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ATTEMPTS TO PREPARE NITROSYL AZIDE AND A STUDY OF THE DECOMPOSITION OF NITROSYL CYANIDE

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Part II

ATTEMPTS TO PREPARE NITROSYL AZIDE AND A STUDY OF THE DECOMPOSITION OF NITROSYL CYANIDE

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ABSTRACT

The synthesis of nitrosyl azide has been attempted using a wide variety of reagents and techniques. Neither matrix isolation nor mass spectral studies of co-condensed hydrazoic acid and nitrosyl chloride provided any evidence for the formation of nitrosyl azide. No evidence has been found to substantiate a claim that nitrosyl azide exists as a moderately stable compound. Nitrosyl cyanide has been made by a slight variation of published methods, a method of purification established, and the decomposition studied. In the dark at room temperature or 75° and at moderate pressures of nitrosyl cyanide, the decomposition products of nitrosyl cyanide which was labeled with nitrogen 15 on the cyanide nitrogen were consistant with two mechanisms occurring simultaneously. Each mole of nitrosyl cyanide decomposed to 1/3 mole each of nitrogen, nitrous oxide, cyanogen, and carbon dioxide.

Part I

I. INTRODUCTION

Nitrosyl azide has been postulated as an unstable intermediate in the reaction between hydrazine and nitrous acid solutions.[1,21,22] For many years attempts to isolate N_4O led only to the formation of equimolar amounts of nitrogen and nitrous oxide.[1,2] In 1958, Lucien claimed the first isolation on nitrosyl azide.[3]

Our study of nitrosyl azide has included and has gone far beyond the reactions and conditions which Lucien reported. The failure of $NOCl$-NaN_3 reactions to yield N_4O led to investigations designed to vary the source of the nitrosyl ion and the azide ion. The object was to find a better source for these reagents. The solvents used were varied in an attempt to find a solvent which would support high concentrations of the reactants, not react with products, and allow the reaction to be carried out at the lowest possible temperature. Our investigation included a matrix isolation program with infrared spectroscopy and also a study using mass spectroscopy.

Conventional chemical analyses of the amounts of reagents introduced and the amount of products recovered were carried out. The mass balances obtained from chemical analyses eliminated the possibility of N_4O forming without detection. Volatile products and reactants were also subjected to infrared and mass spectral analysis. Samples thought to contain N_4O were allowed to stand at room temperature for long periods and then examined for the presence of non-condensible gases. The infrared and the mass spectrum of all volatiles was then recorded. Any N_4O which formed would be expected to yield characteristic decomposition products (N_2O and N_2).

II. MATERIALS

Nitrosyl chloride was purchased (Matheson) and was also prepared by a literature procedure.[4] The NOCl from either source was purified by fractional distillation. Cold traps at -95° (toluene slush), -130° (n-pentane), and -196° (liquid nitrogen) made up the fractionation train. Pure NOCl condensed in the -130° trap. Sodium azide (Matheson) was used as purchased in some experiments and, in others, the sodium azide was recrystallized from water-alcohol mixtures, finely powdered, and dried on the vacuum line. Nitrosyl tetrafluoroborate was prepared by a published method[5] and was purified by sublimation. Hydrazoic acid was prepared by the gradual addition of sodium azide to concentrated phosphoric acid in vacuo. As it was formed, the HN_3 passed through a -78° trap (dry ice-acetone) and collected in a -196° trap. (Danger; HN_3 is highly explosive.[6]) Monoglyme and hexane were distilled from $LiAlH_4$ under reduced pressure. Spectro acetonitrile (MCB), quality analytical reagent-grade ether and carbon tetrachloride (Mallinckrodt) were used as purchased. These solvents were transferred in a dry nitrogen filled glove bag and stored in tightly capped containers. The purity of volatile reactants was checked by mass spectrometry.

III. APPARATUS

The reagents were handled using a glass vacuum line consisting of several manifolds and a series of four U traps separated by greaseless stopcocks (J. Young and Co., Acton, England). The stopcocks were designed so that only Teflon and glass came into contact with materials passed through them. One section of the line was calibrated accurately and could be opened to a mercury manometer. A quartz spiral manometer was attached to another section of the line and was used to measure pressures of NOCl.[7] Large quantities of NOCl were measured by the liquid volumes in a vessel graduated in 0.1 ml increments. This vessel and all of the reaction vessels could be attached as necessary to the vacuum line with a #9 O-ring joints. Buna-N-O-rings were used and were found to be servicable for about 50 exposures to NOCl.

Two low temperature cryostats were used. The first (Fig. 1) was used exclusively in the synthetic and mass spectrometric studies of HN_3-NOCl mixtures. The outer jacket was made with a #75 O-ring joint at the top and 100 mm diameter tubing at the bottom. The bottom had two 1/4 in. o.d. inlets sealed into it. Sixty-five mm down from the O-ring a 10 mm i.d. tube joined the jacket. Uranium glass feed throughs in the side arm provided contacts for connecting thermocouple (copper-constantan) leads to a potentiometer. A greaseless stopcock completed the fittings in the side arm. The bottom one third of the central cold finger was copper, terminating in a 25.4 mm thick copper block fitted with a set screw to secure a thermocouple junction. The copper tubing soldered into the block joined the glass top through a copper to glass housekeeper seal. The top of the cold finger was a

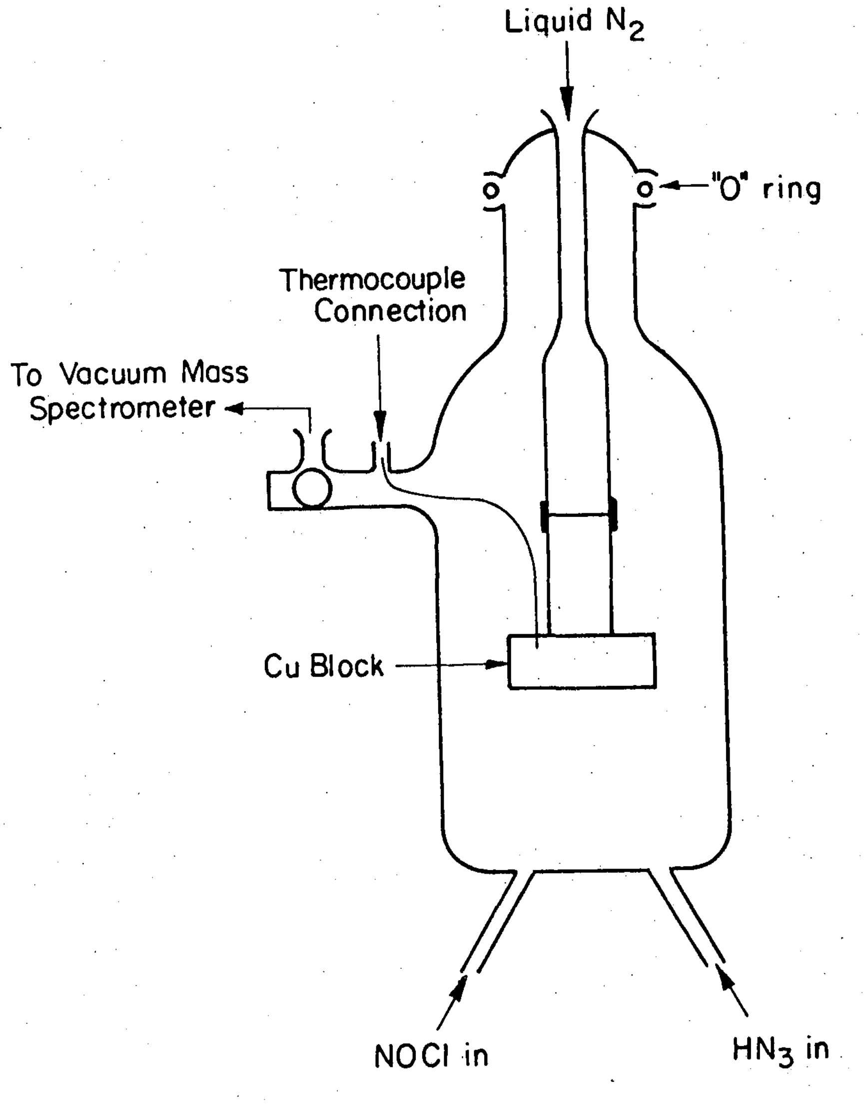

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Fig. 1. Cryostat used in codeposition of HN_3 and NOCl.

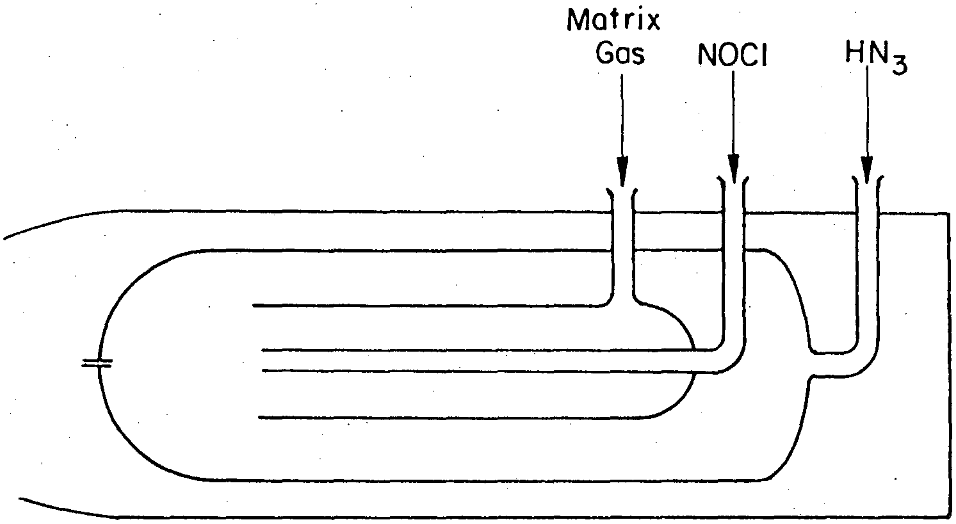

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Fig. 2. Pyrex glass gas mixer used to premix reactants and matrix gas before deposition on the infrared window.

#75 O-ring joint. The entire apparatus was Pyrex except for the copper parts.

The second cryostat was used in the matrix isolation study. It was nickel plated brass and very similar to one described by Meyer.[8] Liquid hydrogen could be used as a refrigerant.

The flow rates of the reactant and matrix gases in the matrix isolation experiments were monitored with sapphire float flow meters. The floats were -0.5 mm in diameter. The gases (two reactants and the matrix) were mixed in a concentric gas mixer (Fig. 2) and then deposited on the window. The auxiliary vacuum line used to handle these gases was all glass with greaseless stopcocks.

Gas analysis was made simple and unequivocal by use of a quadrupole mass spectrometer (Finnigan Instruments, Sunnyvale, CA). The probe chamber was 4 liters in volume. It was pumped by a 6 in. liquid nitrogen trapped diffusion pump and a Kinney KC-5 mechanical fore pump. The probe chamber was maintained at 4×10^{-8} Torr. Spectra could be recorded satisfactorily from 10^{-4} Torr to 10^{-9} Torr. The inlet was differentially pumped and could be used with a micrometer needle valve to regulate flow rates reproducibly. The spectrometer was capable of mass discrimination of better than 0.5 amu from zero to 500 amu and extremely rapid scans (1 millisecond/amu). Ions were produced by 70 eV electrons and detected by a 14 stage Cu-Be electron multiplier with a gain of better than 10^5. The signal from the electron multiplier was input for a PAR (Princeton Applied Research, Princeton, NJ) model 136 electrometer. Spectra were plotted with an x-y recorder. Gaseous materials were also subjected to infrared analysis using a glass gas cell with KBr windows, a 75 mm path length and a greaseless stopcock for evacuation and introduction of samples. Spectra were recorded on a Perkin-Elmer model 337 spectrometer.

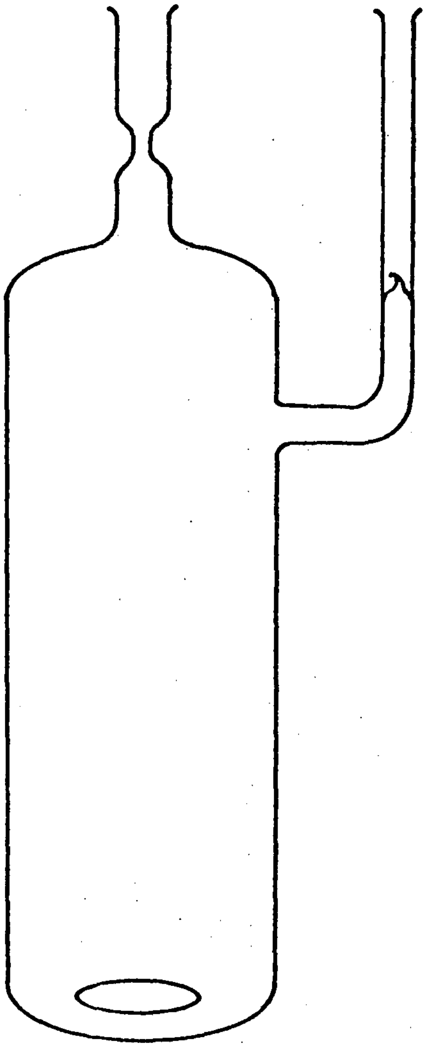

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Fig. 3. Typical all Pyrex glass reaction vessel with a stirring bar sealed in. The break seal was broken with a glass enclosed magnet placed in the side arm.

