and Rideal who, from calorimetric measurements, estimated that active nitrogen had an energy of 42.5 kcaIs per mole.
Ludlam and Easson (1926)\textsuperscript{21} queried Willey and Rideal's \textsuperscript{20} determination of the energy of active nitrogen. They estimated that the atomic iodine line at 2062 Å, observed by Strutt and Fowler\textsuperscript{16}, would require at least 150 kca per mole to excite. Because of the rate at which iodine destroyed active nitrogen, they thought it unlikely that a chemical reaction was taking place; only a direct energy transfer from the active nitrogen to the iodine.

Willey (1926)\textsuperscript{22}, in a reply to Ludlam and Easson, defended his estimation of the energy of active nitrogen at about 45 to 50 kca per mole. He suggested that in the reaction of iodine, unstable molecules of the type \(N_2I_2\) could be formed and then degraded by a further collision with excited nitrogen molecules to give excited iodine atoms. For normal exothermic reactions, there would be insufficient energy transferred to excite the atomic iodine line, but since nitrogen halides were unstable, he postulated that their formation could be by way of an endothermic reaction. The degradation by excited molecules would then give more energy for excitation. Willey remarked that, with the possibility of this sort of multi-step excitation mechanism, the evaluation of spectroscopic data alone was not an accurate method of determining the energy of active nitrogen.

Constantinides (1927)\textsuperscript{23} found that the introduction of iodine into a flow of active nitrogen, changed the conductivity of the gas and concluded that the iodine was being ionized. Since the ionization potential of iodine is about 216 kca per mole, he postulated that active nitrogen must have a greater energy than this.
Wille and Rideal (1927)\textsuperscript{24}, in an attempt to detect compound formation, could not obtain any condensate containing both iodine and nitrogen on cooling the products of the reaction in liquid nitrogen. The addition of molecular hydrogen to the reaction of active nitrogen with iodide did not give any detectable hydrogen iodide as a product. When active nitrogen was reacted with hydrogen iodide, the reaction flame consisted predominantly of the bright blue iodine spectrum, while the products were iodine and ammonium iodide with a trace of halogeno-amine (NH\textsubscript{2}I).

Easson and Armour (1928)\textsuperscript{25} investigated the iodine reaction, and in addition to the spectral features found by Strutt and Fowler\textsuperscript{15}, they found an atomic iodine line near 1850 A. An attempt to follow the kinetics of the reaction by varying the concentration of reactants, photographing the blue iodine emission through various filters, and determining the density of the photographic image, proved unsuccessful. The maximum iodine emission occurred when the iodine concentration was about one fifteenth of the concentration of active nitrogen (considered as N\textsubscript{2}), and even at very low concentrations of iodine the iodine emission was pronounced. From this, they concluded that the iodine was receiving energy from the active nitrogen by an energy transfer reaction and that no chemical reaction was taking place. In an attempt to follow the rate of decay of the blue iodine emission in a static system using cinematic techniques, they found that the blue glow was less than 0.01 seconds in duration and so its decay could not be followed.

Ewart and Rodebush (1934)\textsuperscript{26} reacted active nitrogen with hydrogen iodide and confirmed Wille and Rideal's\textsuperscript{24} observation, that the blue
iodine emission was the predominant feature of the spectrum. They postulated that the initial reaction was:

\[ \text{N} + \text{HI} \rightarrow \text{NH} + \text{I} \]
a reaction that would be about 35 kcal per mole exothermic using data then available. (Recent data would reduce this value to about 15 kcal per mole exothermic.)

Elliott (1940) compared the iodine emission from the reaction of active nitrogen with iodine to the vacuum tube emission of iodine. Although the transitions taking place in each system were the same, mainly \( I_2(\tilde{1}_g^+ \rightarrow \tilde{1}_u^+) \), the intensities of the various bands were different for each system.

Milton et al. (1961) carried out a detailed spectroscopic study of the reaction of active nitrogen with bromine, and found that the majority of the emission could be attributed to the transition \( \text{NBr}(\tilde{1}_g^+ \rightarrow \tilde{2}_u^-) \) where the latter state is the ground state of the NBr molecule. The predominant reactions removing nitrogen atoms were postulated to be:

\[ \text{N}(^4S) + \text{Br}_2(\tilde{1}_g^+) \rightarrow \text{NBr}(\tilde{3}_u^-) + \text{Br}(^2P_{3/2}) - 21 \text{ kcal per mole} \]
\[ \text{N}(^4S) + \text{NBr}(\tilde{3}_u^-) \rightarrow \text{N}_2(\tilde{1}_g^+) + \text{Br}(^2P_{3/2}) - 158 \text{ kcal per mole} \]

These reactions are essentially a catalysed recombination of nitrogen atoms to give ground state nitrogen molecules. Excited NBr was believed to be formed by a wall reaction of a nitrogen atom and a bromine atom. (Colin and Jones observed the \( \tilde{1}_g^+ \rightarrow \tilde{3}_u^- \) transition of NCl, when nitrogen and chlorine were pumped rapidly through a microwave discharge, but these bands have not yet been seen in a normal
active nitrogen reaction.)

Freeman and Phillips (1964)\textsuperscript{12} reported and discussed results obtained by Freeman during a B.Sc. (Hons.) project on the reaction of active nitrogen with iodine in a fast flow system. At low iodine concentrations, they found that the reaction flame was divided into two distinct zones. The zone closest to the iodine inlet jet was pink, and its spectrum showed iodine bands along with the atomic iodine line at 2062 \AA. The intensity of the emission depended on the square of the iodine concentration. The second zone further down the reaction tube was blue, and its iodine band spectrum was better developed than that of the pink zone. The intensity of the emission was directly proportional to the iodine concentration.

The dependence of the iodine emission on the nitrogen atom concentration could not be determined accurately because of the difficulty of measuring the nitrogen atom concentration in the presence of iodine. The intensity of the iodine emission varied only slowly with the nitrogen atom concentration determined in the absence of iodine. The variation of the total iodine emission with time at low iodine concentrations showed a minimum corresponding to the discontinuity between the two zones of iodine emission. At higher concentrations of iodine, the two zones merged and the decay of the iodine emission became exponential for the length of the reaction tube.

A similar reaction mechanism to that proposed by Milton et al.\textsuperscript{28} was envisaged. The iodine emission of the initial pink zone was attributed to the recombination of iodine atoms, so that the emission would be
expected to depend on the square of the iodine concentration, which it did. The decay of the iodine emission of the blue zone appeared to be too slow to correspond to iodine atom recombination, and the possibility of it being due to metastable iodine molecules was ruled out because of the high intensity of the emission and its wide spectral distribution. The most promising explanation appeared to be that the iodine emission in the blue zone was being excited by a long-lived energetic species. The intensity of the iodine emission would thus be dependent on the concentration of the energetic species.

A calculation based on the conservation of angular momentum suggested that the second reaction proposed by Milton et al. would give triplet nitrogen molecules eleven times out of fifteen, and since the A state nitrogen molecule \( ^3\Sigma_u^+ \) was believed to be the commonest metastable nitrogen molecule, it was postulated that the energetic species involved in the iodine excitation would be A state nitrogen molecules.

Freeman and Phillips advanced the following mechanism for the reaction between active nitrogen and iodine:

\[
\begin{align*}
N + I_2 &\rightarrow NI + I \\
N + NI &\rightarrow N_2(A) + I \\
N_2(A) + I_2 &\rightarrow N_2(X) + I_2^* 
\end{align*}
\]

where the excited iodine molecule formed in the third reaction can receive enough energy to excite the observed emission bands. Collision of A state nitrogen molecules with iodine atoms would probably explain the lines at 2062 Å and 1830 Å. Other reactions, for example the wall
reactions of the various species and the recombination of the iodine atoms leading to iodine band emission, can also occur.

If the only reactions removing the A state nitrogen molecules are:

\[
N_2(A) + I_2 \rightarrow N_2(X) + I_2^* \quad \text{rate constant, } k_1
\]

\[
N_2(A) \rightarrow N_2(X) + h\nu \quad \text{rate constant, } k_2
\]

and if the intensity of the blue iodine emission is proportional to the concentration of A state nitrogen molecules, then the rate expression for the destruction of A state nitrogen molecules becomes;

\[-d \ln I/dt = k_1[I_2] + k_2\]

where I is the intensity of the blue iodine emission. Thus the values of the rate constants \(k_1\) and \(k_2\) can be obtained from measurements of the decay of the blue iodine emission with time for various iodine concentrations. The value obtained for \(k_1\) was \(3.4 \times 10^{-13}\) cm\(^3\) molecules\(^{-1}\) sec\(^{-1}\). The inverse of \(k_2\) gives the lifetime of the A state nitrogen molecules, and Freeman and Phillips found it to be about one second.

From studies of the decay of the afterglow emission with time in the presence of varying concentrations of iodine, they were able to determine the rate of the initial reaction of nitrogen atoms with iodine as \(9 \times 10^{-14}\) cm\(^3\) molecules\(^{-1}\) sec\(^{-1}\).

Raxworthy and Phillips (1964)\(^3\) studied the reaction of active nitrogen with bromine and chlorine but, in contrast to the iodine reaction, could find no evidence of halogen emission. The implication of this is that either no A state nitrogen molecules were being formed in the reaction, or else they were not transferring their energy to the
halogen molecule. Iodine, when added downstream from the bromine inlet, did not give any blue emission, showing that A state nitrogen molecules were not produced in the reaction.

The reaction:

\[ \text{H} + \text{NX} \rightarrow \text{N}_2 + \text{X} \]

where X is a halogen, is more than 140 kcals per mole exothermic for chlorine, bromine, and iodine, when all reactants and products are in their ground states. It would be expected that the nitrogen molecule could be formed in the A state for all of these halogen reactions, but the formation of excited nitrogen molecules apparently occurs only for the iodine reaction. The iodine reaction is the most exothermic of the reactions of the halogens considered, and it could be envisaged that some other state of nitrogen with an energy between the exothermicity of the iodine reaction and the exothermicity of the bromine reaction. A possible candidate for this species is the \( ^3\Delta_u \) state of nitrogen with an energy of about 175 kcals per mole\(^{31} \).

Phillips (1965)\(^{32} \) reinvestigated the reaction of active nitrogen with iodine, using a similar method to that used by Freeman and Phillips\(^ {13} \), but with improved apparatus, and redetermined the rate constants for the various major reactions taking place. Values obtained were \( 2.6 \times 10^{-14} \exp(-68/RT) \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1} \) for the initial reaction of nitrogen atoms with iodine, \( 8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1} \) for the deactivation of the metastable species by iodine, and 1.1 seconds for the radiative lifetime of the metastable species. The difference between these values and those determined earlier\(^ {13} \), was attributed to
difficulty in determining iodine concentrations accurately in the earlier experiment.

In addition, it was found that the decay of the iodine emission was not dependent on the surface area of the reaction vessel, on the temperature over the range 15°C. to 50°C., or whether the iodine band studied was at 2600 A. or 4600 A. The lifetime determined in this paper for the metastable species, appeared to be very close to those determined for A state nitrogen molecules by Carleton and Oldenberg (2.0 ± 0.9 seconds)\textsuperscript{33}, Noxon (about 1 second)\textsuperscript{34}, and Zipf (0.9 seconds)\textsuperscript{35}.

The possibility that the metastable species were $^3\Delta_u$ nitrogen molecules, as proposed in a previous paper\textsuperscript{30}, was thought unlikely. If the $^3\Delta_u$ state of nitrogen had a greater energy than the $B^3\Pi_g$ state of nitrogen, then it would undergo collision induced transitions to this state and its lifetime would be short and pressure dependent. Conversely, if it had less energy than the B state, then transitions to the ground state of nitrogen would be forbidden and, since these have not been observed, would require the $^3\Delta_u$ state to have a longer lifetime than the A state of nitrogen. vibrationally excited ground state nitrogen molecules would also be expected to have a short, pressure dependent lifetime because of the ease of collision induced relaxation at pressures of several torr.

For this thesis, it was initially planned to study the reactions of A state nitrogen molecules. The first section describes an attempt to produce a stream of nitrogen, enriched with A state nitrogen molecules, by reacting active nitrogen with iodine and removing the iodine with a
cold trap before it could deactivate the A state nitrogen molecules. This proved impossible with the apparatus used because the occurrence of any enrichment would only be marginal and would be hidden by the inevitable fluctuations in reaction conditions.

The second section deals with attempts to determine the rate constants of the reaction of various compounds with A state nitrogen molecules by adding them to the reaction system of active nitrogen and iodine. By simultaneously following the decays of the blue iodine emission and the afterglow emission, it was hoped to determine separate rate constants for the reaction of oxygen and nitrous oxide with nitrogen atoms and A state nitrogen molecules. This work also proved unsuccessful for a different reason.

In the conclusion to this part of the thesis, the review given in this introduction on the reaction of active nitrogen with iodine, is continued to the end of 1967.
CHAPTER 1. ISOLATION OF A-STATE NITROGEN MOLECULES.

EXPERIMENTAL.

REAGENTS:


Iodine: A.R. grade. Used as supplied by Riedel de Haen, Germany.

APPARATUS:

The apparatus was modified considerably over the period when this work was being done, and the apparatus described here represents the final form in use before this line of investigation was abandoned. The apparatus consisted of a power supply delivering a condensed D.C. voltage to a discharge tube. Nitrogen atoms produced in the discharge tube were carried in a stream of nitrogen gas into the reaction vessel where iodine was added through various jets and trapping took place. A number of pieces of ancillary equipment metered and measured gas flows and produced iodine vapour.

The power supply used consisted of a centre-tapped transformer capable of delivering 500 milliamperes at 3.5 kilovolts. The input power supplied to this transformer was controlled by a "Variac" variable transformer. The output of the high voltage transformer was rectified by two mercury rectifier tubes (866A) and was delivered through a 2.4 kilohm resistor (to limit the current) to a 4 microfarad capacitor.
A 0 to 500 milliammeter in one of the high voltage leads to the capacitor enabled the charging current to be kept constant. The output of this power supply, when connected to the electrodes of the discharge tube, consisted of a number of short pulses of high current. Although provision was made for cooling the power supply, some of the components tended to overheat, and as a result there was little long term stability.

The discharge tube, where the molecular nitrogen was dissociated into atoms, was in the form of a large Y. In each arm of the discharge tube, pure aluminium electrodes were hung by brass rods from glass-to-metal seals. The electrodes consisted of hollow cylinders, about 16 cm. long and 2 cm. diameter. Copper and aluminium electrodes were also tried but sputtering, with its attendant production of impurity atoms, made them unsuitable. Nitrogen gas was admitted to the discharge tube through two side arms above the electrodes, so that the gas flowed down past the electrodes. The leads from the power supply to the discharge tube and the two arms of the discharge tube were electrostatically shielded to reduce electrical interference with the light meter.

The stream of nitrogen atoms from the discharge tube passed from the base of the Y into the reaction vessel. About 9 cm. below the junction of the two arms of the discharge tube, a jet enabled iodine to be added to the gas stream, and 4 cm. below this jet, the gas stream entered the central tube of a large trap of conventional design. This trap consisted of a central tube about 2.5 cm. diameter and 8 cm. long, surrounded by an envelope about 4 cm. diameter and 11 cm. long. The
stream of gases left this trap by a sidearm and flowed through a horizontal tube about 2.5 cm. diameter and 80 cm. long before being pumped away through a cold trap by an Edwards ISC 450 rotary vacuum pump. About 6 cm. from this trap along the horizontal tube, a second jet enabled more iodine vapour to be added to the gas flow.

The iodine vapour was supplied to the two inlet jets, in a stream of nitrogen, by two separate saturators. These saturators had to be heated to above room temperature to supply sufficient iodine vapour without the need of using abnormally high flows of nitrogen. This necessitated the wrapping of all glass tubes carrying the nitrogen - iodine mixture from the saturators to the reaction vessel with heating wire. Although care was taken, it proved difficult to prevent iodine from crystallizing out of the nitrogen stream, especially in the glass taps, and in the iodine inlet jets themselves. Thus, it was difficult to achieve stable flows of iodine vapour over a long period of time.

Gas flows were controlled by Edwards LB1A needle valves and were measured by capillary flowmeters. All flowmeters were filled with mercury that had a covering of dibutyl phthalate to prevent mercury vapour entering the reaction vessel, and were calibrated so that the difference in levels in the manometer tubes could be expressed as gas flows through the flowmeters. The nitrogen flow to the discharge tube was kept constant at a value that a preliminary investigation had shown to give the maximum concentration of nitrogen atoms in the issuing gases.

Intensities of the reaction flames were measured using a 1P 21 photomultiplier tube in combination with various filters. For the
nitrogen emission in the presence of iodine emission, a "Spectrolab" Type P interference filter of 16 Å half band width and with a peak transmission at 6250 Å was used to pick up the (11,8) band of the first positive system of nitrogen, having a head at 6252.8 Å. For the iodine emission, a Wratten blue filter (No. 50 with maximum transmission at 4600 Å) was used, and for the nitrogen afterglow in the absence of iodine, a Wratten No. 22 filter was used. Attached to the photomultiplier tube was a collimating system consisting of two 4 mm diameter holes before and behind the filter. The photomultiplier tube was connected through a cathode follower to a 0 to 250 microammeter from which relative light intensities could be read directly. Light intensities were usually measured at a fixed distance from the second iodine inlet jet and provision was made to prevent stray light from reaching the photomultiplier tube.
RESULTS AND DISCUSSION.

Freeman and Phillips\textsuperscript{13} found that at certain concentrations of iodine, the reaction flame for the reaction of active nitrogen with iodine was divided into two distinct zones. They attributed the emission from the first zone to the radiative recombination of iodine atoms produced in the reactions;

\[ \text{N} + \text{I}_2 \rightarrow \text{NI} + \text{I} \]

\[ \text{N} + \text{NI} \rightarrow \text{N}_2^* + \text{I} \]

where $\text{N}_2^*$ is an electronically excited nitrogen molecule. The emission from the second zone was attributed to the radiation of iodine molecules excited by energy transfer from the excited nitrogen molecules produced in the first zone;

\[ \text{N}_2^* + \text{I}_2 \rightarrow \text{I}_2^* + \text{N}_2 \]

In this section of the thesis, it was hoped that all the iodine could be removed by a cold trap at the point in the reaction tube where the ratio of the concentration of the excited nitrogen molecules to the concentration of nitrogen atoms was at a maximum. The excited nitrogen molecules appeared to have a relatively long lifetime and their concentration would thus remain close to this maximum value, while the nitrogen atoms would continue to undergo their normal termolecular recombination reaction, thus decreasing in numbers down the reaction tube. With this source of excited nitrogen molecules, contaminated by only minor amounts of nitrogen atoms, it was hoped to establish their identity and study their reactions with various compounds.
Initially, relatively simple apparatus was used, but as each succeeding attempt to isolate the excited nitrogen molecules proved unsuccessful, the complexity of the apparatus and the sophistication of the techniques used for detection were increased. The form of the apparatus described in the experimental section, represents one of the later stages of development, but basically all stages of the apparatus were to the same overall plan. A stream of nitrogen atoms was initially reacted with iodine to produce the excited nitrogen molecules, and then passed into a cold trap to remove the iodine before deactivation of the excited nitrogen molecules could occur. The presence of any excited nitrogen molecules in the stream of nitrogen leaving the cold trap was determined by introducing iodine through a second jet and estimating the intensity of the blue emission, which was thought to be proportional to the concentration of excited nitrogen molecules.

The various attempts to isolate the excited nitrogen molecules will now be discussed in chronological order.

a). If the production of excited nitrogen molecules in the normal nitrogen afterglow is ignored, then with no iodine flowing through the first inlet jet, no excited nitrogen molecules would be produced. If the flow of iodine through the first jet were very high, all of the excited nitrogen molecules would be destroyed by the excess iodine before they could reach the cold trap. At some optimum iodine flow, the concentration of excited nitrogen molecules passing through the cold trap would be at a maximum. Thus, as the iodine flow through the first jet is increased from zero flow, the number of excited nitrogen
molecules passing through the cold trap should rise from zero to a maximum value, and then decline to almost zero again. With a constant flow of iodine through the second jet, the blue iodine emission close to this jet should likewise pass through a maximum as the flow of iodine through the first jet is increased.

