THE REACTIONS OF ACTIVE NITROGEN WITH BORON TRICHLORIDE, GERMANIUM TETRACHLORIDE, AND GERMANE

by

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INTRODUCTION

During the latter years of the nineteenth century, it was observed that when some gases, or mixtures of gases, were excited by an electrodeless discharge, a luminescence or afterglow with a continuous spectrum was produced. In 1900, Lewis (1) reported that nitrogen subjected to a condensed discharge gave an afterglow different from those previously obtained from other gases. He described it as a "rich chamois yellow fog". It lasted for several seconds after the discharge had been turned off, and its spectrum consisted of narrow bands.

Several years later, Strutt (2), who later became Lord Rayleigh, observed that the spectra of elements and compounds excited in the presence of the yellow nitrogen were the same as those produced by other methods. He also discovered that the glowing gas reacted with metals to form nitrides, and referred to the gas as "active nitrogen". He believed that atoms formed in the discharge were the reactive species in active nitrogen.

When studying the afterglow of active nitrogen, Lewis (1) noted that the intensity varied with the presence of impurities. Trace amounts of oxygen or oxygen-containing compounds, such as water, appeared to be necessary to produce the afterglow, but larger amounts destroyed it. Tiede and Domcke (3) agreed with this view. With pure nitrogen they observed little afterglow, but when oxygen was added to the system, the afterglow became quite intense. From this, they concluded that the afterglow was caused by the oxygen present and not by an active species of nitrogen. However, Baker and Strutt (4) showed that under their conditions the afterglow could be seen even with pure nitrogen. Lewis (5) suggested that impurities form a layer of gas on the walls of the tube which prevents recombination of atoms on the surface. Since there is then more recombination in the gas phase, the afterglow is enhanced. This suggestion was supported by the observation that when the vessel was heated for a long time, no afterglow appeared. Rayleigh's experiments (6) gave similar results. He found that the oxygen apparently did not take part in producing the afterglow, but only conditioned the walls. To increase the intensity of the afterglow, the walls of the vessel may be poisoned by certain substances, such as phosphoric or sulphuric acid, while other materials, such as Apiezon oil, have the reverse effect.

The result of passing active nitrogen between two electrodes indicated high electrical conductivity in the gas. Constantinides (7) found that the ion current as a function of the plate potential followed Ohm's Law up to the saturation potential, but that an increase in the ion current occurred near the ionization potential of nitrogen. He found the saturation current to be proportional to the area of the cathode, and that, between electrodes external to the discharge tube, the current remained constant when the potential between the first pair was increased from 0 to 250 volts. He concluded, therefore, that ions from the discharge could not account for the conductivity of the gas, and that the electrons emitted from the electrodes photoelectrically, or by the action of active nitrogen on the metal, caused the current. Using a hot cathode, Rayleigh (8) found that the saturation current decreased when he expected it to increase. Because of this, he thought that there were positive ions present. However, Benson (9) was unable to detect positive ions in active nitrogen, and concluded that electrons, the concentration of which was less than 10^{-6} that of the active species, were the charged particles responsible for the ion current.

Another unusual property of active nitrogen, studied by Rayleigh in 1911 (10), was a negative temperature coefficient associated with the process responsible for the afterglow. He found that the intensity of the afterglow was proportional to $T^{-0.64}$ where T is the absolute temperature. Debeau (11) noted that when part of a vessel containing discharged nitrogen was immersed in liquid air, the afterglow increased in intensity and then disappeared. As the vessel was warmed up, the afterglow reappeared at the cool surface first, and then spread throughout the vessel. If the afterglow were destroyed completely by heating, the gas still remained chemically reactive (12). Kaplan and Cario (13) found that this "dark modification" could excite sodium D lines in the spectrum. In contrast to Rayleigh, Back et al. (14) have recently observed a slight positive temperature coefficient in the homogeneous decay of active nitrogen over a temperature range up to about 1000°C.

NATURE OF ACTIVE NITROGEN

Several theories about the nature of active nitrogen have been proposed, but no definite conclusion has yet been reached. The number and kind of chemically active constituents and the exact mechanism for producing the afterglow are still in doubt.

Strutt (2) considered the reactive species of active nitrogen to be nitrogen atoms. Sponer (15) agreed with him and suggested a mechanism for the emission of the afterglow,

$$N + N + M \longrightarrow M + N_2^{**}$$

$$N_2^{**} \longrightarrow N_2 + h\nu$$

This would explain the long life of the afterglow (because three-body collisions are rare), but not the different intensities of various vibrational bands or the electrical properties. Birge (16) and Herzberg (17) supported Sponer's theory, but Bonhoeffer and Kaminsky (18) claimed that there were no triple collisions.

Trautz (19) also believed atoms to be present. He proposed a mechanism for the production of the afterglow which included triatomic nitrogen as one of the species present, although Strutt (2) had shown that nothing analogous to ozone could be condensed in liquid air. Recently Peyron et al. (20) discovered N_3 in the solid condensed by liquid helium from discharged nitrogen, but this appeared to be weakly bound N_2 --- N, probably formed in the solid phase, and not similar to ozone.

Several workers (21 - 24) have shown that atoms are present in active nitrogen and probably take part in the process which emits the afterglow. The question remains, however, whether the atoms are in the ground state or in an excited state.

Kaplan and Cario (25) suggested that the atoms in active nitrogen were in a metastable state, being formed by dissociation of an excited molecule which had been formed from two atoms, or by the dissociation of one excited molecule when it collided with another. A collision between an excited atom and a molecule in the A state could provide just enough energy for a molecule in the twelfth vibrational level of the B state. (See energy diagram, Figure 1.) This would account for the high intensity of the band of that level in the spectrum of the afterglow. The B state might then revert to the A state to produce the afterglow,

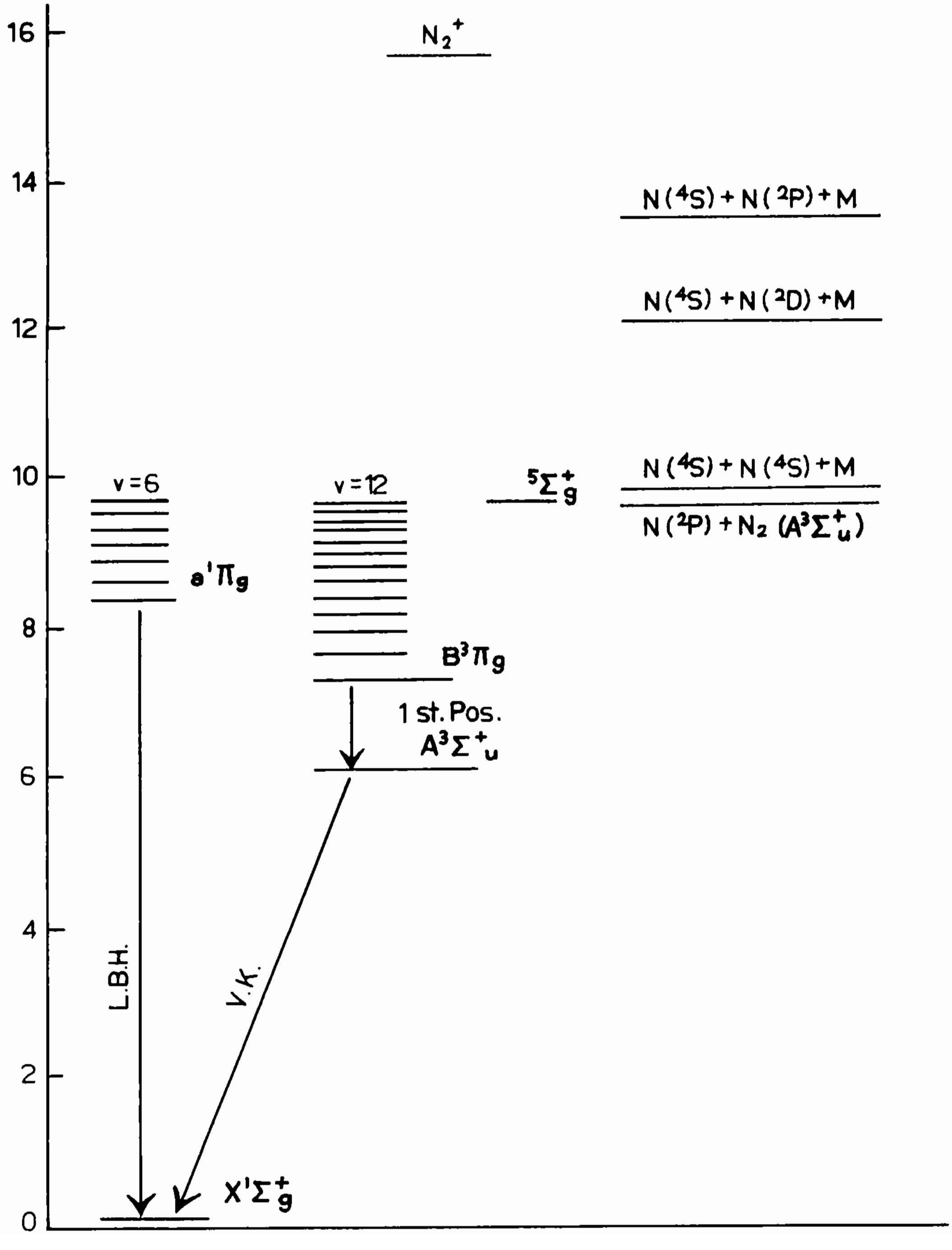
$$N\ ({}^2P) + N_2\ (A^3\Sigma_u^+) \longrightarrow N_2\ (B^3\Pi_g) + N\ ({}^4S)$$

$$N_2\ (B^3\Pi_g) \longrightarrow N_2\ (A^3\Sigma_u^+) + hv$$

A Stern-Gerlach experiment made by Jackson and Broadway (24) supported this theory. They observed brown traces on a silver nitrate screen when a narrow beam of discharged nitrogen hit the target. From the difference between the width of those traces and the traces obtained when the nitrogen beam was passed through a nonhomogeneous magnetic field, they concluded that metastable ^2P atoms were present

FIGURE 1

Energy Levels of Nitrogen Relative to the
Energy of the Ground State Molecules


16
14
12
10
8
6
4
2
0
N2+
N(4S) + N(2P) + M
N(4S) + N(2D) + M
N(4S) + N(4S) + M
N(2P) + N2 (A3Σ+u)
5Σ+g
v = 6
a'Πg
v = 12
B3Πg
1 st. Pos.
A3Σ+u
L.B.H.
V.K.
X'Σ+g

in active nitrogen. On the other hand, Herbert et al. (26) found no evidence for metastable atoms; their concentration was, perhaps, too small to be detected by the vacuum ultraviolet absorption method used. Also, Worley (27) and Frost and Oldenberg (28) did not observe any absorption due to the metastable $A^3\Sigma$ state of the molecule, indicting a low steady-state concentration of molecules in this energy state. The lifetime of the A state, estimated by Lichten (29) to be one tenth of a second, is much too short to account for an afterglow of long duration produced according to the mechanism suggested by Kaplan and Cario (25), involving, as this does, a collision between an $A^3\Sigma_u^+$ state molecule and a ^2P atom.

Because of the electrical conductivity of active nitrogen, Mitra (30) suggested that the active species was a mixture of N_2^+ ions and electrons, and that the long life of the afterglow was due to a three-body collision,

$$N_2^+ + e + N_2 \longrightarrow N_2\ (B^3\Pi_g) + N_2\ (A^3\Sigma_u^+)$$

$$N_2\ (B^3\Pi_g) \longrightarrow N_2\ (A^3\Sigma_u^+) + hv$$

In the first step of the mechanism, there is an energy deficiency of 0.27 ev which Mitra thought could be made up by kinetic energy. Worley (27) supplied evidence against Mitra's theory when he found no absorption by N_2^+ ions, while Benson (9) verified Strutt's results that the removal of charged particles did not affect the afterglow or activity of the gas, and also showed that a magnetic field did not deflect a beam of the glowing gas. Since the concentration of electrons determined by Benson was 10^{-6} that of the active species, it was impossible for the behaviour of active nitrogen to be ascribed to a mixture of N_2^+ ions and electrons.

