# THE REACTIONS OF ACTIVE NITROGEN WITH ALKYL CHLORIDES<sup>1</sup>

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#### ABSTRACT

The reactions of active nitrogen with methyl, ethyl, vinyl, propyl, and isopropyl chlorides yielded hydrogen cyanide and hydrogen chloride as the main products. Small amounts of cyanogen and a polymer were formed from all the halides, and all except methyl chloride also yielded small amounts of  $C_2$  and  $C_3$ hydrocarbons. The observed changes in amounts of products recovered with different reactant flow rates were characteristic of a fast reaction in which complete consumption of either reactant occurs when the other is present in excess. Mechanisms for the reactions are suggested on the basis that relatively longlived complexes are formed in the initial attack of a nitrogen atom on the alkyl chloride.

### INTRODUCTION

A number of reactions of active nitrogen, produced in a condensed electrical discharge, have been studied in this laboratory. Emphasis has been placed largely, though not exclusively, on the reactions with hydrocarbons (2, 3, 9, 11, 13, 14, 17, 18, 19). Hydrogen cyanide is the main nitrogen-containing product of these reactions, which implies that the reactions with saturated hydrocarbons involve direct attack at a completely shielded carbon atom. They are much faster than would be expected from the principle of least motion enunciated by Rice and Teller (15).

In an attempt to elucidate further the mechanism of the reactions, it appeared desirable to investigate the effect of a chlorine substituent on the reactivity. Accordingly, the reactions of active nitrogen with methyl, ethyl, vinyl, propyl, and isopropyl chlorides have been studied.

## EXPERIMENTAL

The reactions were studied with conventional fast-flow techniques (11). Active nitrogen was produced by a condensed discharge and mixed with the halides in a reaction vessel that was sufficiently far from the discharge tube to prevent back diffusion into the discharge. The flow and activation of the nitrogen were kept constant in experiments with a given halide and the effects of change in flow rate of the halide determined. The reaction vessel could be surrounded by a furnace to study the effect of temperature. Condensable products were trapped with the usual arrangement of liquid air traps, and were analyzed by low temperature fractionation (12) and with a mass spectrometer.<sup>3</sup> The hydrogen cyanide, cyanogen, and hydrogen chloride produced in the reactions were estimated by titration (16, 20). The hydrogen produced in the reaction with methyl chloride was determined mass spectrometrically on samples of the gas issuing from the vacuum pump.

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## RESULTS

All the reactions produced a peach-colored flame of fairly high luminosity, which was confined to the upper part of the reaction vessel at the higher flow rates.

The main products of all the reactions were hydrogen cyanide and hydrogen chloride; small amounts of cyanogen were also formed. In all the reactions, significant amounts of a brown polymer were formed on the walls of the reaction vessel but not in the traps. This polymer was quite inert, and had properties somewhat resembling those of paracyanogen. Its composition varied appreciably with the different alkyl chlorides and to a lesser extent with different flow rates of a given alkyl chloride. It contained nearly equal amounts of carbon and nitrogen (on a mole basis) together with smaller amounts of chlorine and hydrogen.

The formation of polymer on the walls of the reaction vessel made it difficult to obtain reproducible results at higher flow rates. (The concentration of active nitrogen is very sensitive to wall conditions, and the polymer itself was probably formed by a wall reaction.)

## Methyl Chloride

The rates of production of hydrogen cyanide, hydrogen chloride, and hydrogen, and the rate of consumption of methyl chloride, all varied linearly with methyl chloride flow rate up to a flow rate of about  $3 \times 10^{-6}$  mole/sec., and were independent of temperature in this linear region (Fig. 1). In<sup>\*</sup><sub>4</sub> this



FIG. 1. Relations between methyl chloride flow rate and rates of methyl chloride consumption and product formation.

region, only 89% of the methyl chloride was consumed, independently of flow rate or temperature. At higher flow rates the yields of products approached a limiting value which was the greater, the higher the temperature.

The curves in Fig. 1 have only qualitative significance, since deposition of polymer changed the surface condition of the thermocouple wells at the center

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and top of the reaction vessel and the thermocouple readings were therefore only a rough measure of the reaction temperature. Quite marked changes in the readings were observed both during an experiment and in successive experiments. In addition, the reaction was sufficiently exothermic to create marked temperature gradients in the reaction vessel. The temperatures at the center of the reaction vessel have therefore been recorded, rather arbitrarily, as "low" and "high" corresponding roughly to 100° and 300°C. respectively.