This experiment was attempted both with visual observation of the intensity of the blue iodine emission, and when this did not prove sensitive enough, with a photomultiplier tube. Three different cold baths were used to cool the trap for the iodine: liquid nitrogen, dry-ice acetone, and a salt-ice mixture. With a liquid nitrogen bath cooling the trap, no reactive species reached the second iodine inlet jet irrespective of the iodine flow through the first jet. The salt-ice bath was not sufficiently cold to trap any of the iodine, and when the flow of iodine through the first jet was increased, the blue iodine emission from the second jet decreased without any evidence of a maximum. The dry-ice acetone bath was sufficiently cold to trap out iodine, and did not deactivate all of the reactive species present, but there was no evidence of any maximum in the blue iodine emission as the iodine flow through the first jet was increased.

b). From the attempt to detect excited nitrogen molecules just described, it became apparent that the excited nitrogen molecules could not be separated completely from the nitrogen atoms. The most evidence for their existence that could be expected would be a slight enhancement of the blue iodine emission at the second iodine inlet jet over that expected for the particular nitrogen atom concentration used.
With a dry-ice acetone bath cooling the trap, but no iodine flowing through either jet and the power supplied by the condensed discharge reduced to a low level, the intensity of the yellow nitrogen afterglow was measured. With a flow of iodine through the second jet, the intensity of the blue iodine emission corresponding to this concentration of nitrogen atoms was determined. Next, with iodine flowing through the first jet and none through the second jet, the power supplied to the discharge was increased until the intensity of the yellow afterglow emission reached the previous level, indicating that the concentration of nitrogen atoms was approximately the same. Finally, with iodine flowing through both jets, the intensity of the blue iodine emission was measured to see if there was any increase, that could be attributed to the presence of some other reactive species besides nitrogen atoms.

This experiment proved unsuccessful, mainly because of the difficulty in achieving reproducibility. Although some experimental runs appeared to give an increase in the blue iodine emission, other runs appeared to give a decrease to the same extent. The reason for this lack of reproducibility was the long delays between sets of measurements, either waiting for the cold trap to receive a uniform coating of iodine, or else waiting for this coating of iodine to be removed, coupled with the instability of the condensed discharge, and the iodine crystallizing out in the glass tubes as mentioned earlier.

c). It thus appeared that to get reproducible sets of readings, the time taken for each experimental run would have to be reduced. To achieve this, the cold bath was kept in place and the trap was kept
coated with iodine at all times. Measurements of the intensity of the blue iodine emission and the nitrogen afterglow emission were made, both with and without the iodine flowing through the second jet, as the iodine flow through the first jet was varied.

As the flow of iodine through the first jet was varied over a large range, the two intensities measured varied by only small amounts showing that the major part of the reaction was probably taking place in the trap with the iodine on the walls. Minor differences could be attributed to some of the blue iodine emission passing through the trap and reinforcing the blue iodine emission arising from the addition of iodine at the second jet. Although blank measurements were attempted to eliminate this, they were not entirely successful. Attempts to use these measurements to determine the dependence of the blue iodine emission on the nitrogen atom concentration also proved unsuccessful because of the small differences between the measurements leading to large errors.

At this stage of the investigation, a failure of the high voltage transformer in the condensed discharge power supply necessitated a change to a microwave discharge to produce nitrogen atoms. The concentration of nitrogen atoms from this source was at least an order of magnitude less than that produced by the condensed discharge, and was not sufficient to produce the effects sought. Because the enrichment of the gas stream with excited nitrogen molecules appeared to be only marginal, if occurring at all, and would be too unstable to use as a source of this species, it was decided to abandon this line of investigation.
A number of compounds are known to react very slowly with nitrogen atoms, but have been postulated to react much faster with excited nitrogen molecules. If these compounds were added to the reaction of active nitrogen with iodine, then they should have little effect on the nitrogen atom concentration but would quickly reduce the concentration of the excited nitrogen molecules, and hence reduce the blue iodine emission. A series of experiments, where the effects of oxygen and nitrous oxide on the blue iodine emission and the nitrogen afterglow emission were studied, is outlined in the next chapter.
CHAPTER 2. REACTIONS OF EXCITED NITROGEN MOLECULES.

EXPERIMENTAL.

REAGENTS:

Nitrogen and Iodine: As used in Chapter 1.

Oxygen and Nitrous oxide: Commercial grade, supplied by N.Z. Industrial Gases Ltd. Dried by passing through a trap cooled in dry-ice acetone.

APPARATUS:

The reaction vessel consisted of a glass tube of 18.7 mm. internal diameter and about 60 cm. long, through which the reacting gases passed with velocities of about 10 metres per second, at a pressure of 2.3 torr.

Nitrogen, which was partially dissociated by a microwave discharge (from a Raytheon 2450 Mc., 125 watt, Microtherm generator, Model 3013), passed through a light trap and into the reaction vessel. A jet system, consisting of two small concentric tubes, was used to admit the reactant gases. One jet, terminating in a bulb with six small holes distributed evenly around its circumference, enabled oxygen or nitrous oxide to be admitted to the reaction vessel about 15 cm. downstream from the iodine inlet jet. The other jet, which was concentric with the first jet and joined to it by an internal seal with six small holes distributed evenly around the seal, was used to admit the nitrogen-iodine mixture from the saturator.

The reactant gases flowed out of the reaction vessel, past a side
tube to a McLeod gauge, and through a trap cooled in dry-ice acetone to prevent contamination of the oil in an Edwards ESC 450 rotary vacuum pump.

Gas flows were measured and metered by the same apparatus as was used in Chapter 1. Nitrogen was saturated with iodine vapour at 15°C. by passing it through a packed column of iodine crystals at room temperature (20 to 30°C.), and then through a coiled glass tube in a water bath cooled to 15°C. by circulating tap water.

Light intensities were measured using the same apparatus and filters as were used in Chapter 1. The photomultiplier tube was in a box which could be moved along the length of the reaction vessel so that the emission intensity of the reaction flames could be studied as a function of time. Three sides of the exterior of the reaction vessel and the light trap were covered with black tape or matt black paint to prevent stray light from reaching the photomultiplier tube. A scale marked along the rails for the photomultiplier assembly enabled its position to be set to within 5 mm.

REACTION CONDITIONS:

A stream of nitrogen through the iodine saturator entrained iodine vapour, and it was assumed that the nitrogen was saturated with iodine at 15°C. The vapour pressure of iodine at 15°C. is 0.13 torr. The flow of nitrogen through the microwave discharge was kept constant at 8.1 cm³ sec⁻¹ (measured at one atmosphere and 25°C.) for all of the work described in this chapter, and the total pressure of gases in the reaction tube was 2.3 torr. Assuming that the pressure in the iodine
saturator was the same as that in the reaction vessel, the partial pressure of iodine in the reaction vessel would be given by the expression;

$$P_{\text{torr}} = 0.13f/(8.1 + f)$$

where $f$ is the flow of nitrogen in cm$^3$. sec$^{-1}$. at one atmosphere, through the saturator. The concentration of iodine in molecules cm$^{-3}$ in the reaction can then be determined by multiplying this partial pressure by Lochamidt's number, which at 25$^\circ$C. is $3.24 \times 10^{16}$ molecules cm$^{-3}$. torr$^{-1}$. These values are given in Table 1.

**Table 1. Flows and Concentrations of Iodine.**

<table>
<thead>
<tr>
<th>$f$</th>
<th>0.15</th>
<th>0.29</th>
<th>0.43</th>
<th>0.71</th>
<th>1.00</th>
<th>1.55 cm$^3$. sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>2.4</td>
<td>3.4</td>
<td>6.6</td>
<td>10.5</td>
<td>14.3</td>
<td>20.8 $\times 10^{-3}$ torr</td>
</tr>
<tr>
<td>$[I_2]$</td>
<td>8</td>
<td>11</td>
<td>21</td>
<td>34</td>
<td>46</td>
<td>67 $\times 10^{13}$ molecules cm$^{-3}$</td>
</tr>
</tbody>
</table>

Oxygen and nitrous oxide were admitted to the reaction vessel as undiluted gases and so their partial pressures would be given by the expression;

$$P_{\text{torr}} = 2.3f/(8.1 + f)$$

where, in this case, $f$ is the flow of oxygen or nitrous oxide in cm$^3$. sec$^{-1}$. at one atmosphere. Although the factor in the bottom line of this expression and the one above for the partial pressure of iodine should include the total flow of gases, it was felt that the extra work required to calculate the solutions of these equations for every combination of flows used was not warranted by the quality of the
results obtained. The error introduced would be no more than 15% for the most unfavourable cases. The concentration of oxygen or nitrous oxide in molecules cm\(^{-3}\) in the reaction vessel can be determined in a similar manner to that described above for iodine by multiplying the partial pressures by \(3.24 \times 10^{16}\) molecules \(\text{cm}^{-3} \cdot \text{torr}^{-1}\). These values are given in Table 2.

**Table 2. Flows and Concentrations of Oxygen and Nitrous oxide.**

<table>
<thead>
<tr>
<th>Flow (L/min)</th>
<th>Concentration (molecules cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>6</td>
</tr>
<tr>
<td>0.40</td>
<td>11</td>
</tr>
<tr>
<td>0.66</td>
<td>17</td>
</tr>
<tr>
<td>1.16</td>
<td>29</td>
</tr>
<tr>
<td>1.68</td>
<td>39 (\times 10^{-2}) torr</td>
</tr>
<tr>
<td>1.68</td>
<td>93 (\times 10^{16}) molecules cm(^{-3}).</td>
</tr>
</tbody>
</table>

The cross-sectional area of the reaction vessel was 2.75 cm\(^2\), and the pressure of the reacting gases was 2.3 torr. The velocity of the gas flow through the reaction vessel at a temperature of 25°C is given by the expression:

\[
V_{\text{cm./sec.}} = \frac{760(8.1 + F)}{2.3} \times 2.75
\]

where \(F\) is the total of both the gas flow through the iodine saturator and the oxygen or nitrous oxide flow in cm\(^3\) sec\(^{-1}\). This expression reduces to a value of \((9.7 + 1.2F) \times 10^2\) cm sec\(^{-1}\). The inverse of this velocity gives the time of reaction, which for the work in this chapter, is about 1 millisecond per cm of distance along the reaction tube.
RESULTS.

When the oxygen or nitrous oxide was added to the reaction of active nitrogen with iodine, the blue iodine emission decreased slightly, but there did not appear to be any colour change, although this was not verified spectroscopically.

The dependence of the intensities of the afterglow emission and the blue iodine emission on time were determined by making repeated measurements at 5 cm. intervals up and down the reaction tube, the first measurement being made at 5 cm. from the oxygen or nitrous oxide inlet jet, and the final one at a distance of 60 cm. from the jet, until two consecutive sets of measurements made in opposite directions agreed to within 5 scale units (2% of the full scale of the meter). Several different flows of iodine and oxygen or nitrous oxide were used, and measurements were also made in the absence of each reactant.
DISCUSSION.

The system investigated in this chapter was the reaction between nitrogen atoms, iodine, and another reactant (either oxygen or nitrous oxide). Considering first the variation of the nitrogen atom concentration, iodine reacts quite rapidly with nitrogen atoms\(^\text{32}\), but the added reactant reacts very slowly. Thus, the added reactant could be considered as causing a small perturbation of the iodine reaction system.

If the rate expression for the reaction of nitrogen atoms with iodine is of the form:

\[- \frac{d \ln [N]}{dt} = F([N], [I_2])\]

where \(F\) is a function of each of these variables, then the rate expression when a reactant \(M\) is added, could be considered to be:

\[- \frac{d \ln [N]}{dt} = F([N], [I_2]) + k_1 [M]\]

where \(k_1\) is the rate constant of the slow bimolecular reaction between nitrogen atoms and the added reactant \(M\). If the logarithmic decay of the nitrogen atom concentration with time is determined for a constant iodine flow both with and without the addition of the reactant \(M\), then the difference in gradients will be equal to \(k_1 [M]\). The values of these differences are given in Table 3 where the reactant \(M\) is oxygen, and in Table 5 for nitrous oxide, for various flows of these reactants and iodine.

Considering now the reaction of excited nitrogen molecules \((N_2^*\)), formed in the reactions proposed by Freeman and Phillips\(^{13}\), with the
reactant \( M \). Although this reactant probably reacts much faster with excited nitrogen molecules than with the nitrogen atoms, to a first approximation it could still be considered as a minor perturbant in the system and a similar analysis to that used for the nitrogen atom reaction applied. Again the difference in the logarithmic decays of the excited nitrogen molecules measured with and without the addition of the reactant \( M \) would be equal to \( k_2[M] \), where \( k_2 \) is the rate constant of the bimolecular reaction between excited nitrogen molecules and the reactant. The values of these differences are given in Table 4 for oxygen and Table 6 for nitrous oxide.

It was found that to determine the differences in decays, by plotting two separate logarithmic lines and determining the difference in gradients, leads to large errors for the nitrous oxide reaction because of the small differences involved. Instead, since the pairs of intensities were measured at the same points down the reaction tube, the differences between the logarithms of these individual readings were plotted against time and the gradients of the resultant graphs were assumed to be the differences in gradients required.

The graphs of the logarithmic decay of the nitrogen afterglow emission were all initially curved concave upwards with a straight final portion, the gradient of which was used. In general, the curvature was reduced when the third reactant was added. The logarithmic graphs of the decay of the blue iodine emission behaved in a similar manner to those of the afterglow emission, except at low iodine flows, when the initial curvature became convex upwards. The difference plots used for
the nitrous oxide, were curved; concave upwards with a minimum for the nitrogen afterglow emission, and concave down for the blue iodine emission, but they generally terminated in a straight portion whose gradient was determined.

A number of the experimental runs were repeated under the same experimental conditions, but the final results were often very different. This probably indicates the experimental error possible and since no legitimate reason could be seen for discarding any of the measurements, except where the cause of divergence was known, they have all been included and statistical methods used to determine the results.

Although the values in Tables 3, 4, 5, and 6, should be directly proportional to the concentration of the third reactant, and independent of the concentration of iodine and the wall conditions, they appear to be dependent on the iodine concentration and to contain a term independent of both the concentration of the iodine and the third reactant. The terms that are not dependent on the concentration of the third reactant can be eliminated by averaging the values for each reactant concentration (shown in each table along with the standard deviation) and using a least mean squares procedure to determine the rate constant for the reaction with the reactant oxygen or nitrous oxide. The results for each reactant will now be considered.

**Oxygen**:

The differences of the gradients of the logarithmic decays of the nitrogen atom concentration on the addition of oxygen are presented in Table 3.
TABLE 3. Effect of Oxygen on the Nitrogen Atom decay.

\[
\begin{array}{cccc}
[I_2] & 3.4 & 6.6 & 10.5 & 20.8 \times 10^{-3} \text{ torr.} \\
[O_2] & 15.4, 15.4 & 15.0 & 24.7 & \text{Average} \\
& 10.2 & & & 16.1 \pm 4.9 \\
6 & 14.0, 16.7 & 21.4 & 34.7, 28.8 & 34.8 \\
& 29.5, 17.9 & 36.9 & & \text{sec}^{-1} \\
11 & 24.2 & 36.7 & & 30.5 \pm 6.3 \\
17 & & & & \times 10^{-2} \text{ torr.}
\end{array}
\]

These results lead to a value of \((4.5 \pm 1.3) \times 10^{-15} \text{ cm}^3 \cdot \text{molecules}^{-1} \text{ sec}^{-1}\) for the bimolecular rate constant for the reaction of nitrogen atoms with oxygen in the presence of iodine. Values that have been determined by other workers for the rate constant for the reaction;

\[N + O_2 \rightarrow NO + O\]
at 25°C. are \(10 \times 10^{-17} \text{ cm}^3 \cdot \text{molecules}^{-1} \text{ sec}^{-1}\), \(9 \times 10^{-17} \text{ cm}^3 \cdot \text{molecules}^{-1} \text{ sec}^{-1}\), and at 77°C. is \(8 \times 10^{-17} \text{ cm}^3 \cdot \text{molecules}^{-1} \text{ sec}^{-1}\). The rate constant determined in this thesis is about fifty times as fast as that determined by other workers and so probably does not apply to the reaction of nitrogen atoms with oxygen alone.

An attempt was made to determine the rate constant for the reaction of active nitrogen with oxygen in the absence of iodine. This was unsuccessful because of the non-logarithmic decay for the nitrogen atom concentration and the large errors arising from the small differences between the experimental measurements with and without the addition of oxygen. In spite of these factors, it was estimated that the rate
constant for this reaction was more than an order of magnitude less than that determined in the presence of iodine and would probably be close to the values determined by other workers.

Because the results used to derive the rate constant were dependent on the concentration of iodine present, it is probable that some reaction between oxygen and either iodine or one of the intermediates in the iodine reaction was occurring and was leading to the formation of species that reacted rapidly with nitrogen atoms. A possible candidate would be the intermediate NI giving the reaction:

$$\text{NI} + \text{O}_2 \rightarrow \text{NO} + \text{IO}$$

Nitrogen atoms would react with both of these products with the reaction with nitric oxide being fast. The postulated production of the oxide IO is supported by the formation of $\text{I}_2^\text{O}_{141}$ on the walls of the reaction vessel.

The corresponding results for the decay of the blue iodine emission are presented in Table 4.

**Table 4. Effect of Oxygen on the Iodine Emission Decay.**

| $[\text{I}_2]$ | 3.4 | 6.6 | 10.5 | 20.8 | $10^{-3}$ torr. |
| $[\text{O}_2]$ | 11.9, 14.0, 14.5, 15.2 | Average: 12.8 ± 2.4 |
| 6 | 8.5 |
| 11 | 14.5, 21.3, 19.7, 29.1, 25.8, 34.8 | Average: 23.3 ± 5.9, sec⁻¹ |
| 17 | 20.7, 34.7, 22.3 | $27.7 ± 7.0$, x $10^{-2}$ torr. |
The bimolecular rate constant derived from this data is $(4.6 \pm 1.1) \times 10^{-15}$ cm$^3$ molecules$^{-1}$ sec$^{-1}$. There is a high probability that this value is the same as that determined from the decay of the nitrogen atom concentration above. A discussion of the significance of the similarity between the two rate constants will be given later.

**Nitrous Oxide**

The differences of the gradients of the logarithmic decays of the nitrogen atom concentration on the addition of nitrous oxide are presented in Table 5.

<table>
<thead>
<tr>
<th>[I$_2$]</th>
<th>[N$_2$O]</th>
<th>( \text{Average} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3.3</td>
<td>5.5 ± 2.2 sec$^{-1}$</td>
</tr>
<tr>
<td>17</td>
<td>7.0</td>
<td>6.5 ± 0.6</td>
</tr>
<tr>
<td>29</td>
<td>5.7</td>
<td>8.0 ± 2.1</td>
</tr>
<tr>
<td>39</td>
<td>13.6</td>
<td>11.6 ± 2.0</td>
</tr>
</tbody>
</table>

These results lead to a value of $(4.1 \pm 1.0) \times 10^{-16}$ cm$^3$ molecules$^{-1}$ sec$^{-1}$ for the rate constant of the bimolecular reaction between nitrogen atoms and nitrous oxide in the presence of iodine. Although many people have attempted to determine the rate constant for the reaction:

$$N + N_2O \rightarrow N_2 + NO$$

the reaction is too slow to be easily measured, and the only value given in the literature is that the rate constant is less than $2 \times 10^{-16}$ cm$^3$. 
molecules$^{-1}$ sec$^{-1}$ (38). An attempt to determine the rate constant of this reaction in the absence of iodine was unsuccessful.

The rate constant determined in this thesis in the presence of iodine is greater than the upper limit given, and since nitrous oxide reacts very slowly with nitrogen atoms, then the nitrous oxide must be reacting with some other reactive species, forming products that react with nitrogen atoms.

The corresponding results for the decay of the blue iodine emission are given in Table 6.

**TABLE 6. Effect of Nitrous oxide on the Iodine Emission Decay.**

<table>
<thead>
<tr>
<th>$[I_2]$</th>
<th>2.4</th>
<th>3.4</th>
<th>6.6</th>
<th>10.5</th>
<th>14.3</th>
<th>$x \times 10^{-3}$ torr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[N_2O]$</td>
<td>6 &amp; 3.3</td>
<td>4.0</td>
<td>3.1</td>
<td>7.0</td>
<td>2.7</td>
<td>8.0</td>
</tr>
<tr>
<td>17 &amp; 5.8</td>
<td>3.0</td>
<td>4.8</td>
<td>5.8</td>
<td>5.2</td>
<td>8.6</td>
<td>7.8</td>
</tr>
<tr>
<td>29 &amp; 10.7</td>
<td>5.8</td>
<td>5.1</td>
<td>6.4</td>
<td>8.3</td>
<td>9.9</td>
<td>10.8</td>
</tr>
<tr>
<td>39 &amp; 7.9</td>
<td>11.7</td>
<td>7.6</td>
<td>11.8</td>
<td>6.9</td>
<td>6.4</td>
<td>5.9</td>
</tr>
</tbody>
</table>

$x \times 10^{-2}$ torr.