In 1953, Mitra (31) revised his theory, but again included ions in the mechanism. He suggested that the active species consisted of ^2D or ^2P metastable atoms formed by the dissociative recombination of an electron and a N_2^+ ion formed in the discharge.

$$N_2^+ + e \longrightarrow N\,(^2D) + N\,(^2P)$$

Since the ^2D atom has a relatively long life, it does not drop to the ground state, but the line for the transition $^2P \longrightarrow {}^4S$ may be observed in the spectrum of the discharge. Mitra was able to explain the properties of active nitrogen using this theory, but it was not generally accepted.

The most popular theory at present is that ground state atoms are the active species in active nitrogen. As mentioned previously, the presence of atoms has been demonstrated by many workers. Wrede (22) allowed active nitrogen to diffuse through a small orifice and obtained a pressure differential, from which he was able to calculate the atom concentration. Debeau (11) assumed that his observations on destruction of the afterglow by heat, and its regeneration at a cool surface, were due to the presence of atoms, but no accurate quantitative measurments were possible in his studies.

The paramagnetic resonance spectrum of active nitrogen recorded by Heald and Beringer (32) showed the presence of ground state atoms and molecules only. However, up to 1% of the total nitrogen atom concentration might consist of excited atoms which could not be detected. This spectrum was the first definite proof of the state of the atoms. Two recent mass spectrometric investigations of active nitrogen by Jackson and Schiff (33) and Berkowitz, Chupka, and Kistiakowsky (34) have confirmed Heald and Beringer's results.

The present theory of the production of the afterglow in active nitrogen assumes that ground state atoms unite to give a quintet state of the molecule, which may then undergo different transitions, as follows:

$$\begin{tikzcd}[column sep=small]
 & & a^1\Pi_g \arrow[r] & X^1\Sigma_g^+ \\
 & & \text{Lyman-Birge-Hopfield Bands} & \\
N\,(^4S) + N\,(^4S) + M \arrow[r] & N_2(^5\Sigma_g^+) \arrow[uur] \arrow[r] \arrow[ddr] & B^3\Pi_g \arrow[r] & A^3\Sigma_u^+ \\
 & & \text{First Positive Bands} & \\
 & & Y\text{ state} \arrow[r] & Z\text{ state} \\
 & & \text{Proposed New Bands} &
\end{tikzcd}$$

A three-body collision is assumed to produce the weakly bound nitrogen molecule in the $^5\Sigma_g^+$ state, which has been observed spectroscopically by Herzfeld and Broida (35-37). The three suggested transitions give rise to different bands in the afterglow spectrum. Herzberg (38) observed the Lyman-Birge-Hopfield bands in the vacuum ultraviolet region for vibrational levels of the B state lower than v' = 6. Of the First Positive system, selected bands are enhanced. They are of transitions from vibrational levels v' = 12, 11, 10 and, less intense, 6, 4, 3 and 2. Kistiakowsky and Warneck (39) have suggested that the weaker bands do not belong to the First Positive system, but are produced by a transition from an unknown state, Y, to another unknown state, Z. Further studies of these bands by LeBlanc et al. (40) and Bayes and Kistiakowsky (41) have indicated that the Y state is probably $^3\Delta_u$, or, less likely, $^3\Sigma_u^-$, and is formed by a radiationless transition from the $^5\Sigma_g^+$ state. The Z state is believed to be the $B^3\Pi_g$ state. The transition from the $A^3\Sigma_u^+$ state to the ground state produces the Vegard-Kaplan bands. When these bands were discovered (42), the relative energies of the singlet and triplet states were fixed. Recently Beale and Broida (43) have observed these bands in a pinkish glow, immediately preceded and followed by the usual yellow afterglow.

The mechanism outlined above is in accordance with the fact that the decay of active nitrogen is termolecular, but bimolecular in respect of the active species, nitrogen atoms. The order of the reaction has been known for a long time (44, 45), and recent mass spectrometric work by Berkowitz et al. (34) has confirmed it.

The rate of recombination of nitrogen atoms has been studied lately, and several values for the rate constant have been recorded. Wentink et al. (46), by measuring the rate of decrease of the afterglow intensity with a photomultiplier, obtained a value of 1.2 x 10^{16} cm. ^{6}/mole ^{2}/sec. The rate constant determined mass spectrometrically by Herron et al. (47) was 5.7 x 10^{15} cm./mole ^{2}/sec. Harteck et al. (48) determined the absolute nitrogen atom concentration at one point, and then, with a photomultiplier, followed the decrease in the intensity of the afterglow down the tube. Their value of the rate constant calculated from this information was 1.7 x 10^{-32} cm. ^{6}/molecule ^{2}/sec. Kelly and Winkler (49) found a value varying from 1.09 x 10^{-33} to 13.2 x 10^{-33} cm. ^{6}/molecule ^{2}/sec., depending on the temperature. This was contrary to the conculsion of Herron et al. (47) that there was no temperature dependence of the rate constant between 200 and 450° K.

ENERGY OF ACTIVE NITROGEN

Not only has the nature of active nitrogen been disputed for years, but also the value of its energy.

Strutt (2) believed that active nitrogen, although atomic, did not contain a large amount of energy. He found that the temperature rise of a copper probe in the gas alone was similar to that of a probe in the gas which had reacted with nitric oxide.

From the reaction with nitric oxide, Willey and Rideal (50) concluded that the energy of active nitrogen, which they believed to consist of metastable molecules, was about 2 ev/ mole of total nitrogen.

Rudy (45) obtained a value of 11 ev, and Saha and Sur (51) a value of 8.5 ev for the energy of the active species which they, too, thought to be metastable molecules.

Birge and Sponer (52) considered the energy of active nitrogen to be the dissociation energy of nitrogen. From the value of the eleventh vibrational level of the B state of the molecule, they found it to be 11.4 ev, which agreed with the spectroscopic value of 11.9 ev. By measuring the temperature increase of metal foil in a stream of active nitrogen, Rayleigh (53) obtained a much higher value of 12.9 ev/ mole of total nitrogen. However, it was shown later by Benson (11) that much of the heating was due to electron bombardment.

The energy of active nitrogen and the dissociation energy of nitrogen are now considered to be the same. The most contested values for the dissociation energy were 7.38, 8.57, 9.76, and 11.8 ev. Gaydon (54) suggested that the true value was 9.76 ev, and this is now generally accepted. The results of Kistiakowsky, Knight and Malin (55), Douglas (56), Thomas, Gaydon, and Brewer (57), Brook and Kaplan (58), Christian, Duff, and Yarger (59), and Toennies and Greene (60), based on a variety of experimental techniques including shock wave (59, 60) and spectroscopic (56, 57) studies, all support this value.

In a discussion of the two more acceptable vaules, 7.38 and 9.76 ev, Martin, Harnisch, and Pohl (61) concluded that the higher value was more reasonable.

Hendrie (62) heated nitrogen at a pressure of about 1 mm. of Hg to a temperature of 3450° K. in a tungsten furnace. Under these conditions, there should be 20% dissociation of nitrogen for a dissociation energy of 7.385 ev, but only 0.5% dissociation if the dissociation energy were 9.765 ev. Since no dissociation was detected, he concluded that 7.385 ev was not the correct value, and was able to set a lower limit of 8.80 ev for the dissociation energy of nitrogen. Later, Herzfeld and Broida (35) obtained a lower limit of 9.632 ev from spectroscopic studies of the solid condensed by liquid helium from discharged nitrogen.

CHEMICAL PROPERTIES OF ACTIVE NITROGEN

In early work on active nitrogen reactions, only qualitative observations were made. The emission by metals placed in the glowing gas and the spectra of other substances introduced into the gas were studied. Strutt (2) found that nitrides were formed when active nitrogen was mixed with the vapours of many metals and those of some non-metals. The spectrum of the flame resulting from the reactions of active nitrogen with organic compounds showed the red and violet CN bands very intensely. Inorganic compounds, on the other hand, gave spectra that showed little in common with one another.

During the past fifteen years, extensive quantitative studies of active nitrogen reactions have been undertaken.

Reactions with Organic Compounds

Although the present study is concerned with reactions of active nitrogen with inorganic molecules, a brief review of studies made with organic molecules will be given, since such studies have provided considerable information about the behaviour of active nitrogen.

The majority of organic compounds react with active nitrogen to form hydrogen cyanide as a main product. From alkyl chlorides, hydrogen chloride is also obtained as a major product, while some cyanogen and small amounts of hydrocarbons are generally formed from all organic reactants. Formation of a polymer containing nitrogen sometimes occurs, particularly at low temperatures. The extent of polymer formation is very variable, from traces only to relatively large amounts, and the same may be said of ammonia production (63). Nelson et al. (64) have recently measured the yield of ammonia from ethylene, ethane, n-butane, and butene-2, and found it to pass through a maximum value at flow rates of reactant roughly equivalent to the active nitrogen concentration, while at high reactant flow rates ammonia production was never more than 2% of the maximum hydrogen cyanide production.

The reaction with ethylene was the first one to be studied thoroughly (65, 66). At high flow rates of ethylene, the amount of hydrogen cyanide recovered reached a constant value which increased with temperature up to about 300°C. Above that temperature it remained constant and approximated the nitrogen atom concentration obtained by Wrede gauge (22) measurements. This indicated complete consumption of the atoms, and led to the use of hydrogen cyanide production from ethylene at high temperatures as a measure of the atom concentration in active nitrogen. Recent work (64) has shown that the temperature dependence is a characteristic of the system. A cylindrical reaction vessel showed no variation in hydrogen cyanide production with temperature, but a spherical vessel did.

The mechanism suggested for the reaction involves a relatively long-lived complex of a nitrogen atom and an ethylene molecule,

$$N + C_2H_4 \longrightarrow N.C_2H_4$$

Hydrogen cyanide may be formed by decomposition of the complex,

$$N.C_2H_4 \longrightarrow HCN + CH_3$$

and by reaction of methyl radicals with a nitrogen atom,

$$N + CH_3 \longrightarrow HCN + 2H$$

Reaction of the complex with another nitrogen atom would lead to disruption of the organic molecule and possibly cyanogen or acetylene formation. Methane and ethane may be attributed to hydrogenation of methyl radicals or ethylene, respectively.

Methane was found to react with active nitrogen to a limited extent only at low temperatures (67, 68). However, above 250°C., the amount of hydrogen cyanide recovered increased rapidly with increase in methane flow rate. It is believed that hydrogen atoms may be formed by attack of two nitrogen atoms in successive collisions with methane, and these then react with methane to form methyl radicals which readily react with nitrogen atoms,

$$N + CH_4 \longrightarrow N.CH_4 \xrightarrow{N} CH_3 + H + N_2$$

$$H + CH_4 \longrightarrow CH_3 + H_2$$

$$CH_3 + N \longrightarrow HCN + 2H$$

In general, alkanes reacted with active nitrogen more slowly than did alkenes, while the rate of alkyl chloride reactions (69) was comparable with that of alkene reactions.

Reactions of many organic compounds with active nitrogen are reviewed by Evans, Freeman, and Winkler (70). A unified mechanism, exemplified by the reactions of C_3 hydrocarbons, is postulated to explain the result of these reactions. Two assumptions made are (a) that nitrogen atoms constitute the only reactive species in active nitrogen, and (b) that the collision complexes formed between propylene, propyl chloride or propane and a nitrogen atom are essentially the same.

$$N + C_3H_6 \longrightarrow N.C_3H_6$$

$$N + C_3H_7Cl \longrightarrow N.C_3H_6 + HCl$$

$$N + C_3H_8 \longrightarrow N.C_3H_6 + H_2$$

The stability of the complex may increase from propylene to propane and account for the different products obtained in the three reactions.

