THE REACTIONS OF ACTIVE
NITROGEN WITH CHLOROMETHANES

by

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Section I

INTRODUCTION

The Physical Properties of Active Nitrogen

Active nitrogen, as it is now commonly known, was first discovered by Lewis (1) in 1900. He used relatively pure nitrogen, through which a condensed discharge was passed. He noted that the discharge tube was filled with a "beautiful chamois-yellow mist," which persisted for several seconds after the current was interrupted. The spectrum of this afterglow was banded and could be identified with part of the nitrogen spectrum. The use of sodium to remove the last traces of oxygen and water eliminated the afterglow. He therefore concluded that traces of oxygen or water vapor were necessary for the production of the afterglow. In 1911, Strutt--later the second Lord Rayleigh--began a series of investigations with active nitrogen produced in a discharge tube. He was unable to condense active nitrogen at low temperatures and concluded, by analogy with oxygen, that N_3 was not one of the constituents of active nitrogen (2). Strutt also observed that the afterglow was first intensified and then quenched on cooling (3, 4, 5) and on compression (4), which indicated that the process responsible for the afterglow was probably poly-molecular.

The spectrum of the afterglow was investigated by

Strutt (6, 7, 8). Its behavior under various conditions has been studied extensively and a review of the results up to 1928 was made by Kaplan (9). That the afterglow is not due to the presence of ions has been shown by Burke (10), Constantinides (11, 12) and Strutt (5), since neither the intensity nor the nature of the afterglow changed when it travelled past gauzes charged to high potentials.

The influence of gases on the production of the afterglow has been the subject of much controversy. At first Strutt maintained that the afterglow could be produced in very pure nitrogen, as well as in nitrogen containing impurities. A number of investigators thought that oxygen was necessary for the production of the afterglow. Tiede and Domcke (18, 19, 20) in particular went so far as to suggest that there was no such species as active nitrogen. Strutt (21, 22, 23) then maintained that absolutely no impurities were necessary for the production of active nitrogen, and he was supported in this view by Koenig and Eloed (24, 25). A joint effort by Tiede and Domcke (26, 27) in Strutt's laboratory was unsatisfactory in that the results were still in conflict. Later Strutt (28) found that very pure nitrogen indeed showed practically no afterglow and that a trace of oxygen, or almost any other gas, restored its brilliance. He also found that there was a time lag between introduction of oxygen and

the intensification of the afterglow (29). Bonhoeffer and Kaminsky (30) showed that when an amount of a foreign gas sufficient to enhance the brilliance of the afterglow was added, its spectrum did not appear in the afterglow. This, and other evidence (31, 32, 33, 34), indicated that impurities acted as catalytic wall poisons to the decay process of the afterglow.

The importance and effect of wall conditions on the rate of decay of the afterglow had been noted by Strutt (13), and he suggested that the catalytic action of the walls on the rate of decay of the afterglow could be minimized by a coating of sulphuric or metaphosphoric acid. He was able to maintain an afterglow, after interruption of the discharge, for six hours in a large vessel coated with metaphosphoric acid. On the other hand, Herzberg (14) found that thoroughly baked out vessels did not allow the afterglow to form even with traces of oxygen present.

The importance of wall conditions in the production of the afterglow, plus the effect of compression and of temperature variation led Strutt to postulate that active nitrogen was atomic in character, and that the afterglow was due to a radiation accompanying the recombination of atoms in a second order process (5). With surface effects excluded, the decay of the afterglow seemed to be

second order in the active species and first order in normal molecular nitrogen. Strutt showed that the increase in luminosity at low temperatures, although partly caused by increased concentration, was also partly due to a negative temperature coefficient of the afterglow decay process. A negative temperature coefficient may be expected for a recombination process if its activation energy is low (36); this has been found to be so for the recombination of iodine atoms in mixtures with several different gases (35). Willey (37) has concluded that foreign gases could replace nitrogen molecules as third bodies for the recombination of the active species.

Direct evidence has been reported for the presence of atoms in active nitrogen. Debeau (38) produced active nitrogen in one of two connected bulbs containing nitrogen at a pressure of 0.5 mm Hg. He used an electrodeless discharge in his experiments. The yellow afterglow diffused into the second bulb and the pressure in the system nearly doubled. But at the same time the temperature of the walls increased only slightly. When liquid air was applied to a small area on the surface the pressure returned to its original value. The intensity of the afterglow increased in the cooled region and then disappeared completely. After the liquid air was removed the afterglow reappeared, first at the cooled surface,

and its appearance was accompanied by a pressure increase. The rapid drop in pressure and the extinction of the afterglow occurred after application of the liquid air to less than one per cent of the area, showing that gas currents were carrying the active nitrogen to the cooled surface where it was destroyed. Debeau suggested that these currents resulted when pressure differences were established, due to the recombination of atoms on the cold surface. Wrede (39) also claimed to have obtained evidence for the presence of atoms by direct pressure measurements. He assumed that if a mixture of molecules and atoms were allowed to diffuse through an orifice under conditions such that complete recombination would take place, only molecules would diffuse back. After reaching a steady state, there would be a pressure differential across the orifice due to the difference in diffusion velocities of atoms and molecules. This pressure differential was in fact observed with active nitrogen, and Wrede used it to estimate nitrogen atom concentrations. Undoubtedly the accuracy of Wrede's measurements of atom concentrations are open to criticism (40), but there can be little doubt that these experiments demonstrated the existence of appreciable concentrations of nitrogen atoms in active nitrogen.

A mass spectrometric study on active nitrogen has

been made by Jackson and Schiff (41). Their results indicate that nitrogen atoms are present in active nitrogen, and that the concentration of excited nitrogen molecules must be much less than the nitrogen atom concentration. No evidence for the existence of the species N_3 was found. Kistiakowsky and coworkers (42) obtained essentially the same results.

The experimental evidence, both physical and chemical, which may be used in elucidating the reactive components in active nitrogen has recently been reviewed by Evans and Winkler (43). They conclude that "critical examination of the available experimental information provides rather convincing evidence that atomic nitrogen is the main reactive species in active nitrogen evidence exists, however, for the presence of more than one active species, and a plausible suggestion would seem to be that the second species is vibrationally excited molecules." If a second species is present in active nitrogen it is not possible, at present, to estimate the extent of its contribution to the chemical activity of active nitrogen. In the present study it will therefore be assumed that nitrogen atoms are responsible for the chemical reactivity of active nitrogen.

Reactions of Active Nitrogen with Inorganic Molecules

The chemical reactivity of active nitrogen was first studied by Strutt (2). He found that active nitrogen converted sulphur and the more volatile metals to nitrides. A nitrogen sulphide polymer was obtained with carbon disulphide, sulphur chloride, and hydrogen sulphide. The main product from the reaction of hydrocarbons with active nitrogen was hydrogen cyanide. The halogenated hydrocarbons yielded products which were hydrolyzed to cyanates in alkaline solution.

Hydrogen

B. J. Lewis (44) studied the reaction of active nitrogen with molecular and with atomic hydrogen. He found that if both gases were activated, ammonia was the only product formed. There was no reaction when only one of the gases was activated. Steiner (45) investigated the same reaction in more detail and confirmed the results of the previous work; but he also found traces of hydrazine in the active nitrogen--atomic hydrogen reaction. He also noted that some hydrazine was produced in the reaction of active nitrogen with molecular hydrogen. Steiner suggested the occurrence of the reactions,

It was shown (46) that when the activated gases met on a metal surface the ammonia yields were increased, indicating the necessity of a third body in the reaction resulting in ammonia.

Oxides of Nitrogen

The reactions of active nitrogen with NO and NO₂ were studied by Spealman and Rodebush (47). Their results could be explained by the reactions

Reaction (5) must be slower than reaction (2) since enough oxygen atoms were formed to produce the active oxygen afterglow. They confirmed these results by studying the reactions of NO and NO₂ with oxygen atoms.

Ammonia

The reaction of active nitrogen with ammonia was studied by Freeman and Winkler (48). No condensable products were found. Ammonia alone, and in mixtures with ethylene, was destroyed to an optimal extent which

appeared to be independent of temperature variation over a wide range. The amount of ammonia destroyed represented about one-sixth of the total reactivity of the nitrogen as determined by its ability to form hydrogen cyanide from ethylene. It was suggested that such behavior might be caused by two reactive species in active nitrogen; one species capable of reacting with ammonia, while the other, or both, reacted with ethylene. No decision could be made as to the identity of a second species.

Hydrazine

Freeman and Winkler (49) also studied this reaction. The only condensable product was ammonia, but the hydrazine was completely destroyed at both 105°C and 480°C up to a critical reactant input of 22 micromoles per second. Ammonia production only became appreciable at hydrazine flow rates of 10 micromoles per second. The suggested mechanism for the reaction was

The argument would be essentially the same for either N or N₃ as the reactive species.

Comparison of the rate of hydrazine destruction with the rate of hydrogen cyanide production from ethylene seemed to indicate that excited nitrogen molecules did not make any large contribution to the chemical reactivity of active nitrogen.

Reactions of Active Nitrogen with Organic Molecules

Ethylene

This reaction was first studied by Greenblatt and Winkler (50) in a conventional Wood-Bonhoeffer type of fast flow system. Water vapor in the nitrogen served as a wall poison. A nitrogen atom concentration of about 40% was measured with a Wrede gauge (39) having a sintered glass disc as a diffusion orifice (51). The products were identified as hydrogen cyanide and some ethane. A viscous polymer, probably polymerized hydrogen cyanide, was also formed. With increasing ethylene flow rate the yield of hydrogen cyanide increased linearly to a maximum, and then remained constant. The Wrede gauge measurements of nitrogen atom concentrations corresponded roughly with the maximum yields of hydrogen cyanide. The ethane yield increased as the excess of ethylene over nitrogen atoms increased.

The reaction was also investigated (52) by the same authors with a diffusion flame technique. Calcula-

tions of rate constants for several temperatures indicated an activation energy of approximately 3 k cal. and a steric factor of 10^{-2} .

A more detailed study of the reaction was made by Versteeg and Winkler (53). Improved experimental techniques eliminated the polymer formation and confirmed hydrogen cyanide to be the principal product. Lesser amounts of ethane, methane, cyanogen and acetylene were found. At the flow rate where ethylene and nitrogen atoms were both completely consumed, the relative amounts of the various products were hydrogen cyanide (75%), ethane (10%), methane (9%), acetylene (3%) and cyanogen (2%).

This reaction has been extensively studied in this laboratory and the reaction mechanisms involved appear to be fairly well understood. At elevated temperatures the maximum yield of hydrogen cyanide does not change with increasing temperature. Under the same experimental conditions none of the other hydrocarbon reactions studied have produced a greater hydrogen cyanide yield than the "plateau" yield of the ethylene reaction at elevated temperatures. Therefore it has become the practice in this laboratory to employ the active nitrogen-ethylene reaction as a means of estimating the nitrogen atom concentration. At temperatures above 250°C

the nitrogen atom concentration is equated to the maximum hydrogen cyanide yield.

Propylene

The products of this reaction (54) were hydrogen cyanide and ethylene, together with small amounts of ethane and propane. Trace amounts of acetylene and of a C_4 hydrocarbon were also detected. The saturated hydrocarbons were likely the result of hydrogenation of the olefins.

Butenes

The reactions of active nitrogen (56) with butene -1, cis-butene -2, and isobutene were found to produce mainly hydrogen cyanide, propylene and ethylene. Lesser amounts of butane, propane, ethane, methane and hydrogen were also obtained. At higher butene flow rates traces of acetylene and hydrocarbons higher than C_4 were also detected. Complete consumption of nitrogen atoms was attained with excess reactant present. The order of reactivity of the series of butenes was:

butene -1 > cis-butene -2 > isobutene

Acetylene

This reaction (55) yielded hydrogen cyanide and smaller amounts of cyanogen, methane and hydrogen among

the gaseous products. A polymer containing about 32% nitrogen was also formed in significant quantities. At very low reactant flow rates, the only product detected was polymer. The hydrogen cyanide and polymer formation became constant above a critical acetylene flow rate.

Methane

At temperatures above 280°C the production of hydrogen cyanide became significant in the methane reaction (57, 58). It was the only product detected. An "induction" effect in the hydrogen cyanide production was observed at lower methane flow rates. This "induction" effect decreased with increasing temperature and was shown to be due to the reaction of methane with hydrogen atoms.

Ethane

The only product formed in this reaction was hydrogen cyanide (57, 58). At temperatures above 165°C complete consumption of nitrogen atoms was achieved with excess ethane present. There was some indication that hydrogen atom reactions also occurred.

Propane

This reaction (59) produced hydrogen cyanide as the main product with complete consumption of nitrogen

atoms occurring in the presence of excess propane. Acetylene, ethylene, and ethane were also detected. Since the unsaturated reaction products were much more reactive than propane, the recovered unsaturates could represent only a fraction of the amounts formed.

Butanes

Both n-butane and isobutane with active nitrogen yielded hydrogen cyanide as the main product together with lesser amounts of ethylene and acetylene.

As in the propane reaction the amounts of unsaturates formed in the course of the reaction must have been considerably greater than the quantities recovered.

Neopentane

Large quantities of hydrogen cyanide and small amounts of ethylene, acetylene, propylene and propane were recovered in this reaction. At higher reactant flow rates complete consumption of nitrogen atoms was attained at 250°C. An Arrhenius plot showed a pronounced curvature with definite indication of two activation energies. Second order rate constants were calculated for the reaction at eight temperatures from -40° to 350°C.