The bimolecular rate constant derived from this data is $(3.3 \pm 1.0) \times 10^{-16}$ cm$^3$ molecules$^{-1}$ sec$^{-1}$. Although this value is different from the value determined from the decay of the nitrogen atom concentration, the difference is within the limit of error, and arises predominantly from only one of the four pairs of averages used. The probability that the rate constants determined for the nitrous oxide by either the decay
of the nitrogen atom concentration or the blue iodine emission are measures of the same quantity is high.

There are a number of ways in which nitrous oxide could react with a species, thought to be present in the reaction system of nitrogen atoms and iodine, but not in active nitrogen alone, that would lead to an increased removal of nitrogen atoms. Of these, two will be considered. The reaction:

\[ \text{N}_2\text{O} + \text{N}_2^* \rightarrow \text{N}_2 + \text{N}_2 + \text{O} \]

would be exothermic (by about 70 kcals per mole), and the reaction:

\[ \text{N}_2\text{O} + \text{N}_2 \rightarrow \text{N}_2 + \text{N}_2 + \text{O} \]

where \( \text{N}_2^* \) is an excited nitrogen molecule, would be exothermic if the excited nitrogen molecule had more energy than 40 kcals per mole (A state nitrogen molecules have about 140 kcals per mole energy and other electronic states are more excited). Both of these reactions would lead to the chain removal of nitrogen atoms by the reactions:

\[ \text{O} + \text{I}_2 \rightarrow \text{IO} + \text{I} \]
\[ \text{N} + \text{IO} \rightarrow \text{NO} + \text{I} \]
\[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \]

With the information at present available, it is difficult to choose between the various mechanisms for this reaction system.

The similarities in the effects of the oxygen and nitrous oxide on both the logarithmic decays of the nitrogen atom concentration and the blue iodine emission can be related to the observation by Young\(^{15}\), that the logarithmic decay of the blue iodine emission is the same as that of the nitrogen atom concentration. If the mechanism proposed by Freeman
where the asterisk denotes an excited molecule, then the steady state concentration of the excited molecules is:

\[ [N_2^*] = \frac{k_1 [N]}{k_3} \]

provided the last reaction is negligibly slow. If this expression is assumed to apply in the regions investigated, then it would account for the above similarities in the logarithmic decays, although alternative explanations could apply.
CONCLUSION.

In the introduction to this part of the thesis, work on the reaction of active nitrogen with iodine was reviewed, from Strutt's original work in 1912 through to early in 1965. At the time when the investigation outlined in this part of the thesis was carried out, one of the main reactants in the reaction system appeared to be an energetic, long-lived species. This species was tentatively identified as the A state of nitrogen, mainly on the basis of its lifetime and its apparent energy. In Chapters 1 and 2 of this thesis, it was shown that this species cannot easily be separated from the other reactive species involved in the reaction.

The review of the reaction of active nitrogen with iodine is now continued to the end of 1967.

Walton et al (1965) detected the absorption of A state nitrogen molecules in both the (0,0) and (1,0) bands of the nitrogen first positive system, for the iodine reaction. Using a condensed discharge to produce nitrogen atoms and high iodine concentrations, it was estimated that the average concentration of nitrogen atoms was about $10^{15}$ to $10^{16}$ atoms cm$^{-3}$. The steady state concentration of A state nitrogen molecules was expected to be about one third of this concentration, but the concentration determined appeared to be $10^{13}$ to $10^{14}$ molecules cm$^{-3}$; about two orders of magnitude less than that expected.

Young (1965) failed in an attempt to detect the emission of
Vegard-Kaplan bands of nitrogen ($A ightarrow X$) from the iodine reaction, when the steady state concentration of the A state nitrogen molecules was expected to be $10^{15}$ molecules cm$^{-3}$. From the sensitivity of his apparatus, he estimated that the concentration of A state nitrogen molecules was less than $10^9$ molecules cm$^{-3}$; a value considerably lower than that found by Walton et al.$^{14}$.

On examining the data Phillips$^{32}$ used to calculate the lifetime of the A state of nitrogen, Young found that the blue iodine emission appeared to decay at the same rate as the nitrogen atom concentration. Thus, the rate constant determined was not that of the deactivation of the A state nitrogen molecules by iodine. The supposed lifetime of the A state of nitrogen could be reinterpreted as the catalytic efficiency of the walls of the reaction vessel for nitrogen atom recombination. The independence of this quantity on an increase in surface area was attributed to the new surface being much less catalytic than the existing surface, and so not affecting the decay appreciably.

Young (1966)$^9$ in an extension of his earlier work$^{15}$, failed to detect the emission of the Vegard-Kaplan system from active nitrogen without any added reactants. Since A state nitrogen molecules are known to be formed in active nitrogen in concentrations that should have been detectable, he assumed that they were being removed by some fast reaction. He postulated a reaction with nitrogen atoms;

$$N + N_2(A, v = 0) \rightarrow N + N_2(X, v = 25)$$

and since this is a simple atom-atom interchange reaction, it would be expected to be fast. The existence of this reaction deactivating the A state nitrogen molecules had also been predicted by Wray$^{10}$ and was
confirmed by Dugan, who estimated that the concentration of excited nitrogen molecules in active nitrogen was at least three orders of magnitude less than the nitrogen atom concentration.

If the A state nitrogen molecules were excited above the vibrational level \( v = 6 \), it is possible, but not probable, that other excited electronic nitrogen molecules could be formed. It would also be possible for other electronic states to be deactivated by a similar mechanism.

Young suggested that the unusual effects observed by various workers in the reactions of active nitrogen, that had hitherto been attributed to reactions of A state nitrogen molecules, would probably be due to vibrationally excited ground state nitrogen molecules. Although these vibrationally excited molecules have been proposed as one of the main active species in the pink afterglow, it would not seem feasible that they could exist in high concentrations in the normal afterglow at pressures of several torr, because of the ease with which collision-induced vibrational relaxation could occur.

Grigor and Phillips (1966) reported and discussed work done by Grigor during a B.Sc. (Hons) project in which the reactions of active nitrogen with a number of iodine compounds was studied. Methyl iodide gave only CN emission and no detectable iodine emission, and so was not investigated further.

Iodine monochloride and monobromide gave similar reaction flames to that obtained from iodine (an initial pink zone followed further down the reaction tube by a blue zone) with iodine monochloride giving the
brighter flame of the two interhalogen compounds. Iodine monobromide decomposes slightly at room temperature to iodine and bromine, and so the blue iodine emission could be attributed to the reaction of the molecular iodine formed with active nitrogen. Iodine monochloride is stable at room temperature, and so the iodine band emission that occurs must arise from iodine formed in the reaction.

Most of the emission bands seen could be attributed to iodine emission, with minor contributions from excited ICl and IBr in each case. There was no evidence of any IBr emission from the iodine monobromide reaction. The iodine monochloride reaction gave some wall emission which was attributed to iodine monochloride absorbed on the walls of the reaction vessel.

The intensity of the blue and ultraviolet emission from the blue zones of the flames was directly proportional to the concentration of the iodine monohalide for both compounds. The variation of the intensity of this emission with respect to the concentration of nitrogen atoms, was first order for the iodine monobromide reaction, and second order for the iodine monochloride reaction. (The intensity of the blue iodine emission from the blue zone in the iodine reaction varied first order with respect to the iodine concentration, but was almost independent of the nitrogen atom concentration.) Because the maximum emission occurred at a little distance down the reaction tube, it was assumed that the blue emission was being excited by energy transfer from some excited species in the same manner as in the iodine reaction.

As Young had shown\textsuperscript{15}, the decay of the blue iodine emission with
time closely followed that of the nitrogen atom concentration. Young had also postulated a fast reaction between nitrogen atoms and A state nitrogen molecules giving vibrationally excited ground state molecules. Grigor and Phillips conceded that these vibrationally excited molecules could have been the immediate precursors of the iodine emission and not the A state nitrogen molecules. However, the observation that blue and ultraviolet emissions from iodine decay at the same rate is evidence against this.

The initial attack of nitrogen atoms on the iodine monobromide could be by either of two reactions:

$$N + IBr \rightarrow NI + Br$$

$$N + IBr \rightarrow NBr + I$$

The initial attack on iodine monochloride appeared to be much slower, and because the intensity of the blue iodine emission produced depended on the square of the nitrogen concentration, it was considered to be either a termolecular recombination of nitrogen atoms with the iodine monochloride acting as the third body, or the kinetically similar reaction of iodine monochloride with an excited nitrogen molecule produced during nitrogen atom recombination. Either of these reactions would be expected to give excited ICl, which would subsequently decompose to atoms, giving the various spectral features of the flame.

Smith (1966) investigated the vacuum ultraviolet emission from the iodine reaction, and a number of atomic iodine lines down to the line at 1799 Å were detected. To both dissociate the molecular iodine and excite the atoms formed to give this line would require about 183 kcaes
per mole. This is more energy than would be available from the A state nitrogen molecules (142 kcals per mole) and so Smith suggested that the state of nitrogen with an energy of about 222 kcals per mole could be the reactive species exciting the iodine. This species has been assumed to be present in active nitrogen as a precursor of the nitrogen afterglow\(^7\), and as a reactive species in some active nitrogen reactions\(^6\). However its concentration should vary as the square of the nitrogen atom concentration\(^6\).

McNaughton (1967)\(^4\) attempted to determine the concentration of A state nitrogen molecules arising from the reaction of active nitrogen with iodine, iodine monobromide, and iodine monochloride, by measuring the absorption of the nitrogen first positive bands in a similar manner to Walton et al\(^1\), but instrumental difficulties prevented him doing more than verifying that absorption did occur in the active nitrogen iodine flame.

Phillips (1967)\(^4\) extended Smith's\(^4\) work on the vacuum ultraviolet emission from the reactions of active nitrogen with iodine, iodine monochloride, iodine monobromide, and iodine cyanide. A number of atomic iodine lines down to that at 1261 A., along with some atomic chlorine and atomic bromine lines from the binary halogen compounds, were seen. The dependence of the intensities of some of these atomic lines on the concentration of nitrogen atoms was determined by making simultaneous measurements of the intensity of the selected line, and the intensity of the nitrogen afterglow emission.

The dependence of the atomic iodine lines from the iodine cyanide
reaction appeared to be rather slight (corresponding to a variation with about [N]$^2/2$) and the iodine cyanide flame was not considered further.
The atomic iodine lines resulting from the iodine reaction could be divided into two separate groups. Those lines requiring an excitation energy of up to 181 kcal per mole were bright and their intensity varied directly with the nitrogen atom concentration, while those lines where the iodine atoms required an excitation of over 189 kcal per mole were weaker and their intensities depended on the square of the nitrogen atom concentration. Iodine monobromide gave similar results to iodine, while lines from the iodine monochloride varied as the square of the nitrogen atom concentration, with one exception. This is the same as the variation found for the banded emission with ICl$^{43}$. 

To account for the two distinct mechanisms of the excitation of the atomic iodine lines, depending on the degree of excitation, Phillips proposed that the group of atomic lines whose intensities were directly proportional to the nitrogen atom concentration, were being excited by energy transfer from a metastable species formed in an earlier reaction$^{13}$. If the energy of this species were between 181 and 189 kcal per mole, it would have sufficient energy to excite the atomic lines up to this energy but not above. The atomic iodine lines requiring a greater excitation were thought to be excited by a slower termolecular mechanism involving the recombination of nitrogen atoms, giving the observed dependence of the intensity of these lines on the square of the nitrogen atom concentration.

The identity of this metastable species was proposed as being the
$3 \Delta_u$ state of nitrogen. In an earlier paper$^{30}$, it had been shown that this species could be expected to form from the reactions of nitrogen atoms with NI, but not with NBr or NCl, hence giving the reason why the reaction of iodine with active nitrogen is different from the reactions of the other two halogens. Because of this difference, the possibility that the energetic species involved was vibrationally excited ground state nitrogen molecules appeared to be ruled out.

The earlier observation of the A state nitrogen molecules$^{14}$ was attributed to their formation from the $3 \Delta_u$ state of nitrogen either directly, or by way of vibrationally excited nitrogen molecules in a reaction with nitrogen atoms in a similar mechanism to that proposed by Young$^9$, viz.;

$$N + N_2(3 \Delta_u) \rightarrow N + N_2(A, v_1)$$
$$N + N_2(3 \Delta_u) \rightarrow N + N_2(X, v_2)$$
$$N + N_2(X, v_2) \rightarrow N + N_2(A, v_3)$$

The existence of the $3 \Delta_u$ state of nitrogen has been predicted on theoretical grounds for a number of years, but no spectra from transitions either to or from it have yet been positively identified.

Hepner and Herman (1957)$^{47}$, from a discharge through a helium-nitrogen mixture, obtained a new band system in the 1.5 to 3 $\mu$ region that they tentatively assigned to a $^5 \Sigma_u^+ \rightarrow ^5 \Sigma_g^+$ transition of nitrogen. This assignment has been questioned by Lofthus$^{48}$ and Phillips$^{49}$ suggested that the bands could belong to the $3 \Delta_u \rightarrow 3 \Sigma_g$ transition of nitrogen.

Kent (1961)$^{50}$, using a similar discharge system to Hepner and
Herman's\textsuperscript{4,7}, but with a much lower current, found evidence for the presence of a metastable energy carrier. The addition of barium vapour enabled the energy of this metastable species to be set at between 182 and 191 keals per mole, and its lifetime to be estimated at several seconds. Kenty postulated that the species involved was the $3\Delta_u$ state of nitrogen because no other excited nitrogen molecules had the right properties.

Phillips (1967)\textsuperscript{4,5} searched the infra red emission of the reaction of active nitrogen with iodine from 1.5 to 3\m, in an attempt to detect bands of the $3\Delta_u \rightarrow 3\Pi_g$ transition of nitrogen. Although emission bands, similar to those observed by Hepner and Herman\textsuperscript{4,7} were found, their resolution was not sufficient for a positive identification to be made.

On the addition of very small amounts of iodine to active nitrogen, the first positive bands of nitrogen were enhanced, indicating that the population of the B state of nitrogen was being increased. This may have been due to the reaction;

$$N + N_2\left(3\Delta_u\right) \rightarrow N + N_2\left(B, v > 0\right)$$

where the $3\Delta_u$ state nitrogen molecules were being formed in the reaction with iodine.

Current work in this field by McCowan includes the operation of a discharge tube similar to those used by Kenty\textsuperscript{50}, and Hepner and Herman\textsuperscript{4,7}, in an attempt to detect and identify emission bands from the $3\Delta_u \rightarrow 3\Pi_g$ transition of nitrogen in the infra red. To date (the end of 1967) little progress has been made.
In a current paper, Kenty discards his previous estimate of the energy of the $^3\Delta_u$ state of nitrogen in favour of a value near 170 kca/s per mole. Thus the $^3\Delta_u$ molecules involved in the vacuum ultraviolet emission must have some excess vibrational energy, if this new value is correct. The next higher metastable state of nitrogen; the $a^1,^1\Sigma_u^-$ state at 190 kca/s per mole, has too much energy to be produced by the reactions:

\[
\begin{align*}
N + I_2 & \rightarrow NI + I \\
N + NI & \rightarrow N^* + I
\end{align*}
\]

Kenty also gives a figure showing the spectrum of his Xe-N$_2$ discharge between 1 and 3 $\mu$. This spectrum contains a broad feature near 1.5 $\mu$, which he attributes to a XeN$_2$ molecule, but which could also be the predicted $^3\Delta_u \rightarrow B^3\Pi_g$ transition of nitrogen.
PART II. THE EXCITATION OF CN EMISSION BY ACTIVE NITROGEN.

INTRODUCTION.

The emission spectrum of the CN radical has been studied by many workers for over fifty years, and the wavelengths of the predominant emission bands are well known. The main CN emission arises from two transitions: the "red" system ($A^2 \Pi \rightarrow X^2 \Sigma$), and the "violet" system ($B^2 \Sigma \rightarrow X^2 \Sigma$). There are a number of less important transitions, that arise mainly in the discharge tube under special conditions, and these are included in Douglas and Routly's system. The violet system of CN is further subdivided into a main system, with bands arising from the lower vibrational levels of the B state (up to $v' = 5$), and the tail bands arising from the higher vibrational levels of the B state (emission from levels $v' = 5$ to $v' = 19$ has been tabulated).

The important sources of CN emission that have been investigated, include discharge tubes containing cyanogen, carbon arcs in air or nitrogen, combustion flames of cyanogen burning in oxygen, and the reaction of active nitrogen with carbon and its compounds. Although the populations of the vibrational levels, and hence the intensity distribution of the CN emission, is thermal for some sources like cyanogen burning in oxygen, other sources present anomalous population distributions; for example, the emission arising from active nitrogen reactions may give a rotational temperature close to room temperature and a vibrational temperature of several thousand degrees. A chronological review of the various attempts to explain this phenomenon
of anomalous population distributions is now presented. This field, along with most other aspects of active nitrogen chemistry, was pioneered by R.J. Strutt (later to become the second Lord Rayleigh) who added a considerable number of compounds to active nitrogen, and investigated the line and band spectra that resulted.

Strutt (1911)\(^5\)\(^2\) by observing the spectra of organic compounds with active nitrogen, found that although all gave well developed CN spectra, compounds containing halogens (chloroform and carbon tetrachloride) gave a bright orange flame, while organic compounds not containing a halogen atom (hydrocarbons, both saturated and unsaturated, alcohols, ethers, and cyanogen) gave a weaker lilac flame with a different intensity distribution amongst the various bands. He postulated that the active nitrogen attacked the organic compound forming CN radicals, which were then excited by a further reaction with active nitrogen.

Strutt and Fowler (1912)\(^1\)\(^6\) continued the investigation of the reaction and showed that for reactions that gave the orange flame, the CN red system was more strongly developed than the CN violet, while in the lilac flames, the converse applied. There were also different intensity distributions within each system. The group of bands in the CN violet in the region of 4216 Å. (with \(v'' - v' = +1\)) were graded evenly in intensity in the carbon arc from the brightest (0,1) band. However, in active nitrogen the bands alternated in intensity; the (0,1) and (2,3) bands being developed and the (1,2) and (3,4) bands suppressed, with a number of intense, and apparently new bands appearing. The tail bands of the CN violet system, although not well developed, also appeared to
be modified. When hydrogen atoms were present in the organic compounds, CN emission bands often appeared, but with a different intensity distribution to those arising from an oxy-coal gas flame.

Fowler and Shaw (1912) compared the intensity distribution of various bands of the CN red system, arising from different sources. The sources used included cyanogen burning in oxygen, an electrical discharge through cyanogen, and the reaction of active nitrogen with carbon tetrachloride. All gave markedly different emission distributions.

Strutt (1913) found that the main product of the reaction of active nitrogen with hydrocarbons was not cyanogen, as he had previously assumed from the presence of CN radicals, but hydrogen cyanide, with only a trace of cyanogen. He also found that there was little correlation between the amount of hydrogen cyanide produced, and the intensity of the CN emission. The reaction of active nitrogen with cyanogen gave a flame comparable in intensity to the hydrocarbon reactions, but the reaction with hydrogen cyanide gave only a very weak flame, revealing that the emission from the hydrocarbon reaction did not originate from the reaction of active nitrogen with either hydrogen cyanide or with the cyanogen produced. The flame from the hydrogen cyanide would be too weak, while there was insufficient cyanogen present, to account for the observed intensity.

For the reaction of halogenated hydrocarbons with active nitrogen, Strutt assumed that the orange flame arose from the reaction of active nitrogen with a cyanogen halide that he postulated to be produced in the
reaction. However it has since been shown that the intensity distributions of the CN emission from the reaction of active nitrogen with halogenated hydrocarbons and the cyanogen halides are different, indicating that the cyanogen halide is probably not an intermediate in the emission mechanism for hydrocarbon flames.