Unsaturated compounds could be formed from the complex in the following manner:

$$N + N.C_3H_6 \longrightarrow C_3H_6^* + N_2$$

$$C_3H_6^* \longrightarrow C_2H_4^* + CH_2$$

or

$$C_3H_6^* \longrightarrow C_2H_4 + CH_2^*$$

$$C_2H_4^* \longrightarrow C_2H_2^* + H_2$$

Hydrogen cyanide could be produced by any of the following reactions:

$$N.C_3H_6 \longrightarrow HCN + C_2H_5$$

$$N + C_2H_5 \longrightarrow HCN + H + CH_3$$

$$N + CH_3 \longrightarrow HCN + 2H$$

Most of the ethylene formed in the reaction of propylene with active nitrogen may come from the decomposition of the C_2H_5 radical,

$$C_2H_5 \longrightarrow C_2H_4 + H$$

The extent of such a reaction with propyl chloride or propane as original reactant would be very small because the radicals would not have enough energy to split off a hydrogen atom.

This unified mechanism may be adapted to most reactions, possibly with some modification, to give satisfactory explanations for the results obtained. The relatively small amounts of ammonia among the products indicate that hydrogen abstraction by a nitrogen atom is not significant, and it is certainly energetically unfavourable.

Reactions with Inorganic Compounds

Hydrogen: Willey and Rideal (71) were the first to report the absence of reaction between active nitrogen and molecular hydrogen. Lewis (72) and Kistiakowsky and Volpi (73) confirmed these results. However, they all found that atomic hydrogen reacted with active nitrogen to form ammonia. In his experiments with molecular hydrogen, Varney (74) did recover some ammonia, but this could be explained by back diffusion of the hydrogen into the discharge tube.

Hydrogen Halides: Among the reactions with active nitrogen studied by Willey and Rideal (71) were those involving the hydrogen halides. Hydrogen iodide and hydrogen bromide were found to decompose, but there was no apparent reaction with hydrogen chloride. Ewart and Rodebush (75) reported that hydrogen iodide gave a brillant blue flame and hydrogen bromide a bright orange one, but that hydrogen chloride only destroyed the afterglow. Ammonium bromide and bromine were found in the reaction with hydrogen bromide (75, 76).

Recent work by Wiles and Winkler (77) showed that some hydrogen chloride was destroyed by active nitrogen to produce chlorine. The maximum amount of decomposition was less than one-sixth of the nitrogen atom concentration. The suggested mechanism for the reaction involved catalytic recombination of nitrogen atoms,

$$N + HCl \longrightarrow N.HCl$$

$$N + N.HCl \longrightarrow N_2 + H + Cl$$

At high flow rates, the reaction might be

$$2\ N.HCl \longrightarrow HCl + H + Cl + N_2$$

Several back reactions were assumed, the most important being

$$H + Cl_2 \longrightarrow HCl + Cl$$

<u>Ammonia</u>: Willey and Rideal (71) found that ammonia decomposed easily in active nitrogen. Recently Freeman and Winkler (78) studied the reaction and found that nitrogen and hydrogen were the only products. The extent of decomposition corresponded to only about one-sixth the amount of reaction that occured with ethylene under comparable conditions, and appeared to be independent of temperature.

The explanation offered for these results is that there is a second reactive species in active nitrogen which reacts with ammonia but not with organic compounds. This species might be the vibrationally excited ground state molecules suggested by Evans and Winkler (79). Kistiakowsky and Volpi (73) supported the view that ammonia is decomposed by an excited nitrogen molecule (78). They found that ammonia decreased the intensity of the afterglow, but did not alter the nitrogen atom concentration. This suggests that the excited molecules are in the $B^3\Pi_g$ state. Kelly (80) showed that the second reactive species is probably formed by the decay of nitrogen atoms, but its exact nature is still unknown.

Nitrous Oxide: Kistiakowsky and Volpi (81) found no reaction between active nitrogen and nitrous oxide in the temperature range of 25° to 280°C. However, Nelson et al. (64) found a small amount of decomposition at room temperature, and more at high temperatures.

Nitric Oxide and Nitrogen Dioxide: Spealman and Rodebush (82) discovered that both nitric oxide and nitrogen dioxide react rapidly with active nitrogen. Further study of these reactions was made by Kistiakowsky and Volpi (81) and Verbeke and Winkler (83).

The primary reaction with nitric oxide appears to be

$$N + NO \longrightarrow N_2 + O$$

followed by a chain reaction involving oxygen atoms,

$$O + NO \longrightarrow NO_2^*$$

$$NO_2^* + M \longrightarrow NO_2 + M$$

$$O + NO_2 \longrightarrow NO + O_2$$

Verbeke and Winkler (83) found that, at 2 mm. of Hg pressure, the amount of nitric oxide destroyed was about 1.6 times the nitrogen atom concentration determined from the maximum amount of reaction with ethylene. As one possible explanation, they suggested the formation of a collision complex, N.NO, which might react with another nitric oxide molecule to regenerate the nitrogen atom,

$$NO + N.NO \longrightarrow N_2 + O_2 + N$$

However, no trace of nitrous oxide was found among the products, although some might have been expected from de-excitation of the N.NO complex. This suggestion was therefore rejected in favour of the view that a second reactive species, possibly vibrationally or electronically excited molecules might be present in active nitrogen, and be capable of causing the decomposition of nitric oxide,

$$N_2^* + NO \longrightarrow N_2 + N + O$$

An excited nitrogen molecule, in the fourth vibrational level of the $A^3\Sigma_u^+$ state, would have enough energy to dissociate the nitric oxide molecule. If this is the same species that also reacts with ammonia, the quenching of the afterglow in that reaction, reported by Kistiakowsky and Volpi (73), remains unexplained. The nature of a second, or even a third, reactive species in active nitrogen is still to be determined. However, Kaufman and Kelso (84) have shown that molecules in the first vibrationally excited level do exist in active nitrogen, and are probably formed in the discharge. Dressler (85) later confirmed these results by a study of the vacuum ultraviolet absorption spectrum of active nitrogen. These results give some support, perhaps, to the suggestion of Evans and Winkler (79) that vibrationally excited ground state molecules might represent a reactive species in active nitrogen.

There is more than one possible initial reaction between nitrogen dioxide and a nitrogen atom,

$$N + NO_2 \longrightarrow N_2O + O$$

$$N + NO_2 \longrightarrow N_2 + O_2 \qquad \text{(slow)}$$

$$N + NO_2 \longrightarrow 2NO$$

Oxygen atoms may then attack either a nitric oxide or a nitrogen dioxide molecule, as described for the nitric oxide-active nitrogen reaction, or a nitrogen dioxide molecule might react with an excited nitrogen molecule, the proposed second reactive species in active nitrogen,

$$N_2^* + NO_2 \longrightarrow N_2 + NO + O$$

Boron Trichloride: Jevons (86) observed the spectrum of the boron trichloride flame in active nitrogen. There were three intense bands which he showed to be due to BN. A white deposit on the walls gave a positive test for nitrogen.

Silicon Tetrachloride: In the reaction of silicon tetrachloride (87) with active nitrogen, chlorine and a white solid containing nitrogen were formed. SiN bands and unquenched afterglow bands were observed in the spectrum of the flame.

Silane: Recently Dewhurst (88) reacted silane with active nitrogen and recovered no condensable products. With methyl silanes, ammonia and hydrogen cyanide were formed. Experiments using CH_3SiD_3 showed that the ammonia was not formed by hydrogen abstraction from the silane molecule. The main ammonia product formed in the reaction,

NH_2D, indicates the intermediate in the formation of ammonia to be NH_2, formed from hydrogen atoms attached to the carbon atom.

Dewhurst suggested that the initial reaction might be

$$SiH_4 + N \longrightarrow SiH_3 + NH$$

The analogous reaction with methane is endothermic and therefore does not occur to a significant extent. It appears that the NH radical does not take part in ammonia formation, but either reacts with a nitrogen atom,

$$NH + N \longrightarrow N_2 + H$$

or disproportionates,

$$2\ NH \longrightarrow N_2 + H_2$$

Other Compounds: Several other inorganic compounds have been caused to react with active nitrogen, but the studies have been qualitative only, and have given no definite information about the nature of the reactive species in active nitrogen.

THE PRESENT PROBLEM

Reactions of organic compounds with active nitrogen can be explained by assuming that the reactive species is atomic nitrogen. However, it appears that not all inorganic reactions may be explained in the same way. It was thought, therefore, that further study of active nitrogen reactions with inorganic compounds might lead to a better understanding of the nature of active nitrogen.

It seemed possible that boron trichloride, being somewhat similar to ammonia although of different structure, might react with excited nitrogen molecules rather than atoms, and thus provide more information about the existence of a second reactive species.

When it was found that boron trichloride probably reacted with nitrogen atoms, but apparently only to a very limited extent, experiments were made with germanium tetrachloride. This compound seemed to react even less than boron trichloride and study of it was abandoned in favour of germane, which was found to behave more satisfactorily.

EXPERIMENTAL

MATERIALS

Nitrogen, 99.9% pure, was obtained from the Linde Company. To remove traces of water, the gas was passed through a trap immersed in liquid air.

Ethylene, 99% pure, was obtained from the Ohio Chemical Company. It was purified by degassing at liquid air temperature to remove any non-condensable gases, followed by a bulb-to-bulb distillation in which only the middle portion of the distillate was kept.

Nitric oxide was obtained from the Matheson Company, and was purified by distilling it from a trap surrounded by a dry ice-acetone bath and condensing it with liquid nitrogen.

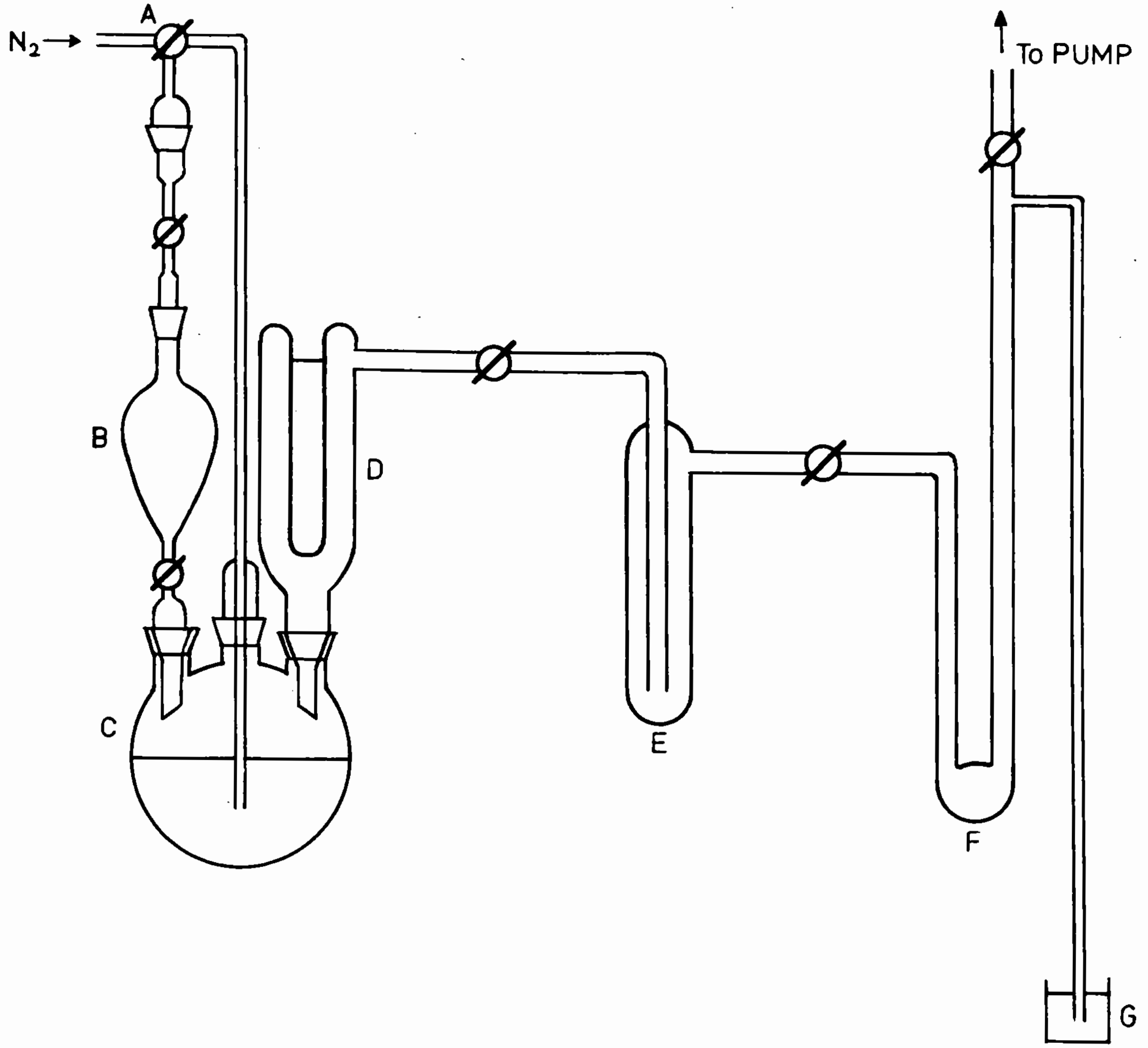
Boron trichloride was obtained from the Matheson Company, and germanium tetachloride from Dow Corning Chemicals. Both were purified in the same manner as ethylene.

