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CHEMICAL AND PHYSICAL PROPERTIES OF NITRYL CHLORIDE

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THESIS

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ABSTRACT

Nitryl chloride ($ClNO_2$) and nitrosyl chloride (ClNO) are pollutants that have been detected in the lower atmosphere.[1] Interconnecting chemical reactions between the chlorine and nitrogen oxide cycles of the stratosphere may also produce these molecules.

Two methods for preparing $ClNO_2$[1,2] were evaluated, and experimental techniques for determining the purity of $ClNO_2$ were developed. The vapor pressure and mass spectrum for $ClNO_2$ and the ultraviolet absorption cross sections of $ClNO_2$ and ClNO were investigated. Preliminary results for the photochemical decomposition of $ClNO_2$ with 253.7 and 350.5 nm radiation are reported, and the energetically possible steps for photochemical dissociation of $ClNO_2$ are summarized.

Data involving the absorption cross sections and primary photochemical processes, such as those that we have studied, are needed as input for calculations modelling the chemistry of the stratosphere.[3] No data on the absorption cross sections of $ClNO_2$ have been previously reported.

1. F.Huillet and P. Urone, J. Gas Chromatog.,4,249(1966)
2. M.Volpe and H. Johnston, J. Amer. Chem. Soc.,78,3903 (1956).
3. R.Hampson, Jr., and D. Garvin, "Chemical Kinetic and Photochemical Data for Modelling Atmospheric Chemistry," NBS Tech. Note 866,National Bureau of Standards, Washington, D.C. (1975)

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ACKNOWLEDGEMENTS

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I. INTRODUCTION

This study was an investigation of some physical and chemical properties of nitryl chloride ($ClNO_2$). Convenient methods for the preparation and purification of the compound were found. A method for determining the purity of nitryl chloride was developed. The vapor pressure, mass spectrum, ultraviolet-visible absorption spectrum, and the photochemical decomposition of nitryl chloride were studied. The cross sections for the absorption of ultraviolet radiation by nitrosyl chloride (ClNO) were also investigated.

Both nitryl chloride and nitrosyl chloride are important molecules in atmospheric chemistry. In the lower atmosphere, nitryl chloride and nitrosyl chloride have been detected in the gaseous emissions of a chemical plant.[1] Nitrosyl chloride is also formed from reactions of nitrogen dioxide with salts.[2]

$$2NO_2 + NaCl \longrightarrow ClNO + NaNO_3 \qquad (1)$$

A possible mechanism by which nitryl chloride is formed in the lower atmosphere is:[3,4]

$$Cl + NO_2 + M \longrightarrow ClNO_2 + M \qquad (2)$$

M is any background molecule.

This mechanism requires the existence of chlorine atoms, a condition that exists at some industrial sites where nitrogen dioxide is also present. For example, the combustion of coal may produce nitryl chloride since coal contains chlorine.[5] Nitrogen oxides are evolved during the combustion of fossil fuels.

The formation of nitryl chloride in the lower atmosphere may also take place by the reactions listed below:

$$Cl_2 + 2NO_2 \rightleftharpoons 2ClNO_2 \qquad (3)$$

$$ClNO + NO_2 \rightleftharpoons ClNO_2 + NO \qquad (4)$$

$$ClNO + O_3 \longrightarrow ClNO_2 + O_2 \qquad (5)$$

The principal sources of chlorine molecules are the emissions from industry and sodium chloride which is released into the atmosphere over the oceans and converted into chlorine by an unknown mechanism.[5] The equilibrium between chlorine and nitrogen dioxide (3) will be discussed in Chapter IV of this thesis. Reaction (4) has been studied and will be discussed later in this section. Ozone, which is a reactant in reaction (5), is produced in the lower atmosphere by the discharges from high voltage lines. Both ozone and nitrogen dioxide are pollutants that are monitored throughout the U.S.

Currently, there is much interest in the gas-phase reactions involving stratospheric pollutants that are capable of reducing the earth's ozone shield.[6-11] As reviewed below, chemical species coming from pollutants may react to produce nitryl chloride and nitrosyl chloride and thus, knowledge of their physical and chemical properties is an important part of atmospheric studies.

Chapman,[12] in 1930, described the following reactions as the principal ones occurring in the ozone belt. These reactions are referred to as the ozone cycle.

$$O_2 + h\nu \longrightarrow 2O \qquad (6)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (7)$$

$$O_3 + h\nu \longrightarrow O_2 + O \qquad (8)$$

$$O + O_3 \longrightarrow 2O_2 \qquad (9)$$

The present ozone distribution cannot be explained on the basis of this mechanism alone, and at least two additional cycles are required, the NO_x and the ClO_x cycles.

The NO_x cycle surfaced during the controversy surrounding the proposed building of a U.S. supersonic transport fleet (SST's). SST's emit nitrogen oxides into the stratosphere,[11] and these nitrogen oxides can catalytically reduce the ozone concentration according to the following reactions.[10, 11, 13]

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (10)$$

$$NO_2 + O \longrightarrow NO + O_2 \qquad (11)$$

$$NO_2 + h\nu \longrightarrow NO + O \qquad (12)$$

The major source of chlorine-containing species in the stratosphere comes from the upward diffusion from the earth of compounds containing chlorine, such as the freons (CF_2Cl_2 and $CFCl_3$), which are mainly used as propellants in aerosol cans and refrigerants in cooling systems.

Chlorine atoms are primarily produced from the photochemical dissociation of these freons with solar radiation.

$$CF_2Cl_2 + h\nu \longrightarrow 2Cl + CF_2 \qquad (13)$$

$$CF_2Cl_2 + h\nu \longrightarrow Cl + CF_2Cl \qquad (14)$$

$$CFCl_3 + h\nu \longrightarrow 2Cl + CFCl \qquad (15)$$

$$CFCl_3 + h\nu \longrightarrow Cl + CFCl_2 \qquad (16)$$

The chlorine atoms initiate a chain catalyzed destruction of ozone similar to the NO_x cycle.