IV. EXPERIMENTAL

A. NaN_3 and NOCl

Anhydrous sodium azide (0.650 g; 10.0 mmol) was placed in an all-glass reaction vessel containing a Teflon-coated magnetic stirring bar (Fig. 3). The opening through which the sodium azide was added was sealed with a hot flame. The glass was allowed to cool, and then the reaction vessel was evacuated to a pressure of 10^{-4} Torr or less. Previously purified NOCl (12.7 mmol) was condensed through a constricted tube onto the liquid nitrogen-cooled walls of the reaction vessel. The constricted tube was sealed off under vacuum with a hot flame. When the glass had cooled nearly to room temperature the vessel was removed from the liquid nitrogen bath and plunged into a bath at -45° (chlorobenzene slush). The reaction vessel was maintained at -45° for four days while continuously stirring the reaction mixture. After 4 days the reaction vessel was cooled with liquid nitrogen and opened to the vacuum line through the break seal. The noncondensible gas was Toepler-pumped from the cold vessel, measured, and then identified with the mass spectrometer. The noncondensible gas was nitrogen (9.2 mmol).

After the noncondensibles were removed, the condensible products were collected as the vessel gradually warmed to room temperature. Traps at -78, -130, -160 (iso-pentane), and -196° were used to separate and collect the volatile products. The -196 and -78° traps were empty. N_2O (9.2 mmol) collected in the -160° trap. It was identified by its infrared[9] and mass spectrum and by its vapor pressure at -112° (carbon disulfide). About one half the material in the -130° trap was condensed into the side arm of a gas infrared cell. The cell was removed from the vacuum line and placed in its holder in the spectrometer. Spectra were recorded immediately following the complete vaporization of the sample, 1/2 hr later, and thereafter a roughly 8 hr intervals for 36 hr. The second half of the original sample was isolated in a trap on the vacuum line and allowed to stand at room temperature for 30 hr. Both samples were finally cooled with liquid nitrogen, opened, and Toepler-pumped. No noncondensible gas was found. The spectra recorded from the first sample showed no change with time and no peaks not attributable to NOCl.

There was little variation in procedure among these reactions. The procedure for those reactions which were carried out in solvents was similar to that used for the preceding reaction except that, before the introduction of NOCl, the solvent was distilled in. Reaction vessels with stopcocks were used in the same manner as all glass vessels except that, after the introduction of NOCl, the stopcock was closed to isolate the vessel from the vacuum line. Although stopcock-fitted vessels were convenient to use, they posed the threat of leakage which the glass vessels did not.

These reactions were analyzed with very similar procedures. For some reactions, the entire contents of the -130° trap were allowed to stand undisturbed at room temperature; in others, the mass spectrum of the material was obtained. The contents of the -130° trap were, for some experiments, condensed completely into a fresh all-glass reaction vessel, the vessel sealed and then allowed to stand. Several days to 1 week later it was cooled with liquid nitrogen, opened, and

Toepler-pumped. In some reactions, the residual NaN_3 was determined. This was done by adding water to the solid residue that remained after the reaction was stopped and the volatiles pumped out. This water solution was degassed on the vacuum line. A degassed solution (1 molar, 15 ml) of ceric sulfate was added to the solution. The N_2 evolved was Toepler-pumped from the reaction vessel and measured. None of the variations in analytical procedure gave results significantly different from what has been previously described. Only NOCl or products from its dissociation (NO + Cl_2) were detected in the -130° trap after it had been closed and had stood at room temperature. Table I shows the results of a series of reactions of NaN_3 with NOCl, both with and without solvent.

B. Moist NaN_3-NOCl

A beaker containing a saturated NaCl solution was placed in an empty desiccator to serve as a hygrostat. Sodium azide (0.650 g; 10.0 mmol) was exposed to the humid atmosphere within the hygrostat for 1 week. The azide was then removed and added to a reaction vessel as before. The vessel was sealed; the bottom portion of the vessel was cooled with liquid nitrogen, and the vessel evacuated. The closed vessel was then allowed to warm until it was at about room temperature. It was then refrozen at the bottom end. The stopcock was reopened and any residual air pumped out. This freeze-thaw cycle was repeated one more time and then NOCl (15.0 mmol) was condensed into the vessel. The sealed vessel was then plunged into a -45 bath to initiate the reaction. The reaction began at a temperature just above the melting point of NOCl (-63.5), as the NOCl

Table I. Summary of reactions of anhydrous NoN$_3$ with NOCl.

-- Reagents --						---- Product Composition ----			
mmol NOCl	mmol NaN$_3$	Temp.	Time	Solvent	Type Vessel	mmol N$_2$O	mmol N$_2$	mmol NOCl	mmol NaN$_3$
11.1	10.14	-78	8 days	None	AG	0.4	0.3	10.7	9.6
10.8	10.98	-78	53 hr	None	HG	0.088	0.088	--	-
11.0	9.29	-78	53 hr	None	AG	0.101	0.105	--	-
2.66	24.03	-78	3 days	None	AG	0.072	0.071	2.52	-
50	10.00	-78	8 hr	None	AG	0.15	0.15	--	-
12.3	10.11	-63	4 days	None	AG	1.3	1.3	11.0	9.7
10.8	10.02	-63	42	None	AG	0.69	0.68	--	-
11.1	10.0	-45	4 days	None	AG	9.2	9.2	2.8	-
13.6	10.00	-22	2 days	None	SC	9.4	9.5	4.0	-
12.1	10.0	0	26 hr	None	AG	8.4	8.4	3.7	-
11.0	10.0	0	4 hr	None	SC	2.1	2.2	8.9	-
11.2	10.02	-78	4 days	5 ml ether	AG	0.2	0.2	10.9	-
10.8	10.00	-63	2 days	5 ml ether	AG	0.1	0.1	10.7	-
11.1	10.00	-45	1 day	5 ml ether	AG	1.1	1.1	10.0	-
11.1	10.03	-10.5	2 days	5 ml CCl$_4$	SC	3.8	3.9	7.3	-
10.8	10.0	0	1 day	5 ml CCl$_4$	SC	3.4	3.6	3.7	-
10.8	10.00	-63	3 days	5 ml monoglyme	SC	3.0	2.9	7.6	6.9
10.5	10.0	-45	2 days	5 ml monoglyme	SC	3.7	3.7	6.5	6.7
10.8	10.0	-45	2 days	10 ml acetonitrile	AG	4.1	4.3	6.6	-
11.0	10.0	-22	1 day	10 ml acetonitrile	AG	4.1	4.1	6.7	-
10.6	10.0	0	1 day	10 ml acetonitrile	SC	4.8	4.8	5.7	-
10.8	10.0	0	14 hr	10 ml hexane	SC	0.1	0.1	10.6	-
35	10.0	-63	4 days	None	SC	8.9	9.0	--	-
41	10.0	-45	1 day	None	SC	9.2	9.2	--	-
50	10.0	-22	8 hr	None	SC	6.4	6.4	--	-
29	10.0	-10.5	3 hr	None	SC	2.1	2.1	--	-

The reaction was also tried with NaN$_3$ as the excess reagent with similar results.

liquified and ran down the walls of the vessel. When the liquid NOCl touched the moist NaN_3, a white froth rapidly formed. The gas evolution subsided after about 5 min. After 4 days the reaction vessel was opened, and the volatile products were removed. Analysis showed the presence of nitrogen (8.1 mmol), NO (0.8 mmol), N_2O (7.1 mmol), HCl (0.2 mmol), NOCl (3.0 mmol) and less than 0.1 mmol each of NO_2 and HN_3. These products were separated and identified as previously described except that HCl and N_2O were not separated. The amount of HCl mixed with N_2O was estimated mass spectrometrically by comparing the height of the parent peaks of each compound against the corresponding peaks in mixtures of HCl and N_2O of known composition. The NO and N_2 were determined similarly. The NOCl fraction did not evolve any noncondensible gas upon standing at room temperature for 14 hr.

Sodium azide was moistened to an even greater extent (to about 5% by weight) by the addition of liquid water. The reaction between NOCl and this moist azide was violent enough to throw the azide all about the inside of the reaction vessel. It was found that the largest amount of water added to the azide produced the reaction of greatest vigor. Table II gives a summary of reactions with moist sodium azide.

C. <u>Gaseous NOCl-NaN_3</u>

Finely powdered sodium azide (5.00 gr) was added to a 6 mm o.d. Pyrex U tube with #9 O-ring joints on it. Glass wool was packed above the azide in each arm of the tube in order to prevent the powder from being carried into the rest of the vacuum line. The tube was slowly evacuated. NOCl at room temperature in a glass gas storage bulb (10.0 mmol) was attached to the vacuum line. The stopcock on the NOCl

Table II. Reactions with moistened NaN_3.

mm NOCl	mm NaN_3	% by weight H_2O	N_2O	N_2	HCl	Temp.	Time	NO
15.1	10.0	0.1%	8.6	9.0	0.3	-63	1 Day	Trace
15.2	10.0	0.3%	7.1	8.1	0.2	-63	4 Day	0.8
15.0	10.0	0.5%	8.8	9.0	0.1	-45	11 Hr	Trace
16.0	10.0	1%	7.6	8.0	Trace	-45	6 Hr	Trace
15.0	10.0	5%	9.0	10.0	0.2 HCl	-45	13 Hr	0.6
35	10.0	20%	8.6	18.9	0.9 HCl	-63	48 Hr	1.1

bulb was opened slightly, so that a small flow of NOCl passed through the tube packed with NaN_3 and into a series of two -196° traps immediately following it. The system was opened to a mechanical pump so that any noncondensible gas was rapidly removed. For efficient condensation of condensible materials, the rate of flow of NOCl was regulated manually so that the pressure of noncondensible gas as measured by a Hastings thermocouple vacuum gauge was never more than 1×10^{-2} Torr. Two hours were required to pass all of the NOCl through the U tube.

The bright yellow orange material in the two liquid nitrogen traps was combined and distilled through traps at -130, -160 and -196°. No volatile product was found in the -196° trap. N_2O (0.70 mmol) was found in the -160° trap along with a trace of HCl. The material in the -130° trap (9.2 mmol) was divided into two portions. One was allowed to stand isolated in a trap on the vacuum line for 24 hr. The second portion was subjected to analysis by mass spectrometer at 8 hr intervals for 24 hr. Only peaks characteristic of NOCl were observed. No nitrogen was found when, after 24 hr, the first portion was cooled with liquid nitrogen and Toepler-pumped.

Both the temperature of the NaN_3 in the U tube and its water content were varied in some experiments. Temperatures of -63, -45 and -22° were tried without significant differences in the results. The water content was varied from 0.0% to 5%. When moist NaN_3 was used, the azide remaining in the tube often had a distinct orange color at the point of first contact with NOCl. The greatest amount of N_2O was recovered from a reaction in which the NaN_3 was moistened 1% by weight.

D. HN_3-NOCl

Nitrosyl chloride (1.04 mmol) was condensed into a previously evacuated all-glass reaction vessel. Hydrazoic acid (1.00 mmol) was condensed in, the vessel was sealed, removed from the vacuum line, and plunged into a -78° bath. The HN_3 soon began to melt and run down the walls of the vessel. When the liquid HN_3 came into contact with the solid NOCl, an audible and visibly violent reaction occurred. For several seconds a smoky white cloud obscured the view into the vessel.

The vessel was removed from its -78° bath, cooled with liquid nitrogen, opened, and Toepler-pumped. Nitrogen (1.00 mmol) was collected and identified mass spectrometrically. The condensible gas was collected in a trap as it evolved from the warming reaction vessel and was measured (1.99 mmol found). The mass spectrum of the condensible gas contained only peaks attributable to HCl and N_2O. Equimolar amounts of each were present (determined by the intensities of the parent peaks as before). The reaction proceeded according to the equation:

$$HN_3 + NOCl = HCl + N_2O + N_2$$

This reaction is very dangerous. At times reaction vessels and nearby equipment were completely shattered by explosions. A face shield, gloves, a thick vest and plexiglass explosion shield were always used. Only the smallest practicable amounts of material were used for each experiment. It was found that explosions which occurred in reaction vessels in which the bottoms had been left deliberately unannealed caused much less damage than similar explosions in uniformly annealed glassware. The major force of the explosion was directed downward and away from other equipment when unannealed vessels exploded.

The reaction between NOCl and HN_3 was rapid in ether. NOCl (1.0 mmol) was condensed into a vessel containing 20 ml of degassed ether and a Teflon clad stirring bar. The vessel was warmed to -60° and stirred to uniformly dissolve the NOCl. The vessel was then refrozen with liquid nitrogen and HN_3 (1.00 mmol) condensed in. The sealed, frozen vessel was placed in a -78° bath. One half hour after all the ether melted, the stirred solution had become colorless and no more gas bubbles could be seen forming in the solution. The vessel was cooled, opened and the noncondensible gas Toepler-pumped from the vessel. Nitrogen (0.99 mmol) was identified as the noncondensible gas. The condensible material was distilled through a -130° trap to remove the ether. The condensible gas separated from the ether was identified (as previously described) as an equimolar mixture of HCl and N_2O (N_2O + HCl = 2.02 mmol).

E. NaN_3-$NOBF_4$

Sublimed nitrosyl tetrafluoroborate (0.351 g) was transferred to a stopcock-fitted reaction vessel in the dry nitrogen atmosphere of a glove bag. A stirring bar, 0.1901 g of NaN_3, and 5 ml of dry monoglyme were added, and the vessel capped and degassed at -78°. The vessel was then placed in a -22° bath and the slurry stirred at that temperature for a total of 9 days. The slush bath was renewed every 4 hr, or the vessel was cooled with liquid nitrogen and allowed to stand at that temperature until it was convenient to resume the reaction at -22°. After 24 hr at -22° the entire apparatus was placed in a large walk in refrigerator maintained at -15° which extended the useful life of the cooling bath to 18 hr.