Germane was prepared in the laboratory (89). A mixture of five grams of germanium dioxide and 625 ml. of 1 M hydrogen bromide in a two-litre, three-necked flask was refluxed for six to eight hours. After most of the solid had dissolved, the flask was connected to the apparatus shown in Figure 2.

Air was excluded from the system by introducing nitrogen through a three-way stopcock, A, and allowing it to bubble through the reaction mixture and out through a mercury safety valve, G. A solution of 25 grams of sodium borohydride in 375 ml. of water was placed

FIGURE 2

Diagram of Apparatus for the Preparation
of Germane


N_2
A
B
C
D
E
F
G
To PUMP

in the dropping funnel, B, and added slowly to the mixture in the reaction flask, C. After the reaction had started, enough hydrogen was produced that the nitrogen could be shut off. The rate of addition of the solution was adjusted according to the rate of evolution of hydrogen. The reaction mixture was stirred continuously with a magnetic stirrer. The inner tube of the condenser, D, was filled with a mixture of dry ice and acetone (-78°C). This prevented most of the water from distilling into the traps, E and F. The remaining volatile compounds were carried into the traps by the hydrogen and condensed by liquid air. When the reaction was complete, the system was connected to the pump and all the hydrogen and nitrogen were removed. The products in the two traps were transferred to a LeRoy still and separated at -145°C. (90). Only germane was recovered at this temperature. The amount obtained was approximately 85-90% of the theoretical yield.

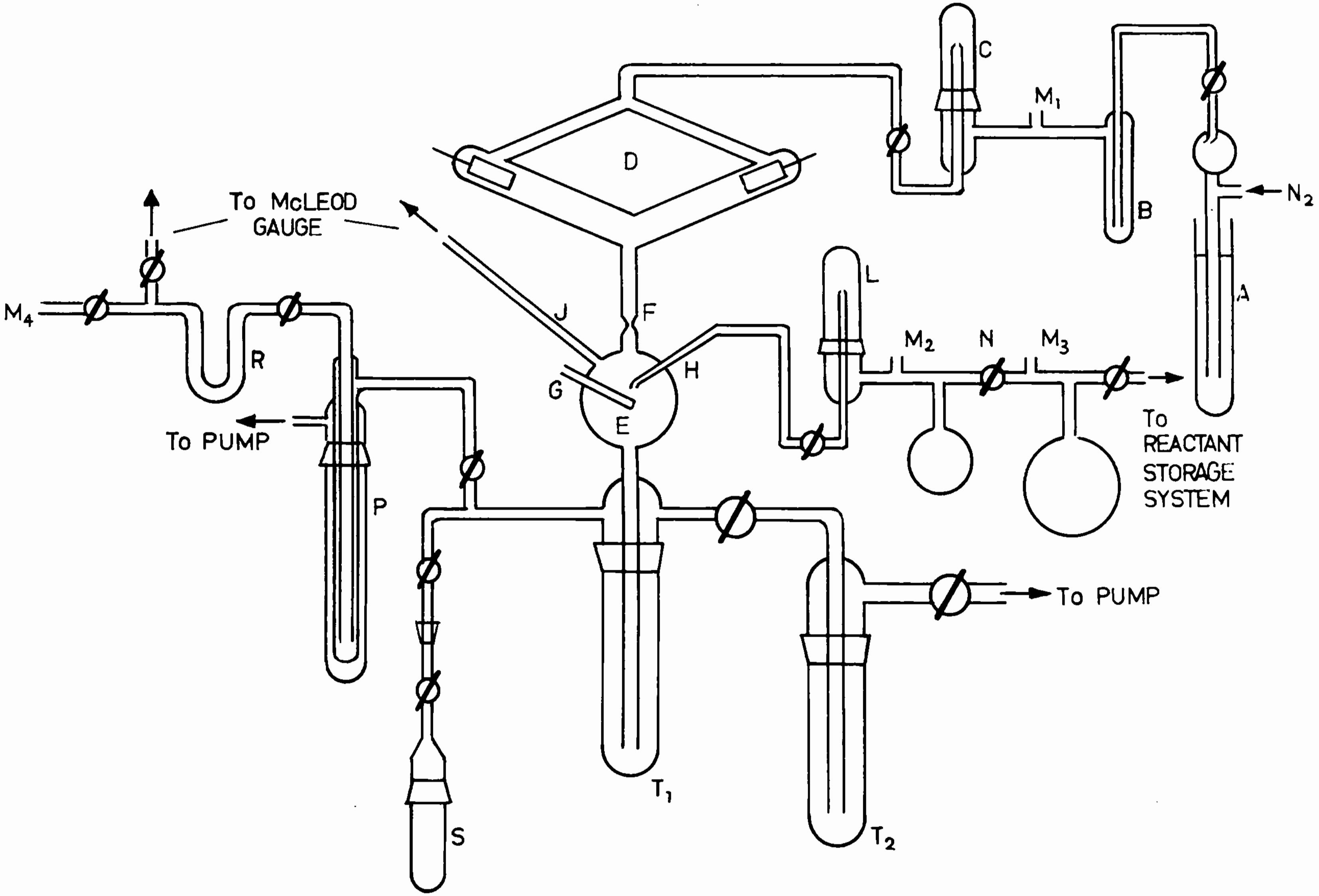
APPARATUS

The active nitrogen apparatus, represented in Figure 3, was made of Pyrex glass. It was similar to others used in this laboratory for studies of active nitrogen reactions.

Nitrogen from a cylinder was introduced into the system through a manostat, A, containing dibutyl phthalate. This was regulated to keep a constant nitrogen pressure head of 77.2 cm. of Hg, measured on the manometer, M_1, when atmospheric pressure changed. A cold trap, B, surrounded by liquid air, removed traces of water

FIGURE 3

Diagram of Apparatus



C
M1
D
B
N2
To McLEOD GAUGE
A
L
M4
R
J
F
M2
N
M3
G
H
E
To PUMP
To REACTANT STORAGE SYSTEM
P
To PUMP
S
T1
T2

from the gas. The gas passed through a capillary flowmeter, C, into the V-shaped discharge tube, D, containing two aluminum electrodes connected by tungsten wire to the discharge circuit. Between the discharge tube and the 500 ml. spherical reaction vessel, E, was a constriction, F, to prevent back diffusion. In the reaction vessel was a thermocouple well, G, with its end just below the reactant inlet, H. Two hemispherical furnaces connected in series could be placed around the reaction vessel to heat it to any temperature up to about 450°C. Reaction products were condensed in the trap, T_1, by liquid air. In the trap, T_2, all waste products were collected to prevent them from going into the pump. A McLeod gauge, connected at J, was used to measure the pressure in the reaction vessel.

The reactant flow system consisted of a bulb, K, of known volume, two manometers, M_2 and M_3, and a flowmeter, L. The gas passed through the flowmeter at a definite rate depending on the pressure measured on M_2. The pressure was regulated by adjusting the scratched stopcock, N, thereby determining the flow rate of reactant.

In the analytical system were a LeRoy still, P, and a U-tube trap, R, connected to a manometer, M_4, and the McLeod gauge. After some reactions, the products were distilled from the trap, T_1, into an absorber, S, for analysis, rather than into the LeRoy still.

The pump used was a Cenco Hypervac 23, guaranteed to produce a vacuum of 5×10^{-4} cm. of Hg.

For the first few experiments the apparatus was poisoned with a 2% solution of phosphoric acid. The solution was slowly drawn up into the reaction vessel and discharge tube. Because of the shape of the discharge tube, its walls could be poisoned up to the electrodes. After the solution was allowed to run out, the system was evacuated and the reaction vessel heated for several hours to remove all the water.

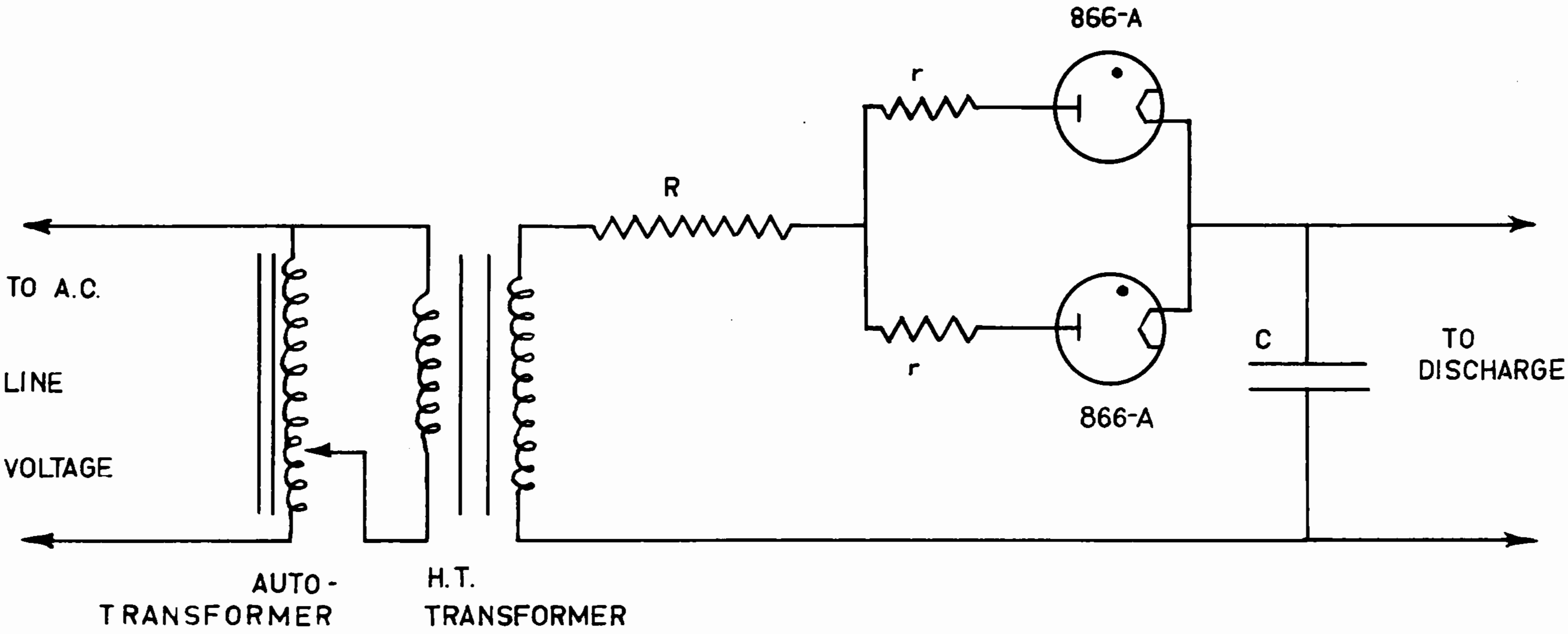
When preliminary experiments indicated that boron trichloride reacted with the poison, the reaction vessel and discharge tube were thoroughly cleaned with a mixture of hot chromic and sulphuric acids, followed by several rinsings with distilled water, and the remainder of the work was done in an unpoisoned system.

