REACTIONS OF NITRYL CHLORIDE (NO₂Cl) WITH AMMONIA,
THE METHYLAMINES, AND TITANIUM TETRACHLORIDE

DISSERTATION
Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

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*****

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INTRODUCTION

The primary objective of this research was the investigation of the gas-phase reactions of nitryl chloride (NO₂Cl) with the methylamines. Other objectives were the search for a feasible method for preparing relatively pure nitryl chloride, the examination of the solid product of the gas-phase reaction of nitryl chloride and ammonia, and the investigation of the reaction of nitryl chloride with titanium tetrachloride.
The Nature of Nitryl Chloride (NO₂Cl)

Physical properties.—Nitryl chloride has a freezing point of -145° and a boiling point of -15°. The compound is white in the solid state and the gaseous form is colorless. The liquid is usually pale-yellow probably due to impurities. Two investigations²,³ have shown that it can be obtained colorless in the liquid state. The gas at 100° has 2.81 times the density of air.⁴ The density of the liquid at 0° is 1.37 g/cc.⁵

The vapor of nitryl chloride has an odor much like that of chlorine, possibly because of the dissociation into dinitrogen tetroxide and chlorine. The vapor pressure has been measured from -80° to -15°.⁶ The rate of thermal decomposition is first order with respect to nitryl chloride and dependent on the initial pressure of nitryl chloride.⁷ The heat of dissociation into NO₂⁻ and Cl⁺ is 32 kcal per mole.⁸

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² Ibid.
³ H.A. Ogg, private communication.
⁴ H.J.Schumacher and G.Sprenger, loc. cit.
⁵ Ibid.
⁶ Ibid.
Structure.—Two structures of nitryl chloride

\[
\begin{align*}
\text{Cl} - \text{N} & \equiv \text{O} \\
\text{O} & = \text{N} \equiv \text{O} - \text{Cl}
\end{align*}
\]

(I) (II)

have been proposed from a consideration of its chemical reactions.

The support for (II), the hypochlorite structure, is due mainly to
the hydrolysis and alcoholysis reactions as represented by the
equations

\[
\begin{align*}
\text{NO}_2\text{Cl} + \text{H}_2\text{O} & \rightarrow \text{HNO}_2 + \text{HOCl} \\
\text{NO}_2\text{Cl} + \text{ROH} & \rightarrow \text{HNO}_2 + \text{ROCl} \setminus \longrightarrow \text{ROH} \rightarrow \text{RONO} + \text{H}_2\text{O}
\end{align*}
\]

However, it has been pointed out\(^9\),\(^10\) that if nitryl chloride were to
split into \(\text{Cl}^+\) and \(\text{NO}_2^-\) or if the \(\text{Cl}-\text{N}\) bond were polarized in such
a way that it could be represented as \(\text{Cl} - \text{N}\), the above reactions
could occur without requiring the hypochlorite structure. Since all
other reactions of nitryl chloride which could not be explained by a
\(\delta^+\) \(-\delta^-\) polarization could be explained by either a \(\delta^-\) \(-\delta^+\) polarization
or by the dissociation into \(\text{NO}_2^+\) and \(\text{Cl}^-\) or into \(\text{NO}_2^-\) and \(\text{Cl}^+\), the
structure \(\text{Cl} - \text{N} \equiv \text{O} \) seemed more acceptable.

The possibility of the existence of an equilibrium mixture of
\(\text{Cl}-\text{N} \equiv \text{O} \) and \(\text{O} = \text{N} \equiv \text{O}-\text{Cl} \) was nevertheless considered, and attempts were

\(^10\)F. Seel, J. Nográdi, and R. Posse, Z. anorg. allg. Chem. 269, 197
(1952).
made to show the presence of the nitrosyl and hypochlorite groups. The results showed that the lack of a reaction of NO$_2$Cl at a tempera-
ture just above its melting point with the azide ion was not typical
for that of a nitrosyl compound, and the lack of a reaction with the
tetramethylammonium ion was not typical for that of a hypochlorite.
The hypochlorite structure was therefore considered untenable.

The infrared spectrum of gaseous NO$_2$Cl and the Raman spectrum
of the liquid were investigated two years later. The structure
was found to be Cl - N$_2$O. However, it could not be ascertained
whether the molecule is planar or pyramidal.

Because of the marked similarity in structure and physical
properties of isosteres and on the basis of the known structures of
molecules which are isosteric with nitryl chloride a planar structure
was predicted in this research. It remained for the technique of
microwave spectroscopy to show experimentally that the structure is
definitely planar.

Correlation of This Research with Previous Work

The preparation of pure nitryl chloride.—A review of the litera-
ture pertaining to the various methods of preparation of nitryl

11 Ibid.
chloride has been compiled by Batey, who experimentally checked many of the syntheses. He was unable to find a convenient synthesis yielding a product sufficiently pure to be colorless in the liquid state.

There are two methods of preparation that yield liquid nitryl chloride that is colorless. The method first reported is the oxidation of nitrosyl chloride with liquid ozone according to the equation

$$\text{NOCl} + \text{O}_3 \rightarrow \text{NO}_2\text{Cl} + \text{O}_2$$

This method has the disadvantage that the product can be safely prepared in only small amounts at a time due to the hazards of working with large quantities of liquid ozone. The second method is the oxidation of nitrosyl chloride with dinitrogen pentoxide according to the equation

$$\text{NOCl} + \text{N}_2\text{O}_5 \rightarrow \text{NO}_2\text{Cl} + \text{N}_2\text{O}_4$$

The details of the latter method of preparation, which have never been published, have only recently become available.

The reaction of nitrosyl chloride and dinitrogen pentoxide may virtually be the only one known which yields nitryl chloride in a degree of purity that renders it colorless in the liquid state. This may be concluded from a study of the mechanism of the reaction between ozone and nitrosyl chloride. Johnson and Leighton have concluded

14 H.R. Batey, dissertation, The Ohio State University, 1951.
16 R. A. Ogg, private communication.
that the reaction of nitrosyl chloride with ozone depends on the presence of impurities such as nitrite oxide or nitrogen dioxide, which are converted by ozone into dinitrogen pentoxide.

During the course of previous research in this laboratory nitryl chloride had only been obtained in a degree of purity which yielded at best a pale-yellow liquid. Impurities have been shown to include chlorine, dinitrogen tetroxide, and nitrosyl chloride. Because of the reactivity of these impurities toward the compounds studied in the present research, a convenient method of preparation of colorless liquid nitryl chloride was desirable.

The reactions of nitryl chloride with ammonia and with amines.—

The work of Batey\textsuperscript{18} on the gas-phase reaction of nitryl chloride and ammonia provided the background for the present research on the reactions with the methylamines. The nitryl chloride-ammonia reaction is reported to proceed according to the equation

\[
\text{NO}_2\text{Cl} + 2\text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_4\text{NO}_2
\]

Chloramine may readily be converted in liquid ammonia or in an aqueous ammonia solution to hydrazine according to the equation

\[
\text{NH}_2\text{Cl} + 2\text{NH}_3 \rightarrow \text{N}_2\text{H}_4 + \text{NH}_4\text{Cl}
\]

Substituted hydrazines of low molecular weight, which have been of general interest in our laboratory, may be prepared by reactions similar to that expressed in the previous equation by substituting either a primary or a secondary amine for ammonia or by substituting a substituted chloramine for chloramine.

\textsuperscript{18}H. H. Batey and F. H. Sisler, loc. cit.
The reactions of nitryl chloride with Lewis acids.—Only two reactions of nitryl chloride have been reported which do not involve oxidation-reduction with Lewis acids. Batey\textsuperscript{19} found that nitryl chloride and sulfur trioxide form \( \text{NO}_2\text{Cl} \cdot 2\ \text{SO}_3 \). Seel, Nográdi, and Posse\textsuperscript{20} using liquid chlorine as a solvent, found that nitryl chloride and antimony pentachloride yield nitryl hexachloroantimonate(V).

\textsuperscript{19}Ibid.

METHODS OF PREPARATION OF NITRYL CHLORIDE

The Reaction of Anhydrous Nitric Acid and Chlorosulfonic Acid

The most convenient and widely used method of preparation of nitryl chloride has resulted from the patent by Dachlauer\(^1\) on the reaction of anhydrous nitric acid and chlorosulfonic acid according to the equation

\[
\text{HNO}_3 + \text{HSO}_3\text{Cl} \rightarrow \text{NO}_2\text{Cl} + \text{H}_2\text{SO}_4
\]

Since a colorless product from this reaction has not been reported, attempts were made to improve the techniques involved in the synthesis. The technique of Batey\(^2\) made no mention of purification of the commercial chlorosulfonic and anhydrous nitric acids.

To purify the chlorosulfonic acid it was refluxed until fumes of dissolved impurities ceased to form. It was then fractionated in a ten-inch column packed with glass helices. Continued heating during fractionation caused decomposition, however, with the result that the highest boiling point of distillate was 138.5\(^\circ\). Distillation under reduced pressure was also known to cause decomposition. However, a rapid distillation at atmospheric pressure using a Claisen column was successful.

The apparatus subsequently used for the distillation of chlorosulfonic acid is shown in Figure 1. A flow of dry nitrogen served

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\(^1\)K. Dachlauer, German Patent 509,405 (1929).
\(^2\)H. H. Batey, dissertation, The Ohio State University, 1951.
FIGURE 1
DISTILLATION OF CHLOROSULFONIC ACID
to displace moist air. The three drying tubes contained a mixture of phosphorus(V) oxide and sand. Volatile, fuming impurities were removed by refluxing for several minutes using only the take-off condenser. The acid was then distilled into the second flask. The rate of transfer of distillate to the second flask was regulated so that a head of liquid was always maintained above the stopcock. Distillation from the second flask through the Claisen column was rapid to prevent decomposition from overheating. A middle fraction was collected which boiled at $150^\circ\text{C}$ (litt.; $151.5^\circ\text{C}$).

Commercial anhydrous nitric acid became unobtainable just prior to this research because of accidents which occurred as a result of its thermodynamic instability. The preparation was effected by a double distillation from an ice bath at about 1 mm Hg using the apparatus shown in Figure 2.

Two hundred milliliters of concentrated nitric acid and 400 ml of concentrated sulfuric acid were cooled to just above their freezing points. The sulfuric acid was poured slowly with constant stirring into the nitric acid. The mixture was cooled to just above its freezing point and shaken vigorously in a glass-stoppered conical flask. After the mixture reached room temperature, it was allowed to stand several hours. After cooling to $0^\circ\text{C}$ it was transferred to the distillation flask (A). The flask was surrounded by an ice bath, and a Dry Ice bath was placed about the safety trap (C). The system was evacuated to about 1 mm of mercury with a mechanical pump. A small amount of

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3 General Chemical Division, Allied Chemical and Dye Corporation, private communication.
FIGURE 2
DISTILLATION OF NITRIC ACID
distillate was collected in the safety trap after which the receiver (B) was cooled to -78°. The level of a Dry Ice–trichloroethylene bath was maintained approximately level with the mouth of the inlet tube of the receiver. The bath surrounding the distillation flask was warmed as the rate of distillation decreased. Approximately 100 milliliters of distillate was collected.

The once-distilled, partially dehydrated acid was accumulated from several distillations and stored in the dark at 0°. Two hundred milliliters of the once-distilled acid was treated with 400 milliliters of sulfuric acid and distilled as above.