The vessel was maintained at -22 except during brief periods when volatile products were removed (during these periods the vessel was cooled to -78°). Condensible gas was collected in a liquid nitrogen cooled trap placed between the reaction vessel and the Toepler pump. This trap was isolated from the vacuum line, warmed with a heat gun for 10 min to about 80° and then allowed to stand overnight. No nitrogen was formed in the trap. Noncondensibles from the reaction vessel were collected in the Toepler pump. Volatiles were identified with the mass spectrometer.

Reaction Time	mmol N_2	mmol N_2O	
24 hr	0.006	0.005	
73	0.015	0.013	
121	0.013	0.014	
170	0.010	0.010	
212	0.008	0.008	
212 hr	0.052	0.050	TOTAL

F. HN_3-$NOBF_4$

Monoglyme (5 ml) and a stirring bar were added to a 25 ml two necked (14/20 ground glass joints) round bottomed flask in a glove bag. The vessel was capped with a ground glass joint joined to a stopcock. A tipper containing 0.403 g of $NOBF_4$ flakes was placed into the other neck of the flask. The apparatus was removed from the dry bag, degassed at -78°, and 1.208 mmol HN_3 was condensed into the liquid nitrogen-cooled vessel. The vessel was immersed in a -45° bath (chlorobenzene). $NOBF_4$ was gradually added to the stirred monoglyme solution. When a particularly large flake of $NOBF_4$ fell into solution bubbles of gas could be seen at the edges of the flake, and it danced like a drop of water in a very hot pan.

After 9-1/2 hr the solution was cooled to -196° and opened to the Toepler pump. Nitrogen (0.803 mmol) was collected, measured, and identified mass spectrometrically. Condensible material from the reaction vessel was distilled from the -78° vessel through a -130° trap into a -196° trap. N_2O (0.798 mmol) was condensed in the -196° trap. The -130° trap was allowed to warm to room temperature and then stand overnight. Hydrazoic acid (0.380 mmol) was detected in the -130 trap. The reaction was also carried out for a period of 2 hr under otherwise identical conditions of temperature, solvent, reagents and vessel. The amounts of products were less (0.15 mmol HN_3 reacted; 1.11 initially present), but their nature was the same.

G. $BF_3N_3^-$, $BCl_3N_3^-$-$NOBF_4$

In an earlier study it was found that a BF_3 or BCl_3 solution in monoglyme dissolves 1 mole of NaN_3 per mole of BF_3 or BCl_3. The ^{11}B NMR signal is a broad single line in the same region as other borane anions[10,11] for either the boron trichloride or boron trifluoride-azide adducts. In contrast to sodium azide, both adducts are soluble in monoglyme.

A three necked 25-ml flask with 14/20 ground glass joints was loaded in a dry bag with 5 ml of dry monoglyme and capped with two tippers, one containing NaN_3 (0.0651 g) the other $NOBF_4$ (0.099 g).

The central neck was capped with an adapter attached to a stopcock and O-ring joint. The joints and stopcock were greased with Kel-F grease. The flask was cooled to -78, evacuated, and then BCl_3 was condensed in. The solution was vigorously stirred while the tipper was rotated to spill the azide into the solution. The azide gradually dissolved until, after 45 min, no solid remained in the monoglyme. The clear colorless solution was cooled to -78, stirred vigorously, and the solid $NOBF_4$ was gradually added. Within 3 hr gas evolution around solid pieces of $NOBF_4$ had stopped, although there was still solid material in the reaction vessel. The vessel was cooled to -196°, opened, Toepler-pumped, and then the condensibles distilled through a -130° trap. Nitrogen (0.98 mmol) was collected with the Toepler pump. The products which were distilled from the vessel at -78° included N_2O (collected in a -196° trap) and BCl_3 (collected in a -130° trap). Similar results were obtained from the reaction of $NOBF_4$ with $BF_3N_3^-$ in monoglyme. The reaction of $BCl_3N_3^-$ and $NOBF_4$ was also carried out at -78° with continuous high speed pumping through two -196° traps during the addition of the $NOBF_4$. The contents of the traps were consolidated and fractionally distilled. No new products were found.

H. $\underline{NaN_3-N_2O_4}$

The high conductivity of liquid N_2O has been explained by autoionization: $N_2O_4 \rightleftharpoons NO_3^- + NO^+$.[12] Although sodium azide is an ionic solid, showing high solubility in solvents of high dielectric constant, it does not dissolve in or react with N_2O_4 at -45 or -22°. It has been reported, however, that HN_3 and N_2O_4 react rapidly to give $N_2 + N_2O + HNO_3$.[34]

Sodium azide (0.0652 g) was added, along with a stirring bar, to a reaction vessel. N_2O_4 (6.0 ml) was distilled into the previously evacuated vessel; the vessel was sealed and then plunged into a -45 bath. The stirred mixture was placed in the -15° cold room and the -45° bath refreshed with liquid nitrogen every 12 hr. The sodium azide did not visibly dissolve. Three days after the initial mixing the vessel was cooled to -196°, opened and Toepler-pumped. Nitrogen (0.011 mmol) was collected with the Toepler pump. The vessel was allowed to warm to room temperature as the condensible products were distilled from it through a series of traps at -78, -95, -130, and -196°. N_2O condensed in the -196° trap (0.014 mmol) and N_2O_4 was found in the -95° and -78° traps. Degassed water was distilled onto the white solid residue remaining in the vessel, 15 ml of 1 M ceric sulfate was added and the nitrogen evolved Toepler-pump, measured (0.98 mmol found), and identified. The material in the -78° and -95° traps was distilled into a third trap which was then warmed to 0 and allowed to stand 48 hr. The trap was then cooled to -196 and Toepler-pumped. No nitrogen was collected.

I. $NOTiCl_5$-NaN_3

Titanium tetrachloride reacts with nitrosyl chloride to form an adduct, $NOTiCl_5$,[13] whose solutions in $TiCl_4$ show conductivity. The charge carriers are NO^+ and $TiCl_5^-$.

NOCl (1.09 mmol) was condensed into 5 ml of degassed $TiCl_4$ in a two necked glass reaction flask containing a stirring bar. A tippable side arm with NaN_3 (0.0653 g) was attached to one neck, a stopcock fitted adapter to the other. The vessel was clamped above a magnetic stirrer in the -15° cold room, the side arm was rotated to spill in the azide, and then the solution was stirred for 4 days. No signs of reaction were observed. The vessel was cooled to -196°, opened, and Toepler-pumped. Condensible volatiles were distilled into a trap on the vacuum line and allowed to stand at room temperature for 3 days. No noncondensible gas was Toepler-pumped from either reaction vessel when it was first opened or from the trap on the vacuum line after it had stood at room temperature.

Impure $TiCl_4$ did react when NaN_3 was dumped into an NOCl solution at -15°. Small but equimolar amounts of N_2O and N_2 were formed. HCl formed in the hydrolysis of $TiCl_4$ was certainly responsible for the formation of HN_3 which in turn reacted with NOCl as previously observed.

J. $\underline{HNO_2-HN_3}$

The nitrosyl (NO^+) ion or the hydrated equivalent the nitrous acidium ion ($H_2NO_2^+$) is thought to be the active species in nitrosation reactions.[14] The equilibrium constant for the reaction: $H^+ + HNO_2 \rightarrow NO^+ + H_2O$ has been reported,[12] and nitrosation reactions in general are well studied. In this study nitrous acid solutions were used as a source of nitrosyl ion.

Hydrazoic acid (1.00 mmol) was made by gradual addition of sodium azide (0.0650 g) to 5 ml of degassed 8 $\underline{M}$ HCl held at -78° in a three necked flask. When all the NaN_3 had been added, the second side arm was rotated to spill the $NaNO_2$ (0.0705 g) into the stirred solution. The solution was stirred and maintained at -78° for 8-1/2 hr after the last of the $NaNO_2$ had been added. The vessel was then cooled to -196°, opened and Toepler pumped. Nitrogen (0.408 mmol) was collected and identified. Condensible gases were distilled from the vessel through a -130° trap and into a -196° trap. N_2O condensed in the -196° trap. It was difficult to measure precisely the amount of N_2O since HCl was also present in the -196° trap. Since the stability of N_4O which might be formed as a product was unknown and its volatility was expected to be similar to HCl and N_2O, no attempt was made to adsorb HCl upon NaOH pellets. The total pressure exerted by the mixture contained in a known volume and, therefore, the total amount of the mixture was well known. The fraction which was N_2O (0.4 mmol) was determined from the intensities of the parent peaks in the mixture as previously described.

Water was identified by its mass spectrum as the sole volatile compound in the -130 trap. The same experimental result was obtained when the order of addition of NaN_3 and $NaNO_2$ was reversed.

The reaction between HNO_2 and HN_3 at -78° in 8 M HCl was also studied when the previously described reaction vessel was constantly open to two -196° traps and a mechanical pump during the gradual addition of the second reagent. When the second reagent added in this manner was $NaNO_2$, substantial amounts of HN_3 accumulated in the -196° traps. An explosion occurred during characterization of the material in -196° traps in one such experiment. When NaN_3 was the second reagent tipped into the cold 8 M HCl, much less HN_3 distilled from the reaction vessel. No products except N_2O, HN_3 and traces of HCl were recovered using the continuous pumping technique. The addition of $NaNO_2$ to a continuously pumped 8 M HCl solution which is warmer than -63° causes the formation of NOCl. At temperatures greater than -45° the principle reaction becomes the formation of NOCl. (There is a literature procedure for NOCl production from a saturated $NaNO_2$ solution and concentrated HCl at room temperature.[4]) When NOCl is formed the solution becomes highly colored red or greenish yellow. The NOCl may be pumped from the 8 M HCl solution along with HN_3. HN_3 and NOCl react when a trap containing them warms enough for liquid HN_3 to mix with NOCl.

K. Transition Metal Azides--$NOBF_4$

Many transition metal azides have been shown to react with sources of NO^+ to give equimolar amounts of N_2 and N_2O.[15,16] There have even been several attempts to determine whether the azide is attacked at the terminal nitrogen or at the substituted one.[23] It is still uncertain which nitrogen is attacked first.

Azidopentaamminecobalt(III) chloride (6.0 mmol), a stirring bar, and 5 ml of dry actonitrile were added to a 2 necked reaction vessel in a dry nitrogen-filled glove bag. A side arm containing $NOBF_4$ (0.706 g) was attached to one neck, and a vacuum line adapter to the other. The vessel was cooled to -196° and degassed in three freeze-thaw cycles. The closed vessel was stirred at room temperature as $NOBF_4$ was gradually added. After 56 hr of continuous stirring at room temperature, the vessel was cooled to -196°, opened, and nitrogen (0.007 mmol) was Toepler-pumped from the vessel. The remaining volatile products were distilled through -95, -130, and -196° traps. N_2O (0.006 mmol) collected in the -196° trap. The -95° and -130° traps were sealed and allowed to stand overnight at room temperature. These traps were separately cooled to -196° and Toepler-pumped. No noncondensible gas was collected from them. Neither $[As(C_6H_5)_4][Fe(N_3)_5]^6$ or $\{[Cu(N_3)][P(C_6H_5)_3]_2\}_2$ showed any evidence of reaction with $NOBF_4$ at room temperature in acetonitrile or dimethylsulfoxide. Azidopentaamminecobalt(III) chloride did react with NOCl slightly faster than $NOBF_4$; however, the final products were identical in either case.

L. Concondensation of HN_3 and NOCl

HN_3 (0.500 mmol) and NOCl (0.513 mmol) were condensed into separate, previously evacuated gas storage bulbs each fitted with a greaseless stopcock. The bulbs were attached to the cryostat system shown in Fig. 1. The connections were made with Swagelock fittings from the 1/4 in. glass tubing at the bottom of the cryostate to 1/8 in. copper tubing for HN_3 and to 1/8 in. monel tubing for NOCl. Swagelock unions were again used to match the metal tubing to the glass #9 O-ring joints used to attach the gas storage bulbs. Once the gas storage bulbs were attached to the system it was evacuated. The system was pumped for a minimum of 2 hr before each experiment.

Each gas flowed through a separate nickel plated brass micrometer needle valve fitted with Buna-N O-rings. During the course of these experiments the nickel plating in the NOCl valve became scored, and rapid attack of the exposed brass by NOCl forced replacement of the valve with one of identical design made of monel. Each valve was calibrated with the appropriate gas under simulated operating conditions, so that the rate of flow for a given valve opening and pressure was known.

All of the material in each gas storage bulb was codeposited on the lower surface of the copper block in the cryostat over a period of 4 hr. During the condensation the temperature of the block was -194° and the pressure in the vacuum system never exceeded 10^{-6} Torr. The condensation was very efficient; the background pressure was the same during and preceeding the condensation.

The liquid N_2 which remained in the cold finger after deposition was complete was blown out with a stream of nitrogen. The block was then allowed to gradually warm up while continuous high speed pumping was maintained directly into the ionization forechamber of the mass spectrometer. The solid mixture of NOCl and HN_3 initially looked pale yellow and had no obvious inhomogenities. The temperature rose gradually (~10/min) until at -127° the color of the deposited material changed very suddenly to an orange color. At the same time a pressure increase to $\sim 10^{-5}$ Torr occurred. It became very difficult to maintain a steady temperature increase. Frequent additions of a few milliliters of liquid nitrogen were required to slow the rate of temperature increase. Pressure variations of an order of magnitude or more accompanied the temperature rise and made recording spectra difficult. At -115° the deposit on the block looked white. Finally, above -100° the bare surface of the block could be seen.