Methyl Chloride

The gaseous products of this reaction (60) were

hydrogen cyanide, hydrogen chloride, and hydrogen, with much lesser amounts of cyanogen. Their rates of production varied linearly with methyl chloride flow rate up to a flow rate of 3 micromole per second and were independent of temperature in this linear region. The rate of consumption of methyl chloride showed a similar behavior. Even in this linear region the methyl chloride consumption was only 89%, independent of methyl chloride input or temperature. At higher reactant flow rates the yields of products tended toward a limiting value which was the greater, the higher the temperature. The cyanogen production seemed to be quite erratic but was always less than 3% of the methyl chloride consumed. No cyanogen chloride, methane, or ethane were detected in the reaction products.

Polymer deposition on the upper walls of the reaction vessel was characteristic for this reaction. Analysis of the polymer indicated that it consisted of carbon, hydrogen and nitrogen in approximately equimolar proportions and a small amount of chlorine.

Ethyl, Vinyl, and Propyl chlorides

In these reactions (60), the main products were hydrogen cyanide and hydrogen chloride. The shape of the curves for hydrogen cyanide production from the

alkyl chlorides is quite similar to that of the analogous curves for the olefins, and is quite typical of a fast reaction in which there is complete consumption of either reactant when the other is present in excess. Although the break in the curve for hydrogen cyanide production at the critical reactant flow rate was not as sharp for vinyl chloride as for the other chlorides, the general character of the reaction and its similarity in behavior to the acetylene reaction indicated that the reaction of active nitrogen with vinyl chloride is fast.

Small amounts of hydrocarbons were formed as secondary products in all the alkyl chloride reactions. Ethyl chloride yielded ethylene with traces of acetylene and ethane, vinyl chloride gave acetylene, and the hydrocarbon products from n-propyl and isopropyl chloride were mixtures of unsaturated and saturated C_3 and C_2 compounds.

The compositions of these products, in the limited range of reactant flow rates where samples sufficiently large for analysis could be recovered, were typically: for ethyl chloride, 94% ethylene, 5% acetylene, 1% ethane; for n-propyl chloride, 34% propylene, 41% ethylene, 17% acetylene, 6% propane, 2% ethane.

Reaction Mechanisms

The yields of products are quite similar in the reactions of active nitrogen with corresponding olefinic and saturated hydrocarbons of more than two carbon atoms. Many of the characteristics of the alkyl chloride reactions also resemble those of the active nitrogen-olefin reactions. It would be reasonable therefore, to suggest similar mechanisms for the reactions of these three series of molecules and, on this basis, Evans, Freeman and Winkler (61) have discussed likely mechanisms for some individual nitrogen atom-organic molecule reactions and have proposed a unified mechanism for the other reactions.

Ethylene

The primary step in this reaction was probably the energetically favorable reaction

The electronegative nitrogen atom could be expected to form a complex with an ethylene molecule having lifetime long enough to permit the necessary change in spin (43) and the migration of a hydrogen atom from one carbon atom to the other. The cyanogen flame observed and the formation of molecular cyanogen in this reaction provide some evidence for the formation of a $\text{N} - \text{C}_2\text{H}_4$

complex. The sharp maximum in the cyanogen production from ethylene at the relative reactant concentrations when the greatest number of complexes would be formed suggests that the cyanogen resulted from the reaction of nitrogen atoms with the complexes. It is possible that some cyanogen might have been formed directly in such an interaction but it seems more likely that the reaction

would result in C_2H_4 dissociation followed by reaction of the fragments with nitrogen atoms to form cyanogen radicals:

The species CH_2^* would represent a methylene radical in the triplet state (62). The production of acetylene could be explained by the reactions

where $C_2H_4^*$ and $C_2H_2^*$ represent ethylene and acetylene in triplet states. These reactions could occur with a fairly high probability (43).

The methyl radicals formed in the primary step apparently react very rapidly with nitrogen atoms (62). The products of this reaction could be hydrogen cyanide plus two hydrogen atoms or alternatively, a cyanogen radical together with a hydrogen molecule and a hydrogen atom. The preponderance of hydrogen cyanide over cyanogen observed in the products indicates that the reaction

is the one more likely to occur. The methane and ethane in the products probably were the result of reactions such as

and

Propylene

The observed production of ethylene indicates that it is a primary product. A reaction similar to that suggested above for ethylene seems plausible for the active nitrogen-propylene reaction,

The exothermicity of this reaction would allow the decomposition of ethyl radicals

if enough of the energy involved in the primary step resided in the ethyl radical as vibrational energy. The ethylene formed would react further with available nitrogen atoms.

Butenes

The primary steps in the reactions of the butenes with nitrogen atoms probably are similar to that of the propylene reaction. In the ethylene and propylene reactions there is the migration of a hydrogen atom from one carbon to the next; with cis-butene-2 a methyl group seems to show a similar behavior:

The favored line of approach of a nitrogen atom to the double bond is probably between the two hydrogen atoms and the closer approach of the nitrogen atom to one carbon atom may prevent the hydrogen atom shift and favor the shift of the methyl group instead.

The Unified Mechanism

The main features of this unified mechanism (61)

can be illustrated by comparing the primary reaction suggested above for the propylene reaction with ones for propane and propyl chloride. The observed products in these reactions can be explained if it is assumed that a chemically identical complex is formed in these reactions:

The differences observed are then ascribed to the relative ease of formation and stability of these complexes.

The structure of the N-C₃H₆ complex is probably cyclic

Evidence in support of this was provided by Jamieson and Winkler (64) in their studies of the hydrogen atom reactions with ethylenimine and N-methyl-ethylenimine. The products obtained were mainly hydrogen cyanide and methane. The initial step probably involved hydrogen abstraction from the imino group, followed by decomposition of the radical, $\text{CH}_2 - \text{CH}_2$ (counterpart of the Natom-ethylene complex), to form hydrogen cyanide.

Spontaneous decomposition of the N - C₃H₆ complex

would occur in like manner

followed by

The relative energy contents of the complexes should be such that the C_2H_5 radical formed in the propylene reaction would receive much more energy than those formed in the propyl chloride or propane reactions. Thus, it seems likely that the reaction

might occur to a significant extent only in the propylene reaction, where it is probably responsible for most of the ethylene formed.

The formation of $\text{N}-\text{C}_3\text{H}_6$ complexes and their spontaneous decomposition should be slowest for propane, and probably somewhat faster for propylene, than for the propyl chlorides. These considerations account for the formation of a much larger acetylene to ethylene ratio in the C_2 products from propane and the propyl chlorides than from propylene, and for the formation of nearly as much propylene as ethylene in the propyl chloride reactions.

The formation of unsaturated hydrocarbons as secondary products could be explained by invoking con-

servation of spin and the reluctance of molecules to transfer large amounts of energy into translational energy. Thus, a reaction scheme than can account for the unsaturated products involves further interaction between nitrogen atoms and the N - C₃H₆ complex:

Similar arguments could be applied to the elucidation of the mechanisms for the reactions of the C₄ hydrocarbons.

Acetylene and vinyl chloride behave similarly in their reactions with nitrogen atoms, and probably the same intermediate is formed in both reactions:

The recovery of a polymer with a composition close to that expected for (N-C₂H₂)_n in the acetylene reaction provides direct evidence for the existence of this complex.

The reaction of ethane however, did not yield appreciable amounts of ethylene or acetylene. It would appear therefore, that a stable N-C₂H₄ complex is not

formed in the ethane-nitrogen atom reaction. Ethane has fewer degrees of freedom than propane and the lifetime of the collision complex would be considerably reduced; the chance for a change in spin during the collision would be correspondingly lessened. Thus the spin-disallowed reaction

is the more likely primary step.

Ethyl chloride, however, appears to be able to form the $\text{N-C}_2\text{H}_4$ complex with the concomitant formation of hydrogen chloride. This behavior would be predicted by a consideration of the ethylene reaction and the unified mechanism outlined for the C_3 compounds.

The reaction of methyl chloride, unlike the reaction of methane itself, appears to involve formation of relatively long-lived complexes. By analogy with the unified mechanism, complex formation would be accompanied by the elimination of hydrogen chloride:

The recovery of some methyl chloride even at the lowest reactant flow rates indicates that the elimination of hydrogen chloride is not essential for the formation of stable complexes, and that nitrogen atoms are destroyed to some extent by a reactant-catalyzed recombination:

The latter reaction is exothermic by more than 200 kcal. A large fraction of these vibrationally excited molecules could be expected to dissociate into reactive fragments that can react very fast with atomic nitrogen. Some of the $\text{CH}_3\text{Cl}^{\text{K}}$ molecules could be de-excited on the cold walls of the trap. Recovery of methyl chloride would also result when $\text{N-CH}_3\text{Cl}$ complexes decomposed via a wall reaction in the cold trap. With increasing temperature the spontaneous decomposition rate of the complex

would increase, as indicated by the observed limiting values of product yields at higher temperatures.

The results obtained in the methyl cyanide-active nitrogen reaction (65) could be interpreted in a similar manner. A quantitative treatment of the data for the methyl cyanide reaction on the basis of nitrogen atom recombination catalyzed by the reactant gives good agreement with experiment.

The Present Investigation

For the methyl chloride reaction, Evans (63) postulated a reaction mechanism assuming the ready formation of a collision complex, of significant life-time, between a nitrogen atom and reactant molecule. The fate

of the complex depends on its tendency to dissociate and the availability of nitrogen atoms to react with it. The availability of nitrogen atoms would be governed by the relative efficiency of other species in the system as catalysts for the atom recombination. Such species would include excess reactant, products of the reaction, and the surface of the reaction system. A mathematical treatment (cf. Appendix B) was developed, which would permit the evaluation of the relative efficiencies of these atom recombination processes compared with the tendency toward formation and spontaneous decomposition of the nitrogen atom-reactant complexes. This generalized treatment was based on the reaction scheme:

where X represents a third body (either N_2 , or the wall of the reaction vessel).

Since this theoretical treatment is a potentially powerful tool in the elucidation of the mechanisms of reactions exhibiting the observed characteristics of the methyl chloride reaction, further opportunities to test its validity and applicability would be desirable.

These considerations prompted the present investigations of the reactions of active nitrogen with carbon tetrachloride, chloroform, and dichloromethane.

Figure 1

Diagram of Apparatus

Section II

EXPERIMENTAL

(1) Materials

Dry pumped nitrogen (99% pure-Dominion Oxygen Co.), was passed through a hot tube (400°C) filled with copper turnings to remove residual oxygen and then through a trap at liquid nitrogen temperature to remove water vapor.

Carbon tetrachloride, chloroform, and dichloromethane, were "Certified Reagent" grade (Fisher Scientific Co.) and were used after double bulb to bulb distillations under vacuum, the middle fractions being retained after each distillation.

(2) Apparatus

The apparatus, constructed entirely of Pyrex glass, was similar in design to the fast flow systems currently in use in this laboratory. A schematic diagram of the apparatus is shown in Fig. 1.

Nitrogen was passed from a cylinder to A through pressure tubing and flowed continuously through a simple dibutylphthalate manostat. By adjusting the level H in the manostat the nitrogen head could be maintained at a pressure of 77.0 ± 0.1 cm. Hg (Manometer M_1) despite daily variations in atmospheric pressure. The nitrogen then passed through the furnace C, which was filled with

copper turnings; and the trap N, cooled with liquid nitrogen. The flow of nitrogen into the reaction system was regulated by a flowmeter L, which consisted of a jet and stopcock. The flowmeter was calibrated by determining the rate of evacuation of a known volume of nitrogen at 77 cm. Hg.

The reaction system proper consisted of a discharge tube D, followed successively by a reaction bulb R and a product trap F. The discharge tube was 18 mm. O.D. and 75 cm. in length. It was bent in the middle so that a solution could be drawn up into the tube without it touching the electrodes. The electrodes consisted of pieces of aluminum tubing about 5 cm. long. One end of the tubular electrode was slotted and the two tabs thus formed were pressed together to attach the tungsten leads. Glass-tungsten seals through the ends of the discharge tube were made with Nonex glass.

The reaction vessel was made of a 500 ml. round-bottom flask. It was equipped with a thermocouple well extending almost into the centre of the bulb, and a jet similarly located for admitting the reactant. The pressure in the reaction system was measured with a McLeod gauge connected directly to the reaction bulb but with a vacuum stopcock in the line so that the McLeod gauge could be isolated from the reaction system.

The condensable reaction products were retained in the product trap F, which was approximately 25 cm. in length. A side arm with the stopcock S₅ and a ground-glass joint beyond the exit tube of the product trap led to the appropriate analysis system. A large 15 mm. stopcock S₆ and a protecting trap, immersed in liquid nitrogen, were inserted between the reaction system and the vacuum pump.

To minimize wall deactivation of the active nitrogen a layer of metaphosphoric acid was deposited on the walls of the reaction system. Hot chromic acid was drawn up into the reaction system and the discharge tube to a level just below the electrodes. This treatment was followed by five washings with distilled water and finally with 3% phosphoric acid. After allowing the acid to drain from the walls for half an hour, the phosphoric acid was washed off the inner tube of the product trap. The outer section of the trap was then replaced and the system pumped dry to the ultimate vacuum.