Since boron trichloride is very reactive towards stopcock grease, an inert fluorocarbon grease, Kel-F, was used. Although there was some reaction with even this grease, the stopcocks and joints did not leak and could still be moved. (When Apiezon and silicon greases were used, the stopcocks "froze".) The Kel-F grease was found to be satisfactory also with the other reactants, germanium tetrachloride and germane.

The electrical ciccuit for the discharge is shown schematically in Figure 4. It consisted of two 866-A rectifier tubes, in parallel, but each in series with a 500 Ω resistor, r. A charge was built up in the 2 μf capacitor, C, through a resistor, R, until the voltage was high enough to ionize the gas in the discharge tube. The capacitor then discharged across the electrodes with a flash. Immediately after this happened, the condenser began to charge again, starting another

<u>FIGURE 4</u>

Diagram of Electrical Circuit


866-A
r
R
TO A.C.
LINE
VOLTAGE
r
866-A
C
TO
DISCHARGE
AUTO-
TRANSFORMER
H.T.
TRANSFORMER

cycle. The discharge frequency depends on the values of R, C, and the transformer out-put voltage, the latter being controlled by adjustment of the auto-transformer. In the present studies, the apparatus was operated with about 10 flashes per second.

DETERMINATION OF FLOW RATES

To determine the flow rate of nitrogen, the apparatus from the nitrogen inlet, A (Figure 3), to the flowmeter, C, was filled with the gas to a pressure of 77.2 cm. of Hg. With the stopcock to the nitrogen cylinder closed, the gas was pumped out through the discharge tube and reaction vessel. The flow rate was calculated from the rate of decrease in pressure, measured on the manometer, M_1. The value was 154×10^{-6} moles/sec.

The flow rates of ethylene, boron trichloride, and germane were determined from P-V measurements, assuming the gases to be ideal. The change in pressure (measured on the manometer, M_3) in the known volume, K, was measured during experiments with different flow heads (measured on the manometer, M_2) to obtain a relation between flow head and flow rate. Several blank experiments (i.e. without the discharge operating), in which boron trichloride was trapped and titrated with standard sodium hyroxide solution, were made over a range of flow rates. From this, a correction curve was established for the flow rates inferred from the P-V measurements for that compound.

Since germanium tetrachloride is a liquid at room temperature, its flow rate could not be calculated from P-V measurements. Blank experiments were therefore made for different pressure differentials across the flowmeter, the germanium tetrachloride being trapped and titrated with standard silver nitrate solution. From the chloride content, the amount of germanium tetrachloride that passed through the flowmeter was determined to obtain the desired relation between flow head and flow rate.

PROCEDURE FOR A TYPICAL EXPERIMENT

Each morning the pressure in the apparatus was measured, to ensure that no leaks had developed, before the nitrogen and reactant flow systems were filled with the appropriate gases.

Nitrogen was then allowed to flow through the discharge tube and reaction vessel. When a constant pressure of 1.45 mm. of Hg was reached, the discharge was turned on for several minutes. During this time some of the reactant was introduced into the reaction vessel. The reaction that occurred served only to condition the system and the products were not kept for analysis.

After the discharge had been operating about five minutes and the temperature recorded by the thermocouple in the reaction vessel was constant, the trap, T_1, was surrounded with liquid air and the reaction begun. The reactant was admitted to the reaction vessel for a definite length of time, usually 100 seconds, although for very low flow rates the time was increased to 200 or 300 seconds.

The flow head was kept constant by adjusting the scratched stopcock, N. Before and after each reaction, the pressure of the gas in the calibrated bulb, K, was noted so that the number of moles of reactant used could be calculated.

At the conclusion of the reaction, the reactant, the discharge, and then the nitrogen were turned off, and the system evacuated. The trap containing the reaction products was then isolated from the pump and the products were distilled out of the trap for analysis.

When ethylene was the reactant, the trap was surrounded with carbon tetrachloride for a few seconds before distillation to allow a layer to freeze on the glass. This decreased the amount of polymerization of hydrogen cyanide by keeping the temperature below the melting point of hydrogen cyanide.

When other reactants were used, the trap was warmed to room temperature immediately, and the distillation was allowed to proceed at that temperature.

ANALYSIS OF PRODUCTS

Hydrogen cyanide from the ethylene reactions was distilled from the trap into an absorber containing distilled water. To this solution were added ammonia and potassium iodide, and the solution was titrated with standard silver nitrate solution to obtain the amount of hydrogen cyanide present. (91)

The products of the boron trichloride reactions were separated in the LeRoy still (90). Chlorine distilled at -110°C. at a pressure of 3 mm. of Hg, and boron trichloride at -80°C. at a pressure of 4 mm. of Hg, leaving tetrachlorodiborine in the still. The tetrachlorodiborine was removed at room temperature.

The amount of chlorine produced in both the boron trichloride and germanium tetrachloride reactions was determined by absorbing it in distilled water and titrating with standard sodium thiosulphate solution, using Thyodene as indicator. (91)

In the blank experiments to determine the boron trichloride flow rate, the chloride was dissolved in distilled water, in which it hydrolysed to form boric acid and hydrochloric acid. Boric acid, being weakly ionized, cannot be titrated directly with a base, but the addition of a polyhydroxy compound increases its ionization. In these determinations, mannitol was used to make titration possible, and standard sodium hydroxide solution was used as titrant, with phenolphthalein as indicator. (91) Four equivalents of hydroxide were needed to neutralize one equivalent of boron trichloride in solution. The amount of boron trichloride in the solution could also be estimated by titration of the chloride content with standard silver nitrate solution, using potassium chromate as indicator (Mohr method). (91) Since the two methods were found to give concurrent results, the simpler titration with the base was used, after the first few experiments, to determine the amount of boron trichloride.

Since tetrachlorodiborine, like boron trichloride, hydrolyses to boric acid and hydrochloric acid, the amount trapped in the reaction between active nitrogen and boron trichloride was determined by titration of a solution of it with standard sodium hydroxide solution in the presence of mannitol. Six equivalents of base were required to neutralize one of tetrachlorodiborine in solution.

As with boron trichloride, the amount of unreacted germanium tetrachloride was determined by a Mohr titation with silver nitrate.

Unreacted germane was transferred to the U-tube trap in the analytical section of the apparatus. From its pressure at room temperature in a known volume, the number of moles was calculated, assuming it to be an ideal gas. This assumption should not introduce appreciable error in the amount of germane reacted, since the amount of germane introduced into the reaction vessel was also determined by P-V measurements.

RESULTS

REACTION OF ACTIVE NITROGEN WITH BORON TRICHLORIDE

The flame produced when boron trichloride was introduced into active nitrogen was a pale green colour. At very low flow rates, the flame formed a sphere around the opening of the reactant inlet, while at higher flow rates it filled the upper part of the reaction vessel but did not extend into the tube above. The yellow nitrogen afterglow was destroyed completely when boron trichloride was added to active nitrogen, and a small amount of white solid was deposited on the walls of the reaction vessel.

The products trapped during each experiment were separated in the LeRoy still (90) by slowly increasing the temperature from that of liquid air to room temperature. Four fractions were obtained, the first of which distilled at -155°C., the second at -110°C., the third at -80°C., and the fourth at room temperature.

The first fraction was unexpected; the only compound that conceivably might have been formed in some way and distil at such a low temperature appeared to be hydrogen chloride. A solution of the fraction in distilled water was therefore titrated as an acid with standard sodium hydroxide solution, and for chloride content with standard silver nitrate solution. The results obtained agreed with those expected for hydrogen chloride. Since it was believed that the hydrogen necessary for its formation might have originated in the poison on the walls of the reaction vessel, the vessel was cleaned and not repoisoned. The amount of hydrogen chloride formed in the poisoned system was comparable with the amount of chlorine produced, but in the unpoisoned system it was much less. Blank experiments showed a neglible amount of hydrogen chloride present in the boron trichloride itself.

Chlorine was the second fraction collected, and the amount was determined by titration with standard sodium thiosulphate solution. The presence of tetrachlorodiborine (B_2Cl_4) among the products was demonstrated by mass spectrometric analysis*, and this was separated from boron trichloride, the third fraction, by distillation when the tetrachlorodiborine remained in the still. The tetrachloride was transferred to a trap containing distilled water and titrated with standard sodium hydroxide solution to determine the amount formed during reaction.

A comparison of the amounts of chlorine formed in a poisoned system at 85°C. and in an unpoisoned system at 100°C. is given in Table I and illustrated in Figure 5. Also shown in Figure 5 is the yield of chlorine corresponding to different flow rates of boron trichloride in an unpoisoned system at temperatures of 353 ± 5°C. The values are listed in Table II. The temperatures mentioned above and in the following sections are those recorded in the reaction vessel when the reaction had proceeded for fifty seconds.

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* This analysis was done by Dr. L. Elias.

TABLE I

Reaction of active nitrogen with boron trichloride.

Poisoned system at 85 ± 5°C.		Unpoisoned system at 100 ± 2°C.	
BCl_3 Flow Rate*	Cl_2 Recovered*	BCl_3 Flow Rate*	Cl_2 Recovered*
8.5	0.27	11.7	0.47
9.6	0.33	12.4	0.41
10.1	0.27	21.9	0.47
13.2	0.27		

TABLE II

Reaction of active nitrogen with boron trichloride.

Temperature = 353 ± 5°C.		Temperature = 395 ± 5°C.	
BCl_3 Flow Rate*	Cl_2 Recovered*	BCl_3 Flow Rate*	Cl_2 Recovered*
1.8	0.36	3.0	0.38
2.5	0.33	3.6	0.48
6.4	0.39	6.0	0.49
13.0	0.47	9.9	0.46
16.3	0.47	10.9	0.58
26.1	0.50	12.0	0.49
27.8	0.48	16.6	0.48