The first volatile materials observed during the warm-up were N_2O and N_2 in equimolar amounts. Their spectra were recorded when the block was at -127°. The amounts of these gases increased erratically until at -110° peaks due to HCl began to be visible in the spectra of the gases pumped out of the cryostat. All three gases increased in amount until at -107° they began to diminish.

The experiment was repeated with nearly identical quantities of HN_3 and NOCl after the temperature of initial reaction had been determined. It was found that this initial reaction temperature was a very sensitive function of the rate of deposition of reagents and their amounts. The temperature at which reaction began varied as much as 20°. Since the variation in initial reaction temperature was so great, the block was allowed to warm until the pressure began to rise and was then immediately quenched to ~5° below that temperature. The block was then allowed to rise in temperature at the rate of 1° per hour. Spectra were recorded every 10 min until the temperature was 1° less than the initiation temperature. Spectra were recorded every 5 min from 1° below to 3° above the temperature of first pressure rise. The very slow rise in temperature was accomplished by small (1-2 ml) additions of liquid N_2 to the cold finger at intervals of 1 min or less.

When the temperature rose very slowly, sudden pressure variations were almost completely eliminated, and the pressure rose steadily with increasing temperature. The highest pressure reached during any experiment whose temperature was well controlled was $\sim 8\times10^{-5}$ Torr. It was possible to quench the reaction and force the pressure very rapidly down to background levels. A steady pressure rise could be maintained if the block was warmed up after a second quenching. When the reaction was carried out with a total of ~1 mmol of reactants, a third quench warm up cycle could be carried out.

The only peaks that were evident during the initial part of any gradual warm up were those due to N_2O and N_2 and the normal daughter peaks associated with these molecules. No peaks from HCl were observed until after those from N_2O and N_2 had been observed. There was no evidence for a parent peak corresponding to N_4O or any variation in the fragmentation pattern of the gas mixture pumped from the cryostat from the pattern produced by mixtures of known composition of N_2O, HCl and N_2. The peaks attributable to the excess reagent were not observed until long after the more volatile materials had been pumped away.

The spectra were all recorded using an ionizing energy of 70 eV. Two attempts were made to alter the ionization conditions in order to investigate electron impact induced fragmentations of higher molecular weight species. First an experiment was conducted in which the accelerating voltage was increased from the nominal -135 volts to -180 volts. The peaks were then about 20% wider than normal but exhibited no unusual assymetry. No new peaks were observed. Next the ionization energy was lowered to 50 eV. The intensity of the spectrum was then reduced by factor of almost two. No other changes were observed.

The relative intensities of the parent peaks were used to establish relative amounts of each gas. Calibration mixtures of gases were run under a variety of pressure conditions to establish the effect of pressure variations on peak heights. In the pressure range from 1×10^{-7} to 5×10^{-5} Torr the peak height was found vary linearly with pressure.

If the deposit on the copper block was laid down faster than about 0.5 millimoles per hour then, when the warm-up began the deposit flaked, peeled off and pitted the otherwise smooth looking mixture of reagents. Careful inspection of rapidly made deposits often revealed regions of crystallinity. The surface of a rapidly deposited reagent mixture looked very much like old peeling paint when it was warmed up. The pressure and temperatures in such an experiment would vary widely as the warm up progressed.

Table III itemizes some experiments done with this technique. Figures 4, 5 and 6 show typical spectra of the pre-initiation, initiation and post initiation phases of the experiment.

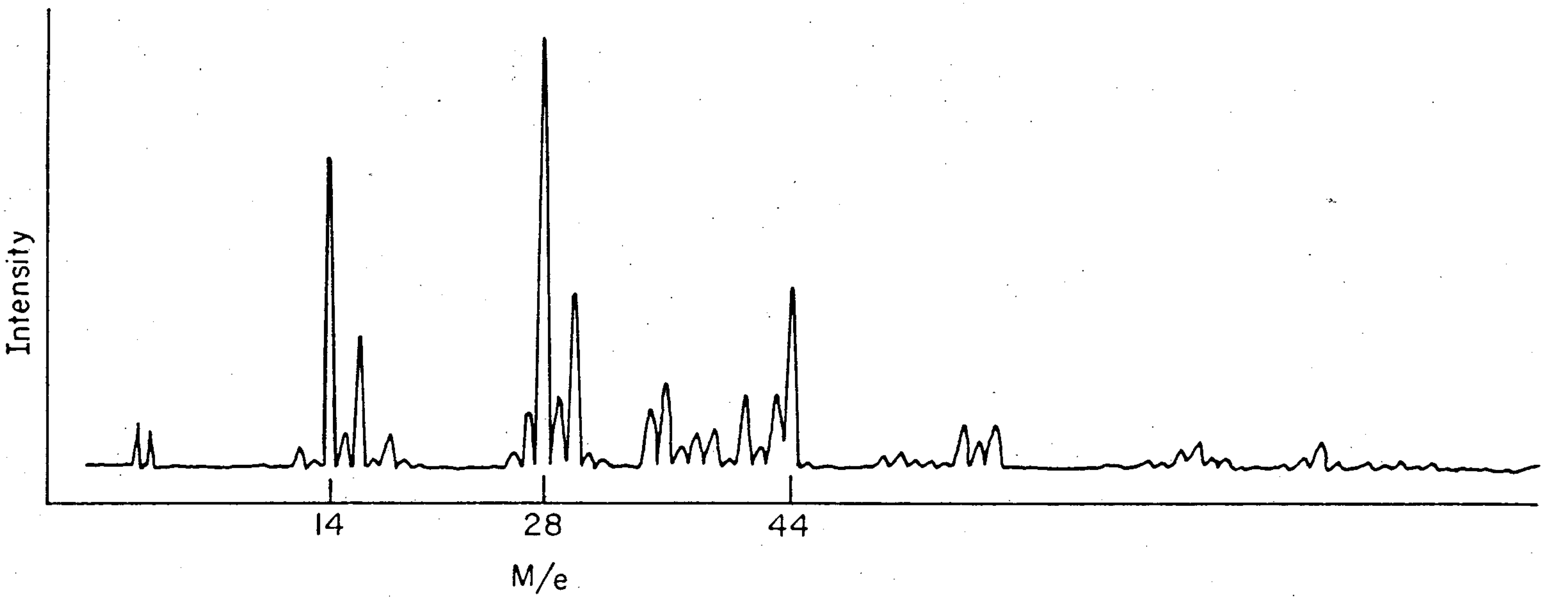
M. Matrix Isolation HN_3-NOCl

One millimole of pure NOCl was condensed into a clean, previously evacuated, glass, 1250 ml gas storage bulb. One millimole of pure HN_3 was condensed into a similar gas storage bulb. Carbon tetrachloride (365 mmol) was condensed into a two liter gas storage bulb. In some experiments SF_6 was used as the matrix gas in place of CCl_4.

The gas storage bulbs were attached to the vacuum system of the cryostat, and the system was evacuated. Pumping with the aid of a liquid nitrogen trapped diffusion pump was rapid. The ultimate pressure of 1×10^{-7} Torr was reached in 10 min. The liquid nitrogen cooling baths were then removed from around the cold fingers of the gas storage bulbs. The bulbs were allowed to warm to room temperature. (Caution: HN_3 is extremely dangerous when it is in the liquid state!) Twenty min after the dewars were removed from around the cold fingers it was judged safe to return to the area of the apparatus. Face shield and protective gloves were always worn when near bulbs containing HN_3. Several explosions occurred during the course of the work with HN_3.

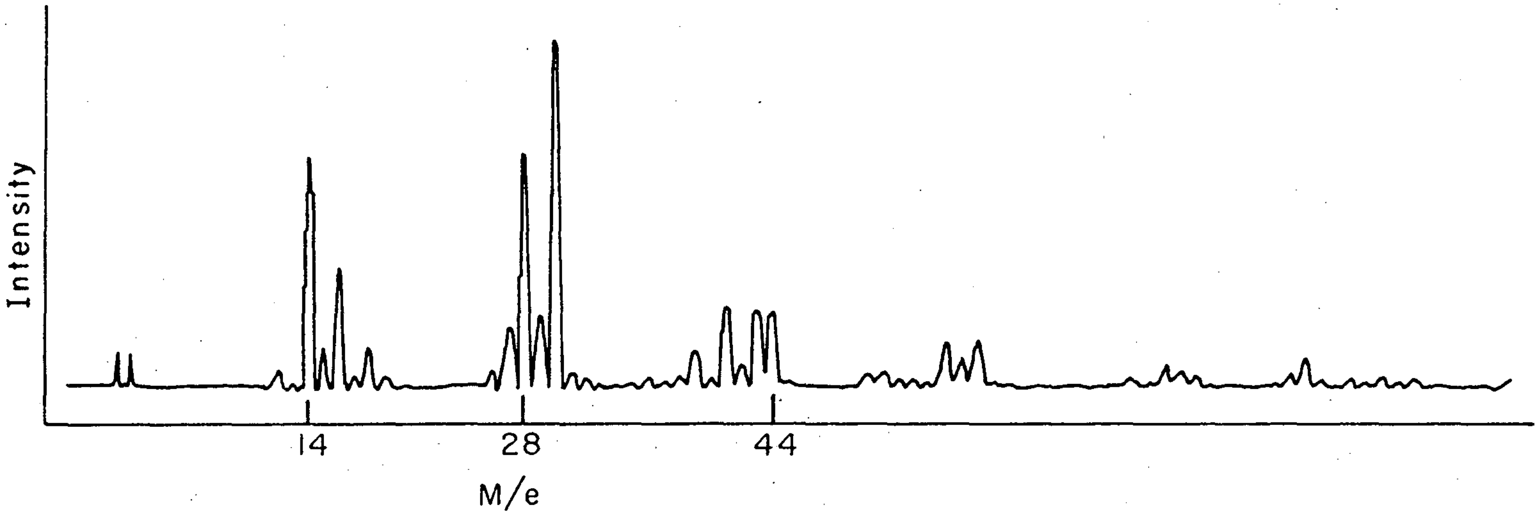
Table III. CO condensation with analysis by mass spectrometer.

Total mmol Deposited (HN_3+NOCl)	Time to Deposit	Initial Reaction Temp. °C	Composition of Initial Products
2.0	6 hr	-106	$N_2 + N_2O + HCl$
1.2	5 hr	-113	$N_2 + N_2O + HCl$
1.0	4 hr	-127	$N_2 + N_2O$
1.0	6 hr	-121	$N_2 + N_2O$
0.4	6 hr	-127	$N_2 + N_2O$
3.7	5 hr	-101	$N_2 + N_2O + HCl$
6.3	12 hr	-113	$N_2 + N_2O + HCl$
1.0	6 hr	-126	$N_2 + N_2O$ SF_6 on matrix 10 to 1 premixed with each reagent



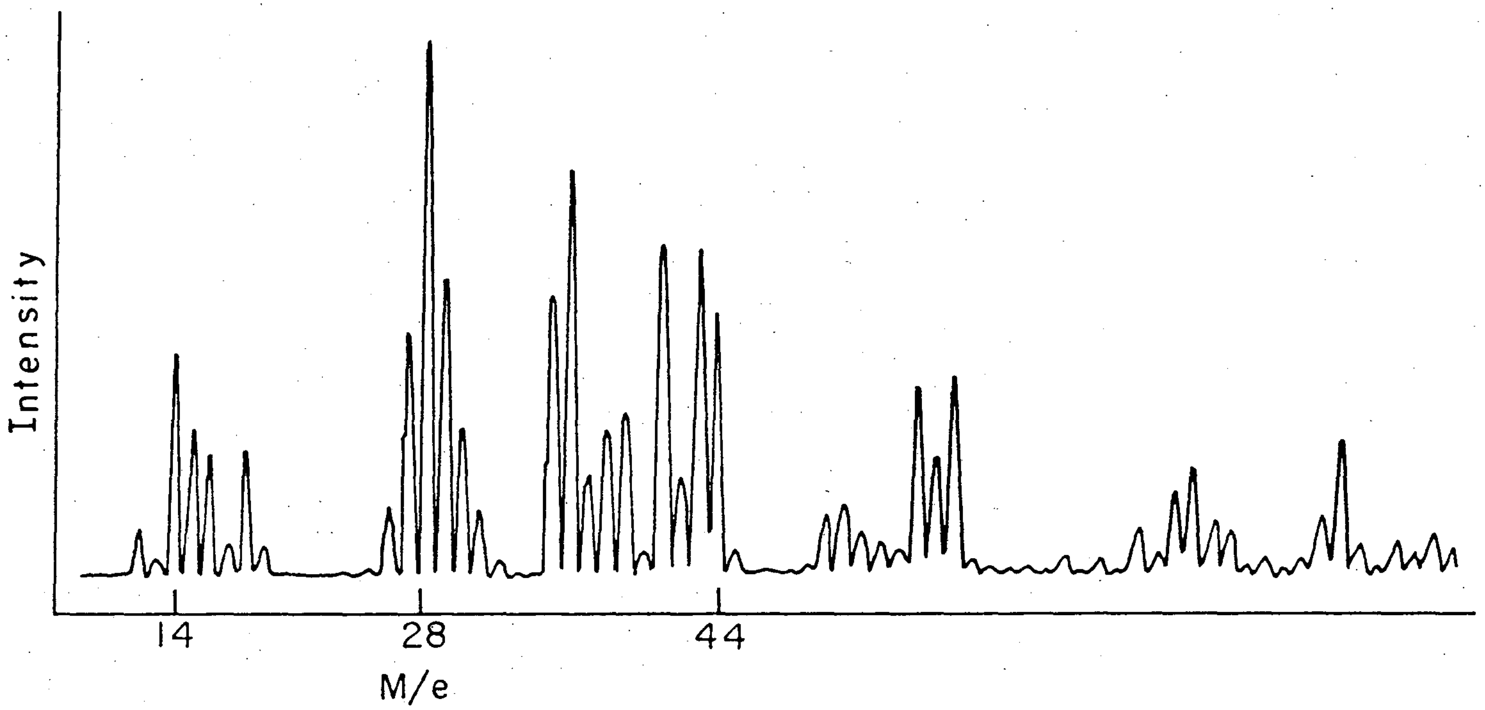
XBL 763-6541

Fig. 4. Mass spectrum from the mass spectrameters cryostat after deposition by before pressure temperature rises occurred. -157° 7.8×10^{-7} Torr.