For the experiments with carbon tetrachloride, continuous pumping on the system was provided by two Cenco-Megavac oil pumps connected in parallel. An ultimate vacuum of 1×10^{-3} mm. Hg was attained with these pumps. An operating pressure of 1.62 mm. Hg resulted with a nitrogen flow rate of 82.1 micromoles per second.

sel. The pressure in the ballast volume, as indicated by manometer M_2 , was kept constant during an experiment to maintain a constant flow of reactant into the reaction bulb. Calibration experiments were made for a range of pressures in the ballast volume up to the vapor pressure of carbon tetrachloride at room temperature. During the measured time of a calibration the usual nitrogen flow was maintained in the reaction system but without the discharge in operation. The carbon tetrachloride frozen out in the product trap was then distilled into a bulb, cooled with liquid nitrogen, attached to the side-arm in the analytical section of the apparatus. When the distillation was completed the reaction system was filled with dry nitrogen. The bulb containing the carbon tetrachloride was removed and capped after carefully removing the grease adhering to the ground-glass joint. The carbon tetrachloride was then melted and its weight determined. The reactant flow rates obtained in this manner were plotted against their respective ballast pressures to give an essentially straight line curve. Two jets, "fine" and "coarse", were calibrated by this procedure. Chloroform flow rates were determined in a similar manner for a series of pressures on the flowmeter. The active nitrogen was produced in a condensed discharge provided by the cir-

cuit illustrated in Fig. 2. The power source (115 volt A.C.) was connected to a Powerstat P, which was connected in turn to the primary of a 6000 volt Hammond transformer T. This arrangement permitted a continuous variation in the output voltage of the transformer from 0 to 6000 volt.

The high voltage current was then rectified by two 866A mercury-filled, half-wave rectifier tubes S, in parallel. The pulsating direct current produced, then charged a pair of 2 microfarad Aerovox condensers C, in parallel, through 2000 ohm resistors, R. When the condensers accumulated sufficient charge, they discharged through the nitrogen between the electrodes in the discharge tube. The discharge potential was approximately 2000 volts and depended on the nitrogen pressure as well as the geometry of the tube.

(3) Experimental Procedure

The reaction system was kept under vacuum at all times except when it became necessary to regrease stopcocks or clean and repair the system. Also, to minimize the effect of changes in wall conditions in the reaction vessel, a "conditioning experiment" preceded each daily series of recorded experiments.

Prior to the commencement of an experiment the

Figure 2

Diagram of Electrical Circuit

furnace C was turned on and brought to 400°C. If the experiment was at an elevated temperature, the current in the electric furnace surrounding the reaction vessel R was then adjusted to give the desired temperature. The liquid nitrogen level in the dewar flask cooling trap N was checked and the heater filaments in the rectifier tubes switched on. With stopcock S₆ closed for about ten minutes the pressure in the reaction system was measured on the McLeod gauge to insure that no leaks had developed. The scratched stopcock S₃ was manipulated until enough reactant had been admitted from the storage bulb into the ballast volume to give the desired head on the flowmeter. The appropriate solution was frozen in the analysis trap which had been attached to the reaction system and also evacuated. With the nitrogen flowing and continuous pumping on the reaction system, the operating pressure was noted and the discharge started. Before the reactant was admitted, the discharge was operated for about ten minutes to attain a steady active nitrogen concentration. The active nitrogen temperature was then read, as registered by the chromel-alumel thermocouple situated in the reaction vessel. To ensure reproducibility, it was necessary that this temperature should not vary by more than five degrees from one experiment to the next. The level of

liquid nitrogen surrounding the product trap was maintained quite constant during an experiment and the same level was used for all the experiments so that there would be minimum variation in the volume of the reaction zone.

The reaction was started by admitting reactant through stopcock S_2 at a known time. By judicious manipulation of the scratched stopcock the head on the reactant flowmeter was maintained at the predetermined value within ± 0.05 mm. Hg at the lower flow rates. This variation in pressure increased somewhat at higher reactant flowrates. The duration of an experiment depended on the time required to introduce sufficient of the reactant to be measured accurately, or to obtain sufficient products for analysis. The reaction time therefore varied from two to six minutes. During an experiment the temperature in the reaction vessel was noted at regular intervals. At the end of an experiment, the reactant feed and the discharge were stopped, but the nitrogen flow was continued for a few minutes to sweep the reaction vessel free from reaction products.

One trap was sufficient to retain all of the condensable products, including hydrogen chloride. In a few experiments the trap that normally served to protect the oil pump was cleaned and used as a second product trap

but no appreciable amounts of condensable products were found to pass the first trap.

If pressure-volume measurements served to determine reactant flow rates, as with dichloromethane and with ethylene, the pressure in the calibrated reactant reservoir was read at the beginning and end of the experiment. With the nitrogen flow cut off at the conclusion of an experiment, the reaction system was evacuated, preparatory to the distillation and analysis of the reaction products.

During the experiments with chloroform a great deal of difficulty was encountered in obtaining reproducible results, owing to variations in the active nitrogen concentrations. All the components of the apparatus were changed, one at a time, with no appreciable improvement. The copper furnace in the nitrogen line was changed, as was the discharge tube. These latter measures decreased the fluctuations in active nitrogen concentration somewhat, but the variation in the results was still excessive. It was then found that by altering the Powerstat setting in the electrical circuit so as to obtain an "equilibrium" temperature of about 105°C with active nitrogen alone flowing through the reaction system, satisfactorily reproducible products yields could be obtained at a particular chloroform

flow rate. This procedure was therefore adopted, with good success, during the remainder of this study.

(4) Analytical Procedures

The analyses were effected by distilling the condensable products from the product trap into an absorber, cooled with liquid nitrogen, and containing the appropriate solution frozen in it. The absorber normally used consisted of two sections. The bottom section was made from a 40/50 ground-glass inner joint with a rounded bottom and approximately 10 cm. in length. The other part of the absorber consisted of a 40/50 ground-glass outer joint connected to a stopcock and a 12/30 ground-glass inner joint, which had its outer counterpart on the side arm leading to the reaction system.

With the appropriate solution in the absorber bulb and ground portions of the two sections greased and fitted together, the assembly was attached to the reaction system, and partially evacuated. The solution in the absorber bulb was then frozen with liquid nitrogen and the absorber assembly completely evacuated along with reaction system at the conclusion of an experiment. When the ultimate vacuum was attained, the stopcocks to the pump and the McLeod gauge were closed, the latter precaution being taken to prevent reaction of the mercury in the gauge with the chlorine present in the prod-

ucts.

The liquid nitrogen surrounding the product trap was then removed and the products distilled into the absorber.

If hydrogen cyanide was among the components in the reaction mixture, a layer of carbon tetrachloride was frozen on to the outside of the reaction trap. This allowed the hydrogen cyanide to distill without liquefaction, and thus minimized its polymerization.

To prevent chlorine from interfering with the analysis of the cyanogen compounds the reaction products of a separate experiment were distilled into the product trap through an intermediate tube containing copper mesh amalgamated with mercury. The amalgam was made by cleaning the copper mesh ("Chore girl" pot cleaners) in strong nitric acid and washing with copious amounts of water. When the copper surface was properly cleaned, a layer of amalgam was produced merely by dipping the mesh into clean mercury. After the mesh had been inserted into the tube it was thoroughly dried by evacuation. Fresh amalgam was prepared for each experiment.

In one experiment where this procedure was followed, the residual products were absorbed in a neutral potassium iodide solution. No iodine was liberated, which showed that the amalgam had removed all the

chlorine present.

Among the anticipated gaseous products of the active nitrogen-carbon tetrachloride reaction were chlorine, cyanogen chloride and cyanogen. A very sensitive test for chlorine consisted of dissolving the reaction products in a neutral (10%) potassium iodide solution. The iodine liberated quantitatively in the reaction,

was then titrated with standard thiosulphate solution. Under these conditions cyanogen chloride does not liberate iodine from an iodide solution (67).

After treating the products of a separate experiment as outlined above to remove chlorine, the remaining mixture of gases was dissolved in N/1 sodium hydroxide. The mixture was allowed to stand at room temperature for about six hours so that the cyanogen chloride and cyanogen present would hydrolyze quantitatively:

An aliquot of this solution was tested for cyanide using the Prussian Blue test (67). Any cyanide present would indicate the presence of cyanogen among the products.

The remainder of the mixture was acidified with 6N nitric acid and boiled for ten minutes to remove the cyanate:

Any chloride present was detected using silver nitrate. This procedure was adopted for the quantitative analysis of chloride and therefore of cyanogen chloride, by using standard silver nitrate solution and either dichloro-fluorescein or potassium chromate as indicator (68). Alternatively, the hydrolyzed solution was treated with 30% hydrogen peroxide, boiled and the liberated ammonia absorbed in an aliquot of standard acid. Back titration of the excess acid using methyl red as indicator gave a measure of the cyanate present. The chloride was determined as before.

In the reactions with chloroform and dichloromethane, hydrogen chloride and hydrogen cyanide were also found in the products. Separation of chlorine and hydrogen chloride from the cyanogen compounds was effected quantitatively by a fractional distillation at -130°C . A simple distillation between the product trap and the analysis absorber was adequate. An inspection of the vapor pressure-temperature curves (Fig. 3) of the components in a typical reaction mixture as encountered here shows that at -130°C the pressures of

Figure 3

Vapor Pressure - Temperature
Relations for Various Substances

the cyanogen compounds are less than 1×10^{-3} mm. Hg whereas the vapor pressure of hydrogen chloride and chlorine are great enough to allow their rapid evaporation.

Two absorbers were prepared; one contained neutral 10% potassium iodide solution, the other N/1 sodium hydroxide. During this stage of the distillation the temperature of the product trap was maintained at -130°C using a pentane slush. The distillation was allowed to proceed into the 10% potassium iodide for $1/2$ to $3/4$ of an hour, to ensure complete separation.

The stopcocks leading to the reaction system and the absorber were then shut and the dewar flask containing the pentane slush replaced by one containing liquid nitrogen. The first analysis trap was then replaced by the one which contained the alkali. The tube containing copper amalgam was also used to remove traces of residual chlorine. The contents of the absorber were then frozen with liquid nitrogen and the bulb evacuated through the reaction system. The stopcock to the pump was shut once more and the distillation completed into the frozen sodium hydroxide solution.

The frozen solution in the absorber was carefully melted by holding the bottom of the absorber in hot water. When some of the solution had liquified it was swirled

around to absorb the gaseous products. The remainder of the frozen solution was then melted and the mixture was ready for chemical analysis. This procedure was followed so that the gaseous products would not vaporize suddenly and cause a pressure greater than atmospheric to build up in the absorber. Also, if hydrogen cyanide was present this procedure prevented its polymerization before the cyanide could dissolve.

The combined amounts of hydrogen cyanide and cyanogen were comparatively small in the reaction with chloroform. The second fraction from the distillation was absorbed in sodium hydroxide and allowed to stand long enough so as to completely hydrolyze the cyanogen chloride and cyanogen present. The trap was then opened and the mixture titrated slowly to the turbidity endpoint with 0.05N Ag NO₃ (69). The alkaline solution was then acidified, boiled to decompose the cyanate and the chloride titrated.

Cyanogen was estimated by the method of Wallis (70) in separate experiments. After the removal of chlorine and hydrogen chloride as outlined above the remaining products were frozen into a special absorber incorporating a bubbler arrangement. It contained slightly acidified silver nitrate solution. After the distillation the solution was melted, nitrogen was bubbled through

the absorber to carry any cyanogen into succeeding bubblers in the train, which contained N/1 sodium hydroxide. The cyanide liberated in the hydrolysis was titrated with standard silver nitrate, 6 ml. of 6 N ammonia and 0.2 gm. of potassium iodide being added to the solution prior to titration (68).

The analytical schemes used in the reaction with chloroform were also used in the dichloromethane reaction with only minor changes. Hydrogen cyanide was produced in much greater quantities than cyanogen chloride. Therefore, after the titration for cyanide to the Liebig end-point (69) and removal of the cyanate, the hydrogen cyanide was again expelled from the acid solution by boiling. Since the chloride resulting from the hydrolysis of cyanogen chloride was not sufficient to remove the silver completely from solution, the excess silver from the cyanide titration was back-titrated with standard thiocyanate using ferric ammonium sulphate as indicator (71).

The quantitative expulsion of hydrogen cyanide from the acidic solution was confirmed by omitting the addition of silver nitrate to the products of one sample, and, after the usual treatment, titrating for chloride only. The cyanogen chloride yield was the same as that determined previously.

In some experiments with ethylene, made for reference purposes, hydrogen cyanide was determined by titration in the usual manner.

Section III

RESULTS

It was not possible to maintain the same reaction conditions, and hence the same active nitrogen concentrations, throughout all the experiments with carbon tetrachloride, chloroform, and dichloromethane. However, for each set of conditions a series of experiments was performed with ethylene, and the relative "plateau" values for the hydrogen cyanide production in this reaction were used to correlate the data obtained with the other reactants.

The hydrogen cyanide "plateau" yields obtained in the ethylene-active nitrogen reaction at 100°C and 425°C were 6.00 ± 0.15 and 9.28 ± 0.12 micromoles per second, respectively, with a molecular nitrogen flow rate of 39.0 micromoles per second and an operating pressure of 0.96 mm. Hg. The equivalent results at 220°C and 385°C were 9.95 ± 0.53 and 14.6 ± 1.2 micromoles per second, respectively, with a nitrogen flow rate of 180 micromoles per second at a pressure of 1.65 mm. Assuming that the hydrogen cyanide production in the ethylene reaction at the higher temperature indicates the nitrogen atom concentration (cf Section I), calculations show that the nitrogen atom concentration was 36% lower during the experiments with carbon tetrachloride than for the experiments with the other two chloromethanes.

During a series of some thirty experiments with carbon tetrachloride the chlorine yields at one reactant flow rate were determined at the beginning, in the middle, and at the end of the series. The mean deviation was only about 2% for this particular series, indicating that it was not necessary to clean and poison the reaction system while the series was in progress.