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (17)$$

$$ClO + O \longrightarrow Cl + O_2 \qquad (18)$$

$$ClO + NO \longrightarrow Cl + NO_2 \qquad (19)$$

Nitryl chloride and nitrosyl chloride may be produced by interconnecting reactions between the above three atmospheric cycles. Some possible sources of these two compounds are listed below:

$$NO_2 + Cl + M \longrightarrow ClNO_2 + M \qquad (20)$$

$$ClNO + O_3 \longrightarrow ClNO_2 + O_2 \qquad (21)$$

$$2ClNO + ClO_2 \longrightarrow ClNO_2 + NO_2 + Cl_2 \qquad (22)$$

$$Cl + NO + M \longrightarrow ClNO + M \qquad (23)$$

$$ClNO_2 + NO \longrightarrow ClNO + NO_2 \qquad (24)$$

Clark and Clyne[3] and Clyne and White[4] have reported a "preliminary" value for the rate constant of reaction (20) at 25° C:

$k_{obs} = 7.2 \times 10^{-31}\ \mathrm{cm^6 molecule^{-2} sec^{-1}}$

Reaction (21) has been used as a method of preparation for nitryl chloride,[14] and nitryl chloride has been detected as a product from reaction (22).[15] Reaction (23) has been studied, using nitrogen, oxygen, and argon as the third body.[4] Freiling, Johnston, and Ogg[16] and Wilkins, Dodge, and Hisatune[17] studied reaction (24). The latter group confirmed the chlorine atom transfer to be:

$$NO + {}^{15}NO_2Cl \longrightarrow {}^{15}NO_2 + ClNO$$

with a rate constant of:

$k_{obs} = 2.34 \times 10^{-12} \exp(-6.89\mathrm{Kcal}/RT)\,\mathrm{cm^3 molecule^{-1} sec^{-1}}$

between 1 and 71° C.

Some reactions that would reduce the concentration of nitryl chloride and nitrosyl chloride include the following:

$$ClNO_2 + Cl \longrightarrow Cl_2 + NO_2 \qquad (25)$$

$$ClNO + Cl \longrightarrow Cl_2 + NO \qquad (26)$$

$$ClNO_2 + NO \longrightarrow ClNO + NO_2 \qquad (27)$$

$$ClNO_2 + h\nu \longrightarrow Cl + NO_2 \qquad (28)$$

$$ClNO_2 + h\nu \longrightarrow ClNO + O \qquad (29)$$

$$ClNO + h\nu \longrightarrow Cl + NO \qquad (30)$$

Other possible reactions would be those between nitryl chloride or nitrosyl chloride and O, H, OH, HO_2, and ClO radicals. Reactions (25) and (26) have been studied at 25° C and the "preferred" rate constants are:[3, 4]

$k_{obs} \gg 3 \times 10^{-14} cm^{-3} molecule^{-1} sec^{-1}$ and

$k_{obs} = 3.0 \times 10^{-11} cm^{-3} molecule^{-1} sec^{-1}$,

respectively.

The absorbance of ultraviolet radiation is important in reactions (28)-(30) and in determining the intensity of radiation that will reach the earth's surface. We have, therefore, studied the ultraviolet absorption cross sections of nitryl and nitrosyl chloride. These data will provide basic chemical information needed as input for calculations involving the modelling of atmospheric chemistry.

Preliminary data are also reported on the photochemical dissociation of nitryl chloride with 253.7 and 350.5 nm radiation. The photochemical decomposition of nitrosyl chloride has been studied by other investigators,[18, 19] and their results are reviewed in Chapter IV.

Nitrosyl chloride has appreciable absorption coefficients at long wavelengths and is rapidly dissociated to regenerate chlorine atoms by the intense solar radiation that exists at these wavelengths.[6]

II. HISTORICAL REVIEW OF NITRYL CHLORIDE

A. Methods of Preparation

Nitryl chloride was first prepared by the reaction between hydrochloric acid and nitrogen tetroxide by Richard Muller in 1862.[22] The compound was prepared by Odet and Vignon[21] in 1870 by passing phosphorous oxychloride vapors ($POCl_3$) over lead nitrate or silver nitrate and by Hassenberg[22] in 1871 by passing nitrogen dioxide and chlorine through a hot tube.

In 1886, Williams[23] and, in 1905, Gunthier and Lohman[24] repeated the experiments of Hassenberg and found no evidence for the formation of nitryl chloride. Geuther[25] also failed in 1888 to obtain nitryl chloride by dropping liquid nitrogen tetroxide onto cooled phosphorous pentachloride (PCl_5).

After these unsuccessful attempts, nitryl chloride was omitted from textbooks and handbooks.[26]

In 1929, however, Schumacher and Sprenger[14] prepared nitryl chloride by the reaction between ozone and nitrosyl chloride, and Dachlauer[27] reported synthesizing nitryl chloride by reacting chlorosulfonic acid ($ClSO_3H$) and anhydrous nitric acid at 0° C.

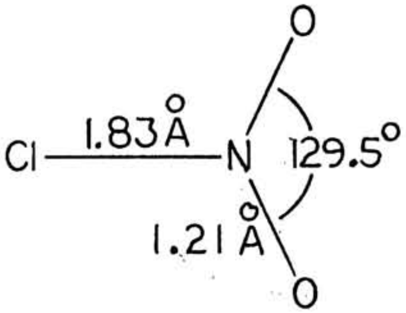
In 1932, Noyes[28] discovered nitryl chloride as one of the products from the gas phase reaction between nitrogen trichloride and nitrogen tetroxide. Wise and Volpe,[29] in

1953, prepared nitryl chloride by reacting hydrogen chloride with a fuming sulfuric acid and nitric acid mixture.

B. The Vibrational Spectrum of Nitryl Chloride

The infrared and Raman spectrum of nitryl chloride were first studied by Ryason and Wilson[30] and Dodd and Woodward.[31] Bernitt, Miller, and Hisatune[32] examined the infrared absorption spectra of isotopic nitrogen -14 and -15 species of nitryl chloride. The assignments for the fundamental modes of vibration by these three groups on the basis of a planar model with C_{2v} symmetry are not in agreement (Table 1). The C_{2v} symmetry was confirmed by Miller and Sinnott,[33] using the microwave absorption spectrum, and by Ray and Ogg,[34] using the nitrogen -14 nuclear magnetic resonance spectrum. The assignment of the types of molecular motion within the symmetry classes were assigned[30-32] (Table 1).

Clayton, Williams, and Weatherly[35] have reported the structural parameters of nitryl chloride as:



Structure of Nitryl Chloride

Table 1. Fundamental Vibrational Frequencies and Assignments of Nitryl Chloride

Assignment	Molecular Motion	Observed Frequency (cm^{-1})		
		Rayson & Wilson[30]	Dodd & Woodward[31]	Bernitt, Miller & Hisatune[32]
$A_1(\nu_1)$	symmetric stretch of NO_2	1293	1293	1267.1
$A_1(\nu_2)$	ONO bend	794	794	792.6
$A_2(\nu_2)$	Cl-N stretch	651	411	369.6
$B_1(\nu_4)$	antisymmetric stretch of NO_2	1685	1685	1684.6
$B_1(\nu_5)$	in plane Cl bend	367	367	408.1
$B_2(\nu_6)$	out of plane Cl bend	411	651	652.3

Arrows show the changes suggested by the latter authors.