XBL 763-6540

Fig. 5. Mass spectrum from the mass spectrometer cryostat at -127°, 8.9×10^{-6} Torr after the reaction began.



XBL 763-6542

Fig. 6. Mass spectrum from the mass spectrometer cryostat after the reaction had progressed beyond in initial temperature and pressure rise -117°, 6.3×10^{-6} Torr.

Liquid nitrogen was poured into the cryostat to cool the target window. The temperature of the target window was monitored with a thermocouple wedged between the target and a target mounting screw. When the target had reached -194°C the CCl_4 bulb was opened and flow from it was established and regulated through a micrometer needle valve. The HN_3 and NOCl bulbs were opened next and ajustments in their respective needle valves made to give identical rates of flow from each bulb. The flow rates from all three bulbs were adjusted to give a mole ratio of 300 to one CCl_4 to HN_3 and NOCl.

The deposition was continued for 9 hr. During this time the pressure in the chamber surrounding the target never exceeded 2.5×10^{-7} Torr. When CCl_4 alone was deposited the pressure in the target chamber was 2.4×10^{-7} Torr. The long deposition times were necessary to put enough material on the window to give a good spectrum and also to ensure good isolation of the reactant gases. Deposition times greater than 9 hr caused a snow effect in the matrix.[24] Scattering then exceeded transmission.

After 9 hr the target was rotated 90° to face the light source. A spectrum was recorded to check the intensity of the spectrum the deposited material produced. The target was warmed by flowing gaseous nitrogen into the liquid nitrogen which remained in the cold finger of the cryostat. When all of the liquid nitrogen had been blown out, the temperature of the target began to rise slowly. The rate of temperature rise of the target was controlled by altering the rate of flow of nitrogen which was blown down into the cold finger. The N_2 was cooled by passing it through an eight turn copper tubing heat exchanger immersed in a liquid nitrogen filled dewar.

Although the guest molecules were significantly lighter than the host (matrix) molecules, the temperature of the CCl_4 matrix was allowed to rise to -109° over a period of 2 hr. There was, however, no change in the spectrum during the warm up period in either matrix. Sulfur hexafluoride matrices were allowed to warm to -168° over a period of about 2-1/2 hr. There was no evidence of aggregate formation[20] or any evidence of an annealing process. When the guest molecules are much lighter than the host molecules, diffusion is often an undesirable process, since the lighter guests tend to form aggregates and lose their isolation.[24] Spectra were all sharp and similar in appearance to gaseous spectra. From -109° with CCl_4 matrices (-168° with SF_6) the rate of temperature rise was maintained at 1/2° per min and spectra were recorded at 5 min intervals. Table IV gives a listing of bands observed.

No changes in the spectrum were observed until the temperature had risen so high that the matrix gas began to sublime away in great quantity. This occurred with CCl_4 at about -65° and with SF_6 at about -128°. As the matrix sublimed away, the pressure in the system went up and became erratic. In an effort to reduce the sublimation of the matrix, pumping was discontinued once the diffusion pump interlock was activated ($\sim 5\times10^{-4}$ Torr). In the recorded spectrum only a steady diminution of the bands due to the reagents was observed. No new bands formed nor were there any changes in band shape or position.

Table IV. Infrared bands observed CCl_4 as a matrix.

Frequency	Intensity
3150 cm^{-1}	weak
2155	medium
1850	medium
1240	strong
1220	strong
995	strong
970	strong

No band ever occurred which could reasonably be assigned to a hydrogen chlorine stretching mode.

Sulfur hexafluoride was the first gas used for a matrix in these experiments. The results that were obtained with it were identical to those for CCl_4 matrices, except that the matrix began to disintegrate at an even lower temperature than the CCl_4 matrices. The reaction between NOCl and HN_3 in either matrix did not take place until a relatively high temperature. When it did occur, the temperature was so high that no volatile products remained trapped in the disintegrating matrix.

When NOCl and HN_3 were condensed without the aid of a matrix, the spectra obtained at liquid nitrogen temperatures were broad and irregular. The broad spectra were similar similar to other amorphous solids. No HCl spectrum could be observed. As the target was gradually allowed to warm up, no change was observed until at about 130°, when the deposit literally exploded off the window. There was not enough material remaining to record any further spectra. The very large pressure increase tripped vacuum alarms through out the cryostat system.

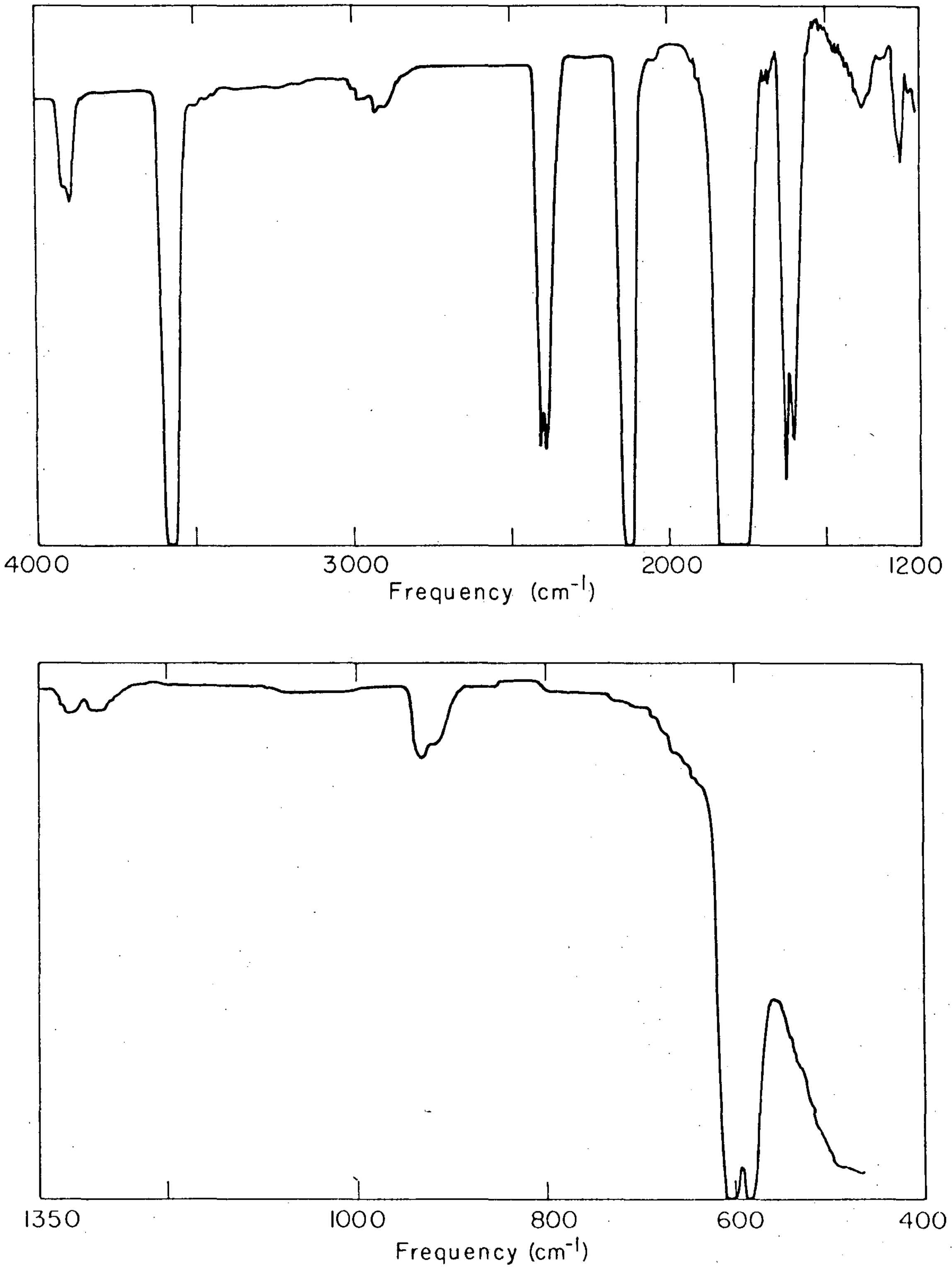
V. DISCUSSION

Lucien's claim of formation of nitrosyl azide rested on an infrared spectrum, the physical properties, and decomposition of a sample.[3] He reported bands in the infrared at 2340, 1850, 2180, and 1350 cm^{-1}. The first two bands were identified and referenced as nitrosyl vibrational modes.[3,25,26] The second pair of bands were identified and referenced by Lucien as azide bands.[3,27,28] The fundamentals of gaseous nitrosyl chloride are observed in 1800, 650, and 332 cm^{-1} (for NOCl with all of the chlorine as chlorine 35)[29] however, overtones and combination bands complicate the NOCl spectrum. Figure 9 shows the spectrum of NOCl. The intensities of these bands are great enough so that they might well be mistaken for fundamentals of a new compound. The combination bands at 2132 and 2405 cm^{-1} are 30 and 25% respectively of the intensity of the 1800 cm^{-1} fundamental. The two lower frequency bands Lucien attributes to N_4O might be due to impurities such as nitryl chloride or products such as nitrogen dioxide from a variety of possible NOCl side reactions. Lucien reported only four infrared bands. If the symmetry of N_4O was C_s analogous to HN_3 then it would be expected to have six infrared and Raman active modes. The bent HN_3 structure seems most likely because the nitrosyl pseudo halide ONCN has such a structure[30] and because the only reasonable reasonance form for N_4O $(O = N - N = \overset{+}{N} = \bar{N})$ implies such a structure. Other resonance structures for N_4O have unfavorable, unreasonable charge separations. Nitrogen is labeling experiments also support the notion that the four nitrogen atoms are bound together momentarily when nitrosyl ion and azide ion react.

It is difficult to rationalize Lucien's report of the growth of bands attributable to nitrous oxide and the concurrent disappearance of bands assigned to nitrosyl azide. Lucien does not describe his gas infrared cell or the procedures used to transfer or record the spectrum claimed to be that of nitrosyl azide. Since nitrosyl chloride reacts with hydrocarbon greases or amine groups in viton rubber, and is adsorbed by silicone greases, reactions between nitrosyl chloride and inappropriate equipment are certain to occur. Such reactions may obscure the significance of a spectrum recorded in apparatus subject to NOCl attack.

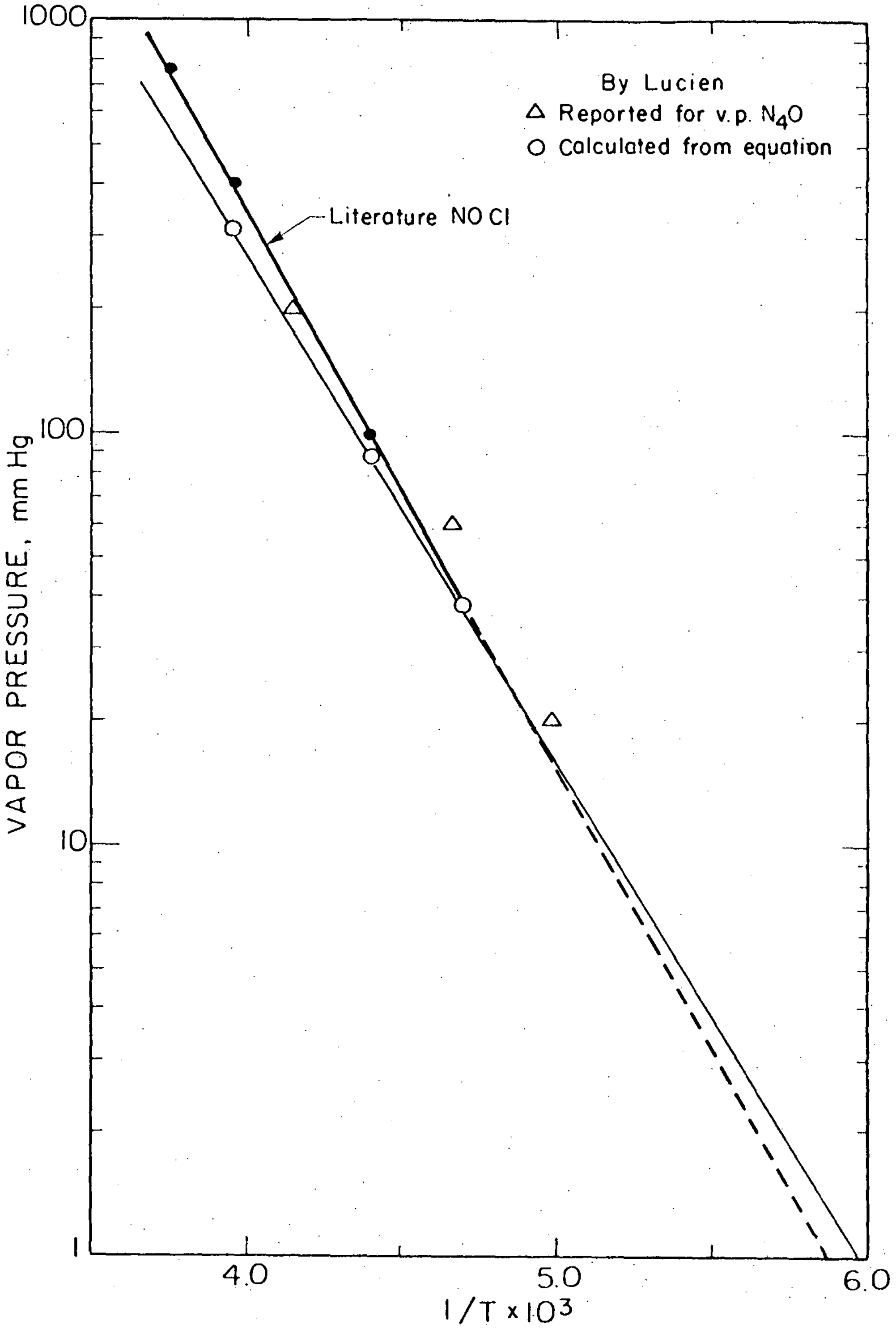
The physical properties reported for nitrosyl azide are remarkably close to those of nitrosyl chloride. The ectrapolated boiling point for N_4O is 1.5°.[3] Nitrosyl chloride boils at 6.5°.[20] Lucien reported that the vapor pressure of nitrosyl azide could be expressed according to: $\log p = 7.306 = \frac{1215.6}{T}$ (T in °K). We applied this equation at -60.2°C and calculated the vapor pressure of nitrosyl azide to be 39.6 mm Hg. At the same temperature the vapor pressure of nitrosyl chloride is 40.0 mm Hg.[31] Figure 7 shows the vapor pressure of NOCl and N_4O (N_4O points calculated using Lucien's equation) as a function of temperature. Three vapor pressures are also plotted that were specifically cited in Lucien's paper.[3] These three points do not fit Lucien's own equation very well.