The apparatus shown in Figure 3 was used in the preparation of nitryl chloride. Nitrogen, which had been passed through a drying train consisting of a tower of calcium chloride, a mercury pressure-relief valve, two gas-washing bottles containing sulfuric acid, and two drying towers of barium oxide, was passed through the apparatus for several hours prior to starting the reaction. One hundred milliliters of anhydrous nitric acid, precooled to 0°, was then transferred to the reaction flask, taking care not to introduce moist air. The reaction flask was surrounded by a salt-ice bath, and 100 milliliters of chlorosulfonic acid was added dropwise under rapid stirring over a period of 4 to 6 hours. The rate of addition of the chlorosulfonic acid was sufficiently slow to preclude the formation of nitrogen dioxide in the reaction flask. The first few milliliters of liquid nitryl chloride were collected in the Dry Ice trap between the receiver and the drying tube containing phosphorus(V) oxide. The remainder of the product was condensed in the receiver, which was then attached to a high-vacuum line. The nitryl chloride was distilled at -78° and condensed by use of liquid nitrogen in the bubbler.
PREPARATION OF NITRYL CHLORIDE

FIGURE 3
shown in Figure 5. After the distillation the pale-yellow product was stored at -78°. The freezing point curve showed a sharp break at -146° (litt.; -145, -146) indicating the preparation was of high purity.

Since nitryl chloride reacts with ordinary stopcock grease, sulfuric acid was used in the early stages of the research to lubricate the ground-glass joint connecting the reaction flask to the receiver. However, it was observed that the gas stream became more highly colored near the joint. Shechter⁴ later reported that nitryl chloride tended to decompose in the presence of sulfuric acid.

More recently Wise and Volpe⁵ showed that nitryl chloride reacts with sulfuric acid according to the equation

\[ \text{NO}_2\text{Cl} + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2\text{HSO}_4 + \text{HCl} \]

The use of a fluorinated grease, du Pont FCX-759, prevented decomposition in this part of the apparatus.

The Reaction of Ethyl Nitrate and Acetyl Chloride

The observation that nitryl chloride reacted with sulfuric acid was of much concern because this then meant that the reaction of anhydrous nitric acid with chlorosulfonic acid yielded a product which would destroy nitryl chloride. Since it was possible that the presence of a strong acid tends to decompose nitryl chloride, a method of synthesis was proposed in which no strong acid would be present.

⁴R. Kaplan and H. Shechter, unpublished work.
This method involved the reaction of acetyl chloride and ethyl nitrate. It was hoped that the reaction would proceed according to the equation

\[ \text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{ONO}_2 \rightarrow \text{NO}_2\text{Cl} + \text{CH}_3\text{COOC}_2\text{H}_5 \]

Five drops of ethyl nitrate were added to 1 ml of acetyl chloride. There was no vigorous reaction, and no apparent heat was evolved. However, the solution became light yellow indicating a reaction had occurred. This reaction was carried out on a larger scale in an all-glass apparatus using traps at 0°, -78°, and -196° to condense any volatile products. No volatile products were observed in the -78° trap, even when the reaction mixture was heated to 5° less than the boiling point of ethyl nitrate. Since ethyl nitrate may detonate when heated above its boiling point, the reaction mixture was not heated over 72°.

The Method of Kaplan and Shechter

The method of Kaplan and Shechter is a variation of the Dachlauer preparation. The primary difference is in the nature of the anhydrous nitric acid. "Fuming" nitric acid was first defumed by bubbling dry air into it for several hours. An amount of "fuming" sulfuric acid was then added which provided a sufficient amount of free sulfur trioxide to react with the water in the nitric acid. The mixture was then used in the reaction with chlorosulfonic acid. This synthesis has been tried in this research and independently by a co-worker but yielded a highly colored product. It is reported by Kaplan and
Shechter that a pale-yellow product is obtained, but a product of such purity does not seem to be obtainable consistently.

The Reaction of Sodium Nitrate, Sulfuric Acid, and Hydrogen Chloride

A synthesis of nitryl chloride was described by Wise and Volpe\(^6\) which gave promise of producing nitryl chloride in a continuous stream from a reaction involving readily obtainable reagents. The reaction is given by the equation

\[
\text{NaNO}_3 + \text{H}_2\text{SO}_4 + \text{HCl} \rightarrow \text{NaHSO}_4 + \text{NO}_2\text{Cl} + \text{H}_2\text{O}
\]

This reaction was investigated in this research by introducing anhydrous hydrogen chloride, which had been diluted with nitrogen, into a solution of 5.4 g of sodium nitrate in 40 ml of sulfuric acid. The temperature of the solution was held at 8\(^\circ\). The first portion of nitryl chloride collected was yellow. When the flow-rate of hydrogen chloride became too excessive, yellow vapor was evolved. The reaction required approximately 30 minutes. The final product was red and was considered unsuitable for use in the present work. The impurities in nitryl chloride prepared by this method were shown by Wise and Volpe to include nitrosyl chloride and chlorine.

The demonstration of the detrimental effect of sulfuric acid on nitryl chloride was a significant outcome of their research. Wise and Volpe\(^7\) showed that only a 60 per cent yield of nitryl chloride

\(^6\) Ibid.

\(^7\) J.R. Wise and M.L. Volpe, private communication.
could be realized by the synthesis. The solubility of nitryl chloride in $\text{H}_2\text{SO}_4$ was then determined. Fifty per cent of a known amount was absorbed by bubbling it into sulfuric acid, but no chloride was found in the sulfuric acid after absorption. Yet 85-100 per cent of the total nitrogen was accounted for. To explain these facts the reaction was assumed to occur according to the equation

$$\text{NO}_2\text{Cl} + \text{H}_2\text{SO}_4 \rightarrow \text{HCl} + \text{NO}_2\text{HSO}_4$$

**The Reaction of Nitrosyl Chloride and Dinitrogen Pentoxide**

It has been reported that colorless nitryl chloride may be obtained in the reaction of dinitrogen pentoxide and nitrosyl chloride. The reaction is represented by the equation

$$\text{N}_2\text{O}_5 + \text{NOCl} \rightarrow \text{NO}_2\text{Cl} + \text{N}_2\text{O}_4$$

Nitrosyl chloride was prepared either by the reaction of hydrogen chloride with nitrosyl hydrogen sulfate or by the reaction of nitrogen dioxide with moist potassium chloride. The nitrosyl chloride was refluxed to remove dissolved hydrogen chloride and distilled in a high-vacuum apparatus.

Dinitrogen pentoxide was prepared by the dehydration of anhydrous nitric acid with phosphorus(V) oxide in the presence of ozone.

The receivers containing the nitrosyl chloride and dinitrogen pentoxide were attached to a high-vacuum apparatus. Nitrosyl chloride

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8R. A. Ogg, private communication.
was allowed to distil onto the solid dinitrogen pentoxide, which was cooled to $-80^\circ$. The bath temperature was then raised sufficiently to allow the nitrosyl chloride to melt and react more completely with the dinitrogen pentoxide. The nitrosyl chloride receiver was then disconnected, and an empty receiver was substituted. The receiver and connection to the reaction flask were opened to the vacuum system and evacuated. Cooling the receiver in liquid nitrogen and opening the stopcock to the reaction flask resulted in a flow of nitryl chloride, which condensed as a white solid in the receiver. On melting, the white solid formed a pale-yellow liquid of higher purity than obtained by the other methods of preparation which were investigated.

The observation that highly colored nitryl chloride could be purified by treatment with relatively small quantities of dinitrogen pentoxide was a significant outcome of the research on this synthesis.

**Conclusions**

The preparation of nitryl chloride as a colorless liquid by the reaction of chlorosulfonic acid and anhydrous nitric acid is probably not possible for various reasons. This reaction was performed recently at low temperature in a vacuum system, and yielded, as in previous investigations carried out under less rigorous conditions, a pale-yellow liquid. Sulfuric acid, a product of the reaction, reacts with nitryl chloride yielding hydrogen chloride. Hydrogen chloride is also an impurity in chlorosulfonic acid. Although the reaction of

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hydrogen chloride and nitryl chloride has not been investigated, oxidation-reduction probably occurs with the formation of chlorine, oxides of nitrogen, and anhydrous nitric acid. The equilibrium amount of water resulting from the self-dissociation of anhydrous nitric acid may also lead to the decomposition of nitryl chloride.

The removal of all impurities from impure nitryl chloride is difficult, if not impossible. Chlorine, which is the most difficult to remove, may account for the color of liquid nitryl chloride. Nitrosyl chloride may be removed by addition of dinitrogen pentoxide. Dinitrogen tetroxide may be removed by a low-temperature vacuum distillation. A self-dissociation of the liquid according to the equation

$$2 \text{NO}_2\text{Cl} \rightarrow \text{N}_2\text{O}_4 + \text{Cl}_2$$

would explain the reason the white solid state melts forming a pale-yellow liquid. This appearance of color on melting casts some doubt on the report of colorless, liquid nitryl chloride. Since the colorless liquid has apparently been obtained only in the presence of dinitrogen pentoxide, the possibility exists that traces of dinitrogen pentoxide may be sufficient to catalytically repress the dissociation, as expressed by the equations

$$\text{NO}_2\text{Cl} \leftrightarrow \text{NO}_2 + \text{Cl} \quad \text{NO}_2\text{Cl}_{2} \rightarrow \text{NO}_2 + \text{NO}_2\text{Cl} + \text{N}_2\text{O}_5$$
THE REACTION OF NITRYL CHLORIDE WITH AMMONIA

A. Preliminary Considerations

The solid products of the gas-phase reaction of nitryl chloride with ammonia have not been thoroughly investigated. If this reaction proceeds by a free-radical mechanism, both of the following reactions could occur simultaneously.

\[ \text{NO}_2\text{Cl} + 2 \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_4\text{NO}_2 \]  \hspace{1cm} (1)

\[ \text{NO}_2\text{Cl} + 2 \text{NH}_3 \rightarrow \text{NH}_2\text{NO}_2 + \text{NH}_4\text{Cl} \]  \hspace{1cm} (2)

Chloramine, ammonium nitrite, and ammonium chloride have been identified as products of the gas-phase reaction.\(^1\) However, the formation of ammonium chloride is assumed to result solely from the decomposition of chloramine according to the equation

\[ 3 \text{NH}_2\text{Cl} + 2 \text{NH}_3 \rightarrow 3 \text{NH}_4\text{Cl} + \text{N}_2 \]

Such an assumption implies that the reaction in equation (2) does not occur and suggests that the reaction in equation (1) does not proceed by a free-radical mechanism. A free-radical mechanism would most likely result in the formation of the products of both reactions (1) and (2). The initiation of the mechanism which occurs, whether it be an ionic reaction or a substitution reaction involving molecular species,

may be explained by a polarization of the Cl-N bond in a nitryl chloride molecule, e.g., Cl-N. Such a polarization would account for the presence of nitrite in the product.

In order to understand the gas-phase reaction, it is necessary to identify the original reaction products with certainty. Indirect determination of the products from their aqueous solutions, as was done previously, could lead to erroneous conclusions, since not only might further reaction occur in solution but also the chemical properties of nitramide are not well known. Consequently, it was believed that an x-ray powder diffraction study of the solid product of the nitryl chloride - ammonia reaction might show the existence of compounds other than those previously reported and lead to a better understanding of the mechanism of the reaction.

B. Experimental

1. Preparation and isolation of the reaction products.—The gas reactor was essentially that described by Batey² and shown in Figure 5, but the trap shown in the figure was omitted. To aid in preventing the decomposition of nitryl chloride, a connector of polyethylene tubing was used between the nitryl chloride receiver and the reactor, and Hooker's Grade S Fluorolube oil was used as a lubricant for the ramrod.

The reactor was dried by passing a rapid stream of ammonia through it for 15 minutes. The high flow-rate of ammonia was continued while

²H.H. Batey and H.H. Sisler, loc. cit.
a slow stream of dry nitrogen was bubbled into the nitryl chloride. The flow-rate ratio of ammonia to nitrogen was estimated to be about 50 to 1. The nitryl chloride receiver was maintained in a Dry Ice bath during the reaction. When a sufficient layer of solid products had accumulated, the reactor was removed to a dry box where capillary tubes were loaded with crystals of the product for x-ray diffraction measurements.