Use of these parameters has resulted in the calculation of Urey-Bradley force constants for nitryl chloride.[32]

Bernitt, Miller, and Hisatune[32] recalculated the thermodynamic functions for nitryl chloride as an ideal gas on the basis of their observed absorption frequencies, Tables 2 and 3.

C. The Thermal Decomposition of Nitryl Chloride

A number of investigators[36-39] have studied the thermal decomposition of nitryl chloride and found it to be unimolecular and in accord with the Lindermann theory:

$$ClNO_2 + ClNO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ClNO_2 + ClNO_2^* \qquad (31)$$

$$ClNO_2^* \xrightarrow{k_2} NO_2 + Cl \qquad (32)$$

where $ClNO_2^*$ denotes the activated molecules. Using a steady-state treatment on $ClNO_2^*$, the rate of disappearance of nitryl chloride is determined to be

$$-d(ClNO_2)/dt = (k_2k_1(ClNO_2)^2)/(k_{-1}(ClNO_2) + k_2)$$

At high pressures, $k_{-1}\ (ClNO_2) > k_2$ and the rate of decomposition is limited by reaction (32). The rate law becomes first order at high pressures

$$-d(ClNO_2)/dt = (k_2k_1/k_{-1})(ClNO_2).$$

Table 2. Thermodynamic Function of $ClNO_2$(cal/deg-mole)[32]

T(°K)	C_p^0	$(H^0-H_0^0)/T$	$-(G^0-H_0^0)/T$	S^0
100	8.439	8.036	45.75	53.79
200	10.75	8.800	51.52	60.32
300	12.76	9.800	55.28	65.08
400	14.28	10.74	58.23	68.97
500	15.44	11.57	60.72	72.29
600	16.32	12.29	62.89	75.18
700	16.99	12.91	64.84	77.75
800	17.51	13.46	66.60	80.05
900	17.90	13.93	68.21	82.14
1000	18.22	14.34	69.70	84.04

Superscripts indicate standard pressure, and subscripts indicate the temperature.

Table 3. Some Thermodynamic Properties of Nitryl Chloride (kcal/mole)[32]

	$ClNO_2$
H^0_f (25° C)	3.39
G^0_f (25° C)	13.34
H^0_0 (NCl bond energy)	32.52
H^0_{298} (NCl bond energy)	33.54
H^0_0 (NO bond energy)	67.38
H^0_{298} (NO bond energy)	68.79

Superscripts indicate standard pressure, and subscripts indicate the temperature.

At low pressures, $k_{-1}(ClNO_2) \ll k_2$ because the rate depends upon the rate at which the activated molecules are produced. The rate law then becomes

$$-d(ClNO_2)/dt = k_1(ClNO_2)^2$$

and the rate is second order.

This unimolecular decomposition has been reported to be within its second-order region below 5 torr.[36] The observed rate of decomposition was proposed to be twice that of the elementary unimolecular decomposition due to the reaction of chlorine produced in reaction (32) with nitryl chloride:

$$ClNO_2 + Cl \longrightarrow NO_2 + Cl_2 \qquad (33)$$

By studying the temperature dependency of the rate constant for the thermal decomposition of nitryl chloride, Cordes and Johnson[38] reported

$$k_{obs} = 9.6 \times 10^{-8}\ cm^3 molecule^{-1} sec^{-1} \exp(-27500\ cal/RT)$$

over the temperature range of 100-250° C for the second-order rate constant.

D. Some Inorganic Reactions with Nitryl Chloride

Batey and Sisler [40] (1952) studied the reaction of nitryl chloride with some metals, some Lewis acids, and ammonia. Zinc, mercury, and bismuth showed evidence of reaction with nitryl chloride by giving positive tests for the metal cations, and the nitrite and chloride. The reactions that occur were reported as probably being:

$$2Zn + 2ClNO_2 \longrightarrow ZnCl_2 + Zn(NO_2)_2 \qquad (34)$$

$$2Bi + 3ClNO_2 \longrightarrow BiCl_3 + Bi(NO_2)_3 \qquad (35)$$

$$2Hg + 2ClNO_2 \longrightarrow HgCl_2 + Hg(NO_2)_2 \qquad (36)$$

$$4Hg + 2ClNO_2 \longrightarrow Hg_2Cl_2 + Hg(NO_2)_2 \qquad (37)$$

Copper, magnesium, iron, aluminum, and tin showed no evidence for reaction with nitryl chloride.

There was also no evidence for a reaction between nitryl chloride and the metals (M) such as:

$$2ClNO_2 + M \longrightarrow MCl_2 + N_2O_4 \qquad (38)$$

or $$2ClNO_2 + M \longrightarrow M(NO_2)_2 + Cl_2 \qquad (39)$$

which involve the displacement of nitrogen dioxide or chlorine.

Oxidation and reduction reactions occurred between nitryl chloride and the Lewis acids studied. Nitryl chloride acts as an oxidizing agent by losing oxygen and forming nitrosyl chloride or losing chlorine and forming nitrogen dioxide.

Batey and Sisler[40] reported that nitryl chloride produces chloramine and ammonium nitrate upon reaction with ammonia at low temperatures, suggesting that nitryl chloride gives positive chloride and negative nitrate ions.

Paul, Singh, and Malhatra[41] (1969) reported that cryoscopic, conductance, Raman, and infrared studies of solutions of nitryl chloride in disulfuric acid confirm that nitryl chloride produces nitronium ions (NO_2+) and not positive chlorine ions. Infrared and Raman studies of some complexes of nitryl chloride, with some strong electron acceptors and with some organic tertiary bases, also show the presence of nitronium ions. The authors suggest that the polarity of the nitrogen-to-chlorine bond in nitryl chloride is less polar than in nitrosyl chloride; however, the chlorine atom retains a negative charge and is not positive, as was previously reported.

Nitryl chloride is readily decomposed by water:[42]

$$ClNO_2 + H_2O \rightleftharpoons HNO_3 + HCl \qquad (40)$$

The products of this reaction also suggest that the chlorine is negative.

III. EXPERIMENTAL

A. Instrumentation

A Perkin-Elmer 621 spectrophotometer, equipped with a Beckman Automatic airdryer, was used to measure infrared absorptions, and a Perkin-Elmer 450 spectrophotometer was used to determine ultraviolet absorptions. The 450 was purged with nitrogen gas when wavelengths below 200 nm were studied. The resolution of the infrared spectrophotometer at 1000 cm^{-1} is 0.5 cm^{-1}, and the wavelength accuracy is 0.5 cm^{-1}.[43] The transmittance accuracy of the ultraviolet spectrophotometer is ± 0.5% of the full-scale, with wavelength accuracy of 0.9 nm at 400 nm and 0.1 nm at 200 nm on the chart. The resolution of the instrument is as listed:[44]

Separation	Wavelength
0.5	600
0.1	250
0.03	175

The 100% transmittance baselines were always adjusted and taken with the evacuated cells in place for both instruments, and the ultraviolet absorption measurements were all made between absorbances of 0.8 to 0.2 (15 to 65% transmittance). In this region, the percent relative error found by setting the second derivative of Beer's Law equal to zero is below 4%.[45] The instrument settings used for both instruments are shown in Tables 4a and 4b.