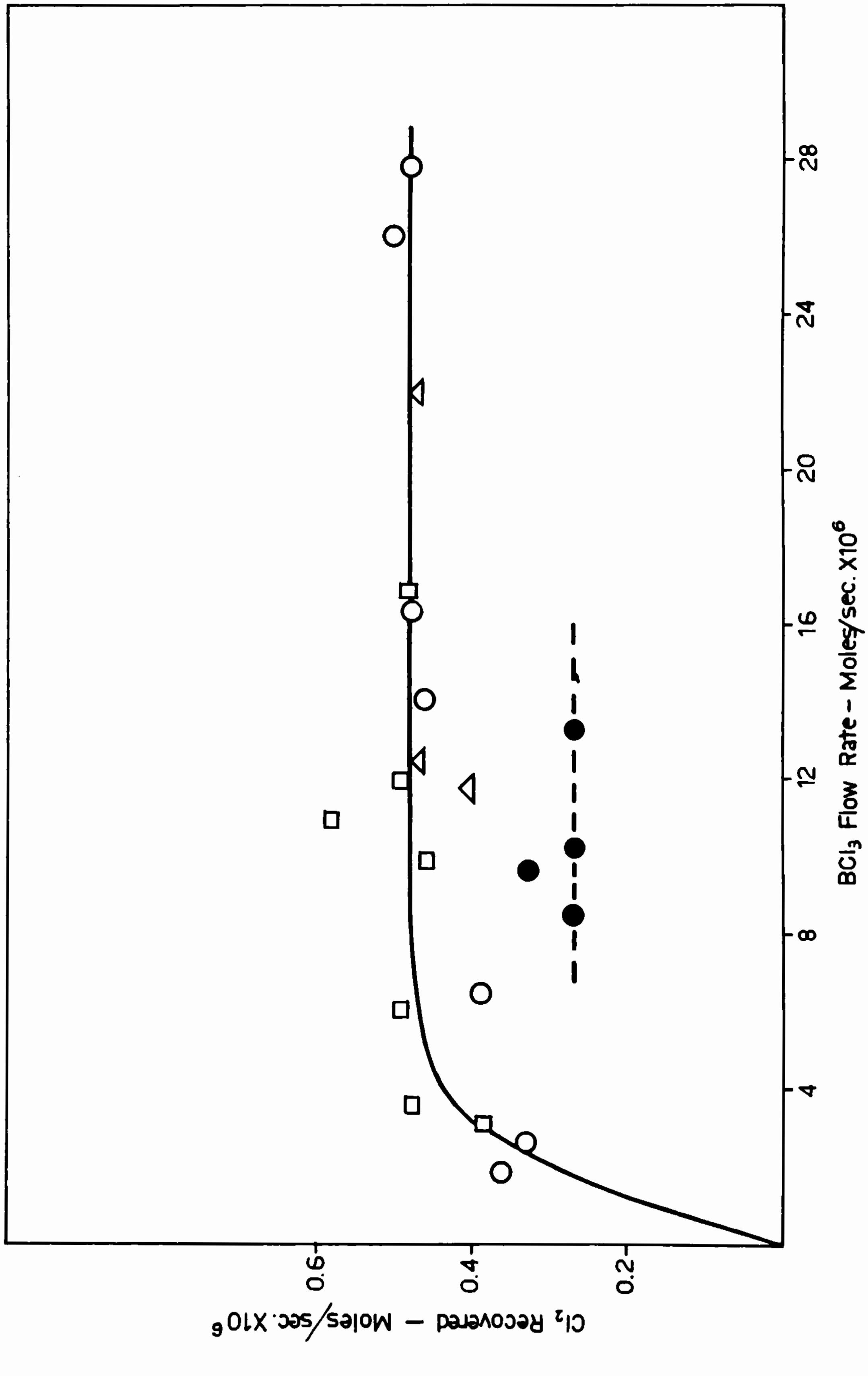
* Units are moles/sec.x 10^{-6}

FIGURE 5

Chlorine Recovered in the Reaction of
Active Nitrogen with Boron Trichloride

Legend:

- ● Poisoned System at 85 ± 5°C.
- △ Unpoisoned System at 100 ± 2°C.
- ○ Unpoisoned System at 353 ± 5°C.
- □ Unpoisoned System at 395 ± 5°C.



Cl$_2$ Recovered — Moles/sec. X10^6
0.2
0.4
0.6
4
8
12
16
20
24
28
BCl$_3$ Flow Rate – Moles/sec. X10^6

The results of the tetrachlorodiborine analysis from reactions at 395 ± 5°C. are summarized in Table III and illustrated in Figure 6. The ratio of the amount of tetrachlorodiborine recovered to the amount of chlorine recovered increases from about 1:10 to 1:2 as the boron trichloride flow rate increases.

The nitrogen atom concentration, determined from the amount of reaction of ethylene with active nitrogen at 350°C., was 14.2×10^{-6} moles/sec. in the poisoned system, and 9.5×10^{-6} moles/sec. in the unpoisoned system.

REACTION OF ACTIVE NITROGEN WITH GERMANIUM TETRACHLORIDE

In the reaction of germanium tetrachloride with active nitrogen, the colour of the reaction flame was royal blue at high flow rates of germanium tetrachloride, but as the flow rate was decreased, the colour became pale blue and finally white at very low flow rates. Except at the lowest flow rates, the nitrogen afterglow was completely destroyed. No noticeable amount of solid was deposited on the walls of the reaction vessel.

The experiments with this compound at room temperature yielded the results summarized in Table IV and illustrated in Figure 7. Poor reproducibility of results is probably due to experimental error in analysing for such small amounts of material.

Since the amount of germanium tetrachloride introduced into the reaction vessel was highly dependent on the flow head, which could not

TABLE III

Reaction of active nitrogen with boron trichloride at 395 ± 5°C.

BCl_3 Flow Rate [*]	B_2Cl_4 Recovered [*]
3.0	0.04
3.6	0.09
6.0	0.09
9.0	0.23
9.9	0.20
12.0	0.24
16.6	0.24
5.9 [**]	0.12

[*] Units are moles/sec. x 10^{-6}

[**] Experiment continued for 10 minutes

FIGURE 6

Tetrachlorodiborine Recovered in the Reaction of Active Nitrogen with Boron Trichloride at 395 ± 5°C.

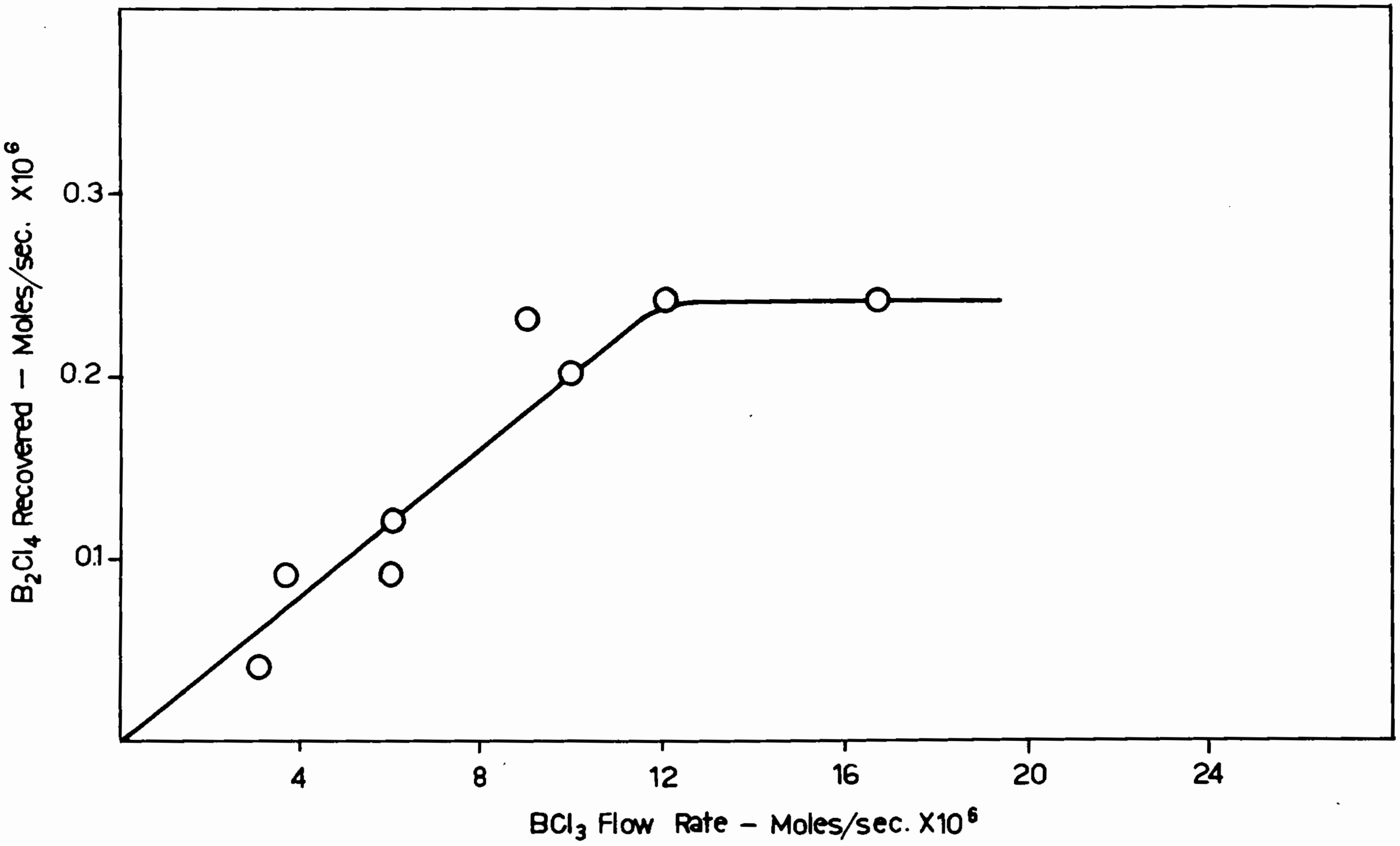

0.3
0.2
0.1
B_2Cl_4 Recovered – Moles/sec. X10^6
4
8
12
16
20
24
BCl_3 Flow Rate – Moles/sec. X10^6

TABLE IV

Reaction of active nitrogen with germanium tetrachloride at 65 ± 5°C.

$GeCl_4$ Flow Rate*	Cl_2 Recovered*
1.5	0.018
1.5	0.045
3.1	0.036
3.55	0.12
6.1	0.10
11.1	0.13
12.75	0.097
19.3	0.08

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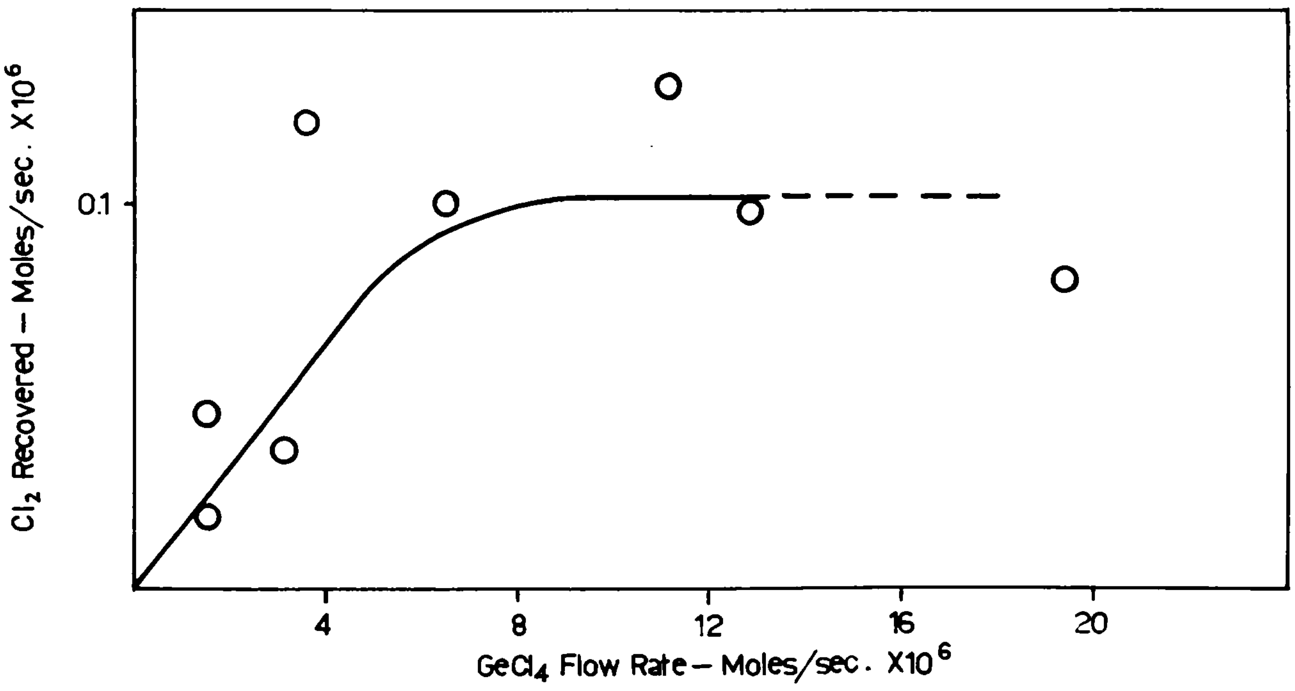
* Units are moles/sec. x 10^{-6}

FIGURE 7

Chlorine Recovered in the Reaction of Active Nitrogen with Germanium Tetrachloride at $65 \pm 5^{\circ}C$.