The flames produced in the three reactions with active nitrogen studied were remarkably similar in color and behavior. The carbon tetrachloride reaction flame had a distinctly orange tint and was also much brighter than the violet flame characteristic for the ethylene-active nitrogen flame. The orange tint of the reaction flame decreased progressively with chloroform and dichloromethane.

At very low carbon tetrachloride flow rates (less than 0.1 micromoles per second), the reaction flame was spherical in shape and centered about the jet. The nitrogen after-glow filled the remainder of the reaction vessel. With increased carbon tetrachloride flow, the flame became progressively larger until at 0.3 to 0.5 micromoles per second of reactant flow the reaction flame had completely displaced the nitrogen after-glow in the reaction bulb. At this stage the flame also streamed downward into the product trap.

With further increase in the carbon tetrachloride flow the main reaction flame started contracting upwards. At the highest carbon tetrachloride flow rates attained in this study, the flame filled the upper half of the reaction vessel and diffused back into the connecting tube leading to the discharge tube for a distance of about one centimeter. This behavior was also exhibited by the reaction flames of chloroform and dichloromethane.

This behavior of the reaction flame would explain the lower temperatures recorded for experiments at the higher reactant flow rates since the thermocouple well extended into the centre of the reaction vessel. It seems likely that the higher temperatures recorded in a series probably were the better approximations to the actual temperatures of the reaction flames.

Polymer formation on the walls of the reaction vessel and product trap seems to be characteristic of the reactions of chloromethanes with active nitrogen. The formation of some brown polymer on the upper parts of the reaction vessel in the active nitrogen-methyl chloride reaction was reported by Evans (62).

In all the reactions of the present study, polymer deposition on the walls of the reaction vessel was slight and of a greenish-brown tinge but only after numerous experiments was there a noticeable opacity.

In the carbon tetrachloride reaction the polymer laid down after several preliminary qualitative experiments was largely removed by introducing chloroform as a solvent into the reaction vessel, but patches of a whitish deposit remained in the lower half of the bulb. This whitish film possibly consisted of hexachloroethane since it was soluble in ether. The slight amount of polymer deposit from the experiments at room temperature was not removed prior to the experiments at higher temperatures. At the end of the series when the furnace enclosing the reaction vessel was removed the opaque polymer film had disappeared leaving the glass walls quite clear. Just below the furnace there was a slight deposit of whitish material on the walls of the exit tube of the reaction bulb. This film could be removed with ether and was probably hexachloroethane which had sublimed to the cooler surface. The colored deposit on the walls of the reaction bulb might have been impure cyanuric chloride; the latter would decompose to cyanogen chloride at about 400°C.

The polymer formed on the walls of the reaction vessel in the reactions with chloroform and dichloromethane seemed to be similar in amount and color to that observed in the carbon tetrachloride reaction, although it did not disappear when the reaction vessel was heated.

The polymer film on the walls of the reaction vessel could be removed quite readily with a 2N ammonia solution. During the series of experiments with chloroform, an aliquot of this ammonia solution was boiled for thirty minutes. The sample was tested for chloride and cyanide. The chloride test gave a slight reaction but the tests for cyanide were definitely positive. Since paracyanogen would be more stable when heated than was experimentally observed for the polymer it seems likely that the constitution of the polymer could not be described in terms of definite compounds like cyanuric chloride or paracyanogen, and the possibility that some of the polymer was partly non-nitrogenous cannot be discounted.

The polymer deposited on the walls of the product trap during the reaction with carbon tetrachloride was slightly darker than that found in the reaction bulb. For the reactions with chloroform and dichloromethane, the polymer on the walls of the trap became progressively darker and in the latter case seemed to be somewhat "granular" in character. This polymer seemed to be comparatively unaffected by the common organic solvents and by concentrated acids and bases. This resistance to solvent action appeared to increase as the chlorine content of the reactant decreased.

At the end of the series of experiments with dichloromethane, when the deposit in the trap seemed most pronounced, an attempt was made to collect sufficient of the material for analysis but this was not achieved. The slight amount of dust obtained glowed and disappeared when heated strongly in air. These observations suggested that this polymer was essentially elemental carbon in the dichloromethane reaction. Some chlorinated hydrocarbon polymer was undoubtedly also formed in the trap in this reaction and progressively larger amounts in the chloroform and carbon tetrachloride reactions.

(1) Active Nitrogen - Carbon Tetrachloride

In all experiments reported with carbon tetrachloride the molecular nitrogen flow was kept constant at 39.0 micromoles per second and the reactant flow rates were varied from 0.3 to 12 micromoles per second. Reaction pressures were in the range of 0.96 to 1.00 mm. Hg. The nitrogen atom concentration obtained under these conditions was 9.28×10^{-6} gram atoms per second, on the basis of constant hydrogen cyanide production in the ethylene-active nitrogen reaction at 425°C with similar operating conditions. This would be equivalent to approximately 12% active nitrogen in the nitrogen

stream.

With active nitrogen alone pumped through the system and with no external heating, the temperature increased to 60°C in the reaction vessel. During reaction the temperature rose to 100 - 105°C at lower carbon tetrachloride flow rates, while at flow rates greater than 5 micromoles per second the reaction temperature was somewhat lower, in some cases being only 85°C. This behavior was probably due to variations in the size and position of the reaction flame described above. In the reactions at 420°C where the reaction vessel was heated externally with a furnace, the active nitrogen flow raised the temperature some 10 to 20°C and a similar increase was noted during reaction.

Studies were made at $100 \pm 10^\circ\text{C}$ and at $420 \pm 5^\circ\text{C}$. The gaseous products were chlorine and cyanogen chloride. In two preliminary experiments the "Prussian Blue" test failed to give any indication in the basic solution containing the products after removal of chlorine from the gas stream. In a third trial the test solution showed a green coloration but no blue precipitate was produced. Consequently, it may be assumed that cyanogen was not among the gaseous products in significant amounts.

The yields of chlorine and cyanogen chloride,

obtained at 100°C and at 420°C in the range of carbon tetrachloride flow rates from 0.3 to 12 micromoles per second, are given in Table I. The chlorine and cyanogen chloride yields at 100°C and 420°C are plotted against carbon tetrachloride flow rates in Figure 4 and Figure 5, respectively. Ratios of the yields of cyanogen chloride to chlorine were calculated from the data at the various carbon tetrachloride flow rates and the two temperatures, and are given in Table II.

At both temperatures, the yields of chlorine and cyanogen chloride seemed to approach constant values at the higher carbon tetrachloride flows. The rate of increase in product yields with increasing carbon tetrachloride flow rates were not constant, even at the lower reactant flow rates. It was apparent therefore, that the over-all reaction was not fast enough to allow complete conversion of carbon tetrachloride to chlorine and cyanogen chloride even at flow rates where the nitrogen atom concentration was well in excess. The average time that the reactants spent in the reaction volume was about 0.24 seconds, although at higher flow rates this would likely be less since the flame contracted somewhat. Absolute carbon balances were not calculated since unreacted carbon tetrachloride was not determined.

Table I
Chlorine and Cyanogen Chloride Production from the
Active Nitrogen - Carbon Tetrachloride Reaction

Temperature $90 \pm 10^\circ\text{C}$

CCl ₄ flowrate moles/sec x 10 ⁶	0.32	0.51	0.96	1.20	1.60	2.32	3.84	4.41	5.09	7.48	9.20
Cl ₂ Yields mole/sec x 10 ⁶	0.40	0.61	1.03	1.09	1.34	1.49	1.39	1.65	1.65	1.72	1.82

Temperature $420 \pm 15^\circ\text{C}$

CCl ₄ flowrate mole/sec x 10 ⁶	0.36	0.96	1.50	2.04	3.00	3.98	4.84	5.66	6.70	9.34	11.7
Cl ₂ Yield mole/sec x 10 ⁶	0.73	1.32	1.38	2/05	2.30	2.60	2.33	2.63	2.93	3.26	3.16

Temperature $90 \pm 15^\circ\text{C}$

CCl ₄ flowrate mole/sec x 10 ⁶	0.96	1.49	1.49	2.46	3.56	4.40	5.30	6.18	7.04	7.70	9.10	9.10	10.6	11.5
CNCl Yield mole/sec x 10 ⁶	0.35	0.33	0.40	0.81	1.00	0.98	1.09	1.37	1.28	1.21	1.06	1.07	0.89	0.93

Temperature $420 \pm 15^\circ\text{C}$

CCl ₄ flowrate mole/sec x 10 ⁶	0.51	0.96	1.50	2.04	3.00	3.98	5.74	7.92	11.5
CNCl Yield mole/sec x 10 ⁶	0.39	0.69	0.98	1.15	1.39	2.10	1.65	1.88	2.01

Figure 4

Chlorine Yield as a Function of
Carbon Tetrachloride Flowrate

PRODUCT YIELDS — MOLE / SEC $\times 10^6$

Figure 5

Cyanogen Chloride Yield as a Function
of Carbon Tetrachloride Flowrate

PRODUCT YIELDS — MOLE / SEC $\times 10^6$

(2) Active Nitrogen - Chloroform

In the series of experiments reported for the chloroform reaction the molecular nitrogen flow was 180 micromoles per second at an operating pressure of 1.62 - 1.70 mm. Hg. The reactant flow was varied from 0.4 to 14 micromoles per second.

The nitrogen atom concentration obtained under these conditions was 14.6×10^{-6} gram atom per second on the basis of the constant hydrogen cyanide yields obtained in the ethylene-active nitrogen reaction at 385°C under similar operating conditions. It is readily estimated that approximately 4% of the molecular nitrogen that entered the reaction vessel was made available as active nitrogen.

With only active nitrogen flowing through the system and no external heating the temperature increased to 110°C. During reaction the temperature increased to about 260°C at the lower chloroform flow rates, while at chloroform flow rates above 4 micromoles per second the reaction temperature generally was somewhat lower. This behavior was quite similar to that observed in the reaction with carbon tetrachloride. In the reactions at 425°C, with external heating of the reaction vessel, the active nitrogen flow increased the temperature approximately 10°C with another increase of about 20°C during

reactions.

Among the gaseous products were hydrogen chloride, cyanogen chloride and chlorine in comparatively large amounts with lesser amounts of hydrogen cyanide and cyanogen. The analytical scheme employed gave the combined yields of hydrogen cyanide and cyanogen. Three experiments were made for chloroform flow rates from 3 to 10 micromoles per second where the cyanogen yields were determined separately. These showed that the "HCN" yields reported were about 60% cyanogen. The product yields obtained at the various chloroform flow rates up to 14 micromoles per second and at 240 - 260°C are recorded in Table III and Fig. 6. The results for the experiments at 425°C $\pm$ 15°C are given in Table IV and shown graphically in Fig. 7. The data plotted in Fig. 6 and 7 are the combined hydrogen cyanide and cyanogen yields.

At 260°C, the yields of hydrogen chloride and cyanogen chloride increased regularly but non-linearly with increasing chloroform flow rates to 7.5 micromoles per second and 5.2 micromoles per second, respectively, for a chloroform flow rate of 11.0 micromoles per second. The combined production of hydrogen cyanide plus cyanogen became constant at 0.9 micromoles per second at the higher reactant flow rates. Chlorine

Table III
Product Yields from the Active Nitrogen - Chloroform Reaction

Temperature $250 \pm 10^\circ\text{C}$										
CHCl ₃ flowrate mole/sec x 10 ⁶	2.85	4.55	6.55	8.20	9.85	10.7	11.4	12.3	14.0	
HCl Yield mole/sec x 10 ⁶	2.80	4.10	5.33			6.97	6.81	7.87	8.24	
CNCl Yield mole/sec x 10 ⁶	1.76	2.99	3.43			4.44	4.80	5.50	6.00	
HCN + (CN) ₂ Yield* mole/sec x 10 ⁶	0.50	0.51	0.77	0.93	0.88	0.96	0.88			
CHCl ₃ flowrate mole/sec x 10 ⁶	0.36	1.58	3.13	4.24	5.45	6.75	6.90	7.40	9.80	13.2
Cl ₂ Yield mole/sec x 10 ⁶	0.26	0.85	1.53	1.82	1.90	1.68	1.80	1.69	1.77	1.71

*(CN)₂ is approximately 60% of Combined values.

Figure 6

Product Yield as a Function
of Chloroform Flowrate

Table IV
Product Yields from the Active
Nitrogen - Chloroform Reaction

CHCl ₃ Flow Rate	HCl Yield	CNCl Yield	HCN+(CN) ₂ Yield	Cl ₂ Yield
Temperature 425 ± 15°C				
3.85	3.72	2.55	1.28	2.17
5.00	5.12	--	1.48	3.15
8.20	8.07	5.79	1.61	--
7.85	--	--	--	3.07
9.05	--	--	--	3.03
11.45	9.70	7.11	1.45	2.86

Figure 7
Product Yield as a Function
of Chloroform Flowrate

Yields increased linearly to a "plateau" value of 1.8 micromoles per second with chloroform flow rates greater than 4.3 micromoles per second.

Similar trends in the yields of the various products were found for the reaction at 425°C although considerably more reaction was observed. At a chloroform flow rate of 11.0 micromoles per second the hydrogen chloride yield increased to 10.2 micromoles per second and that of cyanogen chloride to 7.5 micromoles per second. The "plateau" values for combined hydrogen cyanide plus cyanogen yields and for chlorine production were 1.5 and 3.0 micromoles per second, respectively.