Separation of nitrosyl azide and nitrosyl chloride as Lucien describes by a trap-to-trap distillation is unlikely. Separation by any physical means would be very difficult. Lucien does not report enough information about his claimed separation of N_4O from NOCl to substantiate it.



XBL 761-6120

Fig. 7. Pure nitrosyl chloride showing the many combination and overtone bands and their intensities.



XBL 763-6536

Fig. 8. The heavy solid line shows the vapor pressure-temperature behavior from literature sources for NOCl.[31] The line is broken beyond the freezing point of NOCl. The lighter line is calculated from Lucien's equation.[3] The open trianglular points show how poorly his reported values fit the equation he reports as describing the vapor pressure of N_4O. Clearly separation of two real compounds whose vapor pressures are so close is unlikely.

The decomposition experiment described by Lucien is an incomplete proof for the formation of nitrosyl azide. Lucien does not report the amount of sample used or the amount of each decomposition product. He does report relative pressures which appear to substantiate the claim of formation of equimolar amounts of nitrogen and nitrous oxide from a sample thought to be nitrosyl azide. Since Lucien describes none of the important details of material handling, reactions could have occurred which obscured the meaning of all his data.

The mass spectrometer and matrix isolation studies provided some evidence that no reaction between NOCl and HN_3 occurred in the gas phase. These reagents were co-deposited without increases in the background pressure between the condensation surface and the pumps. The lack of gas phase reaction suggests that NOCl and HN_3 react by an ionic pathway and that a solvent is necessary to lower the energy of ion formation. The solvent most capable of coordinating ionic species would be expected to be the one in which the reaction rate was greatest. Eight molar HCl was the only solvent used whose ability to dissolve ionic species was notable. The nitrous acid-hydrazoic acid reaction in this solvent was, however, one of the slowest reactions studied. Since the overall reaction $NO^+ + N_3 \rightarrow N_2O + N_2$ probably depends on the concentration of the nitrosyl ion, the equilibrium $H^+ + HONO \rightleftharpoons NO^+ + H_2O$ is important. The equilibrium constant for this reaction is 10^{-7} at 20°.[12] Since the concentration of NO^+ or its hydrated equivilent was not high and could not readily be increased in the cold viscous 8M HCl, the reaction was slow. Under the conditions used for the nitrous acid-hydrazoic acid reaction, an alternative reaction path might explain the slow reaction. The reaction may have proceeded according to $2HNO_2 \rightleftharpoons H_2O + N_2O_3$ as a slow first step followed by $HN_3 + N_2O_3 \rightarrow HNO_2 + N_2O + N_2$. At room temperature and down to -63° NO^+ does exist in an HCl solution. When NO_2^- solution or solid MNO_2 (M = Na,K, etc) is added to HCl, nitrosyl chloride is formed and the solution turns yellow or a very deep red color at high concentrations. Nitrosyl chloride can be synthesized in good yield from the reaction between concentrated HCl and a saturated nitrite solution.[4] The nitrous acid solutions we studied were colorless except at temperatures of -63° or higher. Above -63° the solutions were colored straw yellow and NOCl was pumped out as a product along with N_2 and N_2O. We do not, however, have enough data to draw a firm conclusion regarding the detailed mechanism of the nitrous acid-hydrazoic acid reaction in 8M HCl at -78°.

Our results suggest that nitrosyl azide does not exist as a stable chemical compound in the usual sense. It may form in the reaction of HN_3 with NOCl as a very short lived complex in association with HCl. Hydrogen bonding might have prevented observation of an H-Cl stretching frequency in our matrix isolation experiments. The reaction of HNO_2 with HN_3 in 8M HCl may proceed through formation of N_4O as an activated complex. Perhaps all other azide-nitrosyl reactions follow this course. Further kinetic studies might clarify the role of N_4O in such reactions.

Nitryl azide (N_4O_2) has been reported in acetonitrile and carbontetrachoride solutions at -10°.[33] It was prepared from NO_2BF_4 and several azide salts and was characterized in solution by its infrared spectrum. Since it decomposed at 0° producing only N_2O, a cyclic oxatetraazole is probably formed. The mass spectrum is reported to have a peak at m/e 42 corresponding to (N_3^+). Our mass spectrometer experiments provided us with no evidence for N_4O. We observed no parent peak, no peak at m/e 42 (N_3^+) and no other fragment peaks that could be from N_4O. Nitrosyl salts and azide salts did react in acetonitrile and carbontetrachloride at the freezing points of the solvents to form N_2 and N_2O.

Attempts were also made to use silver azide as a reagent to prepare nitrosyl azide. All reactions using silver azide resulted in explosions. Silver azide is a fearfully explosive compound which is very shock sensitive. It was so unpredictable that experiments using it were discontinued.

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Part II

I. INTRODUCTION

For many years chemical study of the cyanide group was restricted to salts, coordination compounds, and a few covalent compounds such as cyanogen chloride, cyanamide, and hydrogen cyanide. Recently, a greater variety of cyanides have been made and studied. Compounds such as OCNCN,[1] NF_2CN,[2] and ONCN[3,4] have renewed interest in the reinvestigation of the volatile cyanides.

Horsewood and Kirby reported the conversion of conjugated dienes into N-cyano-3,6 dihydro-2H-1,2 oxazenes with silver cyanide-nitrosyl chloride mixtures.[4] This fact along with the green colored vapor above the organic solutions, the infrared spectra, and the proton NMR spectra of the organic products led them to propose nitrosyl cyanide had been present in their solutions. Prior to Horsewood and Kirby's report, nitrosyl cyanide had been postulated[6] and some indirect evidence had been accumulated for its existence in photochemical reactions of cyanogen or cyanogen halides with nitric oxide.[7] Tyler et al. reported the microwave spectrum and structure of nitrosyl cyanide.[3] Although no synthetic procedures or physical properties have been published, an infrared study and normal coordinate analysis have been reported for nitrosyl cyanide.[5] We have studied the decomposition of this unique blue gas, investigated its synthesis, and established a purification procedure.

II. MATERIALS AND APPARATUS

Silver cyanide (J. T. Baker) was finely powdered in a darkroom equipped with an X-ray (brown) safe light. Nitrosyl chloride (Matheson) was purified as described in the preceding section. Chloroform was analytical reagent grade and was used as purchased. Potassium cyanide ^{15}N labeled was purchased from Bio-Rad Laboratories in Richmond, CA. It was converted to silver cyanide by adding an aqueous $KC^{15}N$ solution to an excess of aqueous $AgNO_3$ in the darkroom, then filtering the precipitated AgCN, washing the precipitate with water, drying under vacuum, pulverizing into a fine powder, and finally redrying for 2 days under high vacuum. The vacuum drying operations were carried out with partial exclusion of light. The vessels containing the AgCN were loaded in the darkroom, wrapped with Al foil, then attached to the vacuum line, and evacuated. The unlabeled commercial AgCN was often handled with little attempt to exclude light. Light caused the reduction in yield of ONCN because some of the AgCN was converted to silver metal and cyanogen. On the small scale of the isotopic experiments it was necessary to use every possible precaution to insure good yields.

All volatile materials were handled in the glass vacuum line described in the preceding section. A mercury manometer was used to measure the pressures of gases. Its arms were protected from attack of NO_2 or NOCl with a 5 mm depth of Dow-Corning 704 silicon pump oil. A gas distillation column (Fig. 1) was used to purify nitrosyl cyanide. The column was constructed entirely of Pyrex glass including the #9 O-ring joints at the sample inlet, outlet, and nitrogen inlet ports.

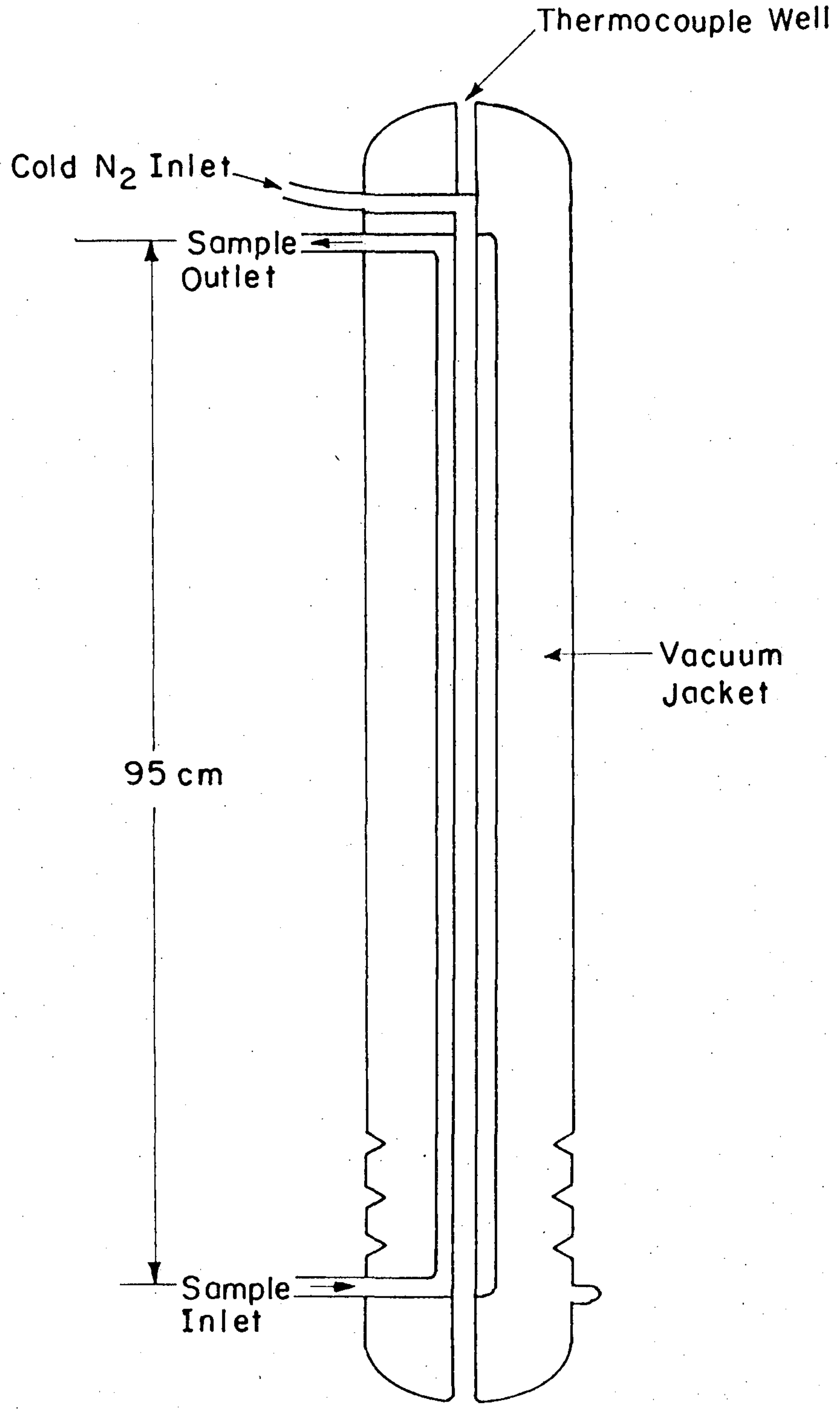

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Fig. 1. Schematic diagram of the gas distillation column used to purify ONCN.

The temperature of the column at its top and the temperature gradient of the column were varied by altering the rate of flow of nitrogen gas through a ten turn copper heat exchanger immersed in a liquid nitrogen filled dewar. The temperature at the top of the column was monitored with a Hewlett-Packard digital thermometer. The temperature was maintained within 0.25° of preselected values for 2 to 3 hr without adjustments to the flow rate. Volatile materials were measured with standard vacuum techniques[8] and analyzed with the mass spectrometer system described in the previous section.