0.1
4
8
12
16
20
Cl_2 Recovered — Moles/sec. X10^6
$GeCl_4$ Flow Rate — Moles/sec. X10^6

always be kept constant, the amount of germanium tetrachloride which reacted could not be determined accurately by the difference between the amount introduced and the amount recovered. The chlorine results, however, should not be affected significantly by small changes in flow head.

Compared with the nitrogen atom concentration, 16.5×10^{-6} moles/sec., determined by the amount of reaction of ethylene with active nitrogen, very little germanium tetrachloride was destroyed, if the amount of chlorine produced is taken as an indication of the extent of decomposition. Assuming this reaction to be similar to the one between boron trichloride and active nitrogen, an increase in the amount of reaction with an increase in temperature seemed unlikely. Since little information could be gathered from such a small amount of decomposition, study of this reaction was discontinued.

REACTION OF ACTIVE NITROGEN WITH GERMANE

The flame of the reaction between active nitrogen and germane was yellowish orange, and no nitrogen afterglow could be seen below the reaction zone. A large amount of dark brown solid was deposited on the walls of the reaction vessel and of the tube leading into the trap below. After about a minute of reaction, the flame could no longer be seen because of the coating on the walls of the vessel.

Before reactions with germane were begun, the nitrogen atom concentration was determined by the reaction of ethylene with active nitrogen at 350°C., and the value obtained was 16.5×10^{-6} moles/sec. After a few experiments with germane had been made, the nitrogen atom concentration was again determined, using ethylene, but at room temperature. The value was 1.8×10^{-6} moles/sec. which, from earlier work on the ethylene reaction, would be equivalent to about 3.6×10^{-6} moles/sec. at the higher temperature. When the temperature of the reaction vessel was increased and a few experiments with ethylene were made at 350°C., the deposit on the walls turned white. Washing the reaction vessel with water appeared to clean it, but when more reactions of ethylene with active nitrogen were done, a metallic layer, presumably germanium, formed on the walls, indicating that an invisible residue had remained on the walls. The nitrogen atom concentration inferred from these last reactions with ethylene varied from 4 to 6×10^{-6} moles/sec. Aqua regia was then used to remove the metal from the reaction vessel, and experiments with germane were completed before ethylene was again used.

The material trapped during the first few experiments with germane was transferred to the LeRoy still, and the temperature of the still was raised from that of liquid air to room temperature. Germane was the only compound removed from the still. The absence of other volatile condensable products was confirmed by mass spectrometric* and infra-red examinations.

Because it took some time for an even layer of solid to be deposited on the walls of the reaction vessel, it was only after several experiments that reproducible results were obtained. Since

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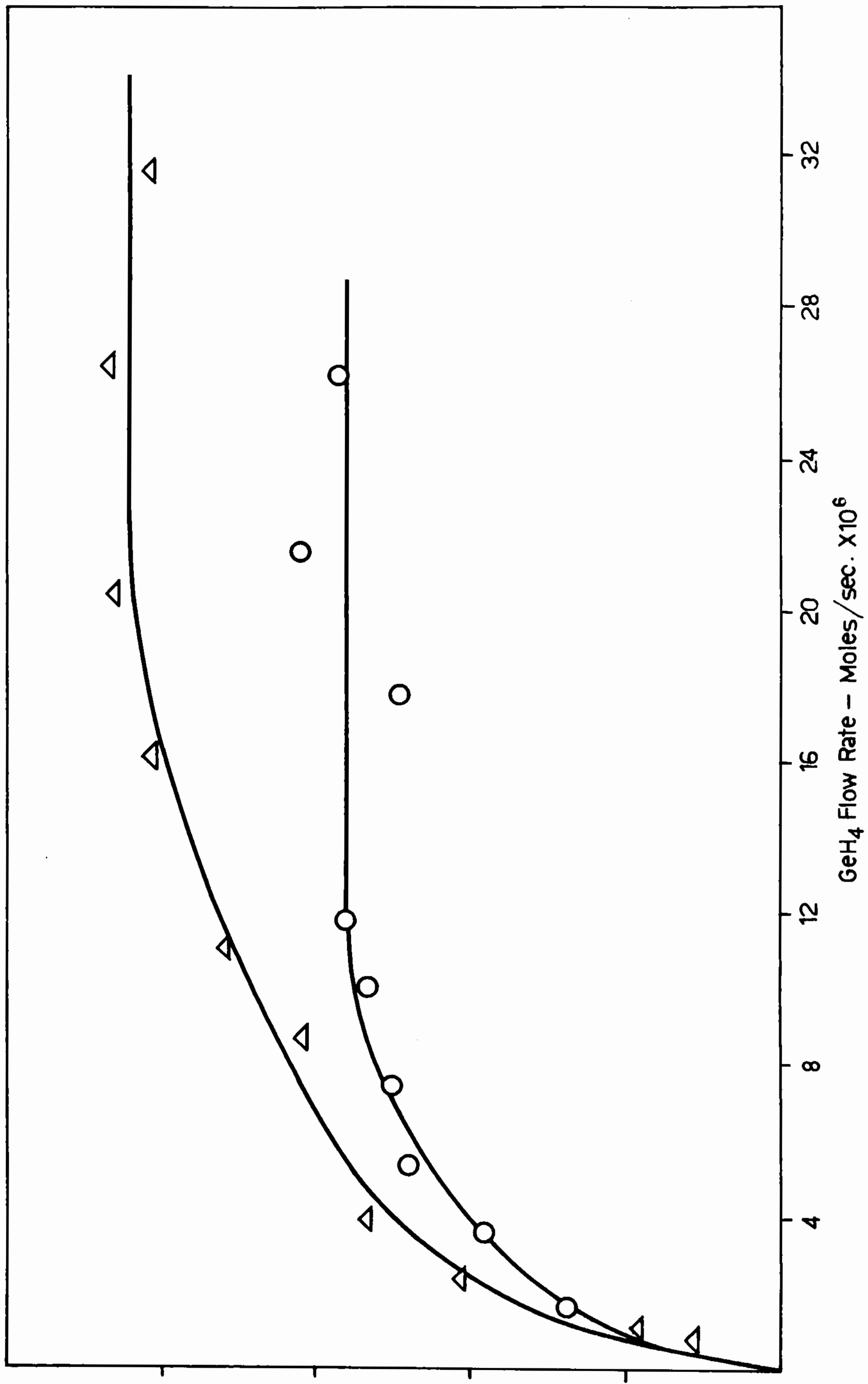
* This analysis was done by Dr. L. Elias.


GeH$_4$ Reacted — Moles/sec. X10^6
1
2
3
4
GeH$_4$ Flow Rate — Moles/sec. X10^6
4
8
12
16
20
24
28
32

germane decomposes at 283°C. (92), one series of experiments was done at 200°C., followed by another series at 100°C. The results of these experiments are summarized in Table V and illustrated in Figure 8.

The nitrogen atom concentration was again determined, following the experiments with germane, and without cleaning the reaction vessel, by reacting ethylene with active nitrogen at room temperature. As indicated previously, the average value obtained, 3.7×10^{-6} moles/sec., may be taken to be approximately one-half the atom concentration at the higher temperature. Since the results of individual experiments did not agree satisfactorily and higher temperatures could not be used because of decomposition of the solid on the walls of the reaction vessel, the maximum amount of nitric oxide destroyed in its reaction with the active nitrogen was determined and found to be 10.5×10^{-6} moles/sec. According to Verbeke and Winkler (83), this would correspond, at the same pressure, to a nitrogen atom concentration of about 7×10^{-6} moles/sec., as inferred from the reaction between ethylene and active nitrogen at high temperatures. From these results, it is apparent that the deposit on the walls of the reaction vessel increased surface recombination of the nitrogen atoms, and therefore decreased the available nitrogen atom concentration from 16.5×10^{-6} to approximately 7×10^{-6} moles/sec.

When no further experiments were to be made, some of the deposit in the reaction vessel was removed and an analysis of it attempted. Since hydrolysis of the solid by alkali caused evolution

TABLE V

Reaction of active nitrogen with germane.

Temperature = 100°C.		Temperature = 200°C.	
GeH_4 Flow Rate*	GeH_4 Reacted*	GeH_4 Flow Rate*	GeH_4 Reacted*
1.6	1.38	0.98	0.92
3.6	1.9	0.64	0.60
5.32	2.39	2.34	2.09
7.44	2.51	3.93	2.71
9.95	2.65	8.55	3.09
11.8	2.80	10.96	3.59
17.8	2.46	16.13	4.07
21.6	3.12	20.4	4.3
26.2	2.85	26.45	4.35
		31.8	4.1

* Units are moles/sec. x 10^{-6}

FIGURE 8

Germane Destroyed in the Reaction of Active Nitrogen with Germane

Legend: ○ 100°C

△ 200°C.

of ammonia, it was concluded that the material was a nitride or mixture of nitrides. There are two known germanium nitrides, germanous nitride (Ge_3N_2) and germanic nitride (Ge_3N_4), each with different properties.

The dark brown solid formed in the reaction between active nitrogen and germane was insoluble in sulphuric and hydrochloric acids, but dissolved in water to form a brown solution and in sodium hydroxide solution to form a colourless solution. When acid was added to the water solution, it became colourless and the brown solid was precipitated. The colour of the solid became lighter when it was left exposed to the air overnight. These observations agree with the behaviour observed by Johnson and Ridgely (93) for germanous nitride, which they noted to be dark brown, to be hydrolysed slowly by water but more easily by alkali, and to react with atmospheric moisture to form white germanic oxide. Johnson (94) found that germanic nitride was insoluble in water and other common inorganic solvents, and that it was not affected by air at ordinary temperatures. From these observations it may be concluded that the solid formed in the germane - active nitrogen reaction was mainly germanous nitride.

Analysis of the solid for nitrogen by the micro-Kjeldahl method gave a value of 5.3% nitrogen, compared with theoretical values of 11.4% for pure germanous nitride and 20.5% for pure germanic nitride. This result is not unreasonable considering that partial conversion to the oxide probably occurred when the brown solid was exposed to the air. A small amount of the solid was oxidized to germanic oxide by perchloric acid, and the acid was evaporated. Assuming the sample to be a mixture of only one of the nitrides with the oxide, it was possible to calculate from the change in weight of mixture, on oxidation, the amount of germanium combined with the nitrogen, and thus determine which nitride was present. It was found that the amount of germanium converted from nitride to oxide was 37% of the original sample. The amount of germanium that would be combined with an amount of nitrogen corresponding to 5.3% of the original sample would be 41% for germanous oxide, and half that value for germanic nitride.

X-ray analysis* of the substance showed only that it was amorphous, and therefore no further information could be obtained from that method of analysis.

From the results of the analyses and the properties observed, there seems little doubt that the deposit formed in the reaction vessel was germanous nitride, and that when it was exposed to the air, some of it suffered change to germanic oxide.

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*Courtesy of the Department of Geology, McGill University.

DISCUSSION

REACTION OF ACTIVE NITROGEN WITH BORON TRICHLORIDE

Since the afterglow is completely destroyed in the reaction of active nitrogen with boron trichloride, the chloride must react with either nitrogen atoms or excited molecules in the $B^3\Pi_g$ (energy of 7.3 ev.) or higher energy state. The results of this reaction can be explained without invoking the presence of excited molecules in active nitrogen, i.e., by considering nitrogen atoms to be the only species in active nitrogen that reacts with boron trichloride. This does not mean, of course, that the results deny the existence of excited molecules in active nitrogen, because they may also be explained by assuming that such a species is involved, as indicated later.