2. Preparation of ammonium nitrite.—Pure ammonium nitrite, used as a reference standard, was prepared by a method similar to one mentioned in Gmelin's Handbuch. Fifteen grams of ammonium sulfate and 30 grams of potassium nitrite were dissolved in separate Erlenmeyer flasks using the least possible amount of water. Each solution was filtered to remove any undissolved solid. On mixing the solutions a precipitate of potassium sulfate formed. The mixture was cooled to 0° and filtered. The filtrate was evaporated to dryness at room temperature using a mechanical pump. A white solid remained.

A sublimation apparatus was designed and constructed as shown in Figure 4. The solid was removed to the sublimation apparatus, heated to 77° with boiling carbon tetrachloride, and subjected to a pressure of about 0.1 mm of mercury by use of a mechanical pump. Sublimate collected on the tip of the cold finger. The sublimation apparatus was removed to the dry box. Precautions were observed so that the

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FRIEDRICH'S CONDENSER

FIGURE 4

SUBLIMATION OF AMMONIUM NITRITE
APPARATUS FOR GAS-PHASE REACTIONS OF NITRYL CHLORIDE WITH AMMONIA OR AMINES

FIGURE 5
sublimate would never come in contact with moist air. Some of the solid, which is capable of detonating, was pulverized carefully by grinding very small amounts at a time in an agate mortar. Samples were loaded in Pyrex capillaries, and x-ray powder diffraction patterns were made.

3. X-ray diffraction measurements.--The calculated x-ray data for the reaction product, for ammonium nitrite, and for ammonium chloride are presented in Tables I, II, and III, respectively. The following notations are used:

$I =$ the estimated intensity based on a maximum value of $I = 10$.

$D =$ the distance in cm, corrected for film shrinkage, between corresponding diffraction arcs. It is numerically equal to $40/10$.

$\Theta =$ the Bragg angle in degrees.

$d =$ the interplanar spacing in Å.

All photographs were made with copper Kα radiation.

The results show that only lines attributable to ammonium nitrite and ammonium chloride are found in the diffraction pattern of the solid produced in the gas-phase reaction of nitryl chloride and ammonia.
<table>
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<tr>
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<th>θ</th>
<th>sin θ</th>
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C. Discussion and Conclusions

The nitryl chloride-ammonia reaction does not yield solid products other than ammonium nitrite and ammonium chloride that can be detected by the x-ray powder diffraction method. Nitramide, being a crystalline solid, should be detectable by this method, but chloramine, a gas, would not. The course of the reaction, as previously reported,⁴

TABLE II
X-RAY POWDER DIFFRACTION DATA FOR AMMONIUM NITRITE

<table>
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<tr>
<th>Line No.</th>
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<th>sin θ</th>
<th>d</th>
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has been substantiated; namely, that the primary reaction proceeds according to the equation

\[ \text{NO}_2\text{Cl} + 2 \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_4\text{NO}_2 \]  

(1)

and that ammonium chloride results from the decomposition of chloramine according to the equation
TABLE III

X-RAY POWDER DIFFRACTION DATA FOR AMMONIUM CHLORIDE

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</tr>
<tr>
<td>1.07</td>
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<td></td>
<td></td>
</tr>
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</table>

3 NH₂Cl + 2NH₃ → 3 NH₄Cl + N₂  \hspace{1cm} (2)

rather than from the reaction

NO₂Cl + 2 NH₃ → NH₂NO₂ + NH₄Cl  \hspace{1cm} (3)

An ionic mechanism, involving Cl⁺ and/or NO₂⁻, for reaction (1) or a mechanism involving a reaction between molecular species, which would involve a nitryl chloride molecule in which the polarization of the N-Cl bond can be represented by the notation N⁻ Cl⁺, may prevail. Either mechanism would be consistent with the fact that nitryl chloride, in the presence of bases, typically behaves as a source of nitrite and positive chlorine.⁶


Although the lack of evidence for the simultaneous occurrence of reaction (3) did not indicate a free-radical mechanism for the nitryl chloride - ammonia reaction, such a mechanism cannot be discounted. If the sum of the free energies of formation of chloramine and ammonium nitrite is algebraically less than that of nitramide and ammonium chloride, the experimentally observed products would still be favored. Relative reaction rates, of course, for reactions (1) and (3) could have a greater influence on the observed products than the relative free energy changes.
THE REACTION OF NITRYL CHLORIDE WITH METHYLAMINE

A. Preliminary Considerations

The gas-phase reaction of nitryl chloride with methylamine offered the theoretical possibility of obtaining a path, by way of formation of methylchloramine, to the substituted hydrazines, which were of considerable interest in our laboratory. If the \( N-Cl \) bond in nitryl chloride were polarized in such a way that the chlorine were positive with respect to the \( NO_2 \)-group, the expected products should be methylchloramine and methylammonium nitrite, according to the equation.

\[
NO_2Cl + 2 \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NHCl} + \text{CH}_3\text{NH}_3\text{NO}_2
\]  

(1)

Methylchloramine, which is unstable, might then be identified by conversion in liquid ammonia to methylhydrazine, according to the equation

\[
\text{CH}_3\text{NHCl} + 2 \text{NH}_3 \rightarrow \text{CH}_3\text{NHNH}_2 + \text{NH}_4\text{Cl}
\]

analogous to the reaction of chloramine with liquid ammonia to produce hydrazine. A further consequence of the formation of methylchloramine would involve its decomposition to give possibly methylamine hydrochloride and other products, somewhat analogous to the decomposition of chloramine in the presence of ammonia to give ammonium chloride and nitrogen.

In addition to methylchloramine, methylammonium nitrite would also be predicted by the \( Cl - N \) polarization. However, methyl-
ammonium nitrite is also unstable at room temperature. One of its modes of decomposition has been given by the equation

\[ 2 \text{CH}_2\text{NH}_3\text{NO}_2 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O} + (\text{CH}_3)_2\text{NNO} \]  

(2)

A polarization of the N-Cl bond in nitryl chloride, in the presence of methyamine, in which the NO₂-group was positive with respect to the chlorine would be expected to lead to the formation of methylnitramine and methyamine hydrochloride, according to the equation

\[ \text{NO}_2\text{Cl} + 2 \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NHNO}_2 + \text{CH}_3\text{NH}_3\text{Cl} \]  

(3)

Evidence indicates that the Cl - N polarization is inherent in nitryl chloride. This factor would favor the reaction in equation (1). A competing factor favoring the reaction in equation (3) is the effect of the basic strength of the amine on the tendency to replace the weaker base, chloride ion, from nitryl chloride.

A free-radical mechanism might influence to a greater extent the course of the reaction. Such a mechanism, which accounts for the products of the reactions of nitryl chloride with some olefins could account for the attack of methyamine by either the chlorine radical or the NO₂⁻ radical.

B. Experimental

1. Introduction.—A preliminary experiment showed that the addition of a few drops of aqueous methyamine to a few drops of

---

nitryl chloride resulted in an explosion. Another experiment showed that the reaction could be controlled if carbon tetrachloride solutions of nitryl chloride and methylamine were cooled with Dry Ice and mixed by means of dropwise addition of one solution and rapid stirring of the second.

The apparatus used for the gas-phase reactions is shown in Figure 5. Preliminary experiments showed that with a large excess of methylamine the reaction occurred with no appreciable liberation of heat. In contrast to the nitryl chloride - ammonia reaction, yellow droplets formed on the walls of the reactor tube in addition to a white solid. Because of the hazardous nature of the substituted chloramines, which were likely products, the reaction was carried out behind safety shields. The vertical position of the reactor afforded the liquid droplets a better opportunity of passing into the trap. The wetting of the solid, due either to its amino-deliquescence or to the presence of the yellow droplets, accounted for the solid not clogging the inlet tubes, thus making use of the ramrod, shown in Figure 5, unnecessary.

2. Investigation of the white solid product.

a. Isolation and purification.—The solid produced in the nitryl chloride - methylamine reaction was yellowish, due to absorption of liquid. The color could not be extracted from the solid with carbon tetrachloride or with ether. The solid was soluble in water and in 95 per cent alcohol. It was hygroscopic and changed to a liquid after
a few minutes' exposure to air. The yellowish solid liberated iodine from a starch-potassium iodide test solution. On heating the solid on a watch glass it became white, then gave off white fumes, subsequently melted, continued to fume, and eventually decomposed.

A small portion of the solid was dissolved in boiling ethyl alcohol forming a light yellow solution. Ether was added, precipitating a white, crystalline solid. The crystals were hygroscopic. The melting point was 232° (litt.; m.p. for methylamine hydrochloride = 226-8°). After one recrystallization the solid still gave a strong test for an oxidizing agent with starch-potassium iodide.

The white solid, accumulated from several runs, was stored under ether. It was recrystallized three times from a mixture of benzene and alcohol. Glistening, white, hygroscopic plates formed, which melted at 230°-234°. These crystals still oxidized starch-potassium iodide to a slight extent. The Franchimont test, characteristic of primary and secondary nitramines as well as of nitrates and nitrites, was also positive, but the test was weak.

b. Analysis.—An analysis for carbon, hydrogen, and nitrogen was performed by standard, microanalytical procedures. Carbon and hydrogen were determined on a single sample by combustion in oxygen to form carbon dioxide and water respectively. Carbon dioxide was absorbed by Ascarite and determined by weighing.

---

3 The compound in acetic acid is added to a one per cent solution of N-diethylamline in acetic acid. Zinc dust is added without shaking the test solution. A green color results with a primary or secondary nitramine.

4 The analyses were performed by W. H. Deebel, Ohio State University.
Water was absorbed by Drierite and also determined by weighing.
Another sample was oxidized in a similar manner. However, the gases
were passed over hot copper, which reduced the oxides of nitrogen to
elemental nitrogen. The nitrogen was determined by measuring its
volume over 50 per cent potassium hydroxide.

Chlorine was determined volumetrically by a modified Volhard
method.\(^5\)

The elemental analysis as compared with that for methylanmonium
chloride showed:

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<tr>
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<td>N</td>
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<tr>
<td>Cl</td>
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</table>

c. Conclusions.---The melting point and analysis indicate that
the white, recrystallized product of the gas-phase reaction of nitryl
chloride and methylvamine is methylvamine hydrochloride. It must be
recognized, however, that the recrystallization of the original solid
product of the nitryl chloride - methylvamine reaction from an alcoholic
solvent may have resulted in its conversion to methylvamine hydrochloride.
The wet solid, however, could not be loaded into a capillary tube for
investigation by x-ray diffraction.

\(^5\)J.R. Caldwell and H.V. Moyer, Ind. and Eng. Chem., Anal. Ed. 7,
38 (1935).
3. **The chlorine-methylamine reaction**—In order to gain further information about the solid product of the nitryl chloride - methylamine reaction, this product was compared with the solid product of the reaction of chlorine with methylamine. The reaction of methylamine with either nitryl chloride or chlorine may involve the reaction of methylamine with chlorine radical. Such a mechanism might yield a stable product common to both reactions. The reaction of chlorine and methylamine was investigated in order to attempt to isolate this common product in a higher degree of purity than might be attained in the nitryl chloride - methylamine reaction.

The gas-phase reaction was performed similar to the nitryl chloride-ammonia reaction described on page 21. X-ray data for the white solid product formed are given in Table IV. Similar data for methylamine hydrochloride obtained from the gas-phase reaction of methylamine and hydrogen chloride and data obtained from the literature are given in Table V. The notations used in the tables are explained on page 25.