The amount of cyanogen formed was quite erratic, but it was always less than 3% of the methyl chloride consumed. A careful search failed to reveal the presence of any cyanogen chloride, methane, or ethane in the products.

## Ethyl, Vinyl, and Propyl Chlorides

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In these reactions, small amounts of hydrocarbons were formed as secondary products. Vinyl chloride gave only acetylene, ethyl chloride gave a mixture of  $C_2$  hydrocarbons, and the propyl chlorides gave mixtures of  $C_2$  and  $C_3$  hydrocarbons. The composition of these products did not change significantly with flow rate in the limited range where samples sufficiently large for analysis could be recovered. Typical values are: for ethyl chloride, 94% ethylene, 5% acetylene, 1% ethane; for *n*-propyl chloride, 34% propylene, 41% ethylene, 17% acetylene, 6% propane, 2% ethane; for isopropyl chloride, 42% propylene, 33% ethylene, 18% acetylene, 6% propane, 1% ethane.

Figs. 2 and 3 show the changes in amounts of products recovered with different reactant flow rates. The different limiting yields with the various reactants may be attributed to changes in operating conditions, particularly the wall conditions in the reaction vessel. The shape of the curves for hydrogen cyanide production from the alkyl halides is quite similar to that of the analogous curves for the olefins (9, 17, 18), and is 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 is not as sharp for vinyl chloride as for the other chlorides, the general character of the reaction and comparison with the similar behavior of acetylene (19) Teave no doubt that the reaction of active nitrogen with vinyl chloride is fast.

The reactions of the higher halides were even more exothermic than the reaction with methyl chloride, and the difficulties of temperature measurement were aggravated to such an extent that it was not possible to obtain meaningful results. A few experiments with ethyl chloride in a heated reaction vessel indicated that the yields of products were independent of temperature within experimental error.

## DISCUSSION

There is some evidence that active nitrogen contains more than one chemically reactive species (7, 8, 14). However, considerations outlined in a further paper (4) suggest that one species, probably atomic nitrogen, is responsible for most of the reaction observed with the hydrocarbons and related compounds, and it is on this basis that the present results will be discussed.

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FIG. 2. Relations between rates of product formation and flow rates of ethyl and vinyl chlorides.

The observed initial linear variation in yield of hydrogen cyanide with methyl chloride flow rate, and its temperature independence, appear to be possible only for a fast reaction. It can be estimated from the experimental conditions that this behavior must correspond to a collision yield greater than about  $5 \times 10^{-5}$ . Similar results would probably be obtained for the higher halides, but the low flow rate region was not investigated as thoroughly for these reactions.

The recovery of methyl chloride at low flow rates might be attributed mainly to decomposition of nitrogen atom – methyl chloride complexes back to methyl chloride and nitrogen on the cold surface of the trap, although some channelling of methyl chloride in the flow through the reaction vessel might have occurred. Competition between a fast reaction of nitrogen atoms with methyl chloride and fast recombination of nitrogen atoms catalyzed by methyl



FIG. 3. Relations between rates of product formation and flow rates of propyl and isopropyl chlorides.

chloride or one of the reaction products can explain the observation that the yields were independent of temperature at low flow rates and increased with temperature at high flow rates. Similar, but more pronounced effects have been found in the reaction of methyl cyanide with active nitrogen where the temperature measurements were more trustworthy (5). A mathematical treatment of the problem is in preparation.

The features of the methyl chloride reaction outlined above suggest that a relatively long-lived methyl chloride – nitrogen atom complex was formed. The assumption that such complexes are formed in the reactions of the higher halides appears to be necessary to explain the formation of the secondary products. Further, the close similarity of the reactions of the higher halides to those of the unsaturated hydrocarbons suggests the possibility that hydrogen chloride is eliminated during formation of the complex, to yield a nitrogen atom complex with the corresponding unsaturated hydrocarbon. This is more fully discussed in the subsequent paper (4) on the basis of which it is possible to suggest the following mechanisms for the formation of the products obtained from the various active nitrogen – alkyl chloride reactions:

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Methyl Chloride

 $\begin{array}{l} \mathrm{CH}_3\mathrm{Cl} + \mathrm{N} \xrightarrow{} \mathrm{N}.\mathrm{CH}_3\mathrm{Cl} \xrightarrow{} \mathrm{HCN} + \mathrm{HCl} + \mathrm{H} \\ \mathrm{H} + \mathrm{H} \xrightarrow{} \mathrm{H}_2 \end{array}$ 