(3) Active Nitrogen - Dichloromethane

In the experiments on the reaction of dichloromethane with active nitrogen, the molecular nitrogen flow, operating pressure, and active nitrogen production were the same as for the chloroform reaction. No major difficulties were encountered in attaining reproducibility of results. The reaction was decidedly exothermic and with no external heating the temperature registered on the thermocouple in the centre of the reaction vessel rose from 105°C to 255°C. Again, there was considerable variation in the "reaction temperature,"

with temperatures up to 270°C registered at low reactant flow rates and 240°C in the experiments at the highest reactant flow rates studied. With external heating of the reaction vessel the temperature increased from 325°C to a mean value of 430°C during two minutes of reaction. The fluctuations from one experiment to the next were again considerable and temperatures quoted may only be taken as a rough indication of the temperature of the reaction flame. As noted previously, the variations in temperature registered during individual experiments were likely due in part to the behavior of the flame and perhaps, to some extent, to polymer formation on the thermocouple well.

The major products obtained were hydrogen chloride, hydrogen cyanide and cyanogen chloride. Much lesser amounts of chlorine and cyanogen were obtained. Separate experiments were made to determine the variation in cyanogen yields with reactant flow rate. The maximum amount obtained was about 0.4 micromoles per second at 255°C. The analytical technique used in the main series was such that cyanogen and hydrogen cyanide were estimated together but separate experiments gave the cyanogen content of the mixture as approximately 10%. The yields of products observed at dichloromethane flow rates from 1.0 to 14.2 micromoles per second, and at

temperatures of $255 \pm 15^{\circ}\text{C}$ and $435 \pm 20^{\circ}\text{C}$, respectively, are given in Table V. The variation of product yield with dichloromethane flow rates at the two temperatures are shown graphically in Figs. 8 and 9, respectively.

At both temperatures hydrogen chloride and hydrogen cyanide production increased linearly with increasing dichloromethane flow rates and became constant at a critical reactant flow rate of 8.0 micromoles per second at 255°C and 9.6 micromoles per second at 455°C .

Above the critical reactant flow rate the product yields became constant. These "plateau" values for hydrogen chloride were 11.75 ± 0.17 and 14.75 ± 0.25 micromoles per second at 255°C and 425°C , respectively. It will be readily seen that the "plateau" value for hydrogen chloride at 425°C is the same as the nitrogen atom concentration estimated from the ethylene reaction. The slope of the linear portion of the hydrogen chloride production curve did not vary appreciably with a change in reaction temperature. On the other hand, the hydrogen cyanide production was somewhat greater at 425°C for dichloromethane flow rates up to the critical value. The constant or "plateau" values for hydrogen cyanide production were 4.28 ± 0.10 and 5.62 ± 0.10 micromoles per second at 255°C and 425°C , respectively. The increase in "reaction temperature" from 255°C to 435°C increased

Table V

Product Yields from the Active
Nitrogen - Dichloromethane Reaction

Temperature $255 \pm 15^{\circ}\text{C}$

	CH ₂ Cl ₂ Flow Rate mole/secx10 ⁶	HCl Yield mole/secx10 ⁶	HCN + (CN) ₂ Yield mole/secx10 ⁶	CNCl Yield mole/secx10 ⁶	Cl ₂ Yield mole/secx10 ⁶
C1	2.52	4.16	1.76	0.22	0.21
C3	4.86	8.36	2.85	0.76	0.24
C4	6.77	10.42	3.77	1.02	0.27
C5	8.06	11.61	4.05	1.40	0.21
C2	10.05	13.54	4.22	1.19	0.27
C6	11.15	11.71	4.37	--	0.09
C7	14.16	11.92	4.24	1.14	0.19

*(CN)₂ yield less than 10% of combined yields.

Table V (Continued)

Temperature $425 \pm 20^\circ\text{C}$

CH_2Cl_2 flowrate mole/sec $\times 10^6$	2.85	5.14	5.35	7.14	10.6	12.3
HCl Yield mole/sec $\times 10^6$	5.07	9.30	9.78	12.95	14.97	14.50
$\text{HCN} + (\text{CN})_2$ Yield mole/sec $\times 10^6$	2.33	--	3.76	4.74	5.68	5.55
CNCl Yield mole/sec $\times 10^6$	0.33	--	0.81	1.28	2.06	2.16

Temperature $425 \pm 20^\circ\text{C}$						
CH_2Cl_2 flowrate mole/sec $\times 10^6$	3.02	5.15	7.45	8.80	12.4	
Cl_2 Yield mole/sec $\times 10^6$	0.66	0.92	0.66	0.55	0.49	

Figure 8

Product Yield as a Function
of Dichloromethane Flowrate

the yields of cyanogen chloride from 1.24 to 2.11 micromoles per second at dichloromethane flow rates above 8.0 micromoles per second. The production of chlorine was only significant at the higher temperature when yields up to 0.6 micromoles per second were obtained. The one experiment where the chlorine yield of 0.92 micromoles per second was observed should probably be ignored since it was unique.

Section IV

DISCUSSION

The possibility that more than one species contributes to the chemical reactivity of active nitrogen cannot be precluded, in view of the results obtained for the ammonia-active nitrogen reaction (48). However, atomic nitrogen appears to be responsible for most of the reaction observed with organic molecules (cf. Section I). It will be assumed, in discussing the results of the present study, that atomic nitrogen in the ground state is the chemically reactive species in active nitrogen.

The reactions of active nitrogen with dichloromethane, chloroform, and carbon tetrachloride markedly resemble the corresponding reaction with methyl chloride. The similarities include the color and behavior of the reaction flames observed, the tendency to polymer formation, the exothermicity of the reactions and the tendency to formation of hydrogen chloride whenever possible. It is therefore reasonable to consider the possibility that the mechanism postulated for the reaction with methyl chloride (62) might be applicable to the reactions of the other chlorinated methanes.

This mechanism assumed the ready formation of a collision complex, of significant life-time, between a nitrogen atom and reactant molecule. The fate of this

complex depends upon its tendency to dissociate into products, and on the availability of nitrogen atoms to react with the complex. Further attack of the complex by nitrogen atoms would promote nitrogen atom recombination, and possible dissociation of the reactant molecule if sufficient energy were imparted to it as vibrational energy during the recombination. Nitrogen atom recombination catalyzed by product, rather than reactant, might also occur. The observation that the afterglow was extinguished at very low reactant flow rates seems to indicate that collision with reactant molecules may lead to de-excitation of excited nitrogen molecules ($B^3\Pi_g$) without emission.

The assumption of long-lived collision complexes in these reactions would allow normally rare three-body recombination processes to compete more favorably with direct reaction of nitrogen atoms with reactant molecules.

Flow conditions have considerable influence on the kinetic behavior of reactions in flow systems, as noted by Bodenstein and Wolgast (74). If there is no turbulence in the reaction chamber, the composition of the reaction mixture will be a function of time (or distance from the reactant inlet) and the total amount of product formed in a given reaction will be an integral

over all the infinitesimal concentration increments in a given time element. This type of flow is known as "streamline flow." If on the other hand there is complete turbulence in the reaction volume, the composition of the reaction mixture will be essentially that of the gases leaving the reaction bulb. The absolute amount of product formed will be proportional to the time spent in the reaction volume and to the initial concentrations of the reactants. This type of flow is referred to as "turbulent flow."

These are the two extremes possible, and, obviously, it is only seldom that actual conditions will be essentially one or the other. On the other hand, any mathematical treatment for conditions intermediate between these extremes becomes too complex for practical solution.

The behavior of the reaction flames with variation in reactant flow rate in this, and in previous studies, indicates that for the conditions used, the flow in the reaction vessel was closer to stream-line than to turbulent flow, and the discussion that follows therefore assumes stream-line flow.

A general treatment for the disappearance of nitrogen atoms by direct reaction, in competition with nitrogen atom recombination processes catalyzed by re-

actant, products and vessel surface was developed by Evans (62).

The reaction scheme used was

Where N and M represent a nitrogen atom and reactant molecule respectively, P represents one of the reaction products and X represents other third bodies (either N_2 or the wall) whose effectiveness would not change appreciably with reactant flow rate.

Assuming that the reactions were fast enough to go essentially to completion before the gas stream entered the product trap it was possible to calculate the forms of the curves relating product formation to flow rates of reactant under various conditions. The details of the mathematical treatments and the tables of numerical values derived from these equations are presented in Appendix B.*

The data thus obtained are plotted in Figures 10 to 15. For these theoretically derived curves abscissae are given by $S = M_o/N_o$ corresponding to the

*The theoretical background and mathematics of this general treatment were developed by H. G. V. Evans (62).

Figure 10

Calculated Production vs. Flow Rate

$$\beta = k_2 N_0 / k_1; k_3 = k_4 = 0$$

Figure 11

Calculated Production vs. Flow Rate

$$\beta = k_2 N_0 / k_1; \quad k_3 = 0; \quad \frac{k_4 X}{k_1} = 0.1$$

Figure 12

Calculated Production vs. Flow Rate

$$\beta = k_2 N_0 / k_1; k_3 = 0; \frac{k_4}{k_1} X = 0.5$$

Figure 13

Calculated Production vs. Flow Rate

$$p = k_4 X / k_1; k_2 = k_3 = 0$$

Figure 14

Calculated Production vs. Flow Rate

$$\beta = k_2 N_0 / N_1; k_2 = k_3, k_4 X / k_1 = 0$$

Figure 15

Calculated Production vs. Flow Rate

$$\beta = k_2 N_0 / k_1, \quad k_2 = k_3; \quad k_4 / k_1 = 0.5$$

ratio of reactant input to nitrogen atom input, while the ordinates $W = S(1-X)$ correspond to $M - M_0/N_0$, i.e. the ratio of reactant consumed to the nitrogen atom input. It might be noted that the variable W is proportional to the reactant consumption, whereas the experimental curves under consideration deal with the yields of products resulting from the reactions. However, past studies have shown that the shapes of the two types of curves are similar.

It was implicitly assumed in all the calculations that the total flow remained essentially constant. Back (75) has found that HCN production reached a maximum and then decreased somewhat with increasing reactant flow rate in the N atom-butane reaction. Some of this decrease might have been due to recombination of N atoms by collision with reaction complexes, but it seemed likely that an increase in total flow with increasing reactant flow rates was mainly responsible. The molecular nitrogen flow rate for the reactions with chloroform and dichloromethane was 180 micromoles per second and the error in assuming constant total flow would be less than 6% at the highest reactant flow rates attained. However, in the reaction of active nitrogen with carbon tetrachloride, where the molecular nitrogen flow was 77% lower, the introduction of reactant probably influ-

enced the total flow rate appreciably and would account for the observation that the product yields at the higher carbon tetrachloride flow rates were less than might have been expected from a comparison with similar curves for the other reactions, and with theoretical curves. Sweeping and detailed conclusions from the comparisons of the experimental and theoretical curves must therefore be avoided.

The relations between reactant consumption and flow rate where only reactions (1) and (2) are significant are shown in Fig. 10. It may be readily seen that there is a linear increase in consumption up to a critical reactant flow rate, above which the yield becomes constant. The values of the maximum consumption (and therefore maximum yield) and critical flow rate decrease with an increase in the parameter, where β represents k_2N_0/k_1 . Therefore, increase in β indicates a relative increase in the importance of reaction (2) with respect to reaction (1). It should also be noted that the rate of reactant consumption remains constant below the critical reactant flow rate if reactions (3) and (4) do not contribute appreciably to nitrogen atom recombination.

Figures 11 and 12 illustrate the variation in reactant consumption with reactant input when reaction

(3) is negligible but with an increasing contribution from reaction (4). It will be seen that an increase in reaction (4) tends to depress the higher portions of the consumption-input curves; the initial slopes of the curves do not change.

The results obtained when the only reactions contributing to the disappearance of nitrogen atoms are reactions (1) and (4) are shown in Fig. 13. For increasing values of p (corresponding to k_4X/k_1) the reactant consumption-input curves are depressed and for high enough " p " values even the initial portions of the curves become non-linear. It may be seen that whatever values are assigned to k_2 and k_3 , there can be an initial linear region only if the ratio k_4X/k_1 is less than unity.

Figures 14 and 15 show the form of the curves obtained when $k_2 = k_3$. Fig. 14 shows the effect of various values of β on the consumption versus reactant input curves where k_4 is zero, while Fig. 15 illustrates the effects of the variation in β with an added contribution from reaction (4). Under both sets of conditions the exact values of critical reactant flow rates are obscured and for higher values of β , i.e. increasing contribution from reaction (2), the apparent product yields tend toward constancy more rapidly with increasing reac-

tant input.

As will be shown later, the nitrogen-containing compounds produced in the reactions of the chloromethanes with active nitrogen result mainly from reaction (1), while the yields of non-nitrogenous products like chlorine or hydrogen chloride are probably also affected by reactions (2) to (4). Hence comparisons of the theoretical and experimental curves should be most significant if they are made for the production of chlorine or hydrogen chloride rather than the production of nitrogen-containing compounds.

In the carbon tetrachloride-active nitrogen reaction, comparison of the chlorine yield-reactant input curves (Fig. 4) with the theoretically derived curves indicated that the conditions for the curves in Figures 10 and 11 are not applicable. However, the resemblance between the chlorine production curves at 95°C and 420°C with the set of curves in Fig. 15 for the higher values of β appear to indicate that all of the reactions in the scheme outlined contribute appreciably to the disappearance of nitrogen atoms. The theoretical curves in Fig. 12 for the higher values of β could also be compared favorably with the chlorine production curves. The inability to distinguish between the curves in Figures 12 and 15 indicates some uncertainty with regard to the

importance of product catalyzed recombination of nitrogen atoms in the reaction with carbon tetrachloride.