Johnson and Jenkins (1926) investigated the tail bands of the CN violet system arising from the reaction of active nitrogen with traces of carbon from the electrodes of the nitrogen discharge. The intensity distribution of the CN emission from this system had few similarities with the reaction of active nitrogen with organic compounds, or to the carbon arc. In the reaction with organic compounds, the brightest bands of the CN violet system were found to be transitions from the lowest vibrational levels of the B state. These workers found no emission from the four lowest vibrational levels of the B state suggesting a high vibrational temperature and a non-thermal population distribution.

To achieve these high excitation energies, they postulated the formation of positive cyanide ions and their subsequent neutralization by electrons. However unless the electrons were of high energy, it is doubtful if sufficient energy would be supplied. In this system, where the concentration of energetic species in the active nitrogen would greatly exceed the concentration of CN radicals, the possibility of multiple excitation of each radical must also be considered, thus making it difficult to derive a simple excitation mechanism.

Jevons (1926) extended Strutt and Fowler's observations, on the enhancement and suppression of bands of the transition \( v'' - v' = +1 \) of
the CN violet system, to include the series of transitions \( v'' - v' = 0 \), and \( v'' - v' = -1 \), and also the tail bands of the CN violet system. A study of the rotational distribution indicated that, although the emission from the active nitrogen showed a higher vibrational temperature than the CN emission excited by the carbon arc, the rotational lines, with their maximum intensity at \( j = 8 \) or \( 9 \), revealed a lower rotational temperature than the carbon arc spectrum, which had its maximum intensity in the rotational spectra at \( j = 28 \).

Hersberg (1928)\(^{56} \) found that the intensity distributions of the rotational lines of transitions arising from the vibrational level \( v' = 0 \) of the B state of CN, from the reaction of active nitrogen with organic compounds, were modified from the expected thermal distribution. In particular, the rotational lines for \( k = 4, 7, \) and \( 15 \), were enhanced at low pressures. He attributed this enhancement to a mechanism involving resonance fluorescence.

Byck (1929)\(^{57} \) confirmed Hersberg's\(^{56} \) results, and also showed that the enhancement of the lines decreased as the pressure in the reaction vessel increased. Because he could find no evidence of the resonance fluorescence suggested by Hersberg, Byck concluded that the enhancement was due to collisions of the second kind (energy transfer collisions).

Beutler and Fred (1942)\(^{58} \) continued this line of investigation, and as well as finding the enhanced lines, they found a number of extra rotational lines. They expanded Byck's\(^{57} \) conclusion to say that the enhancement was due to collisions of the second kind between molecules with mutually perturbing levels for which conditions of close resonance
held, and also that the enhancement of selected rotational lines was related to the ratio of the lifetimes of the unperturbed levels of the B and A states of CN. From their calculations on the basis of this theory, they came to the conclusion that the enhancement, as well as disappearing at high pressures as had been observed by Byck, would disappear at low pressures; a prediction that has since been proven wrong.

Wager (1942)\textsuperscript{59} photographed at high resolution, the (0,0) band of the CN violet system resulting from the reaction of active nitrogen with chloroform, and was able to measure the displacement of the rotational lines resulting from perturbations. He was also able to show that this perturbation was caused by certain rotational levels of the $v' = 10$ vibrational level of the A state of CN, and predicted that the population of these levels would be reduced. (In 1948, Herzberg and Phillips\textsuperscript{60} corrected the numbering of the vibrational levels of the A state of CN. In this review, the revised numbering is used.)

Wager (1943)\textsuperscript{61} gave a more detailed account of his earlier work\textsuperscript{59} together with some further results. He was unable to detect any variation in intensity of the perturbing levels of the A state of CN as he had previously predicted, and so concluded that the levels were being repopulated by rotational relaxation as fast as they were being depopulated by perturbation. From his investigation of the reaction of active nitrogen with a number of organic compounds, Wager postulated that the CN radical received energy by acting as the third body in a termolecular nitrogen atom recombination, thus the excitation occurred after it was formed.
Evans et al (1956)\textsuperscript{b2}, by trapping the reaction products and by following the kinetics of the reaction of active nitrogen with various organic compounds, confirmed Strutt's\textsuperscript{17} results, that the main product of the reaction was hydrogen cyanide with only a trace of cyanogen, and postulated that the CN emission arose from the reaction of these products with active nitrogen via a collision complex:

\begin{align*}
N + N.C.N_2 & \rightarrow N_2 + CN + CN \\
N + N.HCN & \rightarrow N_2 + H + CN
\end{align*}

They estimated that both of these reactions were about 110 kca\textper ml exothermic which, they concluded was sufficient to excite the CN radicals formed to the required energy levels for emission. Strutt's\textsuperscript{17} reasoning would appear to eliminate this mechanism. The rates of the initial reactions with active nitrogen indicated that the nitrogen atoms have no difficulty in approaching even completely shielded carbon atoms in organic compounds.

Jennings and Linnett (1957)\textsuperscript{b3} studied the reaction of a number of organic compounds with active nitrogen spectroscopically. As well as CN emission, they found CCl bands, but no NCl bands from the reaction of chlorinated hydrocarbons. Although NCl bands have been observed\textsuperscript{b4}, they have not yet been detected in the reaction of active nitrogen with chlorine where NCl almost certainly occurs as an intermediate.

From the reaction flames with organic compounds containing hydrogen they detected both CH and NH bands that increased in intensity as the ratio of hydrogen to carbon increased in the compound. This behaviour is the opposite to the behaviour of CN emission, as for example, the
reaction of active nitrogen with chloroform gave stronger CN emission but weaker CH and NH emission than with methylene dichloride. Swan bands \( \text{C}_2 \) were only detected in certain instances, but it was believed that often the non-detection of the Swan bands was not because of their absence but because they were overlapped by the stronger CN red system.

A series of hitherto unreported bands in the vicinity of 3290 A. were also observed. These bands were degraded to the violet and were present in the spectra of all reactions except those of carbon tetrachloride, tetrachloroethylene, and chloroform. Since the formation of these bands seemed to require the presence of hydrogen in the compound, and since the variation of their intensity with reactant seemed to follow the variation of the CH and NH emission, Jennings and Linnett initially ascribed them to an unknown transition of hydrogen cyanide. When they reacted active nitrogen with deuterated acetylene, the bands were not displaced indicating that the unknown emitter did not contain hydrogen. (A shift of about 30 cm\(^{-1}\) was expected for a deuterated emitter, and changes as low as 4 cm\(^{-1}\) could have been detected.)

Akriche and Herman (1957)\(^5\) investigated the reaction of active nitrogen with traces of carbon from the electrodes of the nitrogen discharge; the same experimental system as that investigated by Johnson and Jenkins.\(^5\) In contrast to Johnson and Jenkins, they found that the lower vibrational levels of the B state of CN were populated, and their estimates of the populations of the levels \( v' = 0 \) to \( v' = 6 \) showed a similar alternation from level to level as that found by Strutt and
Fowler. To account for the excitation of the CN, they envisaged a similar mechanism to Johnson and Jenkins, where CN + ions were formed as intermediates, with the excitation reaction following:
\[ \text{CN}^+(v = 0) + e \rightarrow \text{CN}(B, v') \]
It is doubtful whether the theories to account for the excitations in this type of system, would have any relevance to the reaction of active nitrogen with organic compounds.

Broida and Heath (1957) compared the reaction of active nitrogen with carbon monoxide at a pressure of 3 torr. with the reaction with acetylene. They found that as well as the intensity and intensity distributions of the CN emission being similar, both reactions also showed rotational perturbations in the lowest vibrational level of the B state of CN.

Sobering and Winkler (1958) found, in the reaction of active nitrogen with chlorinated hydrocarbons, that the orange reaction flame became less prominent as the number of halogen atoms in the organic molecule decreased. Because cyanogen chloride was a major product of the reaction, they reiterated Strutt's theory, that the orange emission arose from the reaction of active nitrogen with the cyanogen chloride formed. The same arguments used against Strutt's theory would, thus also apply.

Dixon and Nicholls (1958), from studies of the intensity of bands in the red system of CN produced in the reaction of active nitrogen with carbon tetrachloride, determined the electronic transition moments, using previously calculated Franck-Condon factors.
Kiess and Broida (1958) studied the spectra resulting from the reaction of active nitrogen with twenty-nine different organic compounds by measuring the intensities of the CN($B \rightarrow X$)(0,0), the CN($A \rightarrow X$) (10,4), (9,4), and (4,0), and the CH($A \rightarrow X$)(0,0) emission bands at several pressures for each reaction.

They considered that the ratio of the CN red system bands (9,4) and (4,0) gave a measure of the vibrational temperature of the A state of CN. All hydrocarbons reactions gave a uniformly high vibrational temperature, but the vibrational temperature resulting from the reaction of halogenated hydrocarbons increased as halogens of higher atomic number were used. They interpreted this increase as a decreasing population of the lower vibrational levels, and not an increasing population of the higher vibrational levels of the A state of CN.

The vibrational temperature of the A state was independent of the number of halogen atoms present in the organic molecule but a greater number of halogen molecules increased the overall intensity of the reaction flame considerably. Kiess and Broida considered that there was some correlation of the vibrational temperatures of the B state with those of the A state because when the vibrational temperature of the A state increased, the tail bands of the CN violet system became more developed.

The brightest flames occurred when the ratio of nitrogen atoms to organic reactant molecules was about one to one, and when the pressure in the reaction system was in the range that gave the brightest afterglow in the absence of any organic compounds (about 3 to 10 torr.).
At low pressures the CN red system gave the most intense emission, while at high pressures the CN violet system predominated (for the chloroform reaction, the ratio of intensities changed by a factor of eight when the pressure was increased from 1 to 30 torr.). Also, the vibrational temperature of the A state decreased as the pressure in the system increased which could be attributed to vibrational relaxation caused by collisions with other molecules. Conversely, an increased pressure developed the tail bands to a greater extent, i.e. increased the vibrational temperature of the B state.

A rotational analysis of the vibrational level $v' = 0$ of the B state of CN at various pressures showed that at low pressures the population of perturbed rotational levels exceeded that of the unperturbed rotational levels. For example, at 0.1 torr, Kiess and Broida found that there was a factor of six difference between the two populations. At higher pressures, the distribution of populations of the rotational levels approached the normal thermal distribution, until at 20 torr, they could detect no anomalies. The perturbation did not vary with the organic compound used which indicated that the effect was a property of the CN radical and not of the reaction producing it.

From their observations, Kiess and Broida postulated that there were at least two different excitation mechanisms producing excited CN, but they were not prepared to advance specific mechanisms.

Haggart and Winkler (1960)\textsuperscript{70}, from their investigation of the products of the reaction of active nitrogen with cyanogen, advanced the mechanism;
The intermediate NCN was then unknown, but has since been identified.

Jennings and Limnett (1960) extended their earlier work on the reaction of active nitrogen with sixteen different organic compounds. Contrary to Kiess and Broida, they found that increasing the ratio of halogen to carbon in halogenated hydrocarbons, enhanced the CN red system compared to the violet system, but they did not advance any explanation.

Further work on the new bands at 3290 Å failed to lead to the identity of the emitter, but they speculated that it could be either of the then unknown species C₂N or NCN. The latter radical had been postulated as a reaction intermediate by various people. Although they did not consider it likely, they did not overrule the possibility that the emission could be some unknown bands of the cyanogen molecule because the new bands appeared to vary in a similar manner to the cyanogen produced in the reaction.

Pannetier et al (1960) cooled the products of the reaction of a number of organic compounds with active nitrogen and photographed the resulting spectra in an attempt to detect unstable intermediates. Their spectra showed no new bands.

Broida and Golden (1960) continued the investigation of the perturbation of the vibrational level \( v' = 0 \) of the B state of CN by the vibrational level \( v = 10 \) of the A state arising from the reaction of active nitrogen with methylene dichloride. They derived a kinetic
model to account for their observations of the effect of pressure, involving the competition between the formation, radiation, and collisional interchange between the two states. Although their theory explains a number of results, they still considered it too simplified to cover all aspects of the phenomenon.

Bayes (1961)\(^7\), determined the population distribution amongst individual vibrational levels of the A state of CN by studying the emission of the CN red system from reactions of active nitrogen with a number of organic compounds. In contrast to Kiess and Broida\(^6\) he could find no variation of the population distributions with pressure in the reaction vessel below 5 torr., for the reaction of carbon tetrachloride. At higher pressures, the population distribution shifted to lower vibrational levels which he attributed to vibrational relaxation caused by collisions with other molecules. A shift to higher vibrational levels (an increase in the vibrational temperature) occurred on lowering the temperature of the reaction system. The reactions of chloroform and bromoform gave similar population distributions to the carbon tetrachloride reaction, but with broader and less pronounced maxima at vibrational levels of \(v' = 5, 6, \) and 7 for the chloroform reaction, and levels of \(v' = 6 \) and 7 for the bromoform reaction. The population of the level \(v' = 10\) was much greater for the bromoform reaction than for the chloroform reaction, i.e., the vibrational temperature was higher.

The reaction of hydrogen cyanide gave only weak emission that was dependent on both the concentration of hydrogen cyanide and the pressure
in the reaction system. The population of the A state passed through a minimum at the vibrational level \( v' = 3 \), so Bayes divided the vibrational levels up into two groups; the \( P_1 \) group consisting of levels with \( v' \leq 3 \), and the \( P_2 \) group with levels \( v' \geq 3 \), with both groups contributing to the population of the level \( v' = 3 \). Since these two groups appeared at lower pressures than the pressure where vibrational relaxation made its appearance in the carbon tetrachloride reaction, and since the population distribution of the \( P_1 \) group was not of the type expected to result from vibrational relaxation, he assumed that the population of the \( P_1 \) group was not derived from that of the \( P_2 \) group by vibrational relaxation. The ratio of the total population of the \( P_2 \) group to that of the \( P_1 \) group increased as the pressure in the system increased and decreased as the concentration of hydrogen cyanide increased.

The population distribution of the A state of CN resulting from the reaction of cyanogen also showed a similar grouping to the hydrogen cyanide reaction but, although the \( P_1 \) group populations were similar to those arising from hydrogen cyanide, the population of the \( P_2 \) group was approximately ten times less. The ratio of the populations of the two groups varied in a similar manner to the ratio of the groups from the hydrogen cyanide reaction as the concentration of cyanogen was varied.

The flames resulting from the reactions of cyanogen chloride and bromide, which were even brighter than that from the carbon tetrachloride reaction, gave a spectral distribution that could also be divided into the two separate groups. Although the ratio of the two
groups did not vary with concentration, the ratio of the $P_1$ emission group to the $P_2$ emission group was greater for the cyanogen bromide reaction than for the cyanogen chloride reaction.

In order to determine the identity of some of the reactants or intermediates, ammonia was added to the reaction of active nitrogen with cyanogen bromide at a point a little distance downstream from the cyanogen bromide inlet jet. The CN emission was reduced by a factor of up to sixty, depending on the concentration of ammonia added, and the nitrogen afterglow, that had been extinguished by the cyanogen bromide reappeared, although weakened. This quenching of the CN emission by ammonia also occurred with the reactions of hydrogen cyanide and carbon tetrachloride.

The intensity of the $(0,0)$ emission band of the CN violet system was compared to the total intensity of emission from the CN red system as the pressure was varied for a number of the reactions. Variations were attributed to vibrational relaxation of the perturbed energy levels.

Bayes assumed that A state nitrogen molecules, not nitrogen atoms, were the main reacting species in active nitrogen for these reactions. Simple considerations based on statistical weights suggest that when nitrogen atoms recombine, approximately three quarters of the recombinations give A state nitrogen molecules. Experimentally, about one recombination in twenty gives rise to the afterglow emission. From this, Bayes estimated that in his system the concentration of A state nitrogen molecules was about one sixth of the nitrogen atom concentration,
and so would be present in sufficient numbers for reaction. Later work has shown that this estimate of A state populations is likely to be wrong by being many powers of ten too high\(^9\).

Bayes considered that the ammonia quenching of the CN emission confirmed the presence of the A state nitrogen molecules as the reacting species because ammonia reacts very slowly with nitrogen atoms but will remove A state nitrogen molecules quite rapidly. On adding methane to the reaction in the same manner as the ammonia was added, he observed only a slight reduction in the intensity of the CN emission, from which he deduced that the reactive species was not vibrationally excited nitrogen molecules which would have been removed almost completely by methane.

He postulated the reaction mechanism for the reaction of cyanogen and its derivatives was as follows:

\[
\text{N}_2(\text{A}) + \text{XCN} \rightarrow \text{N}_2(\text{X}) + \text{XCN}^* \\
\text{XCN}^* \rightarrow \text{X} + \text{CN}^{**}
\]

where XCN\(^*\) is in a repulsive triplet state. The bond dissociation energies of the X-C bond in cyanogen and its derivatives, used by Bayes in his discussion, were: 146 kcales per mole for cyanogen, 130 kcales per mole for hydrogen cyanide, 107 kcales per mole for cyanogen chloride, and 94 kcales per mole for cyanogen bromide. A state nitrogen molecules, with an energy of 140 kcales per mole, would not have sufficient energy to dissociate cyanogen or both dissociate hydrogen cyanide and excite the CN radicals formed to their A state. If the A state nitrogen molecules were in excited vibrational states, then more energy would be
available for excitation and so emission for the unfavourable cases of hydrogen cyanide and cyanogen could occur.

Bayes proposed that this was the reason that the hydrogen cyanide and cyanogen flames were much less intense than those of cyanogen bromide and chloride, but did not indicate why the cyanogen flame was much more intense than the hydrogen cyanide, the opposite of the result to be expected simply from the bond dissociation energies.

The presence of an oscillating flame front under certain experimental conditions showed that a chain reaction was occurring, and he attributed the reappearance of the nitrogen afterglow on the addition of ammonia, to the removal of the A state nitrogen molecules by the ammonia, breaking the chain leading to a reduced requirement of nitrogen atoms. He did not consider an alternative explanation, that the ammonia breaks the chain by removing one of the intermediates.

The addition of molecular hydrogen to the hydrogen cyanide and cyanogen chloride reactions reduced the ratio of the P₂ emission to the P₁ emission. Bayes interpreted this as a reduction of the population of the P₂ group, and since molecular hydrogen is known to remove CN radicals, he assumed that the excitation of the P₂ emission occurred via unexcited CN radicals, whereas the P₁ emission did not. He did not consider the possibility of other intermediates reacting with hydrogen.

Bayes envisaged the excitation of the P₂ group occurring by a mechanism whereby the CN radical catalysed the recombination of nitrogen atoms;

\[ N + CN \rightarrow NCN \]
$\text{N} + \text{NCO} \rightarrow \text{N}_2 + \text{CN}$

Although Bayes wrote this first step as bimolecular, it is probably
termolecular with some other molecule acting as the third body to
remove excess energy. The species NCO, would be stabilized by
several resonance structures, and he assumed that the second reaction
would be sufficiently exothermic to excite the CN radicals to give the
$P_2$ emission. Because the $P_2$ emission from the carbon tetrachloride
reaction was not quenched by hydrogen, he assumed that the excitation
occurred by a different mechanism in this case.

Pannetier et al (1961) studied the spectra of the reaction of
active nitrogen with a number of organic compounds, and amongst the
emission detected bands of CCl$_3$, plus some other bands that they
attributed to hitherto unknown tail bands of the CN violet system.

Kiess and Broida (1961) determined the effect of the pressure of
the reaction vessel on the perturbed rotational levels of the
vibrational level $v' = 0$ of the B state of CN. At 0.1 torr., they
found that the extra rotational lines (those lines which corresponded to
forbidden transitions in the absence of the perturbation) were the
strongest lines present. They assumed that, as well as depopulation of
levels occurring by spontaneous emission, population and depopulation
could occur by collisions with other species.

Kiess and Broida also estimated that CN was formed twenty times as
readily in the A state as in the B state for the reactions they studied.
Other than saying that they reacted organic compounds with active
nitrogen, they do not specify which reactants they used, so this
observation is of little significance.

Setser and Thrush (1963) extended Bayes' division of the CN red system into the $P_1$ and $P_2$ groups, to include the CN violet system. They associated the $P_1$ distribution (levels $v' \leq 3$ of the A state) with the higher vibrational levels of the B state ($P_1'$), and the $P_2$ distribution (levels $v' \geq 3$ of the A state) with the lower vibrational levels of the B state ($P_2'$). The $P_1$ and $P_1'$ groups appeared to arise mainly from the reactions of active nitrogen with compounds in which the carbon-nitrogen bond already existed while the $P_2$ and $P_2'$ groups arose from reactions where the carbon-nitrogen bond was formed in the reaction.