The data show that methylamine hydrochloride is a product of the chlorine-methylamine reaction. This fact together with the identification of the recrystallized product from the nitryl chloride - methylamine reaction add support to the conclusion that the solid product formed in the gas reactor in the reaction of nitryl chloride with methylamine is also methylamine hydrochloride.
### TABLE IV

**X-RAY DIFFRACTION DATA FOR PRODUCT OF THE REACTION OF CHLORINE AND METHYLAMINE**

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</table>

4. **Attempted identification of the yellow liquid product.**

a. An investigation of the absorption spectrum of the yellow liquid produced in the nitryl chloride - methylamine reaction was undertaken. The ultraviolet and visible spectra were obtained on aqueous solutions of unknown concentration, c. Ultraviolet spectra were also obtained at concentrations c/4 and c/400. The only absorption band occurred between 360 and 370 mμ, which was not characteristic of some compounds that might be expected in the reaction, such as
TABLE V

COMPARISON OF X-RAY DIFFRACTION POWDER PATTERNS OF THE PRODUCT OF
THE CHLORINE-METHYLAMINE REACTION AND METHYLAMINE HYDROCHLORIDE

<table>
<thead>
<tr>
<th>Chlorine-Methy lamine Product</th>
<th>Meth ylamine Hydrochloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>I</td>
</tr>
<tr>
<td>---</td>
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<td>5.07</td>
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<td>3.02</td>
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<tr>
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<tr>
<td>2.53</td>
<td>1/2</td>
</tr>
<tr>
<td>2.39</td>
<td>1/2</td>
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<tr>
<td>1.94</td>
<td>1/2</td>
</tr>
<tr>
<td>1.79</td>
<td>2</td>
</tr>
<tr>
<td>1.67</td>
<td>1</td>
</tr>
<tr>
<td>1.46</td>
<td>1</td>
</tr>
</tbody>
</table>

* d represents values from the product prepared in aqueous solution and recrystallized from ethyl alcohol.\(^6\)

** d represents values from the product of the gas-phase reaction of methy lamine and hydrogen chloride.

*** d represents A.S.T.M. values for methy lamine hydrochloride.\(^7\)


methylnitramine, methylchloramine, dimethylchloramine, and methyl dichloramine.

b. A further attempt to identify the liquid as either dimethylchloramine or methyl dichloramine was undertaken by trying to form the diphenylketene derivative. Diphenylketene was prepared, as described by Vanino, by reacting benzil with hydrazine hydrate to form benzil monohydrazone. A benzene solution of the hydrazone was oxidized with yellow mercuric oxide to azibenzil and filtered. The azibenzil in the solution was converted to diphenylketene by heating to 110°.

Two drops of the yellow liquid which formed in the reaction were isolated and dissolved in ether. This solution was poured into a 250-ml conical flask fitted with a 24/40 3 joint. A small piece of Dry Ice was dropped into the solution to expel oxygen from the flask. While the Dry Ice was subliming, a tube containing phosphorus(V) oxide and a Lunge pipet which contained an ether solution of diphenylketene were attached by ground-glass joints to the flask. About 10-20 drops of the ketene solution was introduced while the contents of the flask was being swirled. A white precipitate formed and was filtered and washed with several portions of ether. It was not hygroscopic. It was insoluble in water and ether and melted at 158°-160°. On recrystallization from alcohol it melted at 167°. This melting point did not correspond to that of any of the derivatives of diphenylketene with substituted chloramines but corresponded to that of N-methyldiphenylacetamide (m.p.: 164.5°, 166.5°), the derivative of methylamine.

Thus, the attempt to characterize the yellow liquid was unsuccessful.

c. A final attempt to show whether a substituted chloramine is formed by converting it to a hydrazine was carried out similar to the Raschig synthesis. Eighty milliliters of concentrated ammonium hydroxide containing one gram of dissolved sodium hydroxide was introduced into the trap. To this a solution of 0.4 g of gelatin in 25 ml of water was added. The reaction was run about 4 hours. During this time the liquid in the trap became warm. The trap was surrounded by an ice bath after the reaction had run 2 hours. The solution became slightly yellow and oxidized starch-potassium iodide. The presence of methyl hydrazine was not considered possible in the presence of an oxidizing agent that would oxidize iodide.

C. Discussion and Conclusions

Methylamine hydrochloride has been the only product identified in the gas-phase reaction of nitryl chloride and methylamine. A yellow, liquid oxidizing agent, which could not be identified, was also formed. This liquid did not possess the properties of various, predicted products. Hence, the reaction must be more complex than previously suggested.

From analogy with the nitryl chloride - ammonia reaction a free-radical mechanism is not indicated for the nitryl chloride - methylamine reaction. The $\text{Cl} - \text{N}$ polarization in nitryl chloride should be favored, leading to the reaction:
\[2 \text{CH}_3\text{NH}_2 + \text{NO}_2\text{Cl} \rightarrow \text{CH}_3\text{NH}_3\text{Cl} + \text{CH}_3\text{NH}_3\text{NO}_2\]

The difficulty in identification of the products given in this equation probably arises from their instability. Chloromethylamine is a very volatile, unstable, yellow liquid of irritating odor.\(^9\) The yellow oil produced in the gas reactor may be dichloromethylamine, which might be formed according to the equation

\[3 \text{CH}_3\text{NH}_2 + 2 \text{NO}_2\text{Cl} \rightarrow \text{CH}_3\text{NCl}_2 + 2 \text{CH}_3\text{NH}_3\text{NO}_2\]

Wurtz obtained methylamine hydrochloride and dichloromethylamine, but not chloromethylamine, from the reaction in aqueous solution of chlorine and methylvamine. Methylamine hydrochloride may result from a free-radical mechanism involving the reaction

\[2 \text{CH}_3\text{NH}_2 + \text{NO}_2\text{Cl} \rightarrow \text{CH}_3\text{NH}_3\text{Cl} + \text{CH}_3\text{NHNO}_2\]

but is more likely to result from the decomposition of chloromethylamine, in a manner analogous to the formation of ammonium chloride from the decomposition of chloramine.

Methylammonium nitrite has been obtained as extremely deliquescent, pale-green lustrous crystals, which decompose in a desiccator into methyl alcohol, nitrogen, and other, secondary products.\(^10\) A general decomposition reaction has also been given

\[2 \text{RNH}_3\text{NO}_2 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O} + \text{R}_2\text{NNO} \]

which could account for the formation of dimethylnitrosamine.

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\(^10\)P. C. Ray and J. N. Rakshit, loc. cit.
\(^11\)Ibid.
The ultraviolet spectrum of an aqueous solution of the yellow liquid product showed an absorption peak at 360-370 mμ, which is not characteristic of chloromethylamine or dichloromethylamine. However, the observed peak approaches that of an alcoholic solution of dimethylnitrosamine, shown later in this research to be 346 mμ.
THE REACTION OF NITRYL CHLORIDE WITH DIMETHYLAMINE

A. Preliminary Considerations

The mechanisms theoretically possible for the nitryl chloride - dimethylamine reaction are very similar to those already discussed for the reaction of nitryl chloride and methylamine. Considering first a substitution mechanism involving ionic or molecular species but not involving free radicals; if, in the presence of methylamine, the polarity of the Cl-N bond in nitryl chloride is such that the chlorine is positive with respect to the nitrogen, the following reaction, yielding a product containing nitrite ion, would be expected.

\[ 2 \text{CH}_3\text{NH}_2 + \text{NO}_2\text{Cl} \rightarrow (\text{CH}_3)_2\text{NCl} + (\text{CH}_3)_2\text{NH}_2\text{NO}_2 \]  

(1)

However, the following reaction would be favored if the Cl-N polarization prevails.

\[ 2 (\text{CH}_3)_2\text{NH} + \text{NO}_2\text{Cl} \rightarrow (\text{CH}_3)_2\text{NNO}_2 + (\text{CH}_3)_2\text{NH}_2\text{Cl} \]  

(2)

An inherent polarity of the N-Cl bond in nitryl chloride may result from the greater electronegativity of the nitro group compared with that of the chloro group. Such a polarity would favor reaction (1). On the other hand, the tendency of dimethylamine to replace from nitryl chloride the weak base chloride ion rather than the less weakly basic nitrite ion would favor reaction (2).

A consideration of a free-radical mechanism would allow for either the occurrence of reaction (1) or reaction (2) or for the simultaneous occurrence of both reactions.
If equation (1) represents the actual reaction that occurs, the observed products will depend on the extent of decomposition of dimethylchloramine and dimethylammonium nitrite, both of which are unstable at room temperature. Dimethylchloramine decomposes rapidly to give dimethylammonium chloride,\(^1\) in a manner analogous to the decomposition of chloramine to give ammonium chloride. Dimethylammonium nitrite is reported to decompose according to the following equations.\(^2\)

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{NNO} + \text{H}_2\text{O} & \rightarrow \text{(CH}_3\text{)}_2\text{NH}_2\text{NO}_2 \\
\text{(CH}_3\text{)}_2\text{NH}_2\text{NO}_2 & \rightarrow 2 \text{CH}_3\text{OH} + \text{N}_2
\end{align*}
\]

Thus, the gas-phase reaction of nitryl chloride and dimethylamine may be complex as a result of the formation of unstable, intermediate products.

B. **Experimental**

1. **Introduction.**—The gas-phase reactions of nitryl chloride with dimethylamine were performed in the apparatus shown in Figure 5. The experimental procedure, described on page 21, was similar to that used in the gas-phase reactions discussed previously. During the reaction white clouds of the products formed in the reactor tube. Use of the ramrod, shown in Figure 5, was unnecessary, even when the reaction was continued for 24 hours. When the reaction was discon-

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\(^1\) M.A. Berg, Ann. chim.[7] 3, 289 (1894).

tinned, a flow of nitrogen served to clear the atmosphere of suspended particles and residual vapors in the tube. A white solid and pale-yellow liquid droplets had formed.

2. Identification of the white solid product.—The white solid was too moist and of such consistency that it could not be loaded into a capillary tube for x-ray diffraction analysis. However, a sample of the solid was isolated from the reactor and recrystallized three times from a mixture of alcohol and ether. The resulting crystals gave a positive test for chloride and liberated a gas having the odor of dimethylamine when added to aqueous sodium hydroxide. They melted sharply at 172°; litt.: for dimethylamine hydrochloride, 171°.

3. The chlorine-dimethylamine reaction.—The gas-phase reaction of chlorine and dimethylamine was investigated in order to add possible support to the assumption that dimethylamine hydrochloride was a product formed during the gas-phase reaction of dimethylamine and nitryl chloride. The identification of dimethylamine hydrochloride from the latter reaction was not made without recourse to a recrystallization of the original product. As a result, the possibility was considered that the original solid from the nitryl chloride - dimethylamine reaction might have reacted with the liquid impurities adhering to it during recrystallization and yielded a different compound, namely, the observed compound, dimethylamine hydrochloride.

The chlorine-dimethylamine reaction offered the possibility of yielding a product which would also be a product of the nitryl
chloride - dimethylamine reaction. Both reactions may involve a mechanism in which dimethylamine reacts with either chlorine free-radical or with an electrophilic chlorine in a polarized molecule of chlorine-containing reactant. If dimethylamine hydrochloride were the product of the reaction of dimethylamine and chlorine, this would be evidence that the original product formed in the reactor during the nitryl chloride - dimethylamine reaction was also dimethylamine hydrochloride.

The chlorine-dimethylamine reaction was performed with the apparatus shown in Figure 5 and with the experimental procedure described on page 21. The product was of such consistency that the x-ray powder diffraction technique could easily be applied. The x-ray pattern obtained was compared to that of dimethylamine hydrochloride that had been prepared in this research by the gas-phase reaction of dimethylamine and hydrogen chloride. The data recorded in Tables VI and VII show that the major portion of the solid product in the reaction of chlorine with dimethylamine is dimethylamine hydrochloride.