It would appear then that the active nitrogen-carbon tetrachloride reaction is accompanied by appreciable nitrogen atom recombination catalyzed by reactant molecules and the walls, and possibly some product-catalyzed recombination.

For the active nitrogen-chloroform reaction, a comparison was made of the curves for the production of HCl at 260°C and 425°C with the theoretical curves for reactant consumption versus input. The curves in Fig. 12 (β values from 1.0 to 5.0) and those in Fig. 14 (β values from 1.0 to 4.0) were reasonably similar in shape to the experimental curves for HCl production at the two temperatures. The curves under consideration in both Figures 12 and 14 indicate an appreciable contribution from reaction (2) as well as reaction (1). The curves in Fig. 12 allow for no contribution from reaction (3) while the recombination of nitrogen atoms involving molecular nitrogen and the walls of the bulb contributes to some extent; the reverse was true in Fig. 14 with respect to contributions from reactions (3) and (4).

These comparisons have shown that the reactant-catalyzed recombination of nitrogen atoms is even more significant in the reaction of active nitrogen with

chloroform than with carbon tetrachloride. In both reactions the efficiency of one or more of the products in promoting nitrogen atom recombination cannot be unequivocally evaluated, but the possibility of the latter occurrence certainly cannot be precluded from the reaction mechanism.

The product yield curves for the reaction with dichloromethane all seem to be essentially linear up to the critical dichloromethane flow rate, followed by constant product yields at higher dichloromethane flows. The HCl curves at 425°C especially, bears a very strong resemblance to the curves illustrated in Fig. 10 where reactions (3) and (4) are of negligible importance and the destruction of nitrogen atoms involves only reactant molecules. The HCl curve at 255°C does fall off slightly in the region of the critical reactant flow rate which is the behavior exhibited by the curves shown in Fig. 11. This indicates that reaction (4) competes to some extent with reactions (1) and (2) in the critical flow region.

The product yield curves obtained at the higher of the two temperatures, at which a reaction was studied resembled that curve in a particular family of theoretically derived curves which involved a lower value of β . This observation indicates that reaction (1) is more

important than reaction (2) at the higher temperature in any particular reaction. This behavior was also indicated by the observation that the slope of the initial portion of the curve for the production of HCN increased slightly at the higher temperature. A similar behavior was observed in the reactions of active nitrogen with methyl chloride, azomethane, and ethylene (cf. Section I).

Mechanisms of the Reactions

(a) Active Nitrogen - Carbon Tetrachloride

The behavior of the reaction may be summarized as follows:

- (1) The only gaseous products were chlorine and cyanogen chloride.
- (2) Cyanogen was not found among the products.
- (3) Polymer was formed on the walls of the reaction vessel and product trap. The polymer in the reaction bulb seemed to be a mixture of hexachloroethane with a compound that might have been cyanuric chloride.
- (4) The $\text{Cl}_2:\text{CNCl}$ ratio seemed to be comparatively high at very low CCl_4 flow rates but showed a regular decrease with increasing CCl_4 flow. At 420°C the initial rate of Cl_2 production was greater than

might be expected from the stoichiometric relation

The mathematical treatment of the variation in product yields with reactant flow rate indicated that the collision complex of a nitrogen atom and carbon tetrachloride molecule should be comparatively long-lived and could therefore contribute appreciably to nitrogen atom recombination by further collisions with nitrogen atoms. Taking into consideration the high electron density resulting from the four chlorine atoms bonded to a carbon atom as in carbon tetrachloride, and the electronegativity of a nitrogen atom, this collision complex might be expected to have a reasonably long lifetime.

In this reaction, as in all the reactions of organic molecules with active nitrogen studied in this laboratory, the only products containing nitrogen have a carbon-nitrogen bond. This observation restricts the modes of dissociation of the collision complex formed with carbon tetrachloride:

Reaction (5) is indicated as being endothermic by 7 kcal, but there is a comparatively large uncertainty

in the estimated heat of formation of the CN radical since the bond dissociation energy of the carbon-carbon bond in cyanogen is still in doubt (76, 77). It is conceivable, therefore, that the reaction might be less than 7 kcal endothermic. A more serious objection to reaction (5) as a possible primary reaction is the fact that cyanogen was not among the gaseous products except in minute traces.

The reaction

is energetically favorable and analogous radical reactions with chlorine in the photochemical chlorinations of short chain hydrocarbons occur with activation energies estimated to be less than 5 kcal (78). On the other hand, it seems reasonable that dimerization of CN radicals to cyanogen (79) should have occurred to an appreciable extent if reaction (5) were an important primary step. It may be concluded therefore, that reaction (6) is the only significant mode of dissociation of the collision complex.

The possible presence of hexachlorethane in the polymer found on the walls of the reaction bulb suggests the occurrence of a reaction of the type

followed by recombination of CCl_3 radicals. However,

Schwab (80, 81) studied the reaction of chlorine atoms, produced by the discharge tube method, with CCl_4 and found that CCl_4 did not cause any decrease in the chlorine atom concentration. He estimated the activation energy of reaction (8) to be greater than 12 kcal, which seems reasonable.

The observed increase in the $\text{Cl}_2 : \text{CNCl}$ ratio with decrease in CCl_4 flow rate would seem to indicate that a reaction leading to chlorine but not CNCl occurred to an increasing extent as the CCl_4 flow rate was decreased.

At the lower CCl_4 flow rates where nitrogen atoms would certainly be in excess, such a reaction might be:

followed by decomposition of excited CCl_4 to yield chlorine.

According to Evans (62) there should be little or no activation energy for reaction (9). The heat evolved would be $(225 - q)$ kcal, where q represents the heat of formation of the complex. A considerable proportion of the excess energy could appear in the internal degrees of freedom of the products of reaction (9) and if this occurred the excited CCl_4 molecule might dissociate:

There are other possible modes of dissociation but the possible presence of hexachlorethane on the walls of the reaction bulb and of elemental carbon in the product trap indicate the likely occurrence of reactions (10) and (11) followed by dimerization of the CCl_3 radicals. Another mode of dissociation of vibrationally excited carbon tetrachloride molecules might be

although no definite evidence can be cited to indicate the presence of reaction (12). It is very likely that further reaction would occur rapidly between nitrogen atoms and radicals of the type of CCl_2 . With increasing carbon tetrachloride flow rate the nitrogen atom concentration and therefore the probability for the occurrence of reaction (9) would decrease and the Cl_2 : CNCl ratio decrease as observed.

To summarize, the reaction of nitrogen atoms with carbon tetrachloride probably resulted in a collision complex with a lifetime great enough to allow appreciable further reaction of the complex with excess nitrogen atoms. When the complex decomposed spontaneously it probably resulted in the formation

of cyanogen chloride and chlorine. A fraction of the vibrationally excited carbon tetrachloride molecules produced in reaction of the complex with nitrogen atoms might dissociate into chlorine and radicals. Some polymerization of the radicals formed and, to a slight extent, polymerization of cyanogen chloride would account for the small amount of polymer found in the reaction products.

Active Nitrogen - Chloroform

The experimental observations may be summarized as follows:

- (1) The main products were HCl, CNCl and Cl₂.
- (2) Smaller amounts of HCN and (CN)₂ were observed.
- (3) Some polymer was found of a type similar to that observed in the reaction with carbon tetrachloride.
- (4) The rates of production of HCl at 260°C and 425°C increased linearly with increase of CHCl₃ flow rate up to CHCl₃ flows of approximately 3.0 and 7.0 micromoles per second, respectively. These critical flow rates were not precisely defined and the HCl production fell off at higher CHCl₃ flow rates but did not approach constant values. The CNCl production tended toward linearity with increasing reactant flow rates for the reaction at the higher temperature.

- (5) The chlorine production increased rapidly at the low reactant flow rates and became constant or decreased slightly for CHCl_3 flow rates above a critical flow rate which was greater at the higher temperature.
- (6) The rate of production of HCN was slightly less than that of $(\text{CN})_2$ and the combined yield of HCN and $(\text{CN})_2$ seemed to remain constant at the higher CHCl_3 flows.

The previous comparison of the experimental and theoretical curves of product yields vs. reactant flow rates indicated the formation of a relatively long-lived collision complex of a nitrogen atom and CHCl_3 molecule, and its reaction with excess nitrogen atoms to a considerable extent.

There would seem to be three possibilities for the dissociation of the collision complex:

The relative amounts of the various nitrogen-containing products formed suggest that reaction (13) occurred at least three times as often as the other two combined. It will be noted that all three dissociations are energetically favorable, with reaction (13) the most exo-

thermic.

Assuming recombination of excess chlorine atoms and the formation of molecular cyanogen from the CN radicals produced in reaction (15), it may be readily seen that the quantity of HCl is greater and that of Cl₂ smaller in the reaction products than can be accounted for by dissociation of the NCHCl₃ complexes according to the scheme outlined in reactions (13) to (15). For example, at a chloroform flow rate of 7.0 micromoles per second, the HCl and Cl₂ yields calculated on this basis would be 4.4 and 3.2 micromoles per second, respectively. The yields of these products experimentally observed were 5.6 micromoles per second of HCl and 1.8 micromoles per second of Cl₂, i.e. there is a deficiency of chlorine.

The rapid removal of chlorine atoms by reaction with excess chloroform would seem to be quite possible. A likely secondary reaction involving chlorine atoms might be

This reaction has been found to take place in the reaction of chloroform with chlorine atoms produced in a discharge tube (8, 10). It has also been accepted as a chain carrier in the thermal chlorination of chloroform in the gas phase (11) and in solution (12),

and in the photo chemical chlorination of methane, which resulted in some carbon tetrachloride as an end product (13). An activation energy of less than 4.3 kcal is generally accepted as reasonable for reaction (16). The alternative reaction

cannot compete with reaction (16) because of its endothermicity.

Further reaction of nitrogen atoms with the CCl_3 radical should be rapid and proceed with little or no activation energy (2):

Further disappearance of chlorine is possible by reactions such as:

and by similar reactions with any other radical species present in the system.

Reaction (19) has been postulated by Schumacher and Wolff (12), and others (13, 14) in photo chlorinations; the former also postulated reaction (21) as a chain terminating step with zero activation energy. Since reaction (21) is a three body reaction it would probably be comparatively rare although each collision

extent since the presence of elemental carbon in the product trap was indicated. Other modes of dissociation for CHCl_3^* are possible, but their importance cannot be evaluated.

Previous considerations indicated that the $\text{N} - \text{CHCl}_3$ complex could be expected to react with excess nitrogen atoms to a greater degree than the collision complex formed in the carbon tetrachloride reaction. This conclusion would be strengthened by the observation that more HCl was produced at all reactant flow rates than could be accounted for by primary dissociation of the $\text{N} - \text{CHCl}_3$ complex and secondary reactions stemming from the chlorine atoms produced in these primary steps.

To summarize, the active nitrogen-chloroform reaction is probably characterized by the formation of a collision complex between a nitrogen atom and chloroform molecule, which may dissociate directly into products or suffer further reaction with excess nitrogen atoms to yield molecular nitrogen and vibrationally excited chloroform molecules. Decomposition of the $\text{N} - \text{CHCl}_3$ collision complex probably occurred in more than one way, to yield CNCl , HCN or CN radicals. The CN radicals might form molecular cyanogen although the possibility of CNCl formation by reaction with chlorine

cannot be precluded. Chlorine atoms probably disappeared to a considerable extent by reaction with molecular chloroform to produce HCl.

The excited chloroform molecules could dissociate in several ways.

It would be difficult to assess the contributions of individual secondary reactions; those favoring the production of HCl and the disappearance of gaseous chlorine probably predominated.

(c) Active Nitrogen - Dichloromethane

The experimental data obtained may be summarized as follows:

- (1) The main products were HCl, HCN and CNCl.
- (2) Small amounts of cyanogen and chlorine were recovered.
- (3) Polymer formation occurred on the walls of the reaction vessel at both temperatures; a blackish deposit was found on the walls of the product trap, which seemed to be largely elemental carbon.
- (4) The rates of production of HCl, HCN and CNCl varied more or less linearly with dichloromethane flow rates up to critical flow rates of 8.0 micromoles per second at 255°C, and 9.5 micromoles per second at 425°C.

- (5) At higher reactant flow rates the main product yields were essentially constant and were greater at the higher temperature.

The observed linear variation of product yields with reactant flow rates are typical of a comparatively fast reaction in which there is complete consumption of the reactant present in the lesser concentration. This behavior was also found with the methyl chloride reaction (62). In the dichloromethane reaction the slope of the initial portion of the curve of the HCl yield vs. reactant flow rate was the same at both temperatures. On the other hand, the slope of the initial portion of the HCN production curve, although linear, increased somewhat at the higher temperature. This was also observed for the CNCl production. The behavior of the HCN and CNCl curves indicates that primary dissociation of the collision complex $N - CH_2Cl_2$ was somewhat faster at the higher temperature.

The mathematical and theoretical treatment, discussed previously, seemed to show that the nitrogen atom-dichloromethane reaction was fast enough to prevent significant contribution of wall recombination reactions in the disappearance of nitrogen atoms, and that recombination of nitrogen atoms occurred mainly by reactant molecules (and possibly products) acting as

efficient third-bodies.