Ethyl Chloride

$$\begin{split} C_2H_5Cl + N &\rightarrow N.C_2H_5Cl \rightarrow HCl + N.C_2H_4 \\ N.C_2H_4 \rightarrow HCN + CH_3 \\ CH_3 + N \rightarrow HCN + 2H \\ N + N.C_2H_4 \rightarrow N_2 + C_2H_4 \\ N + N.C_2H_4 \rightarrow N_2 + C_2H_4^* \text{ (possibly } \dot{C}H_2\dot{C}H_2^*\text{)} \\ C_2H_4^* \rightarrow H_2 + C_2H_2^* \text{ (possibly } \dot{C}H=\dot{C}H^*\text{)} \end{split}$$

Propyl Chloride

$$\begin{split} & C_{3}H_{7}Cl + N \rightarrow N.C_{3}H_{7}Cl \rightarrow HCl + N.C_{3}H_{6} \\ & N.C_{3}H_{6} \rightarrow HCN + C_{2}H_{4} + H \\ & N.C_{3}H_{6} \rightarrow N_{2} + C_{3}H_{6} \\ & N + N.C_{3}H_{6} \rightarrow N_{2} + C_{3}H_{6}^{*} \text{ (possibly CH}_{3}-\dot{C}H-\dot{C}H_{2}^{*}) \\ & C_{3}H_{6}^{*} \rightarrow CH_{3}-CH^{*}: + CH_{2} \\ & CH_{3}-CH^{*}: \rightarrow C_{2}H_{4} \\ & CH_{3}-CH^{*}: \rightarrow C_{2}H_{2} + H_{2} \end{split}$$

Vinyl Chloride

 $\begin{aligned} \mathrm{CH}_{2}\mathrm{CHCl} + \mathrm{N} &\rightarrow \mathrm{N} . \ \mathrm{CH}_{2}\mathrm{CHCl} \rightarrow \mathrm{HCl} + \mathrm{N} . \ \mathrm{C}_{2}\mathrm{H}_{2} \\ \mathrm{N} . \ \mathrm{C}_{2}\mathrm{H}_{2} + \mathrm{N} &\rightarrow \mathrm{N}_{2} + \mathrm{C}_{2}\mathrm{H}_{2} \\ \mathrm{N} + \mathrm{N} . \ \mathrm{C}_{2}\mathrm{H}_{2} \rightarrow 2\mathrm{HCN} \end{aligned}$ 

It will be noted that the formation of the secondary hydrocarbon products is accompanied by recombination of two nitrogen atoms. This recombination appears to be the only source of sufficient energy to form these products and, for their formation in significant amounts, it is obviously necessary that a relatively long-lived complex should be formed. Thus, the higher halides might be expected to show the same change in yields with temperature at higher flow rates that was observed for methyl chloride. In spite of experimental difficulties, there was some indication that the effect was less marked for the higher halides. This might indicate a lower activation energy for these reactions. On the other hand, the spontaneous decomposition of complexes containing more than one carbon atom would make available carbon-containing intermediates that should react very rapidly with nitrogen atoms (1) and the direct reaction should be favored over the recombination.

The cyanogen produced in the alkyl chloride reactions was probably formed by the combination of two cyanogen radicals. The recombination of two nitrogen atoms makes available some 225 kcal. of energy, and there is a quite high probability that a substantial part of this energy is transferred from the newly forming N<sub>2</sub> molecule to the internal degrees of freedom of the rest of the complex (4). This can bring about dissociation into very reactive fragments. For methyl chloride, for example, reactions of the following type are all exothermic:

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$$\begin{split} \mathrm{N} &+ \mathrm{N.CH_3Cl} \rightarrow \mathrm{N_2} + \mathrm{CH_2Cl} + \mathrm{H} \\ \mathrm{N} &+ \mathrm{N.CH_3Cl} \rightarrow \mathrm{N_2} + \mathrm{HCl} + \mathrm{CH} + \mathrm{H_2} \\ \mathrm{N} &+ \mathrm{N.CH_3Cl} \rightarrow \mathrm{N_2} + \mathrm{CH_2} + \mathrm{H} + \mathrm{Cl}. \end{split}$$