Table 4. Spectrophotometer Instrument Settings

a. Infrared Spectrophotometer

Instrument Control	Setting
Scale	Change
Mode	Transmittance
Source	0.8 amps
Gain	5
Slit program	1000
Attenuator	1100
Scan time	12
Suppression	5

b. Ultraviolet Spectrophotometer

Instrument Control	Setting
Mode	Transmittance
Resolution	2.5
Speed	1.8
Response time	1
Slit width	Program

A Consolidated Electrodynamics Corporation 21-104 mass spectrometer was used at the following conditions:

background pressure	7×10^{-7} torr
sample pressure	$1 - 1.2 \times 10^{-6}$ torr
ionization voltage	70 eV
accelerating voltage scan	3600-800 volts
magnet current	4-6 amps
anode current	10 microamps
slit	15 mils
scan speed	10
block temperature	175° C

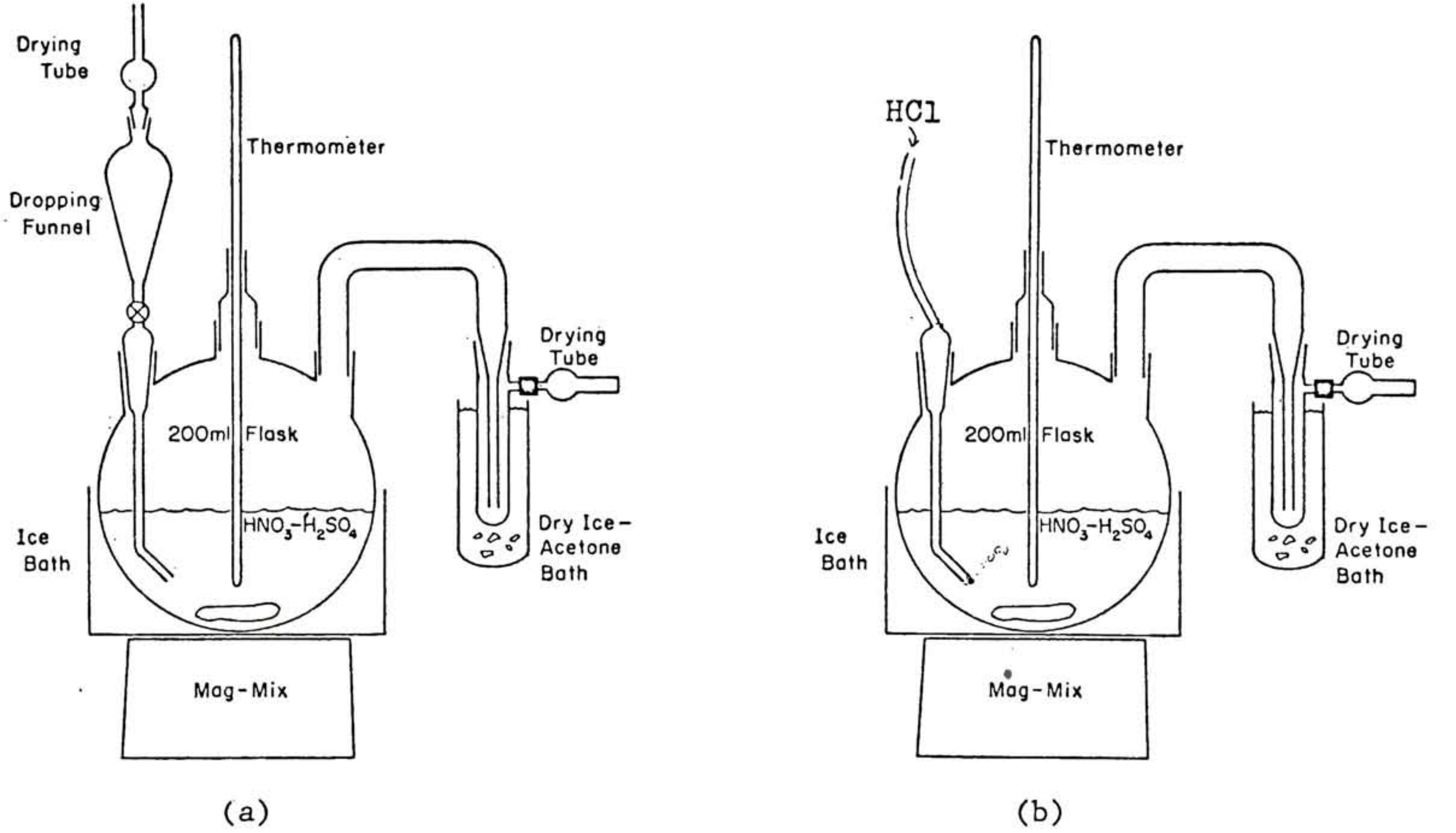
The samples were introduced as gases into a Pyrex vacuum line, equipped with Teflon greaseless stopcocks, at a pressure between 20 and 300 torr. The samples were then introduced into the mass spectrometer through a gold leak. The pressure of the sample in the vacuum inlet system was monitored with a Consolidated Vacuum Corporation thermocouple gauge, while the pressure in the analyzer was measured with a Granville-Phillips Company model 274-12P ion gauge.

Nitryl chloride was photolyzed with a Rayonet Photochemical Chamber Reactor, model RPR-100, at 350.0 and 253.7 nm. A sample holder was constructed from aluminum rod, which enabled the placement of the ultraviolet cells in the center of the chamber. The Photochemical Reactor was operated with the cooling fan on.

B. Synthesis of Nitryl Chloride

Two methods were used to prepare nitryl chloride. The first was a modification of the Dachlauer method.[1] Forty-five grams of chlorosulfonic acid (Eastman Kodak reagent grade) were added from a constant addition funnel to a mixture of 125 grams of 30% fuming sulfuric acid and 61 grams of 20% fuming nitric acid over a three-hour period. The acid mixture was maintained at 0° C and vigorously stirred. The apparatus (Figure 1a) was protected from atmospheric moisture with calcium chloride because of the hydrophilic nature of the acid mixture. The nitryl chloride that evolved was trapped at -77° C by using a dry ice-acetone bath. The nitryl chloride prepared by this method contained approximately 10% chlorine, which could not be removed by bulb-to-bulb distillations from -77° C to -196° C, in which both the first and last portions of the distillate were discarded. The methods used to determine the purity of nitryl chloride are described in Section E of this Chapter.