III. EXPERIMENTAL

A. Synthesis and Purification of ONCN

The original report suggesting the formation of nitrosyl cyanide gave few synthetic details.[4] The reagents NOCl and AgCN were combined in an organic solvent and subsequent reactions occurred in that solvent. The microwave study suggests chloroform as a solvent.[3] The infrared study was completed with nitrosyl cyanide which was made by passing NOCl through a cold (-40°) AgCN packed U tube along with helium as a carrier gas.[5] Although this procedure was successful it had two drawbacks. The yield was low (~8 to 17%) and variable and also undesirable explosive by-products were formed.

We found that silver cyanide powder and excess nitrosyl chloride reacted at -45° to give nitrosyl cyanide in good yield when the following procedure was used. Silver cyanide (0.4321 g, 3.18 mmol) was added to a 200 ml glass reaction vessel in the darkroom along with a Teflon coated magnetic stirring bar. The O-ring cap was placed on the vessel and then it was wrapped in aluminum foil, attached to the vacuum line, and evacuated. During evacuation continuous stirring was maintained to powder the silver cyanide. Previously purified nitrosyl chloride (12.13 mmol) was condensed into the liquid nitrogen cooled vessel through the greasless stopcock attached to it and then the liquid nitrogen cooling bath was removed, the foil removed, and the vessel quickly plunged into a -45° bath (chlorobenzene slush). Over a period of 20 min the stirred vessel gradually warmed to -45° and a blue-green gas became visible in the upper portion of the vessel. The gas (ONCN mixed with NOCl) was pumped from the vessel by briefly opening

(~5 sec) with stopcock to a fractionation train consisting of successive -78 (dry-ice acetone), -95 (toluene), -130 (n-pentane), and -196° traps. Every 10 min during 2 hr of reaction time the stopcock was opened briefly to allow both reactant and product to enter the fractionation train. The bulk of the unreacted nitrosyl chloride was retained in the -95° trap. The -130° trap stopped the nitrosyl chloride which escaped from the -95° trap and allowed nitrosyl cyanide to slowly distill into the -196° trap.

The contents of the -196° trap were distilled into a previously evacuated storage bulb, the bulb attached to the gas distillation column (Fig. 1) using #9 O-ring joints and the column evacuated through the sample outlet port. Pumping on the column was continued for 20 min. During the column evacuation the bulb containing the crude nitrosyl cyanide was kept frozen at -196°. The flow of cold nitrogen into the column was started and then regulated so that a constant temperature of -143° was indicated at the top of the column. The temperature at the nitrogen outlet was about -106°. The bulb containing the sample was allowed to slowly warm until all of the sample vaporized. The sample was then opened to the dolumn and it began to move up the solumn separating as it went into 3 bands. A pale whiteish-blue region moved up the column fastest, a well defined bright blue band followed, and finally a diffuse greenish-blue region moved the slowest. The pale whitish blue material was collected as it came off the column in a -196° trap. It contained some nitrosyl cyanide but it was mainly nitrous oxide and carbon dioxide. The second fraction collected was pure nitrosyl cyanide. The last fraction contained nitrosyl cyanide, nitrosyl chloride, cyanogen, and cyanogen chloride. The pure nitrosyl cyanide (0.89 mmol) was stored at -196° until it was needed. The percentage yield was doubled when the amount of reactants was halved in the same reaction vessel. On an extremely small scale (0.08 g AgCN; 0.7 mmol NOCl) a yield of almost 70% was obtained with the 200 ml vessel.

Two explosive by-products arose from the synthesis of nitrosyl cyanide. Pure liquid nitrosyl cyanide upon standing formed some pale yellow-non-volatile solid which remained when the nitrosyl cyanide was distilled away. Pure ONCN decomposed to the extent of about 5% in 7 hr at -78°. The solid material was unstable and decomposed explosively upon warming to 40°. The principal products of the explosion were carbon, nitrogen and an intractable white solid. When the contact of nitrosyl cyanide with itslf in the liquid phase occurred at the lowest possible temperature for the shortest period of time possible the formation of side products was negligible. Impure nitrosyl cyanide reacted as much as a thousand times faster in the liquid phase than pure material. Nitrosyl cyanide reacted rapidly with nitrosyl chloride when these compounds were co-condensed. The yellow orange solid which formed evolved trace amounts of NOCl upon prolonged pumping (~2 days). Attempts to treat measured amounts of nitrosyl cyanide with equimolar amounts of nitrosyl chloride were not successful because spontaneously explosive products were formed. The yellow orange solid formed from the reaction of trace amounts of NOCl with nitrosyl cyanide decomposed violently upon warming to about 60°. Carbon, nitrogen, and carbon dioxide were formed.

These explosive products were observed in the traps of the fractionation train when the fractionation train was evacuated following the initial purification of nitrosyl cyanide. These products were avoided when the -78, -95, and -130° traps were pumped out slowly while they were still cold. The pump trap protecting the mechanical pump did accumulate all of the by-products. When this trap was removed, warmed, and cleaned, small explosions often occurred. The addition of water to the solids in the trap caused a frequently violent reaction coupled with a flash of light.

B. Decomposition of ONCN

The decomposition of nitrosyl cyanide was studied in all glass break-seal equipped vessels identical to the one illustrated in Fig. 3 of the preceding section except that they contained no stirring bars. The vessels were carefully cleaned in a base bath, rinsed, cleaned in an acid bath, rinsed, and finally placed in an annealing oven. The vessels were dried overnight in an oven immediately prior to use. The vessels ranged in volume from 75 ml to 403 ml.

Pure nitrosyl cyanide (0.0611 mmol) was condensed into an evacuated reaction vessel. The vessel was sealed, wrapped in Al foil, and placed in an oven at 75°. After 10 days the vessel was cooled with liquid nitrogen, attached to the vacuum line, opened, and Toepler-pumped. Nitrogen (0.0207 mmol) was collected and identified mass spectrometrically. The liquid nitrogen cooling bath was then replaced by an empty dewar to allow gradual warming and expansion of the condensible products successively through -95, -130, and -196° traps. Nitrous oxide (0.0205 mmol) and carbon dioxide (0.0202 mmol) condensed in the -196° trap and cyanogen (0.0201 mmol) condensed in the -130 and -95° traps.

Nitrogen oxide and carbon dioxide were condensed into a calibrated volume and the total pressure exerted by the two gases measured. The mixture was then passed into a tube containing Ascarite to absorb the CO_2. The N_2O remaining was passed through a -78° trap and then condensed into the calibrated volume. The volume was sealed, allowed to warm and the pressure measured. The N_2O was identified mass spectrometrically by its peaks of m/e 44, 30, 28, 16 and 14. For some reactions N_2O and CO_2 were not separated but rather the mixture was analyzed with the mass spectrometer. The ratio of the peak height at m/e 12 to m/e 44 for pure CO_2 and also the ratio of m/e 30 to m/e 44 were used to estimate the percentage of the m/e 44 parent due to N_2O and CO_2. The cyanogen was consolodated, measured, and identified with the mass spectrometer by its peaks at m/e 52, 26, 24, 14 and 12.

Decompositions were carried out at room temperature but about 6 weeks were required for complete reaction. The decomposition of nitrosyl cyanide was also studied when the vessels were unprotected from light. The products then included NO, CO and NO_2 as well as the other previously mentioned products. The mass balances for decompositions carried on in the light were poor. It was decided to pursue only a study of the dark reactions. The decomposition products were also dependent on the pressure of ONCN. At high pressures the volatile products only very poorly accounted for the total mass of the system. The non-volatile products were so evenly distributed throughout the reaction vessel they could not be directly observed nor easily accounted for. Table I shows the results typical of decompositions of nitrosyl cyanide carried out at various pressures in the dark.

Labeled nitrosyl cyanide was also decomposed. It was made from labeled $AgC^{15}N$ by the same procedure used to make unlabeled nitrosyl cyanide. It was analyzed in exactly the same way as the unlabeled material. Although the $KC^{15}N$ used in these experiments was purchased as and represented on the bottle as 99.1% nitrogen 15 potassium cyanide, the labeling was actually much less complete.

The weighed sample of $KC^{15}N$ (0.0018 g) was placed in a tippable side arm, then attached to one neck of a two necked, 50 ml round bottomed flask containing 15 ml of concentrated phosphoric acid, and then the flask was evacuated for 30 min. The labeled potassium cyanide was then tipped into the acid. The labeled hydrogen cyanide which bubbled out of the acid was passed through a -78° trap and was collected in a -196° trap. It was distilled into a clean, previously evacuated storage bulb and finally the bulb was attached to the vacuum system of the mass spectrometer. The mass spectrum was recorded and peaks were found at m/e 26, 27, and 28 whose background corrected intensities were 6, 54, and 122 respectively. Pure unlabeled HCN gave a background corrected ratio of 5.42 for ratio of the m/e 27 (HCN^+) peak to the m/e 26 (CN^+) peak. Using this ratio the percentages of the m/e 27 peak observed in the spectrum of the labeled material attributable to HCN^+ and $C^{15}N^+$ were calculated. The HCN^+ m/e 27 peak height was then compared to the peak height from the m/e 28 peak due to $HC^{15}N^+$. The ratio of CN^* to CN was 3.87 corresponding to 20.5%

unlabeled CN and 79.5% labeled CN. Table II lists the background corrected peak heights (in mm) or the cyanogen envelope, nitrous oxide envelope, and nitrogen envelope, and the amounts of each gas.

Because the labeling of the terminal nitrogen atom of the ONCN was far from complete, the percentage peak heights were corrected to 100% label values. For cyanogen the procedure below was used. Background corrected peak heights in the envelopes were first normalized to 100%. For example: the 54 peak height percentage equals

$$\frac{R_2}{R_o + R_1 + R_2} \times 100 \quad ,$$

The 53 peak height percentage equals

$$\frac{R_1}{R_o + R_1 + R_2} \times 100 \quad ,$$

and the 52 peak height percentage equals

$$\frac{R_o}{R_o + R_1 + R_2} \times 100$$

where R_1 = the background corrected peak height at m/e 53 and R_2 = the background corrected peak height at m/e 54 and R_o = background corrected peak height at m/e 52. The percentage peak heights expected if the fractional labeling, α, were unity (F_0 for m/e 52, F_1 for m/e 53, and F_2 for m/e 54) are related to the normalized peak heights through the equations: 54% peak height = $\alpha^2 F_2$, 53% peak height = $F_1 + 2\alpha(1 - \alpha)\ F_2$, and 52% peak height = $F_0 + (1 - \alpha)\ F_1 + (1 - \alpha)^2\ F_2$ where is the fraction of labeling. The peaks at m/e 28, 29, and 30 were used with a similar procedure for nitrogen. Since no doubly labeled N_2O was found, the N_2O percentage peak heights were simply proportional to α. Table III shows the peak percentages corrected to 100% label. The table shows that the $(CN)_2$ is nearly all doubly labeled, that the N_2 is mostly all unlabeled, and that the N_2O is mostly labeled on the terminal nitrogen. (No m/e 31 peak corresponding to $^{15}NO^+$ was ever observed in the N_2O spectrum.) Tables II and III both list the characteristic parent peaks for the nitrogen containing products of the decomposition. Other fragment peaks that were observed in the spectrum and were useful were those at m/e 12, 14, 15, and 16. Since no fragment peak was observed at m/e 31 the implication is that no label found its way to the nitrogen atom of NO. The percentages of unlabeled (m/e 44) N_2O and singly labeled (m/e 29) N_2 are not quite equal to one another. The errors for the N_2 envelope are the largest among the peaks measured since two peaks were (28-CO and 30-NO) were being corrected for the presence of gases other than N_2.

Table I. Distribution of products from the decomposition of ONCN.

Pressure of ONCN in mmHg	mmol ONCN	mmol N_2	mmol N_2O	mmol CO_2	mmol $(CN)_2$	mmol NO	mmol CO
1	0.027	0.008	0.006	0.007	0.010	0.006	
7	0.021	0.006	0.005	0.006	0.008	0.003	
24	0.0611	0.0207	0.0205	0.0202	0.0201	trace	
27	0.080	0.029	0.027	0.027	0.027	trace	trace
33	0.098	0.033	0.032	0.032	0.034	trace	trace
64	0.173	0.058	0.057	0.058	0.058	---	trace
156	0.464	0.167	0.166	0.165	0.170	---	trace
201	0.598	0.225	0.223	0.218	0.231	---	~0.002

Table II. Peak heights, percentage peak heights and mmol of decomposition products from decomposition of nitrogen 15 labeled ONCN.

mmol ONCN	mmol $(CN)_2$	Peak Height/ % Peak Height 54	53	52	mmol N_2O	Peak Height/ % Peak Height 45	44	mmol N_2	Peak Height/ % Peak Height 28	29	30	mmol** NO	mmol* CO	mmol CO_2	
0.0595	0.0190	49.9/53.6	35/37.6	8.1/8.7	0.0193	57.8/67.3	28.1/32.7	0.0197	31.0/74.9	10.4/25.1	6.5/--	0.0003	0.0008	0.0190	1
0.0832	0.0275	29.4/60.3	17.0/35.0	2.2/4.5	0.0274	77.1/65.2	41.2/34.8	0.0279	59.9/64.6	32.8/35.4	-2.35/--	0.0002	0.0004	0.0278	2
0.0487	0.0160	30.6/58.7	19.0/36.5	2.4/4.6	0.0160	57.2/61.1	36.5/38.9	0.0161	88.7/75.6	27.4/24.4	-0.85/--	0.0008	0.0004	0.0162	3
0.0779	0.0250	12.5/59.0	7.8/36.8	0.9/4.2	0.0257	134.0/68.4	62.0/31.6	0.0256	95.0/62.6	56.8/37.4	-2.34/--	0.0004	0.0006	0.0250	4

*CO was determined from the ratio of m/e 12 to m/e 28 known for pure CO. This ratio and the height of the m/e 12 peak in the non-condensible gas mixture allowed us to calculate the portion of the m/e 28 due to CO.