4. Isolation and identification of the yellow liquid product.--
The gas-phase reaction of nitryl chloride and dimethylamine was run for 20 hours according to the procedures used in the gas-phase reactions which have previously been discussed. Liquid dimethylamine was used in the trap, shown in Figure 5, in order to prevent the escape of minute droplets of the liquid product. The residue, after evaporation of excess amine, amounted to 40 ml. A few milliliters of colorless liquid distilled between 35° and 75°. The boiling point of
TABLE VI

X-RAY POWDER DIFFRACTION DATA FOR PRODUCT OF
CHLORINE-DIMETHYLAMINE REACTION

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<th>Line No.</th>
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<th>( \theta )</th>
<th>( \sin \theta )</th>
<th>d</th>
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<td>0.2123</td>
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<td>24.13</td>
<td>0.409</td>
<td>1.88</td>
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</table>

the distillate then rose to 133-135\(^\circ\), at which temperature a yellow liquid distilled. The yellow distillate gave a trace test for chloride as did the colorless, low-boiling fraction. The residue, which represented over half of the solution being distilled, gradually became dark yellow and finally decomposed. The yellow distillate gave a positive test for a nitrosamine with an acetic acid solution of
<table>
<thead>
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<th>Product of Chlorine-Dimethylamine Reaction</th>
<th>Dimethylamine Hydrochloride</th>
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</thead>
<tbody>
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<td>1.88</td>
<td>1/2</td>
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</table>

*d refers to the product prepared in aqueous solution and recrystallized from ethyl alcohol.

**d refers to the 3 strongest lines from the product of the gas-phase reaction of methylamine and hydrogen chloride.
α-naphthylamine. Because the quantity of yellow material in the above solution was too small, sufficient purification by fractionation was not realized for obtaining an accurate boiling point.

The gas-phase reaction of nitryl chloride and dimethylamine was repeated in order to isolate a greater quantity of the yellow liquid product. Approximately 10 ml of liquid nitryl chloride was used. Crystals formed in the trap during the reaction, but on evaporation of excess amine little solid remained. Ether was added to the mixture, which was then subjected to continuous extraction until the yellow color was removed from the amine phase. A flask containing the extract was attached to a vacuum apparatus, and ether was removed by a closed-system distillation using liquid nitrogen as a coolant. More complete removal of ether was accomplished by use of a mechanical pump. The residue was transferred to a small distilling flask. Most of the yellow product distilled at 148.5 - 149.5°. The final fraction distilled at 149.5 - 150°. A slight amount of decomposition, which left a dark residue, occurred at the end of the distillation.

The yellow distillate had an odor similar to that of a sample of diethylnitrosamine and gave a positive Liebermann's nitroso reaction. The boiling point corresponds to that of dimethylnitrosamine (litt.; 153° at 774 mm).

More positive identification of the product as dimethylnitrosamine was obtained from its ultraviolet absorption spectrum. In order to check the experimental method of obtaining the spectra, the ultraviolet spectrum of an alcoholic solution of 0.001 M diethylnitrosamine was obtained with a Beckman DU spectrophotometer and found to be the
same as the spectrophotometric curve recorded in the literature. The ultraviolet absorption curve of the yellow reaction product shown in Graph 1, was compared with the curve in the literature for dimethylnitrosamine. The data for the two experimentally determined curves are given in Table VIII.

The data for the yellow reaction product indicates a double absorption peak may occur around 345 m\(\mu\). In order to ascertain if the double peak were actual or apparent, the spectrophotometric curve was recorded by use of the Beckman DK-2 spectrophotometer. The concentration of the alcoholic solution was again 0.001 M. A single peak appeared at 346 m\(\mu\).

The yellow liquid product, from a consideration of its physical and chemical properties and from theoretical evidence already given, is concluded to be dimethylnitrosamine.

C. Discussion and Conclusions

The formation of dimethylamine hydrochloride and dimethyl-nitrosamine in the nitryl chloride-dimethylamine reaction has added much support to a uniformity regarding the nature of the reactions of nitryl chloride with amines. The reaction is presumed to occur according to the equation

\[ 2 \text{(CH}_3\text{)}_2\text{NH} + \text{NO}_2\text{Cl} \rightarrow \text{(CH}_3\text{)}_2\text{NH}_2\text{NO}_2 + \text{(CH}_3\text{)}_2\text{NCl} \]

\(^{3}\text{E.C.C. Baly and C.H. Desch, J. Chem. Soc. 93, 1759 (1908).}\)
TABLE VIII
ULTRAVIOLET ABSORBANCY, A, OF THE PRODUCT OF THE NITRYL CHLORIDE-DIMETHYLAMINE REACTION AND DIETHYLNITROSAMINE
(Concentration = 1 Drop in 30 cc Ethanol)

<table>
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<th>Product of Nitryl Chloride-Dimethylamine Reaction</th>
<th>Diethylnitrosamine</th>
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</tr>
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<td>330</td>
<td>.718</td>
</tr>
<tr>
<td>342</td>
<td>.999</td>
</tr>
</tbody>
</table>
concentration = 1 drop in 30 ml. ethanol

ABSORBANCE OF THE LIQUID PRODUCT OF THE NITRYL CHLORIDE - DIMETHYLAMINE REACTION

GRAPH 1
Dimethylchloramine is a slightly yellowish liquid boiling at $46^\circ$ at 765 mm.$^4$ It decomposes rapidly, forming dimethylamine hydrochloride. Dimethylammonium nitrite is a pale-yellow liquid, stable at $21^\circ$-$23^\circ$.\textsuperscript{5}

One of its modes of decomposition is the formation of dimethylnitrosamine. The physical properties reported for these compounds agree with those observed for the reaction products.

$^4$M.A. Berg, loc. cit.

$^5$P.C. Ray and J.N. Rakshit, loc. cit.
A. Preliminary Considerations

The predictions of possible products in the reaction of nitryl chloride with ammonia, methylamine, or dimethylamine have been based, in part, on the replacement of an amine hydrogen in some step of the mechanism of the given reaction. Speculation was not offered on the nature of the replaced hydrogen; that is, whether the hydrogen was released as a proton, as part of an electron deficient group, or released in some other form. Such a replacement was requisite to the formation of the ammonium or substituted ammonium ion, which was predicted to be among the reaction products. Because of its tertiary nitrogen, of course, trimethylamine cannot react in this manner. However, trimethylamine has a marked tendency to react in a 1:1 ratio with many simple covalent molecules and form salts. Some examples are the reaction with hydrogen halide or methyl halide to form, respectively, trimethylammonium halide or tetramethylammonium halide; the reaction with chlorine to form chlorotrimethylammonium chloride, the reaction with dinitrogen tetroxide to form trimethylnitrosammonium nitrate, and the reaction with chloramine to form 1,1,1-trimethylhydrazinium chloride.

Let us now consider the general reaction of trimethylamine with the covalent molecule $AB$ to form a salt, where $A$ and $B$ may be either
atoms or small groups of atoms. Two factors governing whether the reaction will yield \([\text{(CH}_3\text{)}_3\text{NA}]\text{B} \) or \([\text{(CH}_3\text{)}_3\text{NB}]\text{A}\) are a kinetic factor, as might be reflected by the relative electronegativities of A and B in the covalent molecule AB and a thermodynamic factor, as evidenced by the relative base strength of the anions \(A^-\) and \(B^-\).

The relative electronegativities of A and B will determine the polarity of the covalent bond joining A and B. If B is more electronegative than A, then the polarity of the bond can be represented by the designation \(\delta^+ \text{A} \rightarrow \delta^- \text{B}\), and the expected product, based on this one factor, would be \([\text{(CH}_3\text{)}_3\text{NA}]\text{B}\); if A is more electronegative than B, then \([\text{(CH}_3\text{)}_3\text{NB}]\text{A}\) would be expected. The relative base strength of \(A^-\) and \(B^-\) will also determine which of these ions will tend to be displaced from the molecule AB as the result of a nucleophilic attack by trimethylamine, which would have a greater tendency to replace the weaker base.

For the previously cited reactions of trimethylamine with covalent molecules, information exists on the relative electronegativities of A and B and on the relative base strengths of \(A^-\) and \(B^-\), in the cases where A-B is H-Cl, CH\(_3\)-Cl, or NH\(_2\)-Cl. The reactions with these three compounds proceed not only according to a displacement of the more electronegative group (Cl is more electronegative than H, CH\(_3\), or NH\(_2\)) but also in agreement with the replacement of the weaker base (Cl\(^-\) is less basic than H\(^-\), CH\(_3\)^-, or NH\(_2\)^-).

In the reaction of trimethylamine with nitryl chloride, however, the formation of chlorotrimethylammonium nitrate according to the equation
\[ \text{NO}_2\text{Cl} + (\text{CH}_3)_3\text{N} \rightarrow [(\text{CH}_3)_3\text{NCl}] \text{NO}_2 \]

would be predicted on the basis of the greater electronegativity of the nitro group compared with that of the chloro group, but the formation of trimethylnitroammonium chloride, according to the reaction

\[ \text{NO}_2\text{Cl} + (\text{CH}_3)_3\text{N} \rightarrow [(\text{CH}_3)_3\text{NNO}_2] \text{Cl} \]

would be favored by the tendency to replace chloride, a weaker base than nitrite.

B. **Experimental**

1. **Preliminary experiments.**—The following preliminary experiments, performed in both the gas and liquid phases to determine the reactivity of nitryl chloride toward trimethylamine, showed that these substances tend to react violently but that the reaction may be controlled.

Gaseous trimethylamine was passed directly from its storage tank into a receiver containing a few milliliters of liquid nitryl chloride. A flash but no sound occurred, and the ground-glass connection of the receiver was forced apart.

In order to carry out the reaction under lower partial pressures of the reactants, two receivers, one filled with gaseous trimethylamine and the other with gaseous nitryl chloride, were connected by means of ground-glass joints to opposite arms of a 2-way stopcock. The stopcock was opened, and the gases were allowed to diffuse together. Some white solid gradually formed on each side of the stopcock. The
pale-yellow color present in the nitryl chloride receiver did not change in one hour, and no color appeared in the other receiver.
In order to effect a more rapid mixing of the reactants a Dry Ice bath was used to cool the nitryl chloride receiver. White solid began to form immediately on the wall of this receiver, and a flash occurred. The solid in the bottom of the cold receiver appeared yellow, and a pink ring was observed about an inch above the bottom.
After warming the receiver to room temperature the solid in the bottom appeared white. A yellow gas was above the solid. The receiver was again cooled with Dry Ice. A ring of red crystals about an inch from the bottom of the receiver indicated the presence of nitrylsyl chloride. Greenish-yellow gas was still present indicating chlorine. The pressure on the white solid was reduced and maintained at 10 mm of mercury for a half-hour. Some droplets collected on the wall of the receiver, but the solid was dry and melted sharply at 78°. A light yellow liquid was formed on melting. The small amount of product formed was insufficient for purification and analysis.

Although the scope of the research with amines was confined to gas-phase reactions, it was of interest to note that the reaction could be controlled in solution. The reactants were diluted with carbon tetrachloride, the nitryl chloride solution cooled to -20°, and the trimethylamine solution added dropwise under vigorous stirring. The solid and/or solution appeared at first to be white, then yellow, and near the end of the reaction, pink. These color transformations are indicative of addition compounds. On allowing the mixture to
warm to room temperature these apparent addition compounds became unstable. A few colorless droplets and a white, hygroscopic solid remained, which was of insufficient amount to be purified and analyzed.