The second method used was a modification from that suggested by Volpe and Johnston[36] and produced nitryl chloride that was purer than that prepared by the modified Dachlauer method.



(a) (b)

Figure 1. Apparatus used in the Preparation of Nitryl Chloride

a) Reaction of the Acid Mixture with Chlorosulfonic Acid

b) Reaction of the Acid Mixture with Hydrogen Chloride

A mixture containing

75 ml of 20% fuming sulfuric acid
75 ml of 98% sulfuric acid
10 ml of 20% fuming nitric acid
and 40 ml of 69% nitric acid

was prepared in a 250 ml, three-necked flask at 0° C. A fine stream of hydrogen chloride (M. G. Scientific) was bubbled through the acid mixture through a porous glass bubbler while the mixture was vigorously stirred with a magnetic stirring bar at 0° C. The nitryl chloride was trapped in a tube maintained at -77° C. The apparatus used is shown in Figure 1b and was also protected from water with calcium chloride.

According to Volpe and Johnston,[36] the preparation of nitryl chloride takes place by the reactions:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (41)$$

$$NO_2^+ + HSO_4^- + HCl \rightleftharpoons ClNO_2 + H_2SO_4 \qquad (42)$$

while chlorine may be produced by:

$$NO_2^+ + HSO_4^- + 2HCl \longrightarrow Cl_2 + NOHSO_4 + H_2O \qquad (43)$$

and nitrosyl chloride by:

$$NOHSO_4 + HCl \longrightarrow ClNO + H_2SO_4 \qquad (44)$$

The product collected by this method of preparation contained less than 0.1% nitrosyl chloride and very little chlorine (see Section E of this chapter). This synthesis was used to produce all the nitryl chloride reported on in the results section of this thesis.

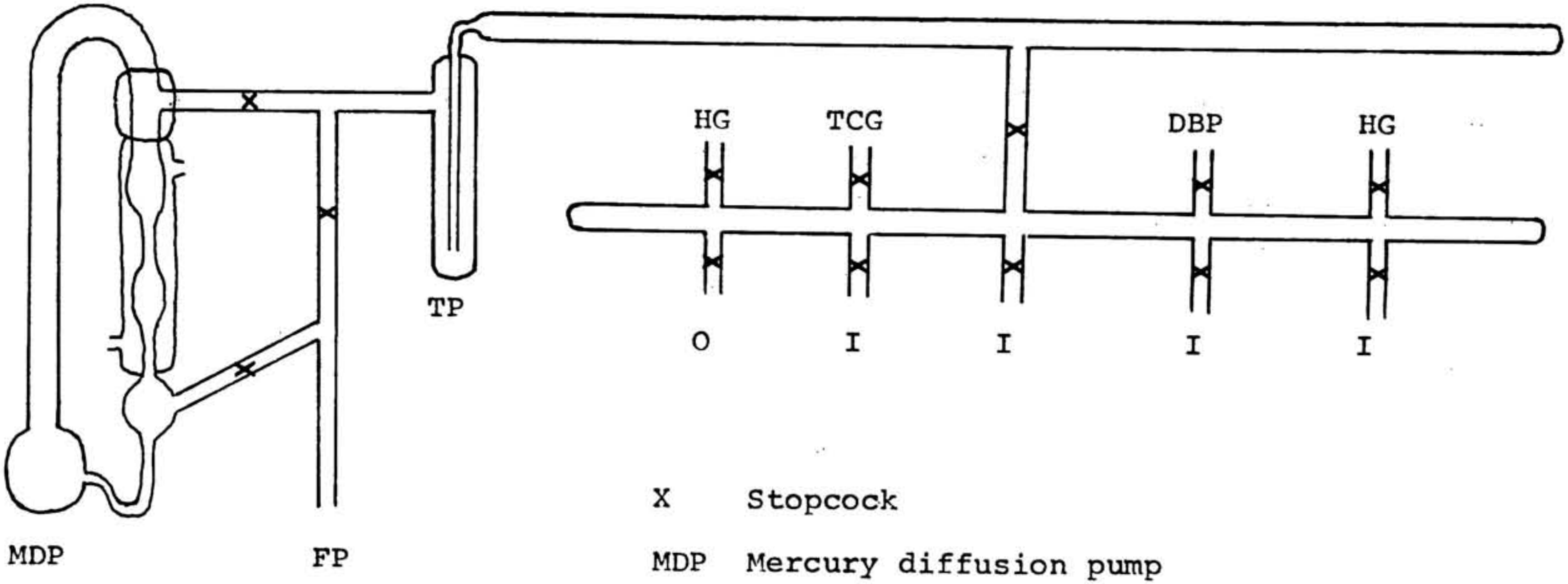
C. Sample Handling

1. The Vacuum Line

The nitryl chloride was handled on a Pyrex vacuum line, diagramed in Figure 2. The vacuum line had a three-stage mercury diffusion pump, separated from the manifold by a trap cooled with liquid nitrogen, which protected the manifold from mercury vapors. All the stopcocks were glass vacuum or greaseless Teflon (vacuum) stopcocks. All the connections between the vacuum manifold and the sample handling bulbs and gas cells were made through glass standard taper joints. The glass vacuum stopcocks were greased with Dow Corning silicon high-vacuum grease, as were the viton "O" rings on the greaseless stopcocks.

2. Pressure Measurements

A Bendix GTC-360 thermocouple gauge was used for leak detection and for determining the extent of the vacuum attainable in the manifold. The glass-to-metal seal for the sensing head was made through a $\frac{1}{4}$-inch brass Cajon fitting. The useful range of the thermocouple gauge was 1 torr to 10^{-3} torr for air. The gauge was not used for the measurement of gas pressures because of the need for



X	Stopcock
MDP	Mercury diffusion pump
FP	Mechanical fore pump
HG	Mercury manometer
TCG	Thermocouple gauge sensor
DBP	Dibutylphthalate manometer
O	Outer standard taper joint
I	Inner standard taper joint
TP	Trap

Figure 2. Vacuum Line

calibration with each different gas; however, the gauge was used to insure that the pressure in the manifold was below 10^{-3} torr before sample manipulation.

All other pressure measurements were taken with a dibutylphthalate manometer or a mercury manometer in which the mercury was covered with six inches of dibutylphthalate to prevent reaction between the gases and the mercury. The mercury manometer was of the open-end type, while the dibutylphthalate manometer was referenced against a vacuum. The manometers were connected to the vacuum line with thick-walled tygon tubing or with conventional vacuum rubber tubing.