All possible modes of dissociation of the collision complex into products would be accompanied by the production of a nitrogen-containing compound:

These reactions are all energetically favorable. The relative amounts of HCN, CNCl, and $(\text{CN})_2$ observed in the reaction products might give a rough estimate of the relative importance of the efficient modes of dissociation outlined. However, reaction (27) might occur with much greater frequency than the cyanogen yields would indicate if further fast reactions of the cyanogen radicals produced HCN and CNCl:

If reactions (27), (28), and (29) contributed significantly to the production of HCN and CNCl it would seem reasonable that with increasing dichloromethane flow rate, the formation of molecular cyanogen would increase to a maximum and then decrease as more and more dichloromethane molecules became available for reactions (28) and (29). Since this was not observed and the highest values of $(\text{CN})_2$ obtained at 255°C did

not exceed 0.4 micromoles per second it may be concluded that reactions (27), (28) and (29) were relatively unimportant.

Therefore the relative amounts of HCN and CNCl found in the products indicates that reaction (25) is much more important than reaction (26) as a primary mode of dissociation of the nitrogen atom-dichloromethane complex.

The observed rate of chlorine production was relatively low in the dichloromethane reaction; a maximum of 0.3 micromoles per second at 255°C and 0.9 micromoles per second for the reaction at 425°C. At the higher temperature this maximum was attained at a dichloromethane flow rate of 5.2 micromoles per second. The chlorine production then decreased with increasing reactant flow rate to 0.5 micromoles per second at the highest dichloromethane flow rate attained. The decrease in the gaseous chlorine production with increasing dichloromethane flow rates indicates that these secondary reactions might involve the reactant,

These reactions are energetically favorable and are comparatively well-known. Reaction (30) has been postulated as a chain carrier in the photo chlorination of

methane (85), and also as one of the chain-initiation reactions in the oxidation of dichloromethane, sensitized photochemically with chlorine (91). Schumacher (78) estimated its activation energy to be less than 8kcal.

Polanyi and co-workers (90) investigated reaction (31) and estimated its activation energy to be about 5.8kcal. They concluded that the reaction

also occurred to some extent since the disappearance of hydrogen atoms was greater than the HCl production. The reaction of nitrogen atoms with the radicals formed might be expected to be fairly rapid. It may be seen that the secondary reactions (30) and (31), followed by nitrogen atom attack on the resulting radicals would give results making this series of reactions indistinguishable from the primary reactions (25) and (26).

Additional reactions of chlorine atoms with radicals might also account to some extent for the disappearance of chlorine atoms:

The need for a third body in these reactions might restrict their occurrence although Kimball (92) was of

the opinion that the occurrence of such reactions should be quite feasible in the gas phase. Kassel (93), however, considered Kimball's classical treatment to be meaningless and insisted that recourse to quantum-mechanical theory was mandatory with these reactions.

The observed yields of nitrogen-containing compounds from reactions (25), (26) and (27) and the secondary reactions of nitrogen atoms with radicals correspond to only about 55% of the HCl produced. This gives an indication of the importance of further reaction of the N - CH₂Cl₂ complex with nitrogen atoms (cf. reaction (2)):

Although, the vibrationally excited CH₂Cl₂^{*} molecule could decompose in a variety of ways, one specific mode might be predominantly favored:

There are two experimental observations that indicate that reaction (36) might be important:

(a) the deposit on the walls of the product trap seemed to be mainly elemental carbon, and (b) the "plateau" values for the HCl production at 425°C in the dichloromethane reaction, and the HCN yields at 385°C in the active nitrogen-ethylene reaction under these experi-

mental conditions were identical within the experimental error. This would seem to indicate that with excess dichloromethane all the nitrogen atoms available for reaction lead to the formation of HCl.

It is probable, then, that the gaseous products observed in the active nitrogen-dichloromethane reaction may be accounted for by assuming a relatively long-lived collision complex between a nitrogen atom and dichloromethane, which dissociated mainly as outlined in reactions (25) and (26), and to a lesser extent via reaction (27). Alternately, they might have reacted further with nitrogen atoms to produce vibrationally excited dichloromethane molecules which dissociated largely to form elemental carbon and HCl. The disappearance of chlorine atoms produced in reaction (25) could occur by secondary reactions with the reactant as shown in reaction (30). Hydrogen atoms produced in reaction (26) might have reacted in a similar manner. Secondary reactions of radicals with nitrogen atoms probably occurred; together with the radical formation reactions they would give relative product yields similar to those from primary complex dissociations.

APPENDIX A

The energy values that have been used to calculate the heats evolved in the reactions have been obtained from two sources. In Table I are given the heats of formation, Q_f^O , of gaseous compounds, i.e. the heat liberated when a compound is formed from its elements; with each substance in its standard state.

Thus $Q_f^O = -\Delta H_f^O$ where ΔH_f^O is the standard heat of formation according to the Lewis and Randall method of notation. In a few cases values for 0°K have been used where the values for 25°C were not readily available; since the error involved is usually about 1kcal this approximation is not serious.

Where bond dissociation energies had to be employed to calculate the heats of formation the values given might only be approximate. These estimated heats of formation are also given in Table VI and the relevant bond dissociation energies in Table VII. In these tables the reference numbers of the sources are also given under the heading of Remarks.

For the sake of simplicity, the "spectroscopists" convention has been followed whereby exothermic reactions are written as

Table VI

Heats of Formation, Q_f^0

Formula	Q_f^0 (kcal)	Remarks
H	-52.089	(94)
H ₂	0	(94)
Cl	-29.012	(94)
Cl ₂	0	(94)
HCl	22.063	(94)
N	-113.0	(94)
N ₂	0	(94)
C	-171.698	(94)
C (graphite)	0	(94)
CH ₄	17.889	(94)
CH ₃ Cl	19.6	(94)
CCl ₄	25.5	(94)
CHCl ₃	24	(94)
CH ₂ Cl	19.6	(94)
CH ₂ Cl ₂	21	(94)
NCN	-31.2 [-29.8]	(94), [(76)]
CNCl	-34.5	(94)
(CN) ₂	-73.60	(94)
CH ₃ CN (gas)	-19.8	(76)
CH	-142.1	(94)
CH ₂	-70 [-66 singlet]	(76) [(62)]
CH ₃	-32	(94)
CN	-94+2 [-100]	(76) [(95)]
C ₂ Cl ₄	3 (liquid)	(94)
C ₂ Cl ₆	48 (solid)	(94)
NH	-86	(94)
CH ₂ Cl	-26	Table VII
CCl ₃	-15.5	Table VII
CH ₂ Cl	-23	Table VII
CCl ₂	-55	Table VII
CCl	-90	Table VII

Table VII
Bond Dissociation Energies

Bond	D (kcal)	Remarks
H ₃ C - CH ₃	83	(95)
H ₃ C - CH ₂ CH ₃	82	(95)
H - CH ₃	101	(95), (96)
H - CH ₂ CH ₃	98	(95)
Cl - CH ₃	80	(95)
Cl - CH ₂ CH ₃	80	(95)
H ₃ C - CN	105	(95)
CH ₂ = HC - CN	121	(95)
NC - CN	114, [116 ± 10] {111.6}	(76), [(96)], {(99)}
C - N	144 [118]	(76), (96)
Cl - CCl ₃	70	(95)
H - CN	120 [117]	(95)
Cl - CN	95	(95)
C - Cl aliphatic	73	(97)
H - CH ₂	86 ± 5	(62)
H - H	103.2	(96)
C - H	80	(96)
Cl - Cl	57.08	(96)
H - Cl	102.1	(96)
D(C - H)	80	(96)
H - CCl ₃	89	(98)
H - C ₂ H ₅	98	(95)

rather than

The value of q is obtained from the relation

$$q = Q_f^{\circ} (C) + Q_f^{\circ} (D) - Q_f^{\circ} (A) - Q_f^{\circ} (B)$$

A positive " q " value denotes an exothermic reaction and a negative value for " q " indicates an endothermic reaction.

APPENDIX B

The Effects of Recombination Reactions on Consumption vs. Flow Rate Curves

The reaction mechanism under consideration is:

where N represents a nitrogen atom, M represents a reactant molecule, P represents one of the products, and X represents a third body (N_2 molecules and/or the wall) whose effectiveness does not change appreciably with a change in reactant flow rate.

Therefore, for "stream-line" flow (flame characteristics indicate that this probably gives a reasonable approximation of reaction conditions)

$$\frac{dM}{dt} = - k_1 MN \quad (5)$$

$$\frac{dP}{dt} = k_1 MN \quad (6)$$

$$\frac{dN}{dt} = - k_1 MN - k_2 MN^2 - k_3 PN^2 - k_4 XN^2 \quad (7)$$

where M, N, P, X represent the concentrations of reactant, nitrogen atoms, product and X is the part of the vessel that is t secs. "away" from the point of entry. From equations (5) and (6)

$$\frac{dP}{dM} = - 1$$

and then integrating for initial conditions of $p = 0$ and

$M = M_0$ have

$$p = M_0 - M \quad (8)$$

Combination of equations (7) and (8) gives

$$\frac{dN}{dt} = -k_1 MN - (k_2 - k_3) MN^2 - (k_3 M_0 + k_4 X) N^2 \quad (9)$$

and similarly from equations (5) and (9)

$$\frac{dN}{dM} = 1 + (k_2 - k_3) N/k_1 + (k_3 M_0 + k_4 X) N/Mk_1 \quad (10)$$

Introducing the dimension less variables

$$x = M/M_0 \text{ and } y = N/N_0$$

and the parameters

$$S = M_0/N_0, \quad p = (k_4 X + k_3 N_0 S)/k_1, \quad (11)$$

$$q = (k_2 - k_3) N_0 S/k_1$$

then equation (10) becomes

$$\frac{dy}{dx} = S + py/x + qy \quad (12)$$

Integration of equation (12), using the initial condition

$y = 1$ for $x = 1$, gives

$$y = x^p e^{-q(1-x)} \quad 1 - \int_1^x SI(x, p, q) \quad (13)$$

$$\text{where } I(x, p, q) = \int_x^1 x^{-p} e^{p(1-x)} dx \quad (14)$$

Where the reactions are fast enough to reach completion before the stream leaves the reaction vessel, the final values of M and N must be such that the right hand sides of equations (5), (6), and (7) are all identically equal to zero. $N = 0$ is the only condition that will satisfy this requirement unless both k_3 and k_4 are

identically equal to zero. The physical basis of this result is that either the product catalyzed, and/or the wall catalyzed reactions, must be fast enough to remove nitrogen atoms completely even at low reactant flow rates. As noted in the description of flame behavior in these reactions (cf. Section III) the nitrogen afterglow was observed leaving the reaction vessel at very low reactant flow rates but it disappeared for reactant flow rates which were still quite small compared with the nitrogen atom flow rate. Therefore, the assumption that N is zero in the gas stream leaving the reaction vessel seems to be justified for all but the very lowest reactant flow rates.

For $N_1 = 0$, the final values of y and x will be given by

$$y_1 = 0 \quad (15)$$

$$0 = x_1^{p_1} e^{-q_1} (1 - x_1) [1 - SI_1] \quad (16)$$

where I_1 stands for $I(x_1, p_1, q_1)$

Equation (16) may be satisfied by either

$$x_1 = 0 \quad (17)$$

or $SI_1 = 1 \quad (18)$

(Note: $e^{-q_1} (1 - x_1)$ cannot be equal to zero since x_1 is less than unity by definition, and only finite values of q are of immediate interest.)

Equation (17) corresponds to complete consumption

of reactant and equation (18) to incomplete consumption of reactant. Thus, there will be complete consumption of chloromethane unless equation (18) has a solution for a value of x_1 between zero and unity. In general, equation (17) will give the only solution for values of S below the critical value, S_0 , and the equation (18) will give the only solution for values of s greater than S_0 . For $S = S_0$, it is obvious that both equations (17) and (18) must be satisfied, i.e.

$$S_0 \int_0^1 x^{-p_0} e^{q_0} (1 - x) dx = 1 \quad (19)$$

where $p_0 = (k_4 X + k_3 N_0 S_0) / k_1$

and $q_0 = (k_2 - k_3) N_0 S_0 / k_1$

It can be shown that equation (19) cannot have a solution for a value of S_0 greater than zero if the value of p_0 is greater than one. This means that there will be no range of S values for which complete consumption occurs unless $k_4 X / k_1$ is less than one.

For direct comparison with the shape of the experimental production vs. flow rate curves, it is necessary to determine w as a function of S , where w is defined by

$$W = S (1 - x_1) \quad (20)$$

Thus $w = S$ for $S \leq S_0$

and $w = S (1 - x_1)$ for $S \geq S_0$

where x_1 is to be determined from equation (18) and S_0 from equation (19).

Special Cases

(a) Recombination Catalyzed by Chloromethane Only.

$$\begin{aligned} & (k_3 = k_4 = 0) \\ \text{For } & k_3 = k_4 = 0 \\ & p = 0 \text{ and } q = \beta S \end{aligned} \quad (21)$$

$$\text{where } \beta = k_2 N_0 / k_1$$

For $p = 0$ the integral in equation (14) is easy to evaluate, and the result is

$$I = (e^{q(1-x)} - 1)/q \quad (22)$$

From equations (13), (21) and (22)

$$y = e^{-q(1-x)} \left[1 + (1/\beta) (1 - e^{q(1-x)}) \right] \quad (23)$$

For $k_3 = k_4 = 0$, it may be seen from equations (5) and (7) that the assumption of fast reactions leads to either $y_1 = 0$, or $x_1 = 0$

If $y_1 = 0$, then from equation (23)

$$e^{-q(1-x_1)} = 1 + (1/\beta) (1 - e^{q(1-x_1)}) \quad (24)$$

$$\text{or } e^{\beta S(1-x_1)} = 1 + (1/\beta) (1 - e^{\beta S(1-x_1)})$$

$$\text{and } W = S(1-x_1) = (1/\beta) \ln (1 + \beta) \quad (25)$$

If $x_1 = 0$ then from equation (23)

$$y_1 = (1 + 1/\beta) e^{-\beta S} - 1/\beta \quad (26)$$

and $W = S$

For both $x_1 = 0$ and $y_1 = 0$, equation (25) shows that

$$S_0 = (1/\beta) \ln (1 + \beta) \quad (27)$$

Since y_1 must be greater than zero by definition, it is evident from equation (26) that the solution $x_1 = 0$ is only possible for $0 \leq S \leq S_0$. Thus, W increases linearly with S , for S less than S_0 and then remains constant at a value determined by the value of β , for S greater than S_0 . Values of S_0 calculated from equation (27) for several values of β are given in Table VIII.