2. The gas-phase reaction of nitryl chloride and trimethylamine.
   a. Introduction.—Several gas-phase reactions of trimethylamine and nitryl chloride were carried out in the apparatus illustrated in Figure 5 and with the technique described on page 21. Considerably more white solid was formed than during the reaction of nitryl chloride with either methylamine or dimethylamine, and the ramrod had to be used frequently. A yellowish band of solid formed near the gas inlet tubes. Some amber liquid generally formed on the upper part of the reactor, possibly accounting for the yellow color of this band and of the solid which adhered to the mouth of the nitryl chloride inlet tube. On some occasions a trap liquid was used, but generally the trap was omitted.

   b. Investigation of the white solid product.—One gas-phase reaction of nitryl chloride and trimethylamine was carried out with liquid trimethylamine in the trap. As the reaction proceeded the trap liquid became cloudy, and a white solid settled out. When the reaction had been discontinued, excess trimethylamine was evaporated, and the system was flushed with dry nitrogen. Some of the solid was yellowish since it contained material forced from the center inlet tube by the ramrod. The solid was insoluble in ether. Sufficient ethyl alcohol was added to dissolve the solid. Ether was again added
until a precipitate formed. The mixture was carefully heated by means of an oil bath to dissolve the solid without decomposing it. White and colorless needles formed on cooling in the refrigerator, but they were generally contaminated with a yellowish substance. They were washed with ether and dried over calcium chloride. The discolored crystals were dissolved in ethyl alcohol, and the solution was decolorized with activated charcoal. Removal of alcohol under vacuum again resulted in a discolored product, which was of insufficient quantity for recrystallization. Some of the crystals which showed no discoloration gave a positive test for chloride. The picrate derivative of this product melted at 210° indicating the original solid might be trimethylamine hydrochloride; the melting point of trimethylammonium picrate is 216°.

A second gas-phase reaction was continued for 8 hours without use of the trap. Glass-wool was used in the reactor to prevent loss of solid products. The products were dissolved in ethyl alcohol, and ether was added until the solid just began to precipitate. The solution after having been warmed until the precipitate dissolved was allowed to cool overnight in the refrigerator. Several dendrites, each about 1 cm long, formed in addition to a small quantity of flocculent particles. The dendrites were filtered, washed with ether and stored over phosphorus(V) oxide and calcium chloride. They were yellowish apparently due to impurity and melted at 157°. Alcohol and benzene were used to recrystallize the solid, which was then washed with ether and dried. The crystals were pale yellow
and melted at 132.5°. Some of them were placed in an oven at 120° for a half-hour during which time they became white. They melted then at 135.5-136.5°. The solid gave the following analysis:

\[ C = 29.58\%, \ H = 8.38\%, \ N = 23.04\% \]

The percentage composition agreed only approximately for that of the possible compound \((\text{CH}_3)_3\text{NNO}_2\text{Cl}\) in which \( C = 32.02\%, \ H = 8.06\% \) and \( N = 24.90\% \).

A third run of about 16 hours duration yielded no liquid droplets. The formation of yellowish solid on the reactor wall just above the gas outlets and the detection of heat on two instances during the run were indications of slight decomposition.

Two separate portions of the reaction products were isolated. The first portion was white with traces of discoloration and constituted the majority of the product. This portion was combined with the white portion of reactor products from a previous run and recrystallized from a mixture of benzene and ethanol. A mixture was indicated by the fact that the crystals melted somewhat at 135°, but most of the melting occurred around 205°. They seemed to be hygroscopic, but after exposure to air they became drier and melted at 138-141°C. The mixture possibly reacted in the presence of absorbed moisture to form a non-hygroscopic substance. A chloride test was positive. An aqueous solution was slightly acidic indicating a hydrochloride. A test for reducing agent with hydrochloric acid and potassium iodate and a test for an oxidizing agent with starch-potassium iodide-acetic acid were negative.

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The analysis was performed by W.H. Deebel of the Department of Chemistry, Ohio State University according to the method cited on p. 33.
The second portion of products was the yellow solid which was scraped from the upper surface of the reactor. Three crops of crystals were obtained using benzene and alcohol as a mixed solvent for the recrystallization. The first crop of crystals melted at 133° and after one recrystallization, melted at 135°. The third crop melted at 180° and after vacuum sublimation at 110° melted at 138-142°.

A solution of 0.3 g of the crystals from this first crop in 3 ml of alcohol was added to 3 ml of a saturated solution of picric acid in 95% alcohol. The picrate derivative, which formed after the reactants had set for a half-minute, was filtered, recrystallized from hot alcohol, and dried over calcium chloride in a vacuum desiccator. The melting point of the picrate derivative was 215°; litt. for trimethylammonium picrate, m.p. = 216°. A sample of the derivative gave the following percentage analysis: C = 37.37, H = 4.36, and N = 18.75; calculated for trimethylammonium picrate: C = 37.50, H = 4.20 and N = 19.44.

A sample from the third crop of crystals gave effervescence when treated with 35% sodium hydroxide. An odor like that of trimethylamine was detected. This crop of crystals melted at 180°. The crystals gave the following percentage analysis: C = 31.04, H = 8.87, N = 21.31. The analysis of a second sample, more finely ground than the previous one, gave the following analysis: C = 31.70, H = 9.09, N = 20.75.
By the assumption of a certain number of carbon, hydrogen, or nitrogen atoms in the formula of the compound and from the percentage composition the molecular weight may be approximated. For example,

$$\text{Mol. wt.} = \frac{\text{No. of carbon atoms} \times \text{at. wt. of carbon} \times 100}{\% \text{ carbon}}$$

In Table IX the calculated molecular weights have been listed for various numbers of atoms in the formula using both sets of the above-mentioned analytical values. From these two sets of data the atomic ratios were calculated to be: C = 2.58, 2.64; H = 8.80, 9.08; N = 1.52, 1.48.

The results indicate that the C:H ratio is about 3:10. The atomic ratios for carbon and nitrogen indicate there must be at least two nitrogen atoms in the formula of the compound. Thus, the molecular weight of the compound must be at least about 115. The molecular weight of one of the likely compounds under consideration, namely (CH₃)₃NNO₂Cl, is 112.5.

The more finely ground analytical sample showed a chloride content of 3.64%.² If the values of the atomic ratio of carbon to chlorine (25.6) and that of nitrogen to chlorine (14.4) are assumed to be prohibitively large, then the chlorine content must be due to impurity of the crystals. Assuming that the chlorine is present as (CH₃)₃NHCl, i.e., C₅H₁₀NCl, and subtracting these coefficients from the atomic ratios based on a value of 1 for chlorine, the corrected atomic ratios now become C₂₂.6 H₇₈.2 N₁₃.₄ O₂₀.₄ or approximately C₅H₁₁N₂O₃.

²The analysis was performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Chlorine was determined gravimetrically by precipitation as silver chloride.
TABLE IX

CALCULATED VALUES* OF THE MOLECULAR WEIGHT OF THE SOLID COMPOUND ISOLATED FROM THE NITRIL CHLORIDE-TRIMETHYLAMINE REACTION

<table>
<thead>
<tr>
<th>Assumed Atomic Composition</th>
<th>Mol. Wt. (1)**</th>
<th>Mol. Wt. (2)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N</td>
<td>65.7</td>
<td>67.5</td>
</tr>
<tr>
<td>2 C</td>
<td>77.4</td>
<td>75.8</td>
</tr>
<tr>
<td>3 C</td>
<td>116.1</td>
<td>113.7</td>
</tr>
<tr>
<td>10 H</td>
<td>113.6</td>
<td>111.0</td>
</tr>
<tr>
<td>2 N</td>
<td>131.5</td>
<td>135.0</td>
</tr>
<tr>
<td>5 C</td>
<td>193.5</td>
<td>189.4</td>
</tr>
<tr>
<td>6 C</td>
<td>232.2</td>
<td>227.3</td>
</tr>
<tr>
<td>17 H</td>
<td>193.1</td>
<td>188.6</td>
</tr>
<tr>
<td>3 N</td>
<td>197.2</td>
<td>202.5</td>
</tr>
</tbody>
</table>

* Each value (columns 2 and 3) is based on an assumed number of carbon, hydrogen, or nitrogen atoms (column 1) in the formula of the compound.

** The values in column 2 were calculated from the analytical data; C = 31.04, H = 8.87, N = 21.31.

*** The values in column 3 were calculated from the analytical data; C = 31.70, H = 9.09, N = 20.75.
3. The chlorine-trimethylamine reaction.--The reaction of chlorine with trimethylamine was investigated in order to compare the solid product formed with the solid formed in the nitryl chloride - trimethylamine reaction. Both reactions may proceed by a free-radical mechanism. Thus, it may be possible to isolate the product of trimethylamine and chlorine radical in purer form by use of chlorine rather than nitryl chloride. The reaction was carried out using the apparatus shown in Figure 5. Chlorine was dried by bubbling through concentrated sulfuric acid. Preliminary runs resulted in the burning of trimethylamine, due to an insufficient excess of amine. During a subsequent run the flow rate of trimethylamine to that of chlorine was still not sufficiently great to prevent the reactor from becoming hot, which resulted in apparent decomposition. A yellowish-brown material solidified on the upper portion of the reactor near the gas inlet tubes. With a still larger trimethylamine-to-chlorine flow-rate ratio, estimated to be about 50:1, no heat due to the reaction could be detected. The only colored material seemed to be that which plugged the chlorine inlet tube. The gases emerging from the reactor were passed into a Raschig solution. The solution gave a negative test for hydrazine with potassium iodate and hydrochloric acid.

In order to facilitate the identification of the solid produced in the nitryl chloride - trimethylamine reaction, as well as that produced in the chlorine-trimethylamine reaction, x-ray diffraction
patterns of the following substances were prepared using copper-Kα radiation:

1) the white solid produced in the nitryl chloride-trimethylamine reaction,
2) the white solid produced in the chlorine-trimethylamine reaction,
3) the brownish solid produced in the chlorine-trimethylamine reaction, which resulted from a higher flow-rate ratio of chlorine to trimethylamine than was used in 2),
4) trimethylamine hydrochloride produced by the gas-phase reaction of trimethylamine and hydrogen chloride.

The interplanar spacings, \( d \), were calculated, and the results are recorded in Tables X, XI, and XII. The data in the literature\(^3\) for trimethylamine hydrochloride is listed in Table XIII. Symbols appearing in the tables are explained on page 25.

The following results were obtained from the x-ray data:

1. The white solid produced in the nitryl chloride-trimethylamine reaction is trimethylamine hydrochloride. All lines from the diffraction pattern for trimethylamine hydrochloride prepared in this research appeared. In addition, lines appeared at \( d = 3.12 \) (I = 1) and \( d = 2.85 \) (I = 1).

2. The white solid produced in the chlorine-trimethylamine reaction is not trimethylamine hydrochloride. The only line which seems to appear from the trimethylamine hydrochloride pattern is \( d = 3.49 \) (I = 7). Others which

### TABLE X

**X-RAY POWDER DIFFRACTION DATA FOR THE WHITE SOLID PRODUCT OF THE NITRYL CHLORIDE - TRIMETHYLAMINE REACTION**

<table>
<thead>
<tr>
<th>Line No.</th>
<th>I</th>
<th>D</th>
<th>θ</th>
<th>sin θ</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>2.90</td>
<td>7.25</td>
<td>0.1262</td>
<td>6.11</td>
</tr>
<tr>
<td>2(?)</td>
<td>1/2</td>
<td>3.51</td>
<td>8.775</td>
<td>0.1525</td>
<td>5.06</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>3.86</td>
<td>9.65</td>
<td>0.1676</td>
<td>4.60</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>5.09</td>
<td>12.73</td>
<td>0.2204</td>
<td>3.50</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.72</td>
<td>14.30</td>
<td>0.247</td>
<td>3.12</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>5.89</td>
<td>14.73</td>
<td>0.2543</td>
<td>3.03</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>6.195</td>
<td>15.49</td>
<td>0.2671</td>
<td>2.91</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>6.28</td>
<td>15.70</td>
<td>0.2705</td>
<td>2.85</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>6.58</td>
<td>16.45</td>
<td>0.2832</td>
<td>2.72+</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>6.695</td>
<td>16.74</td>
<td>0.2880</td>
<td>2.68</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>7.27</td>
<td>18.18</td>
<td>0.3120</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Appeared are \( d = 4.72 \) (I = 10), \( d = 3.35 \) (I = 4), \( d = 2.81 \) (I = 5), and \( d = 2.75 \) (I = 4).