All pressure measurements in this thesis are stated in torr (millimeters of mercury). The conversion from mm of dibutylphthalate (DBP) to torr was calculated from the density ratio[46] of dibutylphthalate and mercury.

$$\text{torr} = \text{mm DBP}\ \left(\frac{1.047\ \text{g/ml}}{13.534\ \text{g/ml}}\right)$$

3. Spectrophotometer Gas Cells

Infrared and ultraviolet gas cells were made from 15/16-inch o. d. Pyrex tubing, onto which greaseless stopcocks and glass standard taper joints were glass-blown (Figure 3). The ends of the Pyrex tubing were cut to the desired length and sanded flush on a flat surface to prevent cracking and to ensure a good fit with the windows,

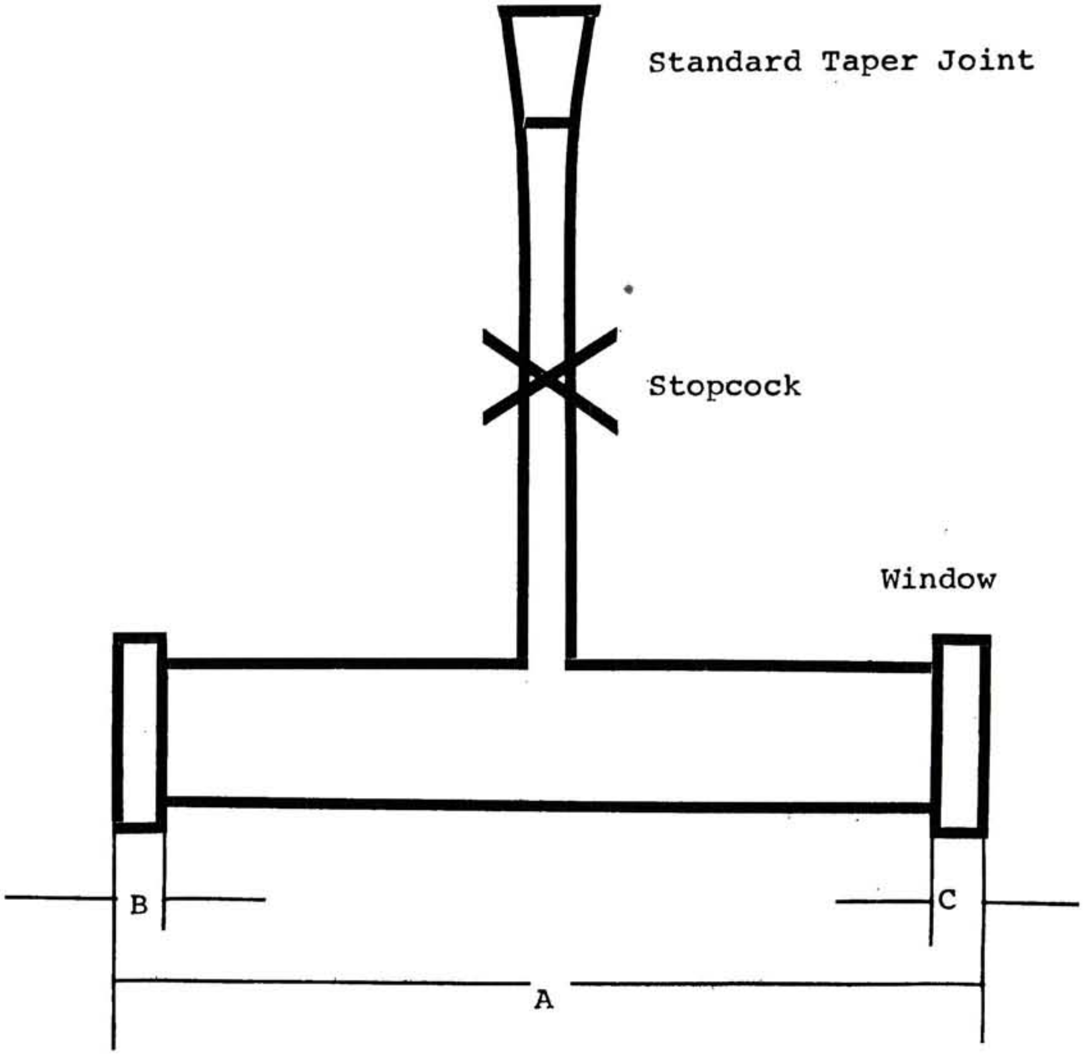


Figure 3. Diagram of gas Spectrophotometer Cells, Path Length = A-B-C.

which were attached with epoxy cement.

Before the windows were attached, their thickness was measured to ± 0.01 cm. They were then glued onto the Pyrex tubing, the length of the entire assembly was measured, enabling the calculation of the path length by subtracting the thickness of the windows with a possible error of ± 0.03 cm.

Two 10-cm path length infrared cells were made. One of these had a small Pyrex test tube glass-blown onto the body of the cell in order to carry out quantitative transfers by using liquid nitrogen to cool the test tube. Both sodium chloride and potassium bromide windows were used. In addition, two 4-cm ultraviolet cells were made with quartz Suprasil-2 windows. Commercially available one- (± 0.01) and two- (± 0.01) cm path length cells with Suprasil windows and a 99.99- (± 0.01) mm path length cell with sapphire windows were also used to make ultraviolet absorption measurements. A wooden cell holder was made for the ultraviolet cells in order to obtain reproducible placement of the cells in the spectrophotometer.

Two 250 ml bulbs and one 500 ml bulb were prepared with greaseless stopcocks and glass standard taper joints for use in sample mixing and handling.

D. Purification of Samples

The nitryl chloride produced from the synthesis and all the other gases used from lecture bottles were degassed at liquid nitrogen temperature (-196° C) on the vacuum line.

The samples were then isolated from the vacuum line by closing the stopcock; they were liquified, refrozen, and degassed again. This process was repeated until there was no deflection on the thermocouple gauge.

The nitryl chloride was always distilled by bulb-to-bulb distillations from -77° C to -196° C after it was degassed, and the first and last portions (approximately 1/8 of the sample) of each distillation were discarded. The distillations were continued until the infrared spectra showed no impurity absorptions; two distillations proved to be sufficient for the samples prepared by the Volpe and Johnston[36] method. After the distillations, the sample was pumped on at dry-ice acetone temperature (-77° C) in order to remove any remaining chlorine.

Nitrosyl chloride (Matheson Gas 97% minimum purity) was degassed and distilled twice from -77° C to -196° C; it was then used without further purification. Thermal decomposition of nitrosyl chloride at 25° C in our experiments is shown to be negligible in Appendix I.