It seems rather likely that cyanogen radicals will be formed by reaction of such fragments with still another nitrogen atom, e.g.

$$N + CH_2 \rightarrow CN + H_2$$
$$N + CH \rightarrow CN + H.$$

These reactions are sufficiently exothermic to give the electronically excited cyanogen radicals that are responsible for emission of the reaction flames (4). For the higher halides it is possible that some cyanogen was formed directly by such reactions as

$$N + N \cdot C_2 H_4 \rightarrow (CN)_2 + 2H_2.$$

However, this type of reaction involves a great deal of rearrangement, and more likely are reactions such as

$$N + N \cdot C_2 H_4 \rightarrow N + 2CH_2$$
$$N + CH_2 \rightarrow CN + H_2$$
$$2CN \rightarrow (CN)_2.$$

The fact that cyanogen production passes through a maximum at low chloride flow rates seems to be good evidence that more than two atoms of nitrogen are involved in its formation. If only two nitrogen atoms were involved, cyanogen production from the ethyl chloride reaction should be similar to the ethylene production, at least at high flow rates where the amount of ethylene reacting with nitrogen atoms can be neglected.

According to the mechanism suggested above, the production of unsaturated hydrocarbons should pass through a maximum as the chloride flow rate is increased. The chloride flow rate at which this maximum should occur will depend upon the relative rates of the reactions of the chlorides and the unsaturated hydrocarbons with nitrogen atoms. Apparently, the maximum yields were not attained in the region studied and this, together with the observation that little or no unsaturated hydrocarbons were recovered at low flow rates, gives some indication that nitrogen atoms react faster with the unsaturated hydrocarbons than with the alkyl chlorides.

The presence of highly reactive intermediate species in the reactions of the halides with nitrogen atoms, and particularly the presence of free CN radicals, probably accounts for the formation of polymer by a wall reaction involving mainly CN radicals with smaller amounts of the other intermediates. This would mean that recombination of two nitrogen atoms was necessary for polymer formation, in agreement with the observation that the polymer was formed near the top of the reaction vessel, especially at higher flow rates. It would also account for the differences in composition of the polymer from the different reactions.

The mechanisms outlined above involve production of hydrogen atoms, and the small amounts of saturated hydrocarbons formed in the reactions of the higher halides probably resulted mainly from hydrogenation of the correspond-

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ing olefin. Failure to detect methane as a product indicates that the concentration of atomic hydrogen was low in all the reactions. Hydrogen chloride (10) and methyl cyanide (6) are efficient recombination catalysts for hydrogen atoms. It seems quite possible that alkyl halides would behave like methyl cyanide in this respect, and in any event there was probably enough hydrogen chloride formed in the reactions to keep the concentration of hydrogen atoms at a low value.

The occurrence of secondary reactions involving more than one nitrogen atom makes it necessary to be cautious in drawing conclusions about the rate of the primary reaction, particularly since many of the products of these secondary reactions are known to react fast with nitrogen atoms. However, it seems likely (4) that the main energy barrier for the reactions is surmounted when the complex is formed. This conclusion would have to be modified if the secondary reactions formed products capable of reacting with alkyl chlorides to set up a chain reaction. For the methyl chloride reaction, hydrogen and chlorine atoms are possible chain carriers. However, the absence of any detectable amounts of methane, ethane, chlorine, cyanogen chloride, or ethylene chloride in the products makes it seem unlikely that there was an important contribution from chain reactions carried by hydrogen or chlorine atoms. It is possible to write a reaction scheme for a chain carried by CN radicals:

> $N + CH_3Cl \rightarrow N.CH_3Cl$  $N + N.CH_3Cl \rightarrow N_2 + CH_2Cl + H$  $N + CH_2Cl \rightarrow CN + HCl + H$  $CN + CH_3CI \rightarrow HCN + CH_2CI.$

The third reaction is exothermic and should be very fast (4), but it is doubtful that the last reaction would be fast enough to be effective as a chain carrier. Absence of a significant contribution from a chain reaction is also indicated by the reactions of the higher halides. In these, the recovery of unsaturated hydrocarbons with the same number of carbon atoms as the parent halide provides good evidence that the main path of the reaction was not hydrogen or chlorine atom abstraction followed by nitrogen atom attack on the resulting radical.

It appears probable, from the foregoing discussion, that the reactions of nitrogen atoms with alkyl chlorides involve direct attack at a shielded carbon atom without requiring a high activation energy.

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