3. The brownish solid produced at higher flow-rate ratios of chlorine to that of trimethylamine is trimethylamine hydrochloride. All lines of the pattern of trimethylamine hydrochloride prepared in this research appeared except \( d = 2.49 \) (I = 2) and \( d = 2.43 \) (I = 1). Others which appeared are \( d = 5.09 \) (I = 1), \( d = 3.26+ \) (I = 3), \( d = 3.11 \) (I = 1), and \( d = 2.54 \) (I = 1).
TABLE XI
X-RAY POWDER DIFFRACTION DATA FOR THE WHITE SOLID PRODUCT
OF THE CHLORINE-TRIMETHYLAMINE REACTION

<table>
<thead>
<tr>
<th>Line No.</th>
<th>I</th>
<th>D</th>
<th>(\Theta)</th>
<th>(\sin \Theta)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>3.755</td>
<td>9.39</td>
<td>0.1632</td>
<td>4.72</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>5.105</td>
<td>12.76</td>
<td>0.2209</td>
<td>3.49</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>5.325</td>
<td>13.31</td>
<td>0.2302</td>
<td>3.35</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>6.35</td>
<td>15.9</td>
<td>0.2740</td>
<td>2.81+</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>6.51</td>
<td>16.28</td>
<td>0.2805</td>
<td>2.75</td>
</tr>
</tbody>
</table>

4. A comparison of the data for trimethylamine hydrochloride prepared by the gas-phase reaction with the data obtained from a sample prepared in aqueous solution, shows a reversal of the relative intensities of lines at \(d = 4.62\) and 3.50.

4. Investigation of the yellow reaction product.—An investigation of the colored reaction product was now undertaken. With the reactor in a horizontal position the procedure involved in the previous runs was employed. Amber droplets were deposited on the upper portion of the reactor wall and white solid settled on the bottom. Some droplets which formed near the gas inlet tubes became reddish. After the reaction had continued for 8 hours, the reactor and glass wool plugs were washed with 100 ml of water. Fifty ml of the resulting deep red solution were subjected to distillation.
TABLE XII
X-RAY POWDER DIFFRACTION DATA FOR THE BROWN PRODUCT
OF THE CHLORINE-TRIMETHYLAMINE REACTION

<table>
<thead>
<tr>
<th>Line No.</th>
<th>I</th>
<th>D</th>
<th>θ</th>
<th>sin θ</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>2.905</td>
<td>7.26</td>
<td>0.1264</td>
<td>6.10</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3.485</td>
<td>8.71</td>
<td>0.1514</td>
<td>5.09</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>3.86</td>
<td>9.65</td>
<td>0.1676</td>
<td>4.60+</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>5.10</td>
<td>12.75</td>
<td>0.2207</td>
<td>3.49</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>5.465</td>
<td>13.66</td>
<td>0.2362</td>
<td>3.26+</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>5.735</td>
<td>14.34</td>
<td>0.2477−</td>
<td>3.11</td>
</tr>
<tr>
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<td>5</td>
<td>5.89</td>
<td>14.73</td>
<td>0.2543</td>
<td>3.03</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>6.19</td>
<td>15.48</td>
<td>0.2669</td>
<td>2.89</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>6.30</td>
<td>15.75</td>
<td>0.2714</td>
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<td>10</td>
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<td>6.555</td>
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<tr>
<td>11</td>
<td>4</td>
<td>6.685</td>
<td>16.71</td>
<td>0.2875</td>
<td>2.68+</td>
</tr>
</tbody>
</table>

Since, in the synthesis of dimethylnitrosamine according to Vanino, an aqueous solution containing the nitrosamine is distilled to dryness, and the nitrosamine is then salted out in the distillate, it was hoped that if dimethylnitrosamine were a product of the trimethylamine-nitryl chloride reaction, it could be isolated in this manner. However, none of the colored material in the aqueous

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TABLE XIII

X-RAY POWDER DIFFRACTION DATA OF TRIMETHYLAMINE HYDROCHLORIDE
FROM THE REACTION OF TRIMETHYLAMINE AND HYDROGEN CHLORIDE

(1) IN THE GAS PHASE AND (2) IN AQUEOUS SOLUTION

<table>
<thead>
<tr>
<th>Line No.</th>
<th>I</th>
<th>D</th>
<th>θ</th>
<th>sin θ</th>
<th>d</th>
<th>(2) AQUEOUS SOLUTION</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>2.895</td>
<td>7.24</td>
<td>0.126</td>
<td>6.12</td>
<td>6.14</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>3.845</td>
<td>9.61</td>
<td>0.167</td>
<td>4.62</td>
<td>4.61</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4.44</td>
<td>11.10</td>
<td>0.1925</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>5.085</td>
<td>12.71</td>
<td>0.167</td>
<td>3.50</td>
<td>3.52</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>5.715</td>
<td>14.29</td>
<td>0.2468</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>5.86</td>
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<td>18.44</td>
<td>0.3163</td>
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solution of reactor products could be distilled. Distillation was discontinued when only 4 ml of solution remained. This residue was also not volatile when subjected to steam distillation.
In a subsequent run after the solid had been recrystallized from a mixture of alcohol and ether, the yellow filtrate was investigated. A few milliliters was made basic with an equal volume of alcohol saturated with potassium hydroxide. The resulting, white precipitate was identified as potassium chloride. Potassium carbonate was added to the solution which had been decanted from the potassium chloride. A small amount of water was added. A pale yellow liquid phase separated from the solution. Applying this technique on a larger scale the remainder of the solution was similarly treated. Potassium chloride was filtered off, and the solution was refluxed for about a half-hour in a 100° bath to expel trimethylamine. The solution still possessed a strong amine odor, but refluxing was discontinued to prevent decomposition. The alcoholic extract of 70 ml was transferred to a round-bottom flask fitted with a take-off condenser. A drying tube containing magnesium perchlorate was attached to the upper end of the condenser. The volume of the solution was reduced to 14 ml by distilling most of the alcohol. This residue was very slightly basic. On raising the temperature of the oil bath which surrounded the flask the residue gradually became dark brown. The highest temperature of distillate was 95°. However, the liquid distilling between 90° and 95° amounted to only a few drops.

In order to investigate the ultraviolet absorption spectrum of the colored product the reaction was run for 9 hours. With the reactor in a vertical position, as illustrated in Figure 5, the trap contained only glass wool to prevent loss of products. A slightly yellowish solid clogged the inlet tube leading to the trap. Some
of this solid was removed and dissolved in ethyl alcohol. The absorption spectrum was plotted from 280-500 m\(\mu\). It showed only one absorption peak, which occurred at 345 m\(\mu\).

C. Conclusions

The solid formed in the gas reactor during the reaction of nitryl chloride and trimethylamine is trimethylamine hydrochloride. While the formation of a salt having the atomic composition equivalent to that of one molecule of nitryl chloride plus one molecule of trimethylamine was postulated, the observed product was not entirely unexpected. Trimethylamine hydrochloride is also the only solid positively identified and formed in appreciable quantity in the nitrosyl chloride - trimethylamine reaction.\(^5\)

The substances obtained by recrystallization of the reaction products from a benzene-alcohol mixture are possibly formed by a reaction with or in the solvent. The analyses of these substances are inconclusive. A small amount of dimethylnitrosamine is indicated by an absorption peak at 345 m\(\mu\) in the ultraviolet spectrum of an alcoholic solution of the products.

A salt other than trimethylamine hydrochloride may be formed if the reaction of trimethylamine and nitryl chloride were performed in a solvent. An acidic solvent would enhance the effective basic strength of trimethylamine and its ability to replace chloride ion.

Such a solvent would also decrease the acidic character of NO$_2^+$ and lessen the tendency for formation of trimethylammonium ion.

While the investigation of the chlorine-trimethylamine reaction was not needed to support the formation of the amine hydrochloride, as was necessary in the reactions of nitryl chloride with methylamine and with dimethylamine, the fact that trimethylamine hydrochloride was not formed was of interest. Although the product was not identified, the formation of chlorotrimethylammonium chloride is postulated.
THE REACTION OF NITRIL CHLORIDE WITH TITANIUM TETRACHLORIDE

A. Preliminary Considerations

Nitryl chloride shows a striking lack of reactivity toward Lewis acids. Although few such reactions have been investigated, it is significant that no reaction occurs with aluminum chloride,\(^1\) tin tetrachloride, silicon tetrachloride, boron trifluoride, molybdenum trioxide, or diiodine pentoxide.\(^2\)

Titanium tetrachloride not only shows pronounced reactivity toward typical Lewis bases but also toward amphoteric Lewis acids such as nitrosyl chloride,\(^3\) dinitrogen tetroxide,\(^4\) dinitrogen pentoxide,\(^5\) and nitric acid.\(^6\) This amphoteric character may result from the possession of an unshared pair of electrons on an oxygen atom or by dissociation to form a base and an acid weaker than titanium tetrachloride.

The investigation of the action of nitryl chloride on titanium tetrachloride could yield new evidence for the amphoteric behavior of nitryl chloride.

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\(^3\) H. Rheinboldt and R. Wasserfuhr, Ber. 60 B, 732 (1927).
1. **Introduction**.—The observation that liquid nitryl chloride and titanium tetrachloride react to form a yellow solid led to the following investigation, which was concerned primarily with the identification of this solid.

2. **Analytical methods**.—The accuracy of the procedures used for the quantitative analysis of each element present in the reaction product was established by analyzing for that element in a known compound. For checking the determination of titanium each sample of 0.2 g C.P. titanium dioxide was dissolved in 7 g of liquid potassium pyrosulfate. The mixture was cooled and treated with boiling 6 N sulfuric acid until the mass dissolved. Hydrated titanium dioxide was precipitated from the solution with ammonium hydroxide. The precipitate was filtered, washed, and ignited and was weighed as titanium dioxide.

   For checking the determination of chlorine each sample of C.P. sodium chloride was dissolved in water acidified with nitric acid and titrated with standard silver nitrate using a modified Volhard technique.7

   For checking the determination of nitrogen each sample of C.P. sodium nitrate, dried at 125°, was reduced in basic solution with Davarda's alloy. Nitrogen was determined as ammonia by the Kjeldahl method.

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3. Preliminary experiments.—An apparatus for preliminary investigation of the action of nitryl chloride on titanium tetra-chloride comprised a nitryl chloride receiver connected by ground-glass joints to a small conical flask containing titanium tetra-chloride. A drying tube containing phosphorus(V) oxide, attached to the receiver, provided access to the atmosphere. Three milliliters of nitryl chloride was maintained at -78°. Titanium tetra-chloride was distilled into the receiver. A yellow product precipitated immediately. The receiver containing the product was disconnected from the apparatus and attached to a second receiver, which was protected with a drying tube containing phosphorus(V) oxide. The Dry Ice bath which surrounded the nitryl chloride receiver was transferred to the empty receiver. Yellow liquid, which was paler than the original nitryl chloride, condensed, and a bright yellow solid formed in the second receiver. The condensed liquid was paler than liquid chlorine and did not freeze at -78°, indicating it to be nitryl chloride rather than chlorine or titanium tetrachloride.

The reaction receiver was surrounded by a water bath at 45°, which served to expel any remaining nitryl chloride and its decomposition products. Two traps at -78° were connected between the receiver and a mechanical pump. The system was evacuated and maintained at -78° for 15 minutes. Some of the yellow product immediately sublimed or was formed by recombination of reactants. The product which formed in the first trap was bright yellow. Some white solid formed in the bottom of the trap. The white solid melted to a colorless liquid.
Ease of hydrolysis accounted for portions of the solid becoming white and the crystals on the inlet tube becoming opaque.