To account for the excitation of the tail bands of the violet system where more than 130 kcales per mole excitation energy was required, Setser and Thrush assumed that the CN was formed and then excited to give the $P_1'$ emission by collision with some excited species present in active nitrogen. They considered that A state nitrogen molecules with an energy of 142 kcales per mole were the most probable species involved in the energy transfer, because the unpaired electron in the CN radical would help the nitrogen molecules to reverse its spin while it gave up its energy. Since the ratio of the intensity of the $P_1'$ emission from the CN violet system, to the $P_1$ emission from the CN red system varied with reactant and reaction conditions, they considered that the $P_1'$ and $P_1$ groups of levels were each populated by different mechanisms.

Setser and Thrush postulated that the excitation of the $P_2$ group occurred by way of intermediates of the type $CX$, where $X$ may be hydrogen.
or a halogen. Reactions of the type:

\[
N + CX \rightarrow CN + X
\]

would be 94 kcales per mole exothermic for hydrogen, and greater than 80 kcales per mole exothermic for chlorine and bromine. Normally these transfer reactions give products with only vibrational excitation and no electronic excitation. The CN radical appears to be a special case in this respect, because the potential curves of the ground state and the A state of CN cross at a bond length of 1.50 Å, an energy of 60 kcales per mole, and at the vibrational level \(v' = 7\) of the A state. Above this point the potential curve of the A state lies below that of the ground state so that CN radicals with a high energy, instead of being formed in the ground state, would be preferentially formed in the A state. The \(P_2\) group has its greatest population in the vibrational level \(v' = 7\) (the point at which the potential curves of the states cross) and the population extends up to the level \(v' = 10\) which has an energy of 74 kcales per mole. Thus the above reaction involving the CX intermediate would be sufficiently exothermic to account for all of the \(P_2\) emission obtained.

To account for the strong \(P_2\) emission from the reaction of cyanogen chloride, Setser and Thrush postulated the mechanism:

\[
\begin{align*}
N + \text{ClCN} & \rightarrow N_2 + \text{Cl} \\
N + \text{Cl} & \rightarrow \text{CN} + \text{Cl}
\end{align*}
\]

where the CN was excited to energy levels leading to the \(P_2\) emission. The first reaction of the cyanogen chloride with nitrogen atoms would be exothermic, but the analogous reaction with hydrogen cyanide;
\[ \text{N} + \text{HCH} \rightarrow \text{N}_2 + \text{CH} \]

would be thermoneutral, probably with a large activation energy and so the resulting \( \text{P}_2 \) emission from this source would not be so prominent.

Radford and Broida (1963)\textsuperscript{18} continued the investigation of the perturbed rotational lines of the vibrational level \( v' = 0 \) of the B state of \( \text{CN} \). From their own work and that of previous workers, they summarized the properties of the perturbations as follows:

At high pressures (10 to 100 torr.):

1) The red system of \( \text{CN} \) was bright and well developed, while the violet system was weak except for intense bands originating from the \( v' = 0 \) vibrational level.

2) Rotational perturbations of the vibrational level \( v' = 0 \) of the B state of \( \text{CN} \) was observed both as line displacements and as intensity anomalies at rotational levels of \( K' = 4, 7, 8, 11 \), and 15, with the perturbation thus being a property of the \( \text{CN} \) radical and not of the reaction producing it. The overall rotational population corresponded to the wall temperature of the reaction vessel; this is usually close to room temperature.

3) An extra line of low intensity accompanied each perturbed line of the main sequence.

4) Normal spin doublets of the rotational lines of the bands of the violet system were seen at levels with \( K' \) greater than 15, with the intensities of the two components different.

5) In the presence of a magnetic field, the perturbed rotational lines broadened and the extra lines split, but the total population
involved did not vary. Unperturbed rotational lines were not affected.

At low pressures (less than 1 torr);

1). The violet system of CN nearly vanished except for the perturbed rotational lines and their companions which, along with the bands of the red system, remained about the same intensity.

2). The extra lines often became the most intense feature of the CN violet system.

3). The rotational levels with \( K' \) greater than 15 did not split into spin doublets.

4). The presence of a magnetic field increased the total population of the main and extra lines at \( K' = 11 \) up to sevenfold and increased the populations of other perturbed levels to a lesser degree. Unperturbed rotational lines remained unchanged.

Radford and Broida's investigation enabled them to explain some of these properties. The perturbation arose because some of the rotational levels of the vibrational level \( v' = 0 \) of the B state of CN, have almost the same energy as some of the rotational levels of the vibrational level \( v' = 10 \) of the A state. A resonance interaction between these pairs of degenerate rotational levels caused the wave functions of each member of the pair to mix slightly and for each to take on some of the properties of the other state. Radford and Broida developed the quantum mechanical expressions to show this effect.

They considered that the presence of the extra lines was direct physical evidence to confirm this theory. These lines arose from the A
state member of the degenerate rotational pair undergoing a transition to the same vibrational level of the ground state that the normal transition from the B state goes to. An example would be that one of the rotational lines of the normal CN violet (0,0) transition would be accompanied by a line from the CN red system (10,0) transition. Since these transitions are from degenerate levels and go to the same ground state level, the energy change for each transition is about the same and so the wavelengths of the resultant radiation would be about the same. The difference in wavelength between the extra line and its perturbed companion is thus a measure of the difference in energy between the two "degenerate" levels. Normally the Franck-Gondon factors for the transitions giving the extra lines are very unfavourable, but the mixing of the wave functions of the degenerate levels increases the transition probability several hundredfold, from almost zero, to a small but significant probability.

The unperturbed rotational levels of the vibrational level \( v' = 0 \) of the B state could be populated by rotational relaxation from the perturbed levels at relatively low pressures because this process is quite efficient. At higher pressures, the B state of CN could be populated from the higher vibrational levels of the A state by collisions with other molecules:

\[
\text{CN}(A, v_1) + M \rightarrow \text{CN}(B, v_2) + M
\]

Although nearly every collision between CN radicals and another molecule changes the rotational energy, only about one collision in a hundred would change the vibronic state, and so this process only
becomes effective at pressures above 10 torr.

Radford and Broida's theory, which applied almost exclusively to Bayes' P₂ emission, postulated that the CN was initially excited to the A state and that the B state was populated from the A state by the various processes outlined above.

When hydrogen cyanide undergoes predissociation, it does so by the reaction;

\[ \text{HCN} \rightarrow \text{H}(2s) + \text{CN}(A) \]

Radford and Broida envisaged a mechanism for the active nitrogen reactions, whereby the hydrogen cyanide produced by the reaction, was excited by collision with some energetic species and dissociated by the above predissociation reaction to give the CN radical predominantly in the A state. They envisaged a similar mechanism involving the cyanogen halides produced in the reaction of halogenated hydrocarbons. This theory has been refuted earlier in this review, the main arguments against it being that when hydrogen cyanide or the cyanogen halides were reacted with active nitrogen, different spectral distributions occurred than for the type of reaction under consideration by Radford and Broida.

Ghosh and Sharma (1963) studied the reaction of active nitrogen with methylene dichloride and found that the intensity of the CN emission increased to a maximum and then declined as the concentration of methylene dichloride was increased. This effect can be interpreted as implying that the chain reaction has more than one reaction involving nitrogen atoms while the formation of excited CN radicals occurred in one of the later reactions, and not in the initial reaction. A high
concentration of methylene dichloride would use most of the nitrogen atoms in the initial reaction, leaving few to take part in reactions giving excited CN radicals.

Herzberg and Travis (1964) analysed the rotational structure of the bands at 3290 Å that Jennings and Linnett found, but could not identify, and showed that they originated from the NCN molecule.

Brown and Broida (1964) found that when active nitrogen reacted with hydrocarbons and chlorinated hydrocarbons, up to four distinct zones could be seen in the reaction flame, depending on the experimental conditions. These zones were characterized by different intensities and spectral distributions of the CN bands, but they conceded that some of the zones could have been due to poor mixing of the reactants. A number of unusual results obtained when the "pink" afterglow was prominent could be attributed to reactions with species not usually present in the normal nitrogen afterglow.

In the reaction with chloroform, "explosive" flashes took place at certain pressures. In these flames, bright flashes of light passed through the reaction vessel in succession, spaced with periods when no light emission occurred. The number of photons emitted was about the same as the number of chloroform molecules present showing that some highly efficient excitation process was occurring. This sort of behaviour is typical of chain reactions.

The zone that Brown and Broida investigated most thoroughly was blue-white, and consisted of bands arising from vibrational levels \( v' = 2 \) to 15 of the B state of CN, together with complex emission from...
the CN red system that was difficult to resolve. The glow was of long
duration, and required very low concentrations of organic reactant for
its production. The intensity of the glow was dependent both on the
pressure in the reaction vessel (high pressures appeared to cause
vibrational relaxation) and on the concentration of nitrogen atoms (the
most intense glows occurring with relatively low concentrations of
nitrogen atoms).

Brown and Broida postulated that the A state of CN was populated by
at least two different mechanisms: some populating vibrational levels
below \( v' = 12 \) and others populating vibrational levels above \( v' = 12 \) and
perhaps some of the lower levels as well. These high vibrational
levels of the A state then populated the higher levels of the B state by
a similar mechanism to that proposed by Radford and Broida\(^7\) for the
population of the low levels of the B state. At high vibrational
levels, the potential curves of the two states lay close together and
above the vibrational level \( v' = 18 \) of the A state, most levels of the A
state became degenerate with the corresponding levels of the B state.
This enabled the vibrational wave functions for each state to overlap to
a considerable extent, and hence cross-transfer collisions became more
efficient for populating the vibrational levels of the B state of CN
from those of the A state.

Evidence that the perturbations of high vibrational levels of the B
state were occurring was found for the level \( v' = 13 \), where certain
rotational lines were enhanced, and the vibrational level \( v' = 10 \), where
the spin components of each rotational level were split, but there was
no evidence of perturbation in the vibrational levels \( v' = 11 \) and 12. They considered that this would indicate that the B state was populated from the A state and not directly, although the evidence was not conclusive.

To achieve the high vibrational levels of the A state necessary for this theory, Brown and Broida used Bayes' mechanism \(^7\);

\[
N + CN + M \rightarrow NCH + M \\
N + NCH \rightarrow N_2 + CN
\]

where the CN was formed in the A state in the second reaction. This second reaction would probably be about 130 kcs per mole exothermic, so although the CN radical could be excited to very high vibrational levels of the A state, unless further energy were added by collisions, vibrational levels up to only \( v' = 10 \) of the B state would be populated. Thus, this excitation mechanism cannot account for all the emission of the tail bands.

Campbell and Thrush (1964) \(^8\) studied the CN emission obtained by passing nitrogen containing traces of methane through a radio frequency discharge. It was found that the CN emission, which arose mainly from low vibrational levels of the A state and vibrational levels \( v' = 0 \), and 5 to 7 of the B state, was proportional to the square of the nitrogen atom concentration. They used a titration with ammonia to establish the concentration of CN radicals;

\[
NH_3 + CN \rightarrow NH_2 + HCN
\]

where the rate constant of this reaction was thought to be about \( 2 \times 10^{-11} \) cm\(^3\) molecules\(^{-1}\) sec\(^{-1}\). This indicated that the concentration
of the CN radicals remained constant at about $3 \times 10^{13}$ molecules cm$^{-3}$. This reaction with ammonia has been considered earlier in the review of Bayes' work, and will be considered further later.

They considered that Bayes' excitation mechanism, involving the NCH species, would be too slow to account for the high intensity of the CN emission. The mechanism proposed by Setser and Thrush, where excitation occurred by energy transfer from a state nitrogen molecules to the CN radical, was reiterated. It was thought that the dependence of the CN emission on the square of the nitrogen atom concentration confirmed this, although there are other possibilities for the identity of the excited molecules involved, notably $5\ge^+_e$, $a^1\ge^-_u$, and $3\Delta_u$.

In this work the organic reactant itself passed through the discharge, along with the nitrogen, where it would come in contact with many short-lived highly excited species not present in a normal afterglow.

Stringal et al (1964) found that the addition of halogen or carbon tetrachloride to the reaction of active nitrogen with organic molecules, altered the CN red and violet systems. Short pulses of a microwave discharge were used to activate a mixture of nitrogen, organic reactant, and the additive in a static system.

Setser and Thrush (1965) continued their investigation of Bayes' classification. They found that measurements on the $P_1$ distribution of the CN violet system required high resolution spectroscopy, because the maximum populations occurred in the vibrational levels $v' = 5$ to 9. For transitions with $\Delta v = 0$ or $\pm 1$, the bands originating from these levels were headless and overlapped, so
were difficult to resolve.

The reason for this was that the equilibrium internuclear distance of the B state of CN was slightly less than that of the ground state for low vibrational levels of each state, but at higher vibrational levels, the reverse situation applied. Thus, initially the value of \( B_v \) for the B state was greater than that of the ground state but decreased more rapidly and became smaller than the value of \( B_v \) for the ground state at higher vibrational levels. The first few emission bands from low vibrational levels of the B state were degraded towards the violet. Emission bands from intermediate vibrational levels (in the region of \( v' = 7 \) of the B state), where the values of \( B_v \) were about the same for each state, were headless, and emission bands from higher vibrational levels were degraded to the red, giving the tail bands. The vibrational spacing of the bands was also dependent on the vibrational level; as the vibrational level increased, the band origin moved first towards higher frequencies, then back towards lower frequencies.

This overlapping of the heads made it impossible to determine the populations of vibrational levels from the intensities of the band heads over the region of maximum population. In contrast, the Franck-Condon factors behaved in a regular manner, being constant for transitions \( \Delta v = 0 \) or \( \pm 1 \), after the first few members of each sequence.

The \( P_1^{-} \) group extended from the vibrational levels \( v' = 0 \) to 13 of the B state with the maximum populations in levels \( v' = 5 \) to 7. There also appeared to be another slight maximum in the population at level \( v' = 10 \). The B state levels \( v' = 0 \) to 4 were populated predominantly
by the $P_2$ group, but there was also a minor contribution to the population of these levels by the $P_1$ group.

The reaction of oxygen atoms with cyanogen gave similar population distributions amongst the vibrational levels of the A and B states of CN as the reaction with active nitrogen, although the ratio of the total population of the B state to that of the A state was up to seven times the corresponding ratio for the active nitrogen reaction. Emission from levels up to $v' = 15$ of the B state was seen but the population of levels $v' = 11$ and above was very low. Some very weak emission from the NCN molecule was detected (about two orders of magnitude less than the intensity of the CN emission), but none from OCN.

For the active nitrogen reactions a number of Stern-Volmer plots of the quenching of the CN emission were determined. Although most of the graphs obtained were first order with respect to the quencher concentration, Setser and Thrush were not prepared to use them to identify any of the intermediates. The quencher could have been acting directly on the CN radical, or an intermediate in the excitation mechanism, or it could have been competing with some of the intermediates for some of the reactive species.

The addition of ammonia appeared to remove the chain carrier in a number of the excitation reactions, but they were unable to establish the identity of any of the species that the ammonia reacted with. Of the two processes leading to the CN violet emission, only one was quenched by the addition of ammonia. Setser and Thrush thought that this could be due to the ammonia removing unexcited CN radicals.
nitrogen molecules while Wright and Winkler believed that ammonia removed nitrogen molecules.) The process that was not quenched by the ammonia appeared to contribute about 20% of the CN violet emission and they postulated that this mechanism formed excited CN radicals directly.

Setser and Thrush envisaged the population of the B state of CN as occurring by way of the A state and not directly. They attributed the lack of emission from the vibrational level \( v' = 20 \) of the A state (which was at the same energy as the maximum population of the B state) to very low transition probabilities for the high vibrational levels, and not to low populations of these levels.

They next considered the excitation reaction proposed by Bayes: \[
N + NO \rightarrow N_2 + CN
\]
where the CN was thought to have been formed in an electronically excited state. If the reactants were in their ground states (\( N(4s) \) and \( NO(2 \underline{g}) \)), and the transition state of the reaction was linear, then the CN radical must have been formed in a \( \underline{2} \rightarrow + \) state, which in this case could have been either the B state or the ground state, but not the A state. This restriction did not apply if the above conditions were not fulfilled. Setser and Thrush thought that it was unlikely for the CN to have been formed in an excited state because this type of transfer reaction normally gave products that were not electronically excited, but if electronic excitation did occur, then the newly formed bond was usually the one excited. In this case, the reaction was not
sufficiently exothermic to have formed electronically excited nitrogen molecules.

For the reaction of the derivatives of cyanogen, Setzer and Thrush considered that the alternative mechanism proposed by Bayes, in which the main reactive species in these reactions was considered to be a state nitrogen molecules, was the most likely excitation reaction. In cases like cyanogen, where the A state nitrogen molecules had insufficient energy, they considered that termolecular nitrogen atom recombination gave excited CN radicals directly. The tail bands required very high excitation energies, and they attributed this to reactions with excited $^2P$ nitrogen atoms (present to less than 0.2% of the ground state nitrogen atom concentration in active nitrogen).

Fontijn (1965) followed the CN emission from a rather complicated reaction system containing acetylene, nitrogen atoms, and varying concentrations of nitric oxide. The system thus contained varying concentrations of oxygen atoms and was of little relevance to this review.

Avramenko and Krasnen'kov (1966) confirmed earlier workers' results, that there was little correlation between the quantity of hydrogen cyanide produced in the reactions of organic compounds, and the intensity of the CN emission. They attributed this to the hydrogen cyanide being formed in a bimolecular reaction, while the CN radicals were excited by a termolecular nitrogen atom recombination. To account for the formation of the various radicals present, they postulated that carbon atoms were formed as intermediates, and their further reaction
gave CN, CH, and C_2. This theory does not seem plausible because carbon was not deposited on the walls of the reaction vessel, and there appears to be little other supporting evidence.

Marsh and Schiff (1967) reacted active nitrogen with a number of ethyl and methyl derivatives of aluminium, boron, and zinc, and obtained CN emission, along with emission from zinc atoms when zinc organometallics were used. The removal of vibrationally excited ground state nitrogen molecules from the active nitrogen had no effect on the flame, indicating that these took little part in the reactions.

They assumed that an intermediate of the type XCN, where X was a metal atom, was formed. A subsequent bimolecular reaction with an energetic species gave CN radicals and metal atoms, where either or both were excited up to about 150 kcals per mole. This amount of excitation, along with the energy to initially break the metal-carbon bond, would require the energetic species to have at least 200 kcals per mole energy available to it. Marsh and Schiff assume that the species were ^\(5^+_2\) nitrogen molecules of energy 220 kcals per mole. They did not offer an adequate explanation as to why the excitation reaction should be a one step, bimolecular reaction.

A considerable amount of work has been done on the investigation of the excitation of CN emission by active nitrogen. A major difficulty in evaluating the significance of earlier work, and even some recent work, is the lack of information on the conditions under which the experiments were carried out. The development of various parts of the CN spectrum appears to depend markedly on the organic reactant used.
the total pressure in the reaction vessel, and even on the relative concentrations of each reactant. Apart from the comprehensive investigations carried out on the effects of the pressure in the reaction vessel on the development of certain spectral features, there has been little work done on the kinetical aspects of the CN emission including simple determinations of the dependence of the emission of CN, and the various other species present, on the concentration of various reactants. In this thesis, an indication is given of how the kinetics of the reactions producing CN emission may be studied and interpreted.

The most fruitful line of investigation of the CN emission appears to have been the division of the CN spectrum into two relatively independent parts as proposed by Bayes and extended by Setser and Thrush. In the preceding review and in the following investigation and discussion, their notation is used to describe the groups of vibrational levels that are populated, the excitation mechanism (or mechanisms) that populate these levels, and the emission arising from these vibrational levels. The notation is, for the A state of CN: \( P_1 \) for levels \( v' \leq 3 \), and \( P_2 \) for levels \( v' > 3 \). For the B state: \( P_1' \) for all levels (with a maximum population at \( v' = 11 \)), and \( P_2' \) for the lower levels (with a maximum population at \( v' = 0 \)).