Nitrogen dioxide (M. G. Scientific Gases), which was contaminated with nitric oxide, as indicated by the blue color of the solid, was purified by cooling to -77° C, whereupon it was pumped on directly until the pressure dropped to 10^{-2} torr (at -77° C, nitrogen dioxide is a solid and nitric acid is a liquid).[46] The sample was then isolated, liquified, cooled, and pumped on again. This purification procedure was repeated until the solid nitrogen dioxide was a pure white color and the liquid was a yellow-brown color with no traces of green.

All other gases used were simply degassed and used with no further purification.

E. Determination of the Purity of Nitryl Chloride

Nitrosyl chloride, nitrogen dioxide, chlorine, and hydrogen chloride are all possible impurities in the nitryl chloride produced. Hydrogen chloride boils at -84° C,[46] and is not trapped out along with the nitryl chloride at -77° C. Nitrogen dioxide, chlorine, and nitrosyl chloride were found in some of our earlier work, when the Dachlauer method was used to prepare nitryl chloride. These compounds were therefore further characterized in order to determine the nitryl chloride purity.

Nitrosyl chloride and nitrogen dioxide were both determined by infrared spectrophotometry. The infrared spectrum of nitrosyl chloride (Figure 4) and nitrogen dioxide (Figure 5) are in agreement with that reported by Burns and Bernstein[47] and Nakamoto.[48] The infrared spectra of nitrosyl chloride and nitrogen dioxide were taken

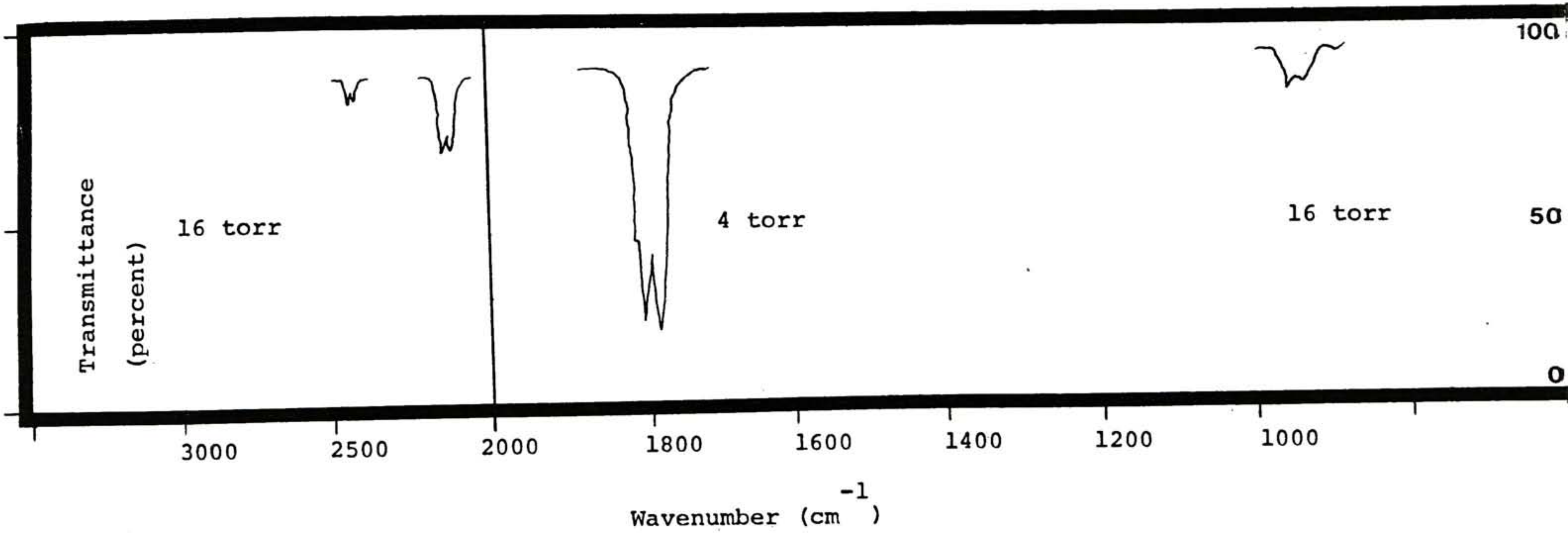


Figure 4. Infrared Spectrum of Nitrosyl Chloride

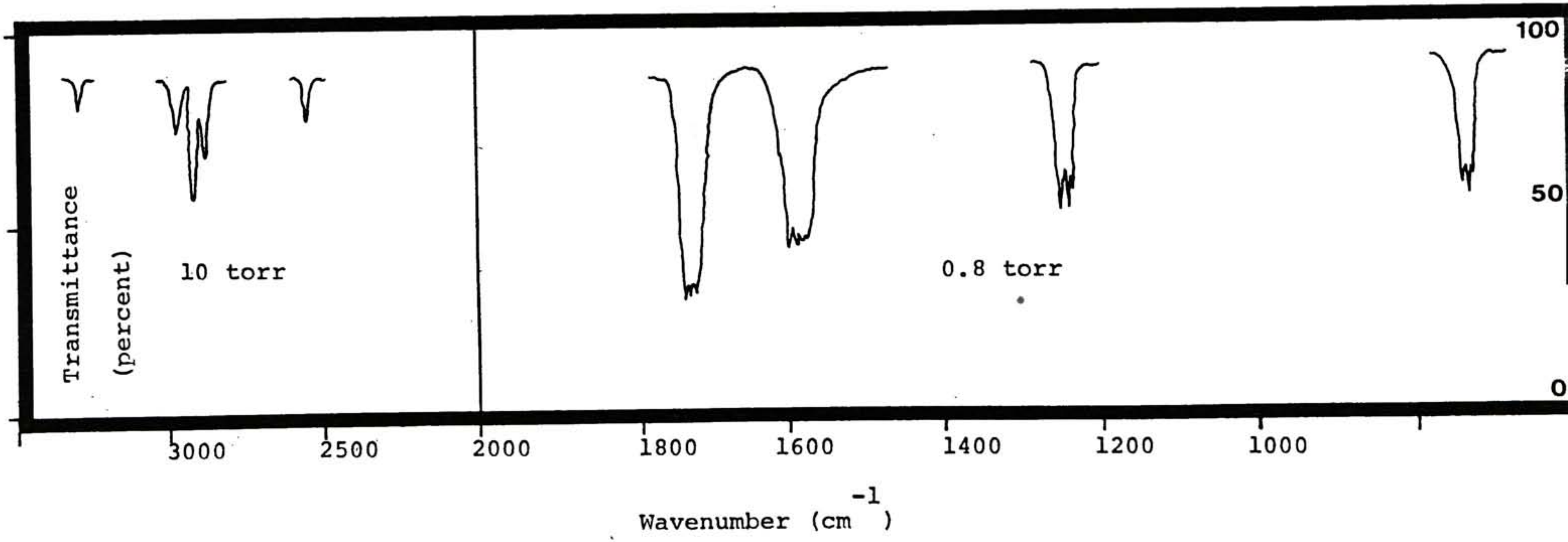


Figure 5. Infrared Spectrum of Nitrogen Dioxide / Nitrogen Tetroxide

at various pressures in order to prepare Beer's Law calibration curves. The infrared absorption data are presented in Tables 5 and 6.