**NO was determined from the known m/e 16 to 30 ratio in pure NO. The m/e 16 peak heights was first corrected for the contribution from CO.

Table III. Peak percentages normalized to 100% label for the decomposition of ONC^{15}N.

	$(CN)_2$ Normalized Percentages			N_2 Normalized Peak Percentages		N_2O Normalized Peak Percentages	
	54	53	52	28	29	45	44
1	84.8	10.0	3.1	68.4	31.6	84.7	15.3
2	95.4	4.9	-0.5	55.5	44.5	82.0	18.0
3	92.9	7.8	-0.9	69.3	30.7	76.9	23.1
4	93.4	8.0	-6.0	53.0	47.0	86.0	14.0

IV. DISCUSSION

Nitrosyl cyanide is a blue gas (λ_{max} = 738 nm, ε = 14.97 l/mol cm) which melts at -108°,[5] has a vapor pressure of 5 mmHg at -95, and is moderately difficult to prepare pure. The mass spectrum of ONCN does not contain a molecular parent ion when the ionizing electrons have energies of 70 or 50 eV. Large peaks at m/e 30 (NO^+) and m/e 26 (CN^+) are the characteristic peaks observed. The ESCA spectrum obtained with Mg $K_{1,2}$ X-rays does contain two nitrogen peaks (cyanide nitrogen at 407.12 eV, nitrosyl nitrogen at 410.91 eV). The oxygen peak is at 543.29 eV and the carbon peak is at 294.38 eV. All of these binding energies are for the 1s levels of each atom. There was some evidence of decomposition of the ONCN during the data collection, because a small peak in the nitrogen region grew in with time and because the storage vessel had pale yellow solid in it after the spectrum was recorded.

Nitrosyl cyanide decomposes at 75° in the absence of light at pressures less than about 1/10 atm according to: $3\ ONCN \rightarrow N_2 + N_2O + CO_2 + (CN)_2$. The decomposition has the same stoichiometry at room temperature but the rate of reaction is small. At the lowest pressures studied significant fractions of NO and increase in $(CN)_2$ are found. At high pressures solid non-volatile products are formed, and we did not pursue high pressure studies. The reactions were studied in the dark, since it was found that light greatly altered and complicated the decomposition reaction. The products formed when ONCN decomposed in the light were: N_2, N_2O, NO, NO_2, $(CN)_2$, CO, CO_2. Since the intensity of light and its frequency cause changes in the mixture of products, we studied only decompositions in the dark.

The following mechanism fits the stoichiometric observations:

$$1\left\{\begin{array}{l} 2\ ONCN \rightarrow 2\ NO + (CN)_2 \\ ONCN + NO \rightarrow ONC + N_2O \\ NO + ONC \rightarrow CO_2 + N_2 \end{array}\right.$$

Other mechanisms also describe the stoichiometry. For example:

$$2\left\{\begin{array}{l} 2\ ONCN \rightarrow 2\ NO + (CN)_2 \\ ONCN + NO \rightarrow NCN + NO_2 \\ NCN + NO \rightarrow N_2O + 1/2(CN)_2 \\ NO_2 + 1/2(CN)_2 \rightarrow CO_2 + N_2 \end{array}\right.$$

or also:

$$3\left\{\begin{array}{l} N\ ONCN \rightarrow 2\ O + N_2 + (CN)_2 \\ O + ONCN \rightarrow N_2O + CO \\ CO + O \rightarrow CO_2 \end{array}\right.$$

or:

$$4\left\{\begin{array}{l} NO + ONCN \rightarrow NO_2 + NCN \\ NO_2 + ONCN \rightarrow N_2 + CO_2 + NO \\ NCN + ONCN \rightarrow N_2O + (CN)_2 \end{array}\right.$$

or

$$5\left\{\begin{array}{l} NO + ONCN \rightarrow OCN + N_2O \\ OCN + ONCN \rightarrow NO_2 + (CN)_2 \\ NO_2 + ONCN \rightarrow N_2 + CO_2 + NO \end{array}\right.$$

or finally:

$$6\left\{\begin{array}{l} ONCN \rightarrow NO + CN \\ NO + ONCN \rightarrow OCN + N_2O \\ NO + OCN \rightarrow NO_2 + CN \\ NO_2 + ONCN \rightarrow CO_2 + N_2 + NO \\ 2\ CN \rightarrow (CN)_2 \end{array}\right.$$

The species NCN in the second mechanism has been identified in NO_x-$(CN)_2$ flames[10] and in photochemical studies of N_3CN.[9] At 75°, however, we found NO_2 and $(CN)_2$ do not react. The labeling experiments are also inconsistent with this mechanism. It requires that half the N_2 be unlabeled and half be singly labeled, that the $(CN)_2$ be half doubly and half be singly labeled, and that the N_2O be half singly labeled and half unlabeled.

The third mechanism suggests that the addition of CO to nitrosyl cyanide would inhibit the formation of N_2O. Experimentally the addition of CO (10 to 1 CO to ONCN) did not affect the formation of N_2O. This mechanism implies that the N_2O should be all singly labeled and that the percentage of doubly labeled $(CN)_2$ should be equal to the percentage of unlabeled nitrogen.

The fourth mechanism implies that all of the N_2 should be singly labeled and that the $(CN)_2$ should be 1/2 doubly and 1/2 singly labeled. The N_2O should be 1/2 singly labeled and 1/2 unlabeled if this mechanism were correct. The experimental labeling data are not consistant with this mechanism.

The fifth mechanism requires that the $(CN)_2$ be 1/2 singly and 1/2 doubly labeled. Since the ONC intermediate can, in principle, be formed from abstraction of either a terminal nitrogen from the cyanide end of the molecule or from a four center reaction of NO and ONCN the N_2O may be either singly labeled or unlabeled. The N_2 arrising from this mechanism should be all singly labeled. The labeling data do not support this mechanism.

The sixth mechanism requires all of the N_2 to be unlabeled. It does not provide a route for the formation of the singly labeled N_2 which is observed as a product. The mechanism further implies that the percentages of doubly labeled $(CN)_2$ and unlabeled N_2O should be equal. This mechanism does not fit the observations.

The seventh mechanism requires the $(CN)_2$ to be all doubly labeled. The percentage of unlabeled N_2O should be equal to the percentage of singly labeled N_2. This last mechanism although it is consistent with the labeling and stoichiometry seems less plausible than the first mechanism because a large number of radical species are formed and must combine to achieve the overall reaction.

The first mechanism is consistent with all the observations without the formation of an unreasonable number of radical species. The fulminate intermediate the mechanism contains does not seem unreasonable since photochemical reactions of cyanogen have been carried out in which the spectrum of ONC has been observed.[11] It also seems possible that the ONC structure may rearrange, before reacting further, to the more stable OCN structure.

The $(CN)_2$ is almost all doubly labeled as the mechanism requires. The N_2O should be all doubly labeled if the terminal nitrogen of the cyanide group were abstracted by the NO. An alternate route to the formation of N_2O can occur by a four center reaction of NO and ONCN to give unlabeled N_2O and the labeled intermediate ONC. The labeled ONC can then give rise to singly labeled N_2 and unlabeled N_2O in equal amounts. The implication is the amount of singly labeled N_2 and N_2O should be the same. An alternate decomposition mechanism:

$$7\left\{\begin{array}{l}NO + ONCN \rightarrow N_2O + OCN \\ ONCN + OCN \rightarrow NO_2 + (CN)_2 \\ NO_2 + ONCN \rightarrow N_2 + CO_2 + NO\end{array}\right.$$

provides an explanation for the larger amounts of singly labeled $(CN)_2$ and N_2 which are found (Table 3) and not predicted by mechanism 1.

The addition of NO_2 to ONCN (in a 9.73 to 1 ratio) resulted in the formation of equimolar amounts of NO and N_2. Nitrogen dioxide (0.321 mmol) and nitrosyl cyanide (0.033 mmol) reacted in the dark for 4-1/2 days at 80°. The glass vessel was then cooled to -196°, opened, and the content Toepler-pumped through a -160° trap as the vessel warmed to room temperature. Nitric oxide and nitrogen (0.021 mmol total) were identified by the m/e 30 and m/e 28 peaks respectively. The ratio of the 28 to 30 peaks was 1.18 corresponding to 54.9% N_2 and 46% NO. The material in the -160° trap was allowed to warm, pass through a -130° trap and condense in a -196° trap. Carbon dioxide (0.010 mmol) and a trace (<0.001 mmol) N_2O were separated as previously described. The large amount of NO_2 was not separated from the small amount $(CN)_2$.

Labeled nitrosyl cyanide decomposed in the presence of NO_2 to give nitrogen that was all singly labeled. Labeled nitrosyl cyanide (0.013 mmol) decomposed in the presence of 0.400 mmol of NO_2 in 28.5 hr at 78° to yield 0.001 mmol of N_2. The vessel was cooled to -196° and the N_2 Toepler-pumped from the cold vessel. The m/e 29 and 28 peaks in mass spectrum of the N_2 were 116.5 and 51 units respectively corresponding to (corrected to 100% label as before) 87.5% N_2 singly labeled and 12.5% N_2 unlabeled. Traces of CO were also observed when the N_2 was toeplered from the cold vessel.

We may calculate the fraction of the decomposition of ONCN proceeding by mechanism 1 and the fraction proceeding by mechanism 2. The fraction proceeding by mechanism 1 plus the fraction proceeding by mechanims 2 is equal to 1, $f_1 + f_2 = 1$. Since the singly labeled nitrous oxide arises from the same reaction (NO + ONCN → OCN + N_2O) in both mechanisms, the fraction of singly labeled nitrous oxide may be a single variable; g. From the experimental fraction of singly labeled nitrous oxide (m/e 45 peak) in Table III we find g. We may then calculate the fraction of doubly labeled cyanogen, $f_{(CN)_2}^{**}$, and the fraction of unlabelec nitrogen, $f(N_2)$, that the interplay of these mechanism cause.

$$f_{(CN)_2}^{**} = f_4 + (1 - f_1)(1 - g)$$

$$= 1 - g + f_1 g$$

$$f_{(N_2)} = f_1 g$$

Table IV. The fraction of the reaction proceeding by mechanism 1, f_1 and the comparison of experimental and calculated doubly labeled $(CN)_2$ percentages.

	Exp $f^{**}_{(CN)_2}$	Calc $f^{**}_{(CN)_2}$	f_1
1	84.8	83.7	0.81
2	95.4	73.8	0.68
3	92.9	92.4	0.90
4	93.4	76.0	0.62

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APPENDIX

The $n \rightarrow \pi^*$ transition which causes ONCN to appear blue is common to a wide variety of nitrosyl containing compounds.[1] Although it is often difficult to unambiguously assign this transition, Table I lists the energies of some transitions thought to be $n \rightarrow \pi^*$ transitions for some compounds considered as a nitrosyl group bonded to various ligands.

The energies of these transitions are also tabulated relative to the $n \rightarrow \pi^*$ transition energy for HNO. The HNO transition is probably the most difficult to assign. The observed bands are broad and weak. Values from 2073Å to 7606Å have been reported.[2-4] To eliminate the uncertainty of the assignment of the $n \rightarrow \pi^*$ transition for HNO, we ignored the experimental values and choose a value which gave a best least squares fit to the rest of the data.

The equation $\Delta E(\text{transition}) = aF + bR$ was used to correlate the data. The values of F and R used as well as the equation itself appeared in a paper by Swain and Lupton.[21] The parameters a and b were determined by least squares. The standard deviation of the calculated value was 3,700 cm^{-1}. Generally those compounds in which the group bonded to the nitrosyl group is a good π aceptor exhibit the lowest energy transition. The calculated transitions do follow the general trends in the data. The errors are not only due to the difficulty in band assignments but also from a relatively small solvent shift. Not all the spectra were recorded in identical solvents.

Table I. $n \rightarrow \pi^*$ transition frequencies correlated with Swain and Luptons F and R values.

	$n \rightarrow \pi^*$ Energy cm^{-1}	ΔE (Relative to HNO) cm^{-1}	R	F	Calc ΔE cm^{-1}	Reference See Text
ONH		-0-	-0-	-0-		
ON NO_2	15,504	1445	0.155	1.109	34.7	5,6
ONOH	26,035	-9086	-0.643	0.487	-10,982	7
$ONCF_3$	14,440	2509	0.186	0.631	1532	8
ONF	32,154	-15,204	-0.336	0.708	-6704	9
ONCl	21.053	-4104	-0.161	0.690	-3960	10,11
ONBr	22,422	-5473	-0.176	0.727	-4271	12
ONϕ	13,115	3834	-0.088	0.139	-1657	13
ONCN	13,550	3399	0.184	0.847	1041	19,20
ONO $CH(CH_3)_2$	25,575	-8626	-0.724	0.488	-12,237	14
ONO CH_2CH_3	25,641	-8692	-0.444	0.363	-7640	15,17
$ONOCH_3$	25,940	-8991			-8613	15,17
$ONCH_3$	16,750	199	0.141	0.052	2070	16

a = 15470

b = -2130

Standard Deviation = 3660 cm^{-1}

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