Radford and Broida have presented a plausible explanation for the connection between the \( P_2 \) and \( P_2' \) groups, but there is yet no satisfactory explanation for the link between the \( P_1 \) and \( P_1' \) groups. Observations on the reactions of various organic compounds, indicate that the \( P_1 \) and \( P_1' \) groups are predominant when the organic reactant is
cyanogen or one of its derivatives, while the \( \text{P}_2 \) and \( \text{P}_2' \) groups predominate for the reactions of most other organic compounds.

Although this group classification can adequately explain the broader features of the CN emission, there are still variations of the spectral distributions within the groups that require a more sophisticated approach. For example, the substitution of different halogens in halogenated hydrocarbons\(^{69} \) varies the population distribution within the \( \text{P}_2 \) group. This behaviour would indicate that the halogen was playing some part in the excitation reaction giving excited CN radicals, and that the CN radical is not formed and excited in two separate steps.

The various mechanisms that have been proposed to account for the formation of excited CN radicals may be divided into three main groups:

1). Reactions involving the organic reactant, an intermediate derived from it, or unexcited CN radicals, acting as the third body in a termolecular nitrogen atom recombination. These reactions will, in general, be too slow to give the majority of the excitation, although they could account for the population of the highly excited levels required to give the tail bands.

2). Bimolecular reactions of vibrationally or electronically excited nitrogen molecules. Vibrationally excited ground state nitrogen molecules apparently do not take any part in the reaction\(^{88} \). Of the electronically excited molecules, \( \text{A} \) state nitrogen molecules have been most considered as the reactive species. In an earlier section of this thesis, it was shown that the concentration of \( \text{A} \) state molecules is
generally very low in active nitrogen \(^8,^9\). Other excited nitrogen molecules are unlikely to be present in sufficient concentration to influence the reactions.

3). Bimolecular reactions of nitrogen atoms. Nitrogen atoms are the main reactive species in active nitrogen and their bimolecular reactions with other species are usually sufficiently fast and energetic to account for most, but not all, of the CN emission.

Setser and Thrush\(^{76}\) have presented a plausible mechanism to account for the excitation of the \(P_2\) emission of CN, and in this thesis, suggestions by several earlier workers \(7,70,80,83\) have been collated and are presented as a possible mechanism for the excitation of the \(P_1^1\) emission.

In the following two chapters, the reaction of active nitrogen with the cyanogen halides is studied. Evidence will be presented to show that the major part of the CN emission arises by way of the reaction of the intermediates NCN and CX (where X is a halogen) to give excited CN radicals. The first chapter describes a spectroscopic study of the CN emission arising from the reaction of active nitrogen with cyanogen chloride, cyanogen bromide, and iodine cyanide. The second chapter consists of a kinetic study of the reaction of active nitrogen with iodine cyanide.
CHAPTER 3. EMISSION SPECTRA OF THE REACTION BETWEEN ACTIVE NITROGEN AND ClCN, BrCN, AND Icn.

EXPERIMENTAL.

REAGENTS.

Nitrogen: Prepurified grade, 99.99 % pure, as supplied by The Matheson Company Inc., U.S.A. Dried by passing through a trap cooled in dry-ice acetone.

Chloroform: A.R. grade, 99 % pure. Used as supplied by Riedel de Haen, Germany.

Iodine cyanide (ICN): Prepared by the method of Goy et al., in which solid iodine was mixed with a stoichiometric excess of mercuric cyanide and sealed in an evacuated tube. The tube was heated, fully immersed in a water bath, until all the iodine had reacted, and was then heated half-immersed until the iodine cyanide (a white crystalline solid) had sublimed to the top of the tube. The iodine cyanide, before use, was pumped under vacuum to remove volatile impurities, and in use was sublimed into the reaction tube, leaving behind any non-volatile impurities.

Cyanogen bromide (BrCN): Prepared by reacting bromine with solid sodium cyanide, subliming the products of the reaction onto an ice-cooled glass surface, pumping under vacuum while cooled in an ice bath, and finally sublimed into the reaction tube when used for spectroscopic studies.

Cyanogen chloride (ClCN): Prepared by passing chlorine through a packed column of sodium cyanide, and then passing the gaseous
products through the saturator cooled in a salt-ice bath that collected the cyanogen chloride formed (M.P. -6°C.) but not the excess of chlorine (B.P. -34.6°C.) or any cyanogen impurity (B.P. -20.5°C.). The cyanogen chloride was pumped under vacuum and sublimed, in use, as above.

**APPARATUS.**

The reaction vessel consisted of a quartz tube about fifteen centimetres long and two centimetres diameter, with a flat quartz window on one end. A stream of nitrogen, partially dissociated by a microwave discharge (from a Raytheon 2450 Mc., 125 watt, Microtherma generator, Model CMD 13) entered the reaction vessel at the opposite end to the window and was pumped out through a side arm close to the window. A trap cooled in dry-ice acetone prevented the contamination of the pump oil in an Edwards ISC 50 rotary vacuum pump.

The cyanogen halide to be reacted with active nitrogen was picked up by a stream of nitrogen passing through the solid compound, packed in the centre tube of a trap type saturator, that was cooled in ice for iodine cyanide and cyanogen bromide, and in a salt-ice mixture for cyanogen chloride. Chloroform was entrained by passing nitrogen over liquid chloroform cooled in ice. These gas mixtures were admitted to the reaction vessel through a jet (concentric with the reaction tube) that terminated in a small bulb with six small holes distributed evenly around its circumference.

Gas flows were controlled by Edwards LB1A needle valves and were adjusted until the intensity of the flame was at its brightest when
viewed through the reaction vessel's window.

Spectra of the reaction flames of active nitrogen with iodine cyanide, cyanogen bromide, cyanogen chloride, and chloroform, were photographed with a Hilger Medium Quartz Spectrograph, using Ilford R40 photographic plates, with exposure times that varied between 10 seconds and 160 minutes. Plates were developed in Ilford ID 2 developer, with continuous agitation, for four minutes at 20°C., and fixed in Ilford IF 2 fixer for ten minutes. The intensity of the spectral lines in the region 4150 to 4200 Å was determined from graphs plotted from the photographic plates using a Joyce Microdensitometer (by courtesy of the Physics Department, University of Canterbury).

The spectrum of the reaction of active nitrogen with iodine cyanide was also recorded, from 1200 to 6500 Å, using a Jarrell-Ash 0.5 metre Ebert Scanning Monochromator in conjunction with a sodium salicylate coated 1P 28 photomultiplier tube, cathode follower, and chart recorder.
Most bands in the spectra could be attributed to the red and violet systems of the CN radical. The only bands of the red system that were within the spectral range of the spectrograph and photographic plates were those of the P\(_2\) group, the P\(_1\) bands being at wavelengths greater than 7800 Å. Of the various bands of the CN violet system, those at 3590 Å could not be resolved, while the bands at 3850 to 3880 Å were represented only by transitions from the vibrational levels \(v' = 0\) to \(v' = 4\) of the B state of CN and so would only contain P\(_2\) group bands together with a mixture of the P\(_2\) and P\(_1\) groups that would be difficult to separate. The region between 4150 and 4220 Å contained both groups, and was studied in detail. The bands between 4500 and 4600 Å were also well resolved and contained both groups of bands. Thus, in the normal spectral range, the two groups of CN emission bands can be easily separated in only two regions.

The intensities of the CN violet system bands in the region 4150 to 4220 Å, as found by measuring peak heights above the base-line of the microdensitometer plots, are presented in Table 7, where the intensities have all been related to that of the (5,6) transition which was arbitrarily assigned the value of 1.0.

The sensitivity of the photographic plates increased by about 5\% with increasing wavelength over this spectral range and although care was taken to ensure that all plates were developed under the same conditions, variations could have occurred. Thus, little reliance should be placed
on the actual figures, and only general trends should be taken into account.

<table>
<thead>
<tr>
<th>Table 7. Intensity of Emission from the CN violet system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibrational transition. (0,1) (1,2) (2,3) (3,4) (4,5) (5,6)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
</tr>
<tr>
<td>4216</td>
</tr>
<tr>
<td>4197</td>
</tr>
<tr>
<td>4181</td>
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<tr>
<td>4168</td>
</tr>
<tr>
<td>4158</td>
</tr>
<tr>
<td>4152</td>
</tr>
<tr>
<td>Spectral group.</td>
</tr>
<tr>
<td>P2'</td>
</tr>
<tr>
<td>Mixture of P2' and P1'</td>
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<tr>
<td>P1'</td>
</tr>
<tr>
<td>Intensity ratios:</td>
</tr>
<tr>
<td>Chloroform.</td>
</tr>
<tr>
<td>1.7</td>
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<tr>
<td>1.2</td>
</tr>
<tr>
<td>0.4</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>0.6</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>Cyanogen chloride.</td>
</tr>
<tr>
<td>0.7</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>0.3</td>
</tr>
<tr>
<td>0.4</td>
</tr>
<tr>
<td>0.7</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>Cyanogen bromide.</td>
</tr>
<tr>
<td>0.8</td>
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<tr>
<td>0.6</td>
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<tr>
<td>0.5</td>
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<td>0.7</td>
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<tr>
<td>0.8</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>Iodine cyanide.</td>
</tr>
<tr>
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</tr>
<tr>
<td>0.2</td>
</tr>
<tr>
<td>0.2</td>
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<tr>
<td>0.3</td>
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<tr>
<td>0.5</td>
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<tr>
<td>1.0</td>
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</tbody>
</table>
CHAPTER 4. KINETICS OF THE REACTION BETWEEN ACTIVE NITROGEN AND IODINE CYANIDE.

EXPERIMENTAL.

REAGENTS.

Nitrogen and Iodine cyanide: As used in Chapter 3.

Nitric oxide: Commercial grade, 99% pure, as supplied by The Matheson Company Inc., U.S.A. Used without further purification.

APPARATUS.

The reaction vessel consisted of a glass tube, of twenty millimetres internal diameter and about fifty centimetres long, through which the reacting gases passed with velocities of about 3 metres per second, at a pressure of about 6.4 torr. This reaction tube was surrounded by a concentric glass water jacket so that it could be cooled (to 15°C.) by circulating tap water, or heated (to 35 or 55°C.) by circulating water from a Tecam Tempunit-controlled thermostat bath.

Nitrogen, which was partially dissociated by a microwave discharge, passed through a light trap and into the reaction vessel. A jet system, consisting of two small concentric tubes, was used to admit the reactant gases. One jet, terminating in a bulb with six small holes distributed evenly around its circumference, enabled nitric oxide to be admitted to the reaction vessel close to the nitrogen inlet. The other jet, which was concentric with the first jet and joined to it by an internal seal
with six small holes distributed evenly around the seal, was used to admit the nitrogen-iodine cyanide mixture from the saturator.

The reactant gases flowed out of the reaction vessel, past a side tube to a McLeod gauge, and through a trap cooled in dry-ice acetone to prevent contamination of the oil in an Edwards ISC 50 rotary vacuum pump.

The nitrogen and nitric oxide flows were controlled by Edwards LB1A needle valves and were measured by capillary flowmeters. The flowmeters for nitrogen were filled with mercury that had a covering of dibutyl phthalate to prevent mercury vapour entering the reaction vessel; dibutyl phthalate alone was used for the nitric oxide flow. The capillary flowmeters were calibrated so that the difference in levels in the manometer tubes could be expressed as gas flows through the flowmeter.

Nitrogen was saturated with ICN by passing it through a packed column of iodine cyanide crystals in the central tube of a trap type saturator, cooled in a constant level ice-water bath.

Intensities of the reaction flames were measured using a 1P 21 photomultiplier tube in combination with a small Hilger monochromator arranged so that the whole assembly could be moved the length of the reaction tube. The photomultiplier tube was connected, through a cathode follower, to a 0 to 250 microammeter from which the relative light intensities could be read directly. The exterior of the water jacket and light trap were covered with matt black paint, except for a
narrow strip along the front face of the reaction vessel, to prevent stray light reaching the photomultiplier tube. A scale on the mounting for the monochromator assembly enabled its position to be read to the nearest millimetre.

The use of the monochromator enabled the intensities of single spectral bands to be studied. The bands investigated, for the major part of this work, were; from the violet system of CN (B \to \Lambda), the (5,6) band at 415 m\mu, and the (0,1) band at 422 m\mu, and from the first positive system of the nitrogen molecule (B \to A), the (11,7) band at 580 m\mu. This last band is the strongest member of the series of first positive nitrogen bands present in the afterglow, and its intensity is proportional to the square of the nitrogen atom concentration.90

**REACTION CONDITIONS.**

A stream of nitrogen, flowing at up to 0.5 cm³. sec⁻¹. (measured at one atmosphere and 25°C.) through the saturator entrained iodine cyanide vapour. It was assumed that the nitrogen was saturated with iodine cyanide at 0°C because the construction of the saturator allowed the nitrogen, at room temperature, to pass through a packed column of the solid iodine cyanide at least four inches long, before passing over a surface, cooled to 0°C. by ice-water, where excess iodine cyanide was deposited.

The vapour pressure of iodine cyanide has not been determined at this temperature, but two groups of workers, who determined the vapour pressures at higher temperatures, give formulae that may be extrapolated
to 0°C. Yost and Stone\textsuperscript{91} measured the vapour pressure over the range 25 to 100°C, and give the formula;

$$\log_{10} P_{\text{torr}} = -13.94/2.303RT + 10.255$$

which gives a value of 0.13 torr at 0°C. Ketelaar and Kruyer\textsuperscript{92} measured the vapour pressure over the range 64 to 153°C, and gave the formula;

$$\log_{10} P_{\text{torr}} = -14.31/2.303RT + 10.46$$

which gives a value of 0.14 torr at 0°C. A value of 0.13 torr for the vapour pressure of iodine cyanide at 0°C will be used in the calculations which follow.

The flow of nitrogen through the microwave discharge was kept constant at 8.1 cm$^3$. sec$^{-1}$. (measured at one atmosphere and 25°C.) for all of the work described in this chapter. It was also assumed that the pressure in the saturator was the same as that in the reaction vessel; the pressure drop between the saturator and the reaction vessel would be unlikely to exceed 0.1 torr at the maximum nitrogen flow used.

The partial pressure of iodine cyanide in the reaction tube can be given by the expression;

$$P_{\text{torr}} = 0.13f/(8.1 + f)$$

where $f$ is the flow of nitrogen, in cm$^3$. sec$^{-1}$. at one atmosphere, through the saturator. The concentration of iodine cyanide in molecules cm$^{-3}$. in the reaction tube can then be determined by multiplying this partial pressure by Lochsmitd's number, which at 15°C. is $3.35 \times 10^{16}$ molecules cm$^{-3}$. torr$^{-1}$, at 35°C. is $3.13 \times 10^{16}$ molecules cm$^{-3}$. torr$^{-1}$, and at 55°C. is $2.94 \times 10^{16}$ molecules cm$^{-3}$. torr$^{-1}$. 
These values are presented in Table 8.

| TABLE 8. Flows and concentrations of iodine cyanide. |
|----------|----------|----------|----------|----------|----------|----------|
| f        | 0.05     | 0.12     | 0.20     | 0.28     | 0.44     | 0.52     |
|          | cm³·sec⁻¹ |
| P        | 0.8      | 2.0      | 3.1      | 4.3      | 5.5      | 6.8      | 7.8 x 10⁻³torr. |
| [ICN]    |          |
| 15°C.    | 3        | 7        | 10       | 14       | 18       | 23       | 26          |
| 35°C.    | 3        | 6        | 10       | 13       | 17       | 21       | 24          |
| 55°C.    | 2        | 6        | 9        | 13       | 16       | 20       | 23          |

Nitrogen atom flows were determined by nitric oxide titrations with a reproducibility of ±1 %. The nitric oxide was a light brown, indicating the presence of nitrogen dioxide and probably nitrogen. Although nitrogen atoms react rapidly with nitrogen dioxide, it is unlikely that the quantity present would affect the titres by more than 10 %. Nitrogen molecules act only as a diluent and again would not affect the titres by more than 10 % making a total error in these titrations of not more than 20 %. This error would be constant for all titrations, and so the gradients of logarithmic graphs would not be altered. The majority of experiments described in this chapter were carried out with a nitrogen atom flow of 0.15 cm³·sec⁻¹. at one atmosphere, equivalent to a partial pressure of nitrogen atoms in the reaction tube of 0.12 torr.

The cross-sectional area of the reaction vessel was 3.14 cm², and the pressure of the reacting gases was 6.4 torr. The velocity of gas
flow through the reaction vessel at a temperature of $T^\circ K.$ is given by the expression;

$$v_{\text{cm. sec}^{-1}} = 760 \times T \times (8.1 + f)/6.4 \times 298 \times 3.14$$

This expression reduces to the values at $15^\circ C.$ of $(296 + 37f)$ cm. sec$^{-1}$, at $35^\circ C.$ of $(316 + 39f)$ cm. sec$^{-1}$, and at $55^\circ C.$ of $(337 + 42f)$ cm. sec$^{-1}$, where $f$ is the flow of nitrogen through the iodine cyanide saturator and is given in Table $8$.

The inverse of these velocities gives the time of reaction, which for the work in this chapter, is about 3 milliseconds per centimetre of distance along the reaction tube.
RESULTS.

When iodine cyanide was added to the afterglow of active nitrogen, a bright blue-white glow was developed, with most of this emission occurring close to the iodine cyanide inlet jet. This emission had decayed almost completely away within twenty milliseconds of the admission of the iodine cyanide. A weak blue emission, that was similar to the iodine emission obtained from the reaction of iodine with active nitrogen, filled the rest of the reaction tube, and even persisted as far as the cold trap. The emission studied in the previous chapter was the bright initial emission from the reaction.

A considerable quantity of a dark brown deposit formed on the walls of the reaction tube. A microanalysis of this deposit (by Dr. A.D. Campbell, Microanalytical Laboratory, University of Otago) gave the composition by weight percentage as; carbon 33.85 %, nitrogen 38.61 %, hydrogen 2.26 %, oxygen 12.15 %, and iodine 10.55 %, which corresponds to a molar composition of $\text{CNH}_2\text{O}_0.8\text{O}_0.3\text{I}_0.03$. The sample thus appeared to be cyanogen polymer with a very small amount of iodine oxide, due to the presence of small quantities of oxygen in the nitrogen. Because no special precautions were taken to keep the sample dry, and because the deposit seemed slightly deliquescent, possibly due to the presence of iodine oxides, it is believed that the hydrogen and oxygen were present as water absorbed from the atmosphere and were not present in the reaction system.

The presence of this deposit, which formed very quickly on freshly
cleaned surfaces, precluded all but a few measurements being made on the initial bright portion of the reaction flame. The deposit was formed for the full length of the reaction tube, but beyond the thick deposition that occupied the first few centimetres of the walls of the reaction tube, it could be seen only as a transparent film which produced noticeable interference colours.

The variation of the intensities of two of the bands of the CN violet system with a number of reaction conditions was investigated. They were the (5,6) band, a representative of the P₁ group, and the (0,1) band, a representative of the P₂ group. Although the P₁ band was much brighter than the P₂ band, their behaviour was, in general, the same within the experimental error. In most of the results following, both of the bands will be considered as CN emission without any group qualification.

The replacement of the iodine cyanide in the saturator by iodine reduced the light intensity at the wavelengths of these CN bands to a negligible level, indicating that the emission measured arose from the CN radical and not from excited iodine molecules.

The variation of the intensity of the CN emission with the nitrogen atom concentration was studied by keeping all the other reaction conditions constant and varying the power supplied to the microwave discharge. Nitric oxide titrations were carried out in the absence of iodine cyanide at each power level and concurrent afterglow intensity measurements were made in the presence of iodine cyanide to determine nitrogen atom concentrations.
The results of these measurements were plotted as graphs of the logarithm of the intensity of the CN emission against either the logarithm of the nitrogen atom concentration, or half the logarithm of the intensity of the afterglow emission. Two different iodine cyanide concentrations were used, and measurements were made at the arbitrary distances of 2 cm., 5 cm., 10 cm., and 20 cm., down the reaction tube from the inlet jet.

The graphs where the afterglow emission was used as the independent variable, gave lines with less curvature than those where the nitrogen atom concentration was used. This result was not unexpected, because the nitrogen atom concentration measured with no iodine cyanide present would only be representative of the nitrogen atom concentration in the presence of iodine cyanide for low iodine cyanide concentrations, and close to the inlet jet. For higher concentrations of iodine cyanide and further down the reaction tube, there would be little correlation between the two measurements.