The first step in the reaction may be a collision between a boron trichloride molecule and a nitrogen atom, with the formation of a relatively long-lived complex which then reacts with another nitrogen atom, with dissociation of the resulting highly energetic boron trichloride molecule.

$$BCl_3 + N \longrightarrow [BCl_3.N] \xrightarrow{N} BCl_3^* + N_2 \longrightarrow BCl_2 + Cl + N_2 \qquad \Delta H = -116 \text{ kcal.} \qquad (1a)$$

$$\longrightarrow BCl + Cl_2 + N_2 \qquad \Delta H = -83.5 \text{ kcal.} \qquad (1b)$$

(Heats of reaction in this and the following sections were calculated from heats of formation and bond dissociation energies listed in the Appendix.) The BCl_2 radical might then react in either of two ways:

(a) in a process involving two nitrogen atoms, in a manner similar to that for boron trichloride above,

$$BCl_2 + N \longrightarrow [BCl_2.N] \xrightarrow{N} BCl_2^* + N_2 \longrightarrow BCl + Cl + N_2 \qquad \Delta H = -135 \text{ kcal.} \qquad (2)$$

or (b) by dimerization to form tetrachlorodiborine,

$$2BCl_2 \longrightarrow B_2Cl_4 \qquad (3)$$

Since the extent of reaction (3) should increase relative to reaction (2) as the flow rate of boron trichloride is increased, and more nitrogen atoms are consumed in reaction (1), the increase in the ratio of B_2Cl_4: Cl_2 with flow rate of boron trichloride is explained by such a mechanism.

The BCl radical formed in reaction (1b) or (2) may react with a single nitrogen atom to form the small amount of boron nitride, which was deposited on the walls of the reaction vessel,

$$BCl + N \longrightarrow BN + Cl \qquad \Delta H = -38.5 \text{ kcal.} \qquad (4)$$

(Although the deposit was not analysed, Jevons has shown this to be the solid product when active nitrogen reacts with boron trichloride (86).)

Much of the chlorine produced, whether atomic or molecular, might be expected to react vigorously with BCl or BCl_2 radicals to re-form, eventually, boron trichloride,

$$Cl + BCl \longrightarrow BCl_2 \qquad \Delta H = -90 \text{ kcal.} \qquad (5)$$

$$Cl_2 + BCl \longrightarrow BCl_3 \qquad \Delta H = -141 \text{ kcal.} \qquad (6)$$

$$Cl + BCl_2 \longrightarrow BCl_3 \qquad \Delta H = -108 \text{ kcal.} \qquad (7)$$

Thus the small amount of chlorine recovered, compared with the nitrogen atom concentration, can be explained by the occurrence of a large amount of back reaction to produce the original reactant, boron trichloride.

Since very little solid was deposited on the walls of the reaction vessel, reaction (4) must be of relatively little importance, which again suggests that the concentration of radicals, such as BCl, must have remained low, presumably because of back reaction.

Less chlorine was recovered in the poisoned system than in the unpoisoned system. Since there would be more nitrogen atoms, and therefore more forward reaction, in a poisoned reaction vessel than in an unpoisoned one, there must also have been more back reaction to explain the results obtained. Since an increase in temperature did not increase the amount of chlorine recovered, presumably the amount of back reaction must have increased with temperature to about the same extent as the amount of forward reaction. This suggests that the activation energies involved were all about equal, and probably all low.

Because of the seemingly extensive back reaction, no relation between the nitrogen atom concentration and the amounts of products formed can be established. To a major extent, the net reaction corresponded simply to catalyzed recombination of nitrogen atoms by the boron trichloride, reflected in the disappearance of the active nitrogen afterglow without substantial product formation.

The reaction of boron trichloride with active nitrogen might also be explained by assuming, as an initial step, its decomposition by excited molecules in active nitrogen, e.g., molecules in the $^3\Pi$ state.

$$BCl_3 + N_2^* \longrightarrow BCl_2 + Cl + N_2 \qquad (8)$$

However, this changes little of the preceding arguments since such a reaction must be followed, presumably, by reactions involving atomic nitrogen, as above, because the afterglow is extinguished even at low rates of boron trichloride.

REACTION OF ACTIVE NITROGEN WITH GERMANIUM TETRACHLORIDE

Since only a few experiments using active nitrogen and germanium tetrachloride were made, very little can be said about this reaction. However, the mechanism is probably similar to that of the reaction between active nitrogen and boron trichloride.

REACTION OF ACTIVE NITROGEN WITH GERMANE

Since germane and silane are similar compounds, it is probable that they both react with active nitrogen in the same way, and the mechanism suggested by Dewhurst (88) for the reaction between silane and active nitrogen may be applied to the germane - active nitrogen reaction.

According to this mechanism, which is similar to that proposed by Wiles (95) for the reaction of phosphine with active nitrogen, a hydrogen atom was abstracted from the germane molecule by a nitrogen atom,

$$GeH_4 + N \longrightarrow GeH_3 + NH \qquad \Delta H = \sim -17 \text{ kcal.} \qquad (9)$$

The same process may occur with the GeH_3 radical,

$$GeH_3 + N \longrightarrow GeH_2 + NH \qquad \Delta H = \sim -25 \text{ kcal.} \qquad (10)$$

and with the GeH_2 and GeH radicals,

$$GeH_2 + N \longrightarrow GeH + NH \qquad \Delta H = \sim -25 \text{ kcal.} \qquad (11)$$

$$GeH + N \longrightarrow Ge + NH \qquad \Delta H = \sim -15 \text{ kcal.} \qquad (12)$$

As an alternative to reaction (12) the hydrogen atom may be replaced by a nitrogen atom to form GeN,

$$GeH + N \longrightarrow GeN + H \qquad (13)$$

Although the heat evolved in this last reaction cannot be calculated because of the lack of information about GeN, the reaction is probably exothermic. Heats of formation of the other radicals have been estimated, as explained in the Appendix, and used to give approximate heats of reaction, which may be considered accurate enough to show that the reactions are thermodynamically possible.

Since no ammonia was detected in the products, the NH radicals must have disproportionated,

$$2NH \longrightarrow N_2 + H_2 \qquad \Delta H = -146 \text{ kcal.} \qquad (14)$$

or suffered further reaction with a nitrogen atom,

$$NH + N \longrightarrow N_2 + H \qquad \Delta H = -133 \text{ kcal.} \qquad (15)$$

Hydrogen atoms, in addition to recombination, would be expected to attack germane molecules or germanium hydride radicals to produce hydrogen,

$$GeH_4 + H \longrightarrow GeH_3 + H_2 \qquad \Delta H = \sim -30 \text{ kcal.} \qquad (16)$$

$$GeH_3 + H \longrightarrow GeH_2 + H_2 \qquad \Delta H = \sim -40 \text{ kcal.} \qquad (17)$$

$$GeH_2 + H \longrightarrow GeH + H_2 \qquad \Delta H = \sim -40 \text{ kcal.} \qquad (18)$$

$$GeH + H \longrightarrow Ge + H_2 \qquad \Delta H = \sim -30 \text{ kcal.} \qquad (19)$$

Catalytic recombination of nitrogen atoms on a germane molecule might also have occurred,

$$GeH_4 + 2N \longrightarrow Ge + 2H_2 + N_2 \qquad \Delta H = \sim -150 \text{ kcal.} \qquad (20)$$

but since this requires a three-body collision, it is less likely than reaction (9), the abstraction of a hydrogen atom by a single nitrogen atom.

Since no volatile, condensable compounds, other then germane, were recovered, there was apparently no significant amount of dimerization of radicals.

The deposition of germanous nitride was, in all probability, the result of a wall reaction involving GeN and germanium formed in the gas phase,

$$2GeN + Ge \longrightarrow Ge_3N_2 \qquad (21)$$

As with boron trichloride, the initial reaction might involve energy transfer from an excited molecule in active nitrogen,

$$GeH_4 + N_2^* \longrightarrow GeH_3 + H + N_2 \qquad (22)$$

followed by reactions of the GeH_3 and other radicals with nitrogen atoms, since the nitrogen afterglow was quenched completely by the introduction of germane.

Since both the boron trichloride and germane reactions may be satisfactorily explained by assuming atomic nitrogen to be the only reactive species in active nitrogen, the results of neither reaction can be considered as evidence for the presence of more than one reactive species in active nitrogen.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. Studies have been made of the reactions of active nitrogen with boron trichloride at temperatures of 85°, 100°, 353°, and 395°C., with germanium tetrachloride at a temperature of 65°C., and with germane at temperatures of 100° and 200°C. All experiments except those with boron trichloride at 85°C. were made in an unpoisoned system.

2. The products of the boron trichloride - active nitrogen reaction were chlorine and tetrachlorodiborine, the maximum amount of tetrachlorodiborine formed being one-half the maximum amount of chlorine formed. The amount of chlorine recovered was independent of temperature, and very low compared with the nitrogen atom concentration. A small amount of boron nitride was also formed and deposited on the walls of the reaction vessel.

3. It is suggested that decomposition of boron trichloride might be due to recombination of nitrogen atoms on boron trichloride molecules, or, possibly, to collisions between excited nitrogen and boron trichloride molecules, to produce atomic chlorine and BCl_2 radicals.

   The low yield of products is explained by assuming a large amount of back reaction to regenerate the reactant.

4. The reaction of active nitrogen with germanium tetrachloride is assumed to be similar to that with boron trichloride. A small amount of chlorine was recovered, but no deposit could be seen on the walls of the reaction vessel.

5. In the reaction between active nitrogen and germane, there were no volatile, condensable products. The only product, besides hydrogen, was germanous nitride, which was deposited on the walls of the reaction vessel. The amount of germane destroyed increased by 50% when the temperature was raised from 100° to 200°C.

6. To explain the results obtained for the active nitrogen - germane reaction, it is assumed that nitrogen atoms abstract hydrogen from germane molecules and germanium hydride radicals, leading ultimately to the formation of germanium atoms and GeN. Stable germanous nitride may then be formed by a reaction, probably at the wall, involving GeN and germanium atoms.

Another possible explanation for the initial step in the reaction is that an excited nitrogen molecule causes dissociation of a germane molecule by energy transfer.

7. Although the reaction of active nitrogen with boron trichloride and with germane may both be explained by assuming reaction of excited nitrogen molecules, no proof of the existence of such a reactive species in active nitrogen was obtained in these experiments.

APPENDIX

In Table VI are listed the heats of formation of the compounds and radicals involved in the reactions discussed, and in Table VII are listed some bond dissociation energies. References are given for values obtained from the literature, but the other values were calculated from the equations

Heat of reaction = (sum of heats of formation of the products) - (sum of heats of formation of the reactants)

and

Heat of reaction = (sum of bond energies of the bonds broken) - (sum of bond energies of the bonds formed).

Since no values could be found for germane, the average bond energy was taken as 70 kcal., slightly lower than the value for silane, 76 kcal. (100), because germane is less stable than silane.

TABLE VI

HEATS OF FORMATION

	ΔH_f kcal. /mole	Source
BCl_3	-97	(96)
BCl_2	-17	Calc.
BCl	44.5	Calc.
BN	90.6	(97)
$GeCl_4$(g)	-118	Calc.
GeCl	32.6	(97)
Ge(g)	91.5	(98)
GeH_4	~20	Rough estimates
GeH_3	~43	
GeH_2	~55	
GeH	66.8	(98)
NH	72.6	Calc.

TABLE VII

BOND DISSOCIATION ENERGIES

	D kcal./mole	Source
BCl_2-Cl	108	(99)
BCl-Cl	90	Calc.
B-Cl	117?	(100)
B-N	155.5	Calc.
E $(GeCl_4)^*$	81	(100)
GeCl	87	Calc.
E $(GeH_4)^*$	~ 70	Rough estimates
GeH_3-H	~ 75	
GeH_2-H	~ 64	
GeH-H	~ 64	
Ge-H	76	(98)
N-H	92	(101)
Cl-Cl	57	(100)

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*Average bond dissociation energies

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