The pale-yellow reaction product reacted rapidly with atmospheric moisture, emitting an odor of hydrogen chloride and becoming white in 30 seconds. It decomposed between $100^\circ$ and $110^\circ$ in a closed capillary forming bright-yellow crystals in the upper portion of the capillary. The pale yellow product was found to be only slightly soluble at best in carbon tetrachloride. In ether the product gave a vigorous evolution of bubbles and became brown as the ether evaporated.

Preliminary analyses of the reaction product were made by removing samples from the reaction tube and transferring them as rapidly as possible to weighed glass-stoppered vials. A partial hydrolysis of the samples caused by atmospheric moisture was evident during the weighings.

A sampling device, Figure 6, was constructed which made possible the transfer of the sample in a current of nitrogen to the weighing bottle. The results of two chlorine determinations were 60.8 and 61.2 per cent. The result of one determination of titanium was 25.8 per cent. The result of one determination of nitrogen was 3.13 per cent. The atomic ratios of titanium to chlorine to nitrogen to oxygen are 2.45 to 7.72 to 1.00 to 2.87.

A single sample of 1.233 g was hydrolyzed in 200 cc water for the purpose of analyzing aliquot portions in order to obtain more consistent analytical data. Oxidation-reduction occurred as evidenced by the formation of nitrogen dioxide. Titanium was present to the extent of 26.1 per cent. Chlorine was determined in the filtrate
FIGURE 6

SAMPLING DEVICE FOR PRODUCT OF NITRYL CHLORIDE - TITANIUM TETRACHLORIDE REACTION
recovered after the precipitation of hydrated titanium dioxide. Chlorine was present to the extent of 57.0 per cent. The atomic ratio of titanium to chlorine was 0.545 to 1.60, or approximately 1 to 3.

4. A closed-system synthesis.—The two subsequent syntheses of the compound of nitryl chloride and titanium tetrachloride were performed in closed systems. For the first synthesis Fisher's C.P. titanium tetrachloride was double-distilled in an all-glass system containing break-seals. The apparatus similar to that shown in Figure 7 was dried thoroughly by flaming and by intermittently evacuating and filling it with dry nitrogen. After evacuating again, the titanium tetrachloride was cooled to \(-20^\circ\), and the break-seals were opened. The Dry Ice bath was removed from the nitryl chloride receiver. On completion of the reaction, excess nitryl chloride was allowed to evaporate through a drying tube of phosphorus(V) oxide. Analytical samples were removed from the apparatus through a ground-glass joint to which a weighing bottle could be attached.

Samples of 0.5 g were dissolved in 200 ml of water. They were titrated for total acidity with standard sodium hydroxide solution. The equivalent-weight determinations were 47.5 and 48.4. A more reliable endpoint resulted using a concentration of titrant of 0.5 N rather than 0.1 N. A pH meter was preferred over phenolphthalein indicator.

Nitrogen determinations using the Dumas method were performed by W. H. Deebel of the Department of Chemistry, Ohio State University. The values were 3.02% and 2.86%.

\[8^G.\text{Brauer, Handbuch der Praparativen Anorganischen Chemie, Ferdinand Enke, Stuttgart, 1954, p. 896.}\]
5. **Summary of analyses of product of the nitryl chloride-titanium tetrachloride reaction.**—The results in the table below were obtained by averaging all the analytical data reported thus far with the exception of the chlorine determination on the 1.253 g sample. This determination is low, as expected, because of loss of products through oxidation-reduction resulting from the hydrolysis of too large a sample. The analytical results are most consistent with the composition \( \text{Ti}_2\text{Cl}_7\text{NO}_2 \).

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>( \text{Ti}_2\text{Cl}_7\text{NO}_2 ) (Theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>61.0%</td>
<td>63.64%</td>
</tr>
<tr>
<td>Titanium</td>
<td>26.0</td>
<td>24.56</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.01</td>
<td>3.59</td>
</tr>
<tr>
<td>Oxygen</td>
<td>10.0*</td>
<td>8.21</td>
</tr>
<tr>
<td>Equivalent Weight</td>
<td>48.0 g/sq.</td>
<td>48.75 g/sq.</td>
</tr>
</tbody>
</table>

*Calculated by difference.

6. **Decomposition of the product of nitryl chloride and titanium tetrachloride at reduced pressure.**—For the second closed-system synthesis Fisher's C.P. titanium tetrachloride was purified according to the method of Clabaugh, Leslie, and Gilchrist.\(^9\) It was first treated with chlorine in the presence of aluminum chloride hexahydrate and water. Dry nitrogen was passed into the solution until dissolved chlorine had been removed. The solution was refluxed over copper and distilled in the absence of moisture. A middle fraction of distillate was collected and sealed in a small Erlenmeyer flask which was fitted with a side-arm containing a break-seal.

Nitryl chloride was prepared by the reaction of nitrosyl chloride and dinitrogen pentoxide. It was preserved at -78 ° in a sealed tube also fitted with a side-arm containing a break-seal.

The apparatus for the reaction is shown in Figure 7. The U-tube shown was not sealed on until mentioned later. The middle portion of the apparatus was dried as described in the previous synthesis and evacuated with a mechanical pump. The break-seals were ruptured. The titanium tetrachloride was maintained from -35° to -25° during the reaction. The nitryl chloride receiver was warmed to -5° to hasten the reaction. To prevent the small amount of higher-boiling impurities from reacting with the titanium tetrachloride, the nitryl chloride receiver was cooled in a Dry Ice bath while the receiver still contained a small amount of liquid. The reaction required two hours. Both receivers were then maintained at -78° for 36 hours. Excess titanium tetrachloride was pumped off and condensed in a liquid nitrogen trap. A yellow sublimate collected on the wall and a purple coloration appeared in the bottom of the trap. The purple color disappeared when a Dry Ice bath was substituted for the liquid nitrogen, but the color did not reappear when the trap was cooled again to -196°. The pale yellow reaction product was exposed to the full vacuum of the mechanical pump for 15 hours. The residue was a paler yellow than the original product.

A U-tube of 8 mm diameter was sealed to the stopcock outlet which connected the apparatus to the trap. After evacuation of the U-tube it was cooled in liquid nitrogen. The stopcock was adjusted to allow the product to sublime. A very small amount of yellow solid and a
FIGURE 7
REACTION OF NITRYL CHLORIDE AND TITANIUM TETRACHLORIDE
purple ring were isolated. The U-tube was sealed off from the apparatus and warmed to room temperature. The yellow solid became brighter yellow on standing, and the purple ring disappeared. Some liquid droplets were present indicating decomposition during sublimation. The purple ring reappeared each time the tube was subsequently cooled with liquid nitrogen. The attempted transfer of the damp, yellow solid to a capillary tube for x-ray diffraction measurements failed.

The apparatus was filled with argon dried over magnesium perchlorate. The conical flask was sealed off at the constriction and transferred to a dry box. The neck of the flask was removed, and samples to be analyzed were transferred to small, glass-stoppered weighing bottles. An x-ray diffraction photograph of the powder after an exposure of 7-1/2 hours using copper-Kα radiation showed no lines, apparently due to extremely small particle size.

The analytical samples were hydrolyzed by removing the stopper and dropping both bottle and stopper into 100 ml of either cold distilled water or cold, 8 M nitric acid. A ground-glass stopper was immediately inserted in the flask. Cloudy solutions resulted with a mist over the liquid if distilled water were used. The mist disappeared on standing. Samples hydrolyzed in 8 M nitric acid gave a clear solution immediately, indicating particles observed after hydrolysis with distilled water did not result from samples which contained titanium dioxide as an impurity.

Two determinations of chlorine by the modified Volhard method were 48.5% and 48.7%. The average value was 48.6%. One determination of titanium was 36.7%. One determination of nitrogen was 0.78%.
The atomic ratio of titanium to chlorine is 0.737 to 1.37, or about 1 to 2. Two determinations of the equivalent weight were 69.6 and 69.7 grams per equivalent. The analytical data are compared below with the calculated values for titanium(IV) oxychloride.

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>TiOCl₂ (Theoretical)</th>
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<tbody>
<tr>
<td>Chlorine</td>
<td>48.6%</td>
<td>52.6%</td>
</tr>
<tr>
<td>Titanium</td>
<td>36.7</td>
<td>35.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.78</td>
<td>0</td>
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<tr>
<td>Oxygen</td>
<td>13.9*</td>
<td>11.9</td>
</tr>
<tr>
<td>Equivalent Weight</td>
<td>69.6 g/eq</td>
<td>67.4 g/eq</td>
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</table>

*Calculated by difference.

C. Conclusions

The reaction of nitryl chloride and titanium tetrachloride produces an unstable, pale-yellow solid, which decomposes under vacuum. The immediate significance of this reaction is that a method of preparing titanium(IV) oxychloride, a product of the decomposition, has been found.

While the apparent composition of the reaction product is Ti₂Cl₇NO₂, further confirmatory work should be done. This compound decomposes on standing, presumably according to the equation

\[ 2 \text{Ti}_2\text{Cl}_7\text{NO}_2 \rightarrow 2 \text{TiOCl}_2 + (\text{NO}_2)_2\text{TiCl}_6 + \text{TiCl}_4 \]

Removal of excess reactant under reduced pressure leads to decomposition. A method which might yield a product of greater purity would involve
the use of excess nitryl chloride and the removal by a stream of nitrogen or, better, argon of the excess remaining after reaction and any chlorine formed, while the product is maintained at low temperature and under considerable, positive pressure. A solvent for the reactants is also recommended.

The accurate analysis of the reaction product is made difficult by its extremely hygroscopic nature. Complete decolorization of the substance was observed after it had been exposed to the atmosphere for 30 seconds. Secondary reactions during hydrolysis result in loss of products due to the formation of chlorine and oxides of nitrogen. The use of the neutralization equivalent has been demonstrated as a satisfactory analytical procedure to aid in the characterization of such compounds.

The relatively small number of compounds of nitryl chloride with Lewis acids may be due to a lack of investigation of proper conditions for reaction. Although no reaction has been reported between nitryl chloride and either aluminum chloride or boron trifluoride, Price and Sears\textsuperscript{10} have noted that the nitrating activity of nitryl chloride is promoted by these two acids and also by hydrogen fluoride. This observation suggests the formation of nitronium ion and the possibility that nitronium salts of these Lewis acids might be isolated at low temperatures. Cases in which oxidation-reduction occurs, rather than formation of a nitronium salt, may be ascribed to the pronounced reactivity of the products of decomposition of nitryl chloride with Lewis acids.

SUMMARY

1. The solid produced in the nitryl chloride - ammonia reaction contains only ammonium nitrite and ammonium chloride.

2. X-ray powder diffraction data for ammonium nitrite have been determined.

3. The solid produced in the gas-phase reaction of nitryl chloride with methylvamine, dimethylamine, or trimethylamine is principally the corresponding amine hydrochloride.

4. The nitryl chloride - dimethylamine reaction yields dimethylnitrosamine in addition to dimethylamine hydrochloride.

5. The solid produced in the gas-phase reaction of chlorine with methylvamine or dimethylamine in the corresponding amine hydrochloride, but the solid produced in the gas-phase reaction of chlorine and trimethylamine is not trimethylamine hydrochloride.

6. The reaction of nitryl chloride and titanium tetrachloride yields an unstable product. Analytical data indicate the compound is $\text{Ti}_2\text{Cl}_7\text{NO}_2$. Removal of volatile components under vacuum yields a residue of titanium(IV) oxychloride.
I, Richard Shubert Shineman, was born in Canajoharie, New York, May 21, 1924. I received my secondary school education in the public schools of Canajoharie, New York, and Deerfield Academy, Massachusetts. My undergraduate training was obtained at Cornell University, from which I received the degree Bachelor of Arts in 1945. After serving in the Army I attended Union College, where I was an assistant in chemistry. In 1950 I received the degree Master of Science from Syracuse University, where I held an assistantship in general chemistry. While completing the requirements for the degree Doctor of Philosophy at Ohio State University I held an assistantship in analytical chemistry and a research assistantship.