Typical plots are presented in figure 1 of the variation of the logarithm of the CN emission against half the logarithm of the intensity of the afterglow emission. Close to the inlet jet, these graphs were curved slightly concave upwards, while further down the reaction tube, the curvature was concave down with a maximum occurring with some of the lines. At intermediate distances from the iodine cyanide inlet jet, the graphs were almost straight.

The variation of the intensity of the afterglow emission with the iodine cyanide concentration was studied by keeping other reaction
conditions constant, and varying the nitrogen flow through the iodine
cyanide saturator. The intensities were measured at distances of 2 cm.,
5 cm., 10 cm., and 20 cm., down the reaction tube. Graphs of half the
logarithm of the intensity of the afterglow emission against the
logarithm of the iodine cyanide concentration gave a series of curves of
varying curvature (concave down) and varying general slope. These
curves represented the variation of the nitrogen atom concentration that
remained unreacted. To convert these to more meaningful graphs, the
quantity; \( \log_{10} \left( 1 - \frac{I}{I_0} \right) \), where \( I_0 \) was the intensity of the afterglow
emission with no iodine cyanide present, and \( I \) was the intensity of the
afterglow emission at a particular concentration of iodine cyanide, was
plotted against the logarithm of the iodine cyanide concentration. The
expression \( 1 - \frac{I}{I_0} \) was a measure of the nitrogen atoms that have
reacted, and although there large errors inherent in its calculation,
the graphs obtained (fig. 2) are straighter than those where the
afterglow emission intensity alone was used. The slopes of these
graphs approximate to unity where the measurements are of significance.

The dependence of the intensity of the afterglow emission on time
was determined by making repeated measurements at 2 cm. intervals up and
down the reaction tube, the first measurement being made 4 cm. from the
iodine cyanide inlet jet, and the final one at a distance of 30 cm. from
the inlet jet, until two consecutive sets of measurements made in
opposite directions agreed to within 5 scale units (2% of the scale).
This was done so that minor variations, due to alterations in wall or
reaction conditions would be negligible during the course of each set of
measurements although, since measurements on the whole series took quite a long time, there was no guarantee that conditions would be exactly the same for different sets of measurements. Seven different iodine cyanide concentrations were used with the reaction carried out at 15°C., 35°C., and 55°C.

The graphs of the logarithm of the intensity of the afterglow emission against time (typical examples are given in figure 3) were straight lines, within experimental error. The gradients of these lines were determined and plotted against the iodine cyanide concentration for each temperature at which the reaction was carried out. These graphs also resulted in reasonably straight lines, although there was a certain scatter of individual points. The graphs are presented in figure 4.

The variation of the intensity of the CN emission with time was determined in the same manner as the variation of the afterglow emission, and the logarithmic plots are presented in figure 5. The graph of the gradients of these lines plotted against the iodine cyanide concentration is given in figure 6. Since these measurements appear to add little of significance to the clarification of the mechanism of the reaction, they will not be considered further.
FIGURE 1.

Variation of $\log_{10} I_{CH}$ with $\log_{10} [N]$. 

$[I_{CH}] = 4.3 \times 10^{-3}$ torr.

2 cm. from inlet jet.

5 cm.

10 cm.

20 cm.

$\log_{10} I_{CH}$ at 422 mp.

0.1 $\log_{10}$ units.

$0.1 \log_{10}$ units.

$\log_{10} [N]$
FIGURE 2.
Variation of $\log_{10}[N]_{\text{reacted}}$ with $\log_{10}[ICN]$.

2 cm. from inlet jet.
5 cm.
10 cm.
20 cm.

$0.2 \log_{10}$ units.

$0.2 \log_{10}$ units.

$\log_{10}[ICN]$
Figure 2.

Variation of $\log_{10} [N]$ with time.

[Diagram showing variation of $\log_{10} [N]$ with time for different temperatures (15°C) and pressures (0.8 to 7.8 x $10^{-3}$ torr).]
Variation of $\frac{d \ln [N]}{dt}$ with $[\text{ION}]$.

$15^\circ C$

$35^\circ C$

$x \times 10^{13}$ molecules cm$^{-3}$. $[\text{ION}]$
FIGURE 6. (Cont'd)

\[ - \frac{d \ln [E]}{dt} \quad \text{sec}^{-1} \]

55°C.

\[ x \times 10^{13} \text{ molecules cm}^{-3}. \]

\[ [ICN] \]
Variation of $\log_{10} I_{\text{CN}}$ with time.

FIGURE 5.

$[\text{CN}] \times 10^{-3}$ torr.

$7.8$

$6.8$

$5.5$

$4.3$

$3.1$

$2.0$

$0.8$

cm. down reaction tube from inlet jet.
Variation of $d \ln I_{GN}/dt$ with $[\text{ION}]$. 

$[\text{ION}] \times 10^{13}$ molecules cm$^{-3}$. 

$\text{d ln } I_{GN}/\text{d}t$ 

sec$^{-1}$

0 10 20 30 

0 10 20 30 40 50 60 

FIGURE b.
Because the graphs of the logarithm of the afterglow emission intensity against time are straight, for constant iodine cyanide concentration, the rate expression must be of the form;

\[-d \ln[N]/dt = K\]
or

\[-d [N]/dt = K [N]\]

where \( K \) is independent of the nitrogen atom concentration. The graphs of this parameter, \( K \), against the iodine cyanide concentration are also straight, indicating that \( K \) is a linear function of the iodine cyanide concentration;

\[ K = k[ICN] + k_w \]

where \( k \) and \( k_w \) are independent of both the nitrogen atom concentration and the iodine cyanide concentration, \( k_w \) being predominantly the rate constant of the unimolecular wall recombination of nitrogen atoms.

Neglecting \( k_w \), the rate expression becomes;

\[-d [N]/dt = k [N] [ICN]\]

a reaction first order with respect to both the nitrogen atom concentration and the iodine cyanide concentration.

This conclusion is confirmed by considering the variation of the number of nitrogen atoms reacted, with the variation of the iodine cyanide concentration. The logarithmic plots of this variation (fig. 2) have gradients of about unity, indicating that there is a one to one correlation between the two variables.
Values of the parameter $K$, determined at various temperatures and concentrations of iodine cyanide, are presented in Table 9.

**Table 9.** Gradients of the plots of $\ln[N]$ against time.

<table>
<thead>
<tr>
<th>[ICH]</th>
<th>0.8</th>
<th>2.0</th>
<th>3.1</th>
<th>4.3</th>
<th>5.5</th>
<th>6.8</th>
<th>7.8</th>
<th>$x 10^{-3}$ torr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values of $K$:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$15^\circ C.$</td>
<td>4.1</td>
<td>6.0</td>
<td>6.7</td>
<td>8.7</td>
<td>9.7</td>
<td>11.0</td>
<td>13.1</td>
<td>9.7</td>
</tr>
<tr>
<td>$35^\circ C.$</td>
<td>3.8</td>
<td>4.5</td>
<td>5.5</td>
<td>6.9</td>
<td>7.6</td>
<td>8.0</td>
<td>11.8</td>
<td>10.8 sec$^{-1}$</td>
</tr>
<tr>
<td>$55^\circ C.$</td>
<td>4.4</td>
<td>4.4</td>
<td>4.8</td>
<td>6.3</td>
<td>8.1</td>
<td>9.9</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>4.8</td>
<td>7.0</td>
<td>8.4</td>
<td>9.2</td>
<td>10.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These values of $K$ have been plotted against the iodine cyanide concentrations given in Table 8, for the various temperatures and are presented in fig. 4. The points have a certain amount of random scatter, so the intercepts and gradients, together with their standard deviations, of the line of best fit have been calculated by the least-squares procedure and these lines have been inserted in fig. 4. The gradients derived correspond to the rate constant for the initial reaction between the active nitrogen and the iodine cyanide, while the intercepts correspond to the rate constant of the unimolecular wall recombination of nitrogen atoms. These results are presented in Table 10.

It was hoped that the rate constants for the reaction of nitrogen
atoms with iodine cyanide could have been used to calculate a
temperature coefficient, and consequently, an activation energy for the
reaction. Grigor and Phillips have found that the temperature
coefficients for the reactions of active nitrogen with iodine, iodine
monochloride, iodine monobromide, bromine, and chlorine, were very small
and so it could reasonably be expected that the temperature coefficient
for the iodine cyanide reaction with active nitrogen would also be small,
and easily hidden by experimental errors arising from variations in the
reaction conditions.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reaction 1 Rate Constant</th>
<th>Temperature</th>
<th>Reaction 2 Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>3.2 ± 0.3 sec⁻¹</td>
<td>15°C</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td>35°C</td>
<td>2.7 ± 0.7</td>
<td>35°C</td>
<td>3.3 ± 0.5 × 10⁻¹⁴ cm³ molecules⁻¹ sec⁻¹</td>
</tr>
<tr>
<td>55°C</td>
<td>2.4 ± 0.6</td>
<td>55°C</td>
<td>3.5 ± 0.4</td>
</tr>
</tbody>
</table>

The rate constant for the wall reaction given in Table can be
recalculated as a recombination coefficient \( \gamma \), which is defined as the
fraction of collisions of nitrogen atoms with the walls of the reaction
vessel, that lead to recombination, and is given by the expression;

\[
\gamma = \frac{4kV}{c}
\]

where \( k \) is the rate constant of the wall reaction (given in Table),
\( V \) is the ratio of the volume of the reaction vessel to its surface area
(0.5 cm. for the apparatus used), and \( c \) is the average thermal velocity
of the nitrogen atoms. The values of the recombination coefficient
become; at 15°C, is \( 10 \times 10⁻⁵ \), at 35°C, is \( 8 \times 10⁻⁵ \), and at 55°C, is
$7 \times 10^{-5}$. As has been observed previously\textsuperscript{94}, the recombination coefficient decreases as the temperature increases, probably due to the increased thermal energy of the nitrogen atoms making them less prone to stick to the walls on collision with them, and also because of the shorter duration of the collisions since the atoms are moving faster.

Values of the recombination coefficient that have been determined recently at room temperature for pyrex are $3.95$, $2.96$, $0.740$, and $< 0.190$, all $\times 10^{-5}$. The differences between each of these values can be attributed to the varying degree of purity of the nitrogen used, leading to varying degrees of poisoning of the walls of the reaction vessel.

It has recently been shown that under certain circumstances, the wall recombination of nitrogen atoms could be bimolecular and not unimolecular\textsuperscript{94}, but this does not entirely abrogate the usefulness of the concept of the recombination coefficient.

The values of the recombination coefficients obtained in this thesis are significantly higher than those obtained by other workers. The walls of the reaction vessel used in this work, were covered with a very thin film of cyanogen polymer ("paracyanogen"), so that the values of the recombination coefficient determined would probably refer to this, and not to clean pyrex. These higher values of the recombination coefficient could be attributed to the cyanogen polymer probably having a more hospitable surface for the nitrogen atoms than clean pyrex.

The first steps of the reaction of active nitrogen with the cyanogen halides can be a termolecular reaction with nitrogen atoms, a bimolecular reaction with nitrogen atoms as used earlier in this
discussion to derive the rate expression and rate constants, or a bimolecular reaction with excited nitrogen molecules. In Part I of this thesis, it was shown that the concentration of excited nitrogen molecules in active nitrogen was too low for them to take any significant part in the reaction.

If this initial reaction is termolecular with the cyanogen halide acting as the third body for nitrogen atom recombination, and in turn being degraded itself, a pseudo rate constant can be determined from the values for the iodine cyanide reaction given in Table 10. Assuming that:

\[ k = k'[N] \]

where \( k \) is the bimolecular rate constant already calculated, then the pseudo termolecular rate constant, \( k' \), can be calculated. The nitrogen atom concentration used has been given as about 0.1 torr partial pressure in the reaction vessel, which is equivalent to about \( 4 \times 10^{15} \) molecules cm\(^{-3}\), hence the value of \( k' \) would be of the order of \( 10^{-29} \) cm\(^6\) molecules\(^{-2}\) sec\(^{-1}\). This is two orders of magnitude greater than the rate of all other known termolecular nitrogen atom recombination rate constants \(^3\), which would indicate that the initial reaction is not termolecular.

There are only a limited number of different bimolecular reactions that can occur between nitrogen atoms and a cyanogen halide. The majority of these reactions can be eliminated on the grounds that their heats of reaction are endothermic, and so this aspect will now be considered. Relevant heats of formation are given in Table 11.
TABLE 1. Heats of Formation of ideal gases at 25°C. in kcais per mole\(^{29}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Formation (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICl</td>
<td>52.4</td>
</tr>
<tr>
<td>BrCN</td>
<td>43.3</td>
</tr>
<tr>
<td>ClCN</td>
<td>32.3 ± 0.3</td>
</tr>
</tbody>
</table>

The heats of formation of the cyanogen halides have been determined by calorimetry from the hydrolysis of these compounds in aqueous solution, and as can be seen from the limits of error given for cyanogen chloride, are known reasonably accurately.

The heat of formation of the CN radical is very controversial and has been determined variously as either 109, 99, or 91 kcal per mole. Although the compilers of the JANAF Thermochemical Tables favoured the highest value, they were not prepared to make a dogmatic selection.

The dissociation energy of CCl was estimated by Gaydon\(^ {97}\), who used a linear Birge-Sponer extrapolation of the ground state, based on data that he considered inadequate. Because these linear extrapolations typically give dissociation energies that are too high, it is probable that the resultant heat of formation is too low.

Milton, Dunford, and Douglas\(^ {28}\) investigated the spectrum of NBr, and used a linear Birge-Sponer extrapolation of the ground state to obtain a value of 71.5 kcal per mole for the bond dissociation energy. Because these extrapolations generally give an energy that is too high, they considered that this value set an upper limit on the dissociation energy. From a study of the populations of vibrational levels of the
excited $^1\Sigma^+$ state of $\text{NBr}$, resulting from the combination of a nitrogen atom and a bromine atom, they found that only vibrational levels up to $v' = 10$ were populated. This level corresponded to an energy of 62 kca\$/\text{mole} when the translational energies of the combining atoms were taken into account. They considered that this value set a lower limit on the bond dissociation energy of $\text{NBr}$ and so they arrived at the range of $67 \pm 5$ kca\$/\text{mole}$ for $D_0$, or $68 \pm 5$ kca\$/\text{mole}$ for the dissociation energy at $25^\circ\text{C}$.

The heats of formation of several other compounds are also required for the following discussion and although some have been determined, the results are of dubious value. Reliable values of the heats of formation of $\text{ClBr}$ and $\text{ClI}$ have not yet been determined.

The heat of formation of NCl has been estimated to be 80 kca\$/\text{mole}$ at $25^\circ\text{C}$, corresponding to a bond dissociation energy of 62 kca\$/\text{mole}$. The more reliable bond dissociation energy of $\text{NBr}$ has been determined as $68 \pm 5$ kca\$/\text{mole}$. In most groups of binary halides, the bond energy of the chlorine compound is greater than that of the corresponding bromine compound. There is no evidence that the nitrogen halides should behave any differently, and so it would appear that this estimate of the bond dissociation energy of NCl is too low, thus making the heat of formation too high.

The bond dissociation energy of HI has been determined from indirect spectroscopic evidence, to be about 40 kca\$/\text{mole}$, corresponding to a heat of formation of 99 kca\$/\text{mole}$.
The bond dissociation energy of NCN has not yet been determined, but bright emission bands have been detected corresponding to an excitation energy of the upper state of 95 kcaals per mole. Until further information is available, this value will be used as a rough lower limit for the bond dissociation energy of NCN. From this value, an upper limit of 127 kcaals per mole can be placed on the heat of formation.

Possible bimolecular reactions of nitrogen atoms with a cyanogen halide will now be considered. (In the subsequent discussion, X will be used to denote a halogen atom.)

\[ \text{N} + \text{XCN} \rightarrow \text{NX} + \text{CN} \]

When the halogen is bromine, this reaction would be \(16 \pm 15\) kcaals per mole endothermic. The large error in this heat of reaction arises predominantly from the uncertainty of the value of the heat of formation for the CN radical. It is probable that the true heat of reaction lies closer to the more endothermic limit of this range and not to the lower limit. Thus, this reaction is probably too endothermic to take any significant part in the reaction mechanism when other more exothermic reactions are possible. (Using the value for the rate constant of the initial reaction determined earlier, and an activation energy of 16 kcaals per mole, the frequency factor of this reaction would become about \(10^{-2}\) \(\text{cm}^3\ \text{molecules}^{-1}\ \text{sec}^{-1}\).)

Using the estimate of the heat of formation of NCl of 80 kcaals per mole given earlier, the reaction for cyanogen chloride would be \(35 \pm 10\) kcaals per mole endothermic (not including any contribution to the error.
from the heat of formation of the NCl), and for iodine cyanide, using the earlier estimate, would be $34 \pm 10$ kcal per mole endothermic (also not including any error inherent in the NCl).

This reaction can be considered as consisting of the breaking of a carbon-halogen bond, and the formation of a nitrogen-halogen bond. To a first approximation, the increment in the bond energy for each type of bond as the halogen is varied would be expected to be the same, and so the heats of reaction for each halogen would be expected to be about the same. Using the cyanogen bromide reaction as a basis, to arrive at the same heat of reaction for each halogen would require the bond dissociation energy of the NCl radical to be $31 \pm 5$ kcal per mole, and that of the NI radical to be $58 \pm 5$ kcal per mole. Although the basis for these estimates is not very sound, it does indicate that the estimated bond dissociation energies of these two radicals $^{14,58}$ could be about 20 kcal per mole too low.

2). $\text{N} + \text{XCl} \rightarrow \text{NCl} + \text{X}$

Using the estimated heat of formation of NCl, this reaction would be $11$ kcal per mole endothermic for the cyanogen chloride reaction, $2$ kcal per mole exothermic for the cyanogen bromide reaction, and $13$ kcal per mole exothermic for the iodine cyanide reaction. Since the estimate of the heat of formation of the NCl is only an upper limit of the true value, it is probable that the heats of reaction are lower than those derived above, enabling the cyanogen chloride reaction to be thermoneutral, if not exothermic.

3). $\text{N} + \text{XCN} \rightarrow \text{CN} + \text{N}_2$
The cyanogen chloride reaction is 13 keals per mole exothermic using Gaydon's value for the heat of formation of CCl. Since this value is probably too low, the reaction is probably not as exothermic as this estimate.

This reaction involves the breaking of a carbon-nitrogen bond, and the formation of a nitrogen molecule. The strength of the carbon-nitrogen bond in the cyanogen halides would be expected to be almost independent of the halogen present. Thus, the overall heat of reaction would also be almost independent of the halogen present, and so the heat of reaction of all the cyanogen halides undergoing this reaction would be about the same. Since the reaction of cyanogen chloride is exothermic, it is probable that the reactions of cyanogen bromide and iodine cyanide would also be exothermic.

\[ N + XCN \rightarrow N_2X + C \]

Because a stable \( N_2X \) molecule is unknown, its heat of formation would probably be high, and besides, this reaction must inevitably be endothermic irrespective of the heat of formation of the \( N_2X \). The reaction is also unlikely because of the extensive geometric rearrangement required for it to occur.

Reactions giving rise to more than one free atom as products are possible, but would be very endothermic and so would be unlikely to occur to any extent.

Of the four reactions considered above, the only ones likely to be exothermic enough to occur are the second and third, that give rise to
NCN and CX molecules respectively. Emission from both of these intermediate species has been detected; CCl emission from the reaction of active nitrogen with chlorinated hydrocarbons, and NCN emission from most reactions with organic compounds. The emission from these species has not been investigated in the reactions of the cyanogen halides, but is expected to be present.

These species could not be detected in the part of this work devoted to the spectral investigation. The resolution of the spectrograph used was not sufficient to separate the NCN bands at 3290 A. from bright CN (5,3) tail bands that occurred in the same region. The photographic plates used were not sensitive in the region (2700 to 2900 A.) where CCl emission occurred.