(b) Recombination Catalyzed by Wall or Nitrogen Only

$$\text{For } k_2 = k_3 = 0$$

$$q = 0 \text{ and } p = k_4 L/k_1 = 1 - \gamma \quad (28)$$

$$\text{where } \gamma = 1 - k_4 L/k_1$$

For $q = 0$, equation (33) gives $\gamma \neq 0$

$$1 = (1 - x_1^\gamma)/\gamma \quad (29)$$

From equations (37) and (48)

$$1 - x_1^\gamma = \gamma/S$$

$$\text{or } x_1 = (1 - \gamma/S)^{1/\gamma} \quad (30)$$

$$\text{For } \gamma > 0, S_0 = \gamma \quad (31)$$

For $\gamma < 0$ there is no linear region.

If $\gamma = 0$, $k_4 L/k_1 = 1$, then I will be given by

$$1 = \ln(1/x) \quad (32)$$

and equations (18) and (32) give

Table VIII

Values of s when $k_3 = 0$

$k_4L/k_1 = 0$ Case (a)

β	$S_0 = v$
0	1.000
0.1	0.953
0.2	0.912
0.4	0.841
0.5	0.811
0.6	0.783
0.8	0.735
1.0	0.693
1.5	0.611
2.0	0.549
4.0	0.402
5.0	0.358
9.0	0.256

$k_4L/k_1 = 0.2$

β	v	S_0
0	1.000	0.800
0.132	0.938	0.757
0.280	0.882	0.715
0.444	0.828	0.676
0.833	0.728	0.600
2.275	0.521	0.440
3.113	0.455	0.386
4.59	0.375	0.327
6.15	0.320	0.276
8.97	0.256	0.223
10.11	0.238	0.208
16.03	0.177	0.156

$k_4L/k_1 = 0.1$

β	v	S_0
0	1.000	0.900
0.111	0.948	0.856
0.233	0.898	0.813
0.369	0.852	0.772
0.518	0.806	0.732
0.683	0.763	0.695
0.865	0.721	0.658
1.066	0.681	0.623
1.288	0.643	0.589
1.533	0.605	0.557
1.804	0.571	0.526
2.102	0.538	0.496
2.432	0.507	0.468
2.796	0.476	0.441
3.196	0.449	0.416
3.639	0.421	0.391
4.02	0.401	0.372
7.50	0.286	0.267
13.18	0.201	0.190

$k_4L/k_1 = 0.5$

β	v	S_0
0	1.000	0.500
0.214	0.906	0.468
0.458	0.823	0.436
0.735	0.750	0.408
1.409	0.624	0.355
2.276	0.521	0.308
4.11	0.396	0.243
5.67	0.334	0.212
8.92	0.257	0.168
11.82	0.216	0.144

$$x_1 = e^{-1/S} \quad (33)$$

From equations (20) and (30),

$$W = S \left[1 - (1 - \gamma/S)^{1/\gamma} \right] \quad (34)$$

It may be shown quite easily from equation (34) that W approaches unity for very large values of S , no matter what the value of γ .

Values of W calculated from these equations for several different values of S , and γ , are given in Table IX.

(c) Catalysis by a Product equal to Catalysis by Chloromethane

$$\text{For } k_2 = k_3$$

$$q = 0 \text{ and } p = 1 - \gamma + \beta S \quad (35)$$

$$\text{where } \gamma = 1 - k_4 L / k_1, \beta = k_2 N_0 / k_1 \text{ and } \gamma^1 = \gamma - \gamma S.$$

The value of I will now be given by equation (29) with $(\gamma - \beta S)$ instead of γ .

$$\text{Thus } I = (1 - x^{(\gamma - \beta S)}) / (\gamma - \beta S)$$

$$\text{and } W = S \left[1 - (1 - \gamma^1/S)^{1/\gamma^1} \right] \quad (36)$$

$$\text{where } \gamma^1 = \gamma - \beta S \quad (37)$$

$$\text{For } x_1 = 0, \gamma - \beta S_0 = S_0 \quad (38)$$

For $S = \gamma / \beta$, $\gamma^1 = 0$, it is quite easy to show that

$$W = S(1 - e^{1/S}) = (\gamma / \beta) \left[1 - e^{\beta/\gamma} \right] \quad (39)$$

It may be shown from equations (36) and (37) that for very large values of S , W approaches the limit

Table IX

Values of w for Case (b) ($k_2 = k_3 = 0$)

$$k_4 L / k = 0.1, \quad \gamma = 0.9$$

S	0.9	1.0	1.2	1.4	1.6	1.8
w	0.9	0.923	0.944	0.957	0.962	0.968

$$k_4 L / k_1 = 0.5 \quad \gamma = 0.5$$

S	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.8
w	0.5	0.583	0.643	0.688	0.722	0.750	0.792	0.821	0.744	0.861

$$k_4 L / k_1 = 1 \quad \gamma = 0$$

S	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
w	0.0	0.199	0.367	0.487	0.571	0.632	0.678	0.714	0.744	0.768

$$k_4 L / k_1 = 2, \quad \gamma = -1$$

S	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
w	0.0	0.167	0.286	0.375	0.444	0.500	0.545	0.583	0.615	0.643

$$k_4 L / k_1 = 5, \quad \gamma = -4$$

S	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
w	0.0	0.107	0.180	0.239	0.289	0.331	0.367	0.400	0.430	0.457

$w = (1/\beta) \ln (1 + \beta)$. Values of w calculated from these equations for different values of s , two values of γ , and several values of β , are given in Table X.

Table X

Values of w for Case (c) ($k_2 = k_3$)

$$k_4 L / k_1 = 0$$

$$\beta = k_2 N_0 / k_1$$

$\beta = 0.1$		$\beta = 0.2$		$\beta = 0.4$		$\beta = 0.6$	
$\underline{S}$	$\underline{w}$	$\underline{S}$	$\underline{w}$	$\underline{S}$	$\underline{w}$	$\underline{S}$	$\underline{w}$
0.909	0.909	0.833	0.833	0.714	0.714	0.625	0.625
1.0	0.922	0.9	0.853	0.8	0.750	0.7	0.666
1.2	0.933	1.0	0.866	0.9	0.770	0.8	0.694
1.4	0.937	1.2	0.880	1.0	0.783	0.9	0.710
1.6	0.940	1.4	0.886	1.1	0.792	1.0	0.722
1.8	0.943	1.6	0.890	1.2	0.797	1.2	0.734
∞	0.953	1.8	0.895	1.3	0.802	1.5	0.749
		∞	0.912	1.5	0.810	1.8	0.755
			∞	1.8	0.815	∞	0.784
				∞	0.842		

$\beta = 0.8$		$\beta = 1.0$		$\beta = 1.5$		$\beta = 2.0$	
$\underline{S}$	$\underline{w}$	$\underline{S}$	$\underline{w}$	$\underline{S}$	$\underline{w}$	$\underline{S}$	$\underline{w}$
0.556	0.556					0.333	0.333
0.6	0.587	0.500	0.500	0.400	0.400	0.4	0.388
0.7	0.626	0.6	0.562	0.5	0.468	0.5	0.432
0.8	0.648	0.7	0.593	0.6	0.503	0.6	0.457
0.9	0.663	0.8	0.610	0.7	0.523	0.7	0.475
1.0	0.672	0.9	0.623	0.8	0.538	0.8	0.486
1.2	0.686	1.0	0.632	0.9	0.548	0.9	0.493
1.5	0.697	1.2	0.646	1.0	0.556	1.0	0.500
1.8	0.706	1.5	0.656	1.2	0.566	1.2	0.509
∞	0.735	1.8	0.662	1.5	0.576	1.5	0.519
		∞	0.693	1.8	0.583	1.8	0.524
				∞	0.611	∞	0.549

$\beta = 4.0$													
$\underline{S}$	0.200	0.250	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.2	1.5	1.8	∞
$\underline{w}$	0.200	0.246	0.277	0.313	0.333	0.346	0.355	0.362	0.370	0.375	0.381	0.385	0.402

$\beta = 9.0$										
$\underline{S}$	0.100	0.2	0.4	0.6	0.8	1.0	1.2	1.5	1.8	∞
$\underline{w}$	0.100	0.165	0.216	0.230	0.236	0.240	0.243	0.246	0.247	0.256

Table X (Continued)

$$k_4 L / k_1 = 0.5$$

$$\beta = k_2 N_0 / k_1$$

$\beta = 0.1$		$\beta = 0.4$		$\beta = 1.0$		$\beta = 2.0$		$\beta = 9.0$	
<u>S</u>	<u>W</u>	<u>S</u>	<u>W</u>	<u>S</u>	<u>W</u>	<u>S</u>	<u>W</u>	<u>S</u>	<u>W</u>
0.454	0.454	0.357	0.357	0.250	0.250	0.167	0.167	0.050	0.050
0.5	0.497	0.4	0.398	0.3	0.299	0.2	0.200	0.1	0.098
0.6	0.570	0.5	0.476	0.4	0.378	0.25	0.246	0.2	0.158
0.7	0.623	0.6	0.532	0.5	0.432	0.3	0.283	0.3	0.185
0.8	0.664	0.8	0.606	0.6	0.471	0.4	0.338	0.4	0.202
1.0	0.722	1.0	0.652	0.8	0.523	0.6	0.402	0.5	0.211
1.2	0.760	1.25	0.688	1.0	0.556	0.8	0.436	0.6	0.218
1.5	0.798	1.5	0.716	1.2	0.578	1.0	0.458	0.8	0.227
1.8	0.824	1.8	0.734	1.5	0.600	1.2	0.473	1.0	0.233
∞	0.953	∞	0.842	1.8	0.616	1.5	0.487	1.2	0.237
				∞	0.693	1.8	0.497	1.5	0.240
						∞	0.549	1.8	0.243
								∞	0.256

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

- (1) The reactions of active nitrogen with carbon tetrachloride, chloroform, and dichloromethane were investigated in a fast flow system. In each reaction nitrogen atom concentrations were kept constant and the effects of change in the reactant flow rates were determined at two temperatures. The general behavior of these chloromethane reactions markedly resembled the corresponding methyl chloride-active nitrogen reaction.
- (2) The flames produced in these reactions were similar in color and behavior, and were brighter than the violet flames characteristic for the hydrocarbon-active nitrogen reactions. The carbon tetrachloride flame had a distinctly orange tint which became progressively less noticeable in the chloroform and dichloromethane reactions.
- (3) This behavior of the reaction flames probably was responsible for the lower temperatures recorded during reactions at higher chloromethane flow rates. The temperatures recorded could therefore only be regarded as approximations of the true reaction temperatures. The possibility that considerable

temperature gradients existed in the vessel during reaction could not be precluded.

- (4) In every one of the chloromethane reactions investigated a slight amount of greenish-brown polymer was observed on the walls of the reaction vessel. The effects of heating and the action of organic solvents on the polymer deposits in the individual chloromethane reactions indicated that in the carbon tetrachloride reaction the deposit possibly contained cyanuric chloride and hexachloromethane; the presence of paracyanogen in the polymers produced in the other reactions was similarly indicated. The deposits formed on the cold walls of the product trap were darker in color than the polymers observed in the reaction vessel. In the chloroform and dichloromethane reactions these deposits seemed to consist largely of elemental carbon.
- (5) The only gaseous products observed in the active nitrogen-carbon tetrachloride reaction were cyanogen chloride and chlorine. The product yields tended toward limiting values at higher reactant flows. At the lower carbon tetrachloride flows the rates of increase of product yields with increasing reactant flow rates were not constant. In the chloroform reaction hydrogen chloride with lesser amounts of

hydrogen cyanide were also produced. The behavior of product yields at different chloroform flows was similar to that observed in the carbon tetrachloride reaction. In the dichloromethane reaction products observed were the same as in the chloroform reaction; but the product yields increased linearly with increasing dichloromethane flows and became constant above a critical reactant flow rate. Generally in these reactions, as in the methyl chloride reaction, the product yields were higher, the higher the reaction temperature; however, the hydrogen chloride yields did not vary with temperature at dichloromethane flows less than the critical flow rate.

- (6) In view of the similarity in behavior of the chloromethane reactions with active nitrogen, the mathematical kinetic treatment developed for the methyl chloride reaction was employed to explain the behavior observed in the chloromethane reactions under consideration. The mechanism proposed involved the formation of relatively long-lived nitrogen atom-chloromethane complexes. This primary reaction competed for nitrogen atoms with atom recombination processes catalyzed by reactant, reaction products, and the reaction vessel wall. The differences observed in the individual chloromethane reactions

would be explained by the relative tendencies of the complexes to dissociate into products, and the relative efficiencies of recombination processes postulated. The fate of excited molecules formed by the interaction of nitrogen atoms with complexes also influenced the overall reaction behavior.

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