The only reaction considered above that formed the CN radical directly is probably endothermic and definitely would not have sufficient energy available if it were exothermic to form electronically excited CN radicals directly. The two intermediates, NCN and CX, formed in exothermic reactions would be expected to react further with nitrogen atoms to give CN radicals and these reactions will now be considered.

\[ \text{H} + \text{NCN} \rightarrow \text{N}_2 + \text{CN} \]

The heat of formation of the CN radical has, as stated before, a large margin of error, but because it is used both in calculating the heat of formation of the NCN molecule and in determining the heat of this reaction, it cancels itself out. The heat of this reaction can thus be determined by using the estimated bond dissociation energy of NCN of 95
From this data, the reaction is 131 kca\ls\ per mole exothermic, although this should only be considered as an upper limit. If this value is correct, then the reaction has sufficient energy to excite the CN radical formed to the vibrational level $v' = 10$ of the B state. Setser and Thrush have determined that, if the transition state of this reaction of NCN is linear, then the CN must be formed in either the ground state or in the B state, but not in the A state. However, this transition state is not known to be linear, so this is not a stringent rule. If the CN were formed in the ground state, it would require excitation before emission could occur, but if formed in the B state, the CN could be sufficiently excited by the energy of reaction to account for most of the $P'_1$ emission except for some of the tail bands.

$$N + CX \rightarrow X + CN$$

For CCl, this reaction would be at least 107 kca\ls\ per mole exothermic, and still more exothermic for bromine and iodine. The 107 kca\ls\ per mole is sufficient to excite the CN to the vibrational level $v' = 15$ of the A state. In transfer reactions of this type, the radical is normally formed in an excited vibrational level of the ground electronic state. However, Setser and Thrush have shown that the CN radical can be an exception to this general rule, because the potential curve of the A state crosses that of the ground state and lies beneath it for energies greater than 60 kca\ls\ per mole. Thus, if the reaction produces CN with a greater energy than this, it will be preferentially formed in the A state with lower vibrational levels of the A state populated by vibrational relaxation. The excitation energy
received from the reaction is sufficient to produce all of the P2 emission.

These two reactions show that it is not impossible to form excited CN radicals from simple bimolecular reactions with known species. An alternative excitation mechanism that has been suggested by a number of workers, is that the CN radicals are formed in the ground state and are then excited by a termolecular reaction with nitrogen atoms. The energy from this excitation reaction, about 225 kcales per mole, would be ample to account for all the CN emission, but does not lead to any plausible reason for the population of only selected vibronic levels.

It should be possible to determine whether the excitation of the CN emission occurs by way of a bimolecular reaction or a termolecular reaction with nitrogen atoms by investigating the dependence of the CN emission on the nitrogen atom concentration. The two reaction mechanisms considered above are:

a). \[\text{N} + \text{XCN} \rightarrow \text{NCN} + \text{X}\]
\[\text{N} + \text{N} + \text{N} + \text{CX} \rightarrow \text{X} + \text{CN}^*\]

b). \[\text{N} + \text{XCN} \rightarrow \text{CX} + \text{N}_2\]
\[\text{N} + \text{CX} \rightarrow \text{X} + \text{CN}^*\]

where \(\text{CN}^*\) is a vibronically excited CN radical. These mechanisms can be summarized as;

\[\text{N} + \text{XCN} \rightarrow \text{M} + \text{Products} \quad \text{Rate constant} \quad k_1\]
\[\text{N} + \text{M} \rightarrow \text{CN}^* + \text{Products} \quad \text{Rate constant} \quad k_2\]

where M is either of the intermediates NCN or CX. The steady state concentration of the species M is given by;
\[ [M] = k_1 [N][XCN]/k_2[M] \]
\[ = k_1[XCN]/k_2 \]

The rate expression for the formation of the excited CN radical is:
\[ d([CN^\ast])/dt = k_2[M][N] \]
\[ = k_1[M][XCN] \]

Thus, to a first approximation, the CN emission should be directly proportional to the nitrogen atom concentration. Similarly, if the CN radical is excited by a termolecular mechanism, the CN emission would be proportional to the square of the nitrogen atom concentration.

The dependence of the intensity of the CN emission on the nitrogen atom concentration was determined for the iodine cyanide reaction for two of the CN violet bands; one from the \( P_1' \) group, and the other from the \( P_2' \) group. No significant difference between the variation of the intensities of these two bands was observed.

The graphs of the logarithm of the intensity of the CN emission against half the logarithm of the afterglow emission intensity, were curved; concave upwards close to the inlet jet, and concave down at a distance from the inlet jet (fig. 1). These effects could be attributed to the varying speed of the reaction, depending on the nitrogen atom concentration. Close to the inlet jet, with low concentrations of nitrogen atoms, the reactions were slow so that they had not taken place to any extent in the part of the reaction tube preceding the point of observation, and so the emission was low, with the flame front quite a distance down the reaction tube. As the nitrogen atom concentration was increased, the flame front brightened and moved up the reaction tube.
towards the inlet jet, but it was only with substantial increases in the nitrogen atom concentration that the flame front approached the observation area and the CN emission increased.

When the observation area was a large distance down the reaction tube from the inlet jet, the increasing brightness of the flame front with increasing nitrogen atom concentration increased the CN emission, but as the flame front passed the observation area, the CN emission tended to become constant and, when measurements could be continued for long enough, started to decline.

The gradients of these graphs were about unity when the excitation reaction was taking place close to the observation area. This could be interpreted as implying that the excitation of the CN emission requires only one nitrogen atom and so must be bimolecular and not termolecular. Although the CN emission appeared to vary in the same manner for bands representative of both the $P_{1}'$ and $P_{2}'$ groups of CN emission bands, this need not imply that only one reaction mechanism was occurring, and exciting both groups of bands. Bayes has shown that the CN bands from the reaction of cyanogen chlorides and bromide are excited by two different mechanisms, and the rate expression derived earlier shows that the two different mechanisms postulated lead to the same nitrogen atom dependencies for the CN emission.

The number of possible reactions for the reaction of the cyanogen halides is limited as shown earlier, and so it could be considered that the CN emission arises predominantly from the two mechanisms involving
the NCN and CX intermediates. It could be considered further that the intermediate NCN, in its reaction with nitrogen atoms, gives rise to the $P_1'$ group of emission bands, and the intermediate CX radical, in its reaction with nitrogen atoms, gives rise to the $P_2$ group of emission bands of CN. Radford and Broida have shown that the lowest vibrational levels of the B state of CN can be populated from the higher vibrational levels of the A state giving the $P_2'$ emission. The connection between the $P_1'$ and $P_1$ emission groups and the excitation of the tail band emission is not yet clear.

If this theory is true, then it would be expected that the intensity of the CN emission would be proportional to the concentration of the intermediates NCN and CX. Although no investigation of this has yet been undertaken for any one particular reaction, a qualitative comparison has been made of the ratios of the intensities of the CN emission and the intensities of the emission of the species CX and NCN for a number of reactions. This work has shown that there is little correlation between the intensities of these emissions. The CCl and NCN bands observed correspond to an excitation of about 90 kcals per mole which is considerably more energy than is available from the initial reaction forming the CX and NCN species, hence these emitters must be receiving excitation energy by some other means. A probable source of energy would be a termolecular reaction of nitrogen atoms, but it is possible that the excited NCN and CX molecules are formed directly in some other side reaction that does not play a major part in the overall reaction. Thus, it is unlikely that the emission of the NCN and CX
molecules would be proportional to the concentrations of the respective ground state molecules.

The excitation mechanism involving the intermediate CX serves to explain the results of a number of earlier workers on the reaction of halogenated hydrocarbons. The effects of different halogens on the spectral distribution of the CN emission have been noted since the earliest investigation by Strutt. Kiess and Broida, in a detailed investigation, found that the substitution of heavier halogens increased the "vibrational temperature" of the A state of CN, i.e. decreased the relative population of the lower vibrational levels. This effect involves only the population of the P₂ group of vibrational levels, and so cannot be explained by considering variations of the ratios of the P₁ and P₂ vibrational level populations. It also cannot be explained by an excitation mechanism involving the formation and termolecular excitation of the CN by nitrogen atoms as two separate steps, or by the reaction of nitrogen atoms with NCN as proposed by Bayes. In the theory presented in this discussion, the variation can be attributed to the reaction of nitrogen atoms with the intermediate CX radical becoming more exothermic as the halogen atom becomes heavier. This would allow more energy for exciting the CN, which could then be excited to higher vibrational levels to the detriment of the populations of the lower vibrational levels.

The two reactions which give the intermediate NCN and CX take place concurrently, and so are in competition. The reaction producing NCN involves the breaking of the halogen-carbon bond in the cyanogen halide,
and so its rate should be dependent on the nature of the halogen present. Conversely, the rate of the reaction that gives the CX radical involves the breaking of the carbon-nitrogen bond, which should be almost independent of the halogen. Thus, the ratio of the \( P_2 \) emission from the reaction of CX, to the \( P_1 \) emission from the reaction of NCN, should decrease as the halogen changes from chlorine, through bromine to iodine.

This general trend appears in Table 2, for the CN violet system, when the results for iodine cyanide are compared with those of the other two cyanogen halides. The results for the cyanogen chloride and bromide are about the same, indicating that some other effect, possibly a difference in the reaction conditions was present. This trend has also been observed by Bayes\(^7\) who, from a study of the emission from individual vibrational levels of the A state of CN, found that the cyanogen bromide reaction gave a lower ratio of \( P_2 \) emission to \( P_1 \) emission to that from the reaction of cyanogen chloride, although the difference was not great.

To conclude, a summary of the basic points of the theory derived in this discussion for the excitation of the CN radical produced in the reaction of active nitrogen with the cyanogen halides, will now be given. The initial reaction of nitrogen atoms with the cyanogen halides is bimolecular. The only two bimolecular reactions that are exothermic are those giving rise to the NCN and CX species. These species can react with nitrogen atoms producing excited CN radicals, and the following reaction mechanisms are obtained.
1). \[ N + XCN \rightarrow NCN + X \]
\[ N + NCN \rightarrow N_2 + CN^* \]

A consideration of the selection rules governing the second reaction\(^{23}\) show that the excited CN is probably formed in the B state with sufficient energy to account for most of the \(P_1\)' emission.

2). \[ N + XCN \rightarrow N_2 + CX \]
\[ N + CX \rightarrow X + CN^* \]

The form of the potential curves leads to the prediction that the excited CN would be formed in the A state with sufficient energy to account for all of the \(P_2\) emission. Other excitation reactions, including a termolecular reaction of unexcited CN radicals with nitrogen atoms could also occur to explain the high energies of the excited CN radicals producing the higher tail bands, but it is unlikely that such reactions are important otherwise.
CONCLUSION.

The excitation mechanism for the reaction of active nitrogen with the cyanogen halides suggested in the discussion, appears to fit the results given in this thesis. Certain other aspects of the CN emission that had not been explained well by other theories could also be explained, but a considerable amount of work remains to be done before the theory could be considered of universal application to cover all CN emission reactions.

Suggestions for further work, although not in order of importance, include a determination and evaluation of the rate constants of the reactions of the other cyanogen halides to ascertain whether the effects of the two competing reactions, forming NCN and CX, can be separated. An investigation of the CH radical to see if it could be included along with the CX radicals in the $P_2$ excitation mechanism. A comprehensive determination of the nitrogen atom dependence of CN emission for all accessible bands and all possible organic reactants, especially to determine how the tail bands receive their large excitation energies.

Finally, the connection between the $P_1$ vibrational levels of the $A$ state of CN, and the $P_1'$ levels of the $B$ state, although important, has not yet been investigated thoroughly.
A paper that has some relevance to the discussion has been published very recently and will now be reviewed. Brodina and coworkers (1967) investigated the population distribution amongst some of the vibrational and rotational levels of the A and B states of CN, resulting from the reaction of active nitrogen with organic compounds which included cyanogen, cyanogen bromide, and methyl cyanide, over a range of pressures from 0.013 to 100 torr. They found that the populations of the A and B states of CN could be separated into the $P_1$ and $P_2$ groups as proposed by Bayes, and Setser and Thrush, although they proposed some minor modifications to the vibrational levels populated by each group. In addition, they placed the higher vibrational levels of each state (along with some of the population of the lower levels) into a third group; the $P_3$ and $P_3'$ groups of levels. These $P_3$ groups populated levels up to at least $v' = 24$ of the A state and $v' = 15$ of the B state and so would include the tail bands of the violet system of CN.

To populate the $P_1$ and $P_1'$ groups (those arising predominantly from cyanogen and its derivatives) they proposed the reaction:

$$N + N + YCN \rightarrow CN^* + N_2(X) + Y$$

where the $CN^*$ is formed either in the A or B states and Y is CN, Br, or $CH_3$ for their reactions. They concluded that the reaction of cyanogen bromide would be about 136 kcal per mole exothermic (about the same as the reaction between nitrogen atoms and NCO discussed in this thesis).
which would be sufficient to excite the \( \text{CN} \) up to the vibrational level \( v' = 10 \) of the \( B \) state. They also considered that kinetically similar reactions of the cyanogen derivatives with excited nitrogen molecules formed in the normal termolecular nitrogen atom recombination (\(^5\Sigma^+ \) and \( B^3\Pi \)) could be the excitation process involved. The possibility of these reactions occurring was considered in the discussion of this thesis and was ruled out, mainly on the grounds that the intensities of the \( \text{CN} \) bands studied (Chapter 4) varied with respect to the nitrogen atom concentration and not with respect to the square of the nitrogen atom concentration.

They considered that the \( P_2 \) levels were populated by the mechanism proposed by Setser and Thrush\(^76\), \(^83\), and considered in this thesis, where nitrogen atoms react with \( \text{C}_X \) radicals formed in the reaction. Because the \( P_3 \) and \( P_3' \) groups required large excitation energies, they postulated a termolecular reaction between nitrogen atoms and unexcited \( \text{CN} \) radicals. This reaction was considered in passing in the discussion of this thesis, but no kinetic data has yet been obtained to justify this postulation.
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APPENDIX A.

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FIGURE 6.

Reaction Vessel used in Chapter 2.
Reaction Vessel used in Chapter 3.

Trap-type Saturator.

N₂

Microwave Discharge

ICN

Quartz Window

N₂ / Reactant

Trap and Pump

Ground Glass Joints

Reactant

Glass Wool Plug

Scale 1:4.
Reaction Vessel used in Chapter 4.
**FIGURE 11.**
Schematic Diagram of Flow Systems used.

\[ \text{N}_2 \rightarrow P \rightarrow X \rightarrow D \rightarrow N \rightarrow F \rightarrow X \rightarrow S \rightarrow X \rightarrow \text{Reaction Vessel} \]

\[ \text{O}_2 \rightarrow P \rightarrow T \rightarrow N \rightarrow F \rightarrow \text{Pump} \]

\[ \text{NO} \rightarrow X \rightarrow T \rightarrow X \rightarrow N \rightarrow F \rightarrow X \rightarrow S \]

**KEY**

- \( P \) Pressure Regulator
- \( D \) De-oxygenator
- \( N \) Needle Valve
- \( F \) Flowmeter
- \( S \) Saturator
- \( T \) Trap
- \( S \) 5 litre Storage Vessel
- \( X \) Tap
FIGURE 12
Variations of Logarithmic Decays with Time.
(from P. 30) \[ [I_2] = 3.4 \times 10^{-2} \text{ torr.} \]

No Oxygen

\[
\log_{10} \frac{L_{\text{blue}}}{L_{\text{blue, initial}}} = 11 \times 10^{-2} \text{ torr.}
\]

No Oxygen

\[
\log_{10} \frac{[I]}{[I, \text{ initial}]} = 11 \times 10^{-2} \text{ torr.}
\]

Gm. down reaction tube from inlet jet.
Gradients of Logarithmic Decays (from P. 30).

\[
\frac{d \log_{10}[N]}{dt} = \frac{d \log_{10}[I_{\text{blue}}]}{dt}
\]

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<tr>
<th>([O_2])</th>
<th>([I_2])</th>
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<td>19.7 9.5</td>
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<td>0.66</td>
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<td>37.1 12.4</td>
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<tr>
<td></td>
<td>45.6 8.9</td>
<td>35.2 0.5</td>
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</tbody>
</table>

\[x 10^{-2} \text{ torr. sec}^{-1}\]

For the effect of nitrous oxide, the identity:

\[d \ln k_1/dt - d \ln B/dt = d (\ln A - \ln B)/dt\]

where A and B are functions of t was used and the differences were calculated directly and are given in the relevant tables (5 and 6).

Typical curves of these differences are given in Figure 13.
Variations of Logarithmic Differences with Time.

(from P. 31) \[ [I_2] = 10.5 \times 10^{-3} \text{ torr.} \]
\[ [\text{N}_2O] = 17 \times 10^{-2} \text{ torr.} \]

Nitrogen Atom

I_{blue} Emission

ca. down reaction tube from inlet jet.
APPENDIX B.  SUMMARY OF REVIEW IN PART I.

The mechanism of the reaction between nitrogen atoms and halogen molecules appeared to have been successfully elucidated when, in 1961, Hilton et al. published a mechanism for the bromine reaction. An attempt to confirm this mechanism by Freeman and Phillips for the iodine reaction brought to light some anomalies that could not be accounted for by the simple mechanism. To explain these anomalies, they extended the earlier mechanism to include the formation and reaction of a metastable nitrogen molecule which was thought to have acted as an energy carrier. They also presented evidence to show that the identity of this species was the $A$ state of nitrogen.

Raxworthy and Phillips found that Hilton's mechanism held for the reactions of bromine and chlorine and that there was no evidence of the formation of any excited molecular states of nitrogen in the reaction of active nitrogen with these reactants. On the basis of the energy that the excited nitrogen molecule would have to have to be formed in the iodine reaction but not in the bromine and chlorine reactions, its identity was tentatively assigned as the $^3\Delta_u$ state of nitrogen and not the $A$ state of nitrogen.

Further studies on the reaction by Phillips established the lifetime of the metastable nitrogen molecules, but his interpretation of the experimental results used to arrive at this lifetime was criticized by Young. A number of attempts to detect the presence of $A$ state nitrogen molecules in this reaction and in active nitrogen alone have shown that its concentration would be too low for it to
take any significant part in the reactions. Recent work on the reaction of active nitrogen with iodine has been mainly concerned with establishing the identity of the excited nitrogen molecules involved. At the end of 1967, the little known $^3\Delta_u$ state of nitrogen was favoured but positive identification had not been made.

The experimental work carried out for this part of the thesis was initially to isolate the excited nitrogen molecules thought to be formed in the reaction of active nitrogen with iodine, and when this proved unsuccessful, to detect their influence on the course of other reactions; an experiment that also failed to give positive results. As this failure to detect the presence of any excited nitrogen molecules could be attributed to the apparatus and methods of detection, no statement could be made as to the existence or non-existence of any excited nitrogen molecules. It is, therefore, worth examining the evidence for their existence in the reaction of active nitrogen with iodine.

The present evidence appears to be based on the division of the reaction flame into two distinct zones, each of which has its own characteristic banded iodine emission$^{13}$, and on the dependence of the various atomic iodine lines on the nitrogen atom concentration, which was assumed to set the energy of the excited nitrogen molecules as 185 kca/s per mole$^{16}$. Sufficient doubt has been cast on evidence based on lifetimes and rate constants$^{15}$ to preclude its use.

The evidence proposed by Phillips and coworkers to explain this evidence is as follows:
It was thought that the iodine atoms produced in the first two reactions would recombine to give excited iodine molecules, leading to the molecular iodine emission of the first zone while the molecular iodine emission of the second zone would arise from the excited iodine molecules produced in the third reaction. Excited iodine atoms would be produced by collisions between free iodine atoms arising from the first two reactions, and the excited nitrogen molecules.

Alternative mechanisms would also appear to explain the above evidence as, for example, a mechanism based on Milton's mechanism for the bromine reaction:

\[
N + I_2 \rightarrow NI + I
\]

\[
N + NI \rightarrow N_2 + I
\]

where in this case, the nitrogen molecules are formed in the ground state. Since the iodine atoms formed in each reaction would probably have different energies, it would be expected that the iodine molecules produced from the recombination of these atoms would also have different energies and hence, different emission. If the intermediate NI has a lifetime of several milliseconds, then the two reactions, and hence the two different iodine emissions, would take place in different regions of the reaction flame giving rise to the two distinct zones observed. The iodine atoms produced in the second reaction could have sufficient
energy to account for the various atomic iodine lines observed provided the heat of formation of NI was about 98 kcais per mole. This corresponds to a dissociation energy for NI of 41 kcais per mole, and although not yet determined experimentally, it would not appear unreasonable as the dissociation energy of NBr has been given as $68 \pm 5$ kcais per mole\textsuperscript{28}.

This mechanism is kinetically similar to that advanced by Phillips but there is yet insufficient evidence to make a choice between them on the basis of kinetic results. The main evidence for preference of any mechanism is expected to arise from the determination of the species present in the reaction system.