Table 5. Infrared Data for Nitrosyl Chloride*

Pressure (torr)	Absorbance
0.04	0.15
1.90	0.561
2.44	0.696
0.70	0.22
1.00	0.319
1.59	0.457

*absorption at 1785 cm^{-1}

Table 6. Infrared Data for Nitrogen Dioxide/Nitrogen Tetroxide*

Pressure (torr)**	Absorbance
2.1	0.085
3.7	0.128
6.9	0.191
11.0	0.308
15.0	0.415
26.1	0.717
49.2	0.969

*absorption at 1600 cm^{-1} (NO_2)

**total pressure of NO_2/N_2O_4 mixture

Figures 6 and 7 show that data follow Beer's Law as determined by a linear regression and the coefficient of determination (r^2):

$$r^2 = \frac{((x-\bar{x})(y-\bar{y}))^2}{((x-\bar{x})^2(y-\bar{y})^2)}$$

The coefficient of determination is a value between zero and one. When $r^2 = 0$, there is no fit to the data, and when $r^2 = 1$, there is a perfect fit.

By using these data and spectra taken of nitryl chloride at 20 torr, less than 0.1% nitrosyl chloride and 2.0% nitrogen dioxide/nitrogen tetroxide could be detected. (See Appendix II for the treatment of the $N_2O_4 \longleftrightarrow 2NO_2$ equilibrium.) Infrared spectra over the pressure range 20 to 60 torr were taken for all nitryl chloride samples to insure their purity with respect to nitrogen dioxide/nitrogen textroxide and nitrosyl chloride.

Chlorine proved to be a more troublesome impurity to detect, since it does not have a dipole moment and therefore may not be detected by infrared spectroscopy. By using ultraviolet spectroscopy, it was only possible to set a maximum limit on the percent chlorine that could be present in the nitryl chloride samples, since both chlorine and nitryl chloride absorb in the ultraviolet region of interest. The absorption maximum of chlorine appears at 330 nm, with an extinction coefficient of 66 liters/

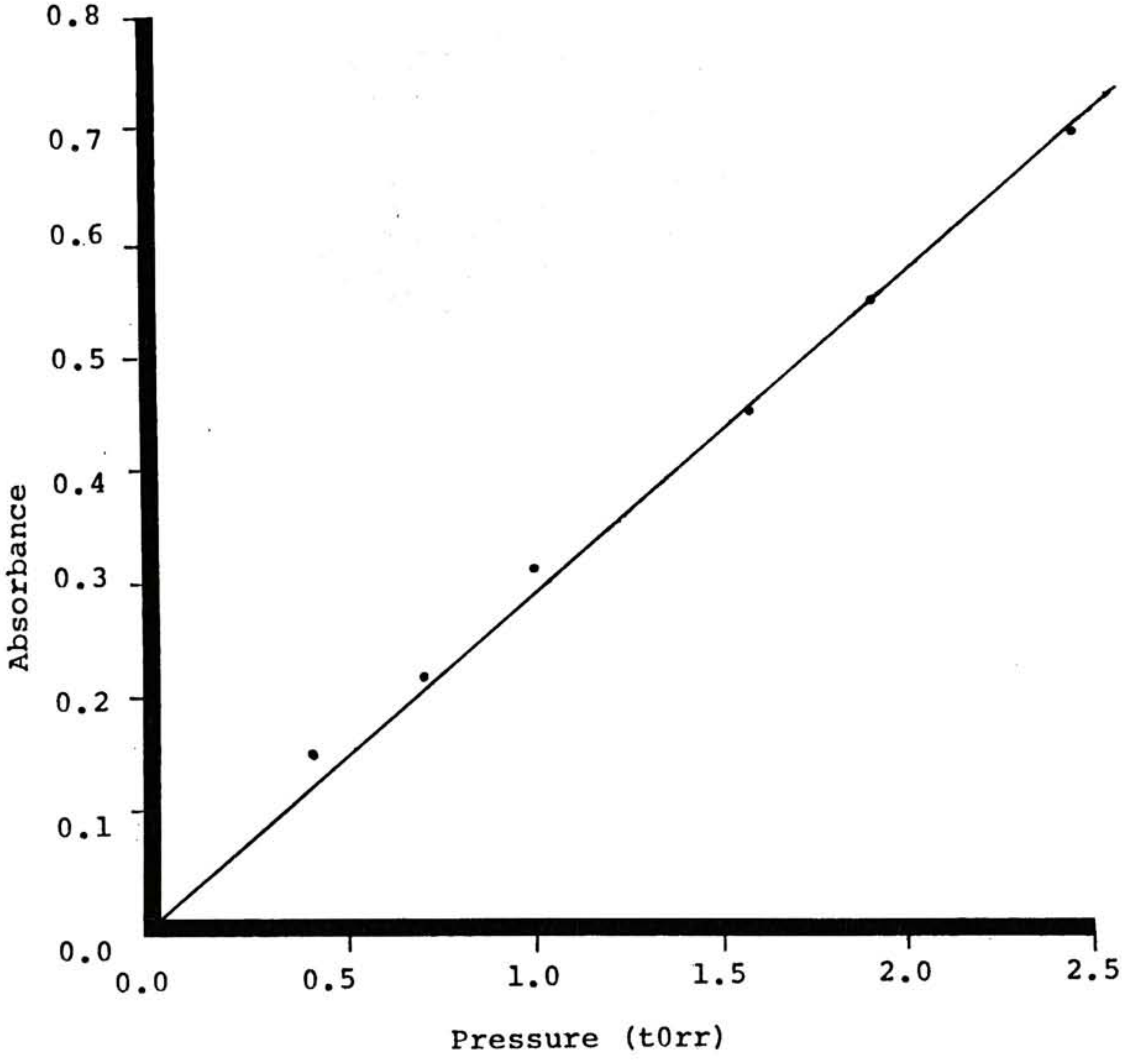


Figure 6. Beer's law plot for the 1785cm^{-1} absorption band of nitrosyl chloride.

coefficient of determination = 0.996

intercept = 0.016

slope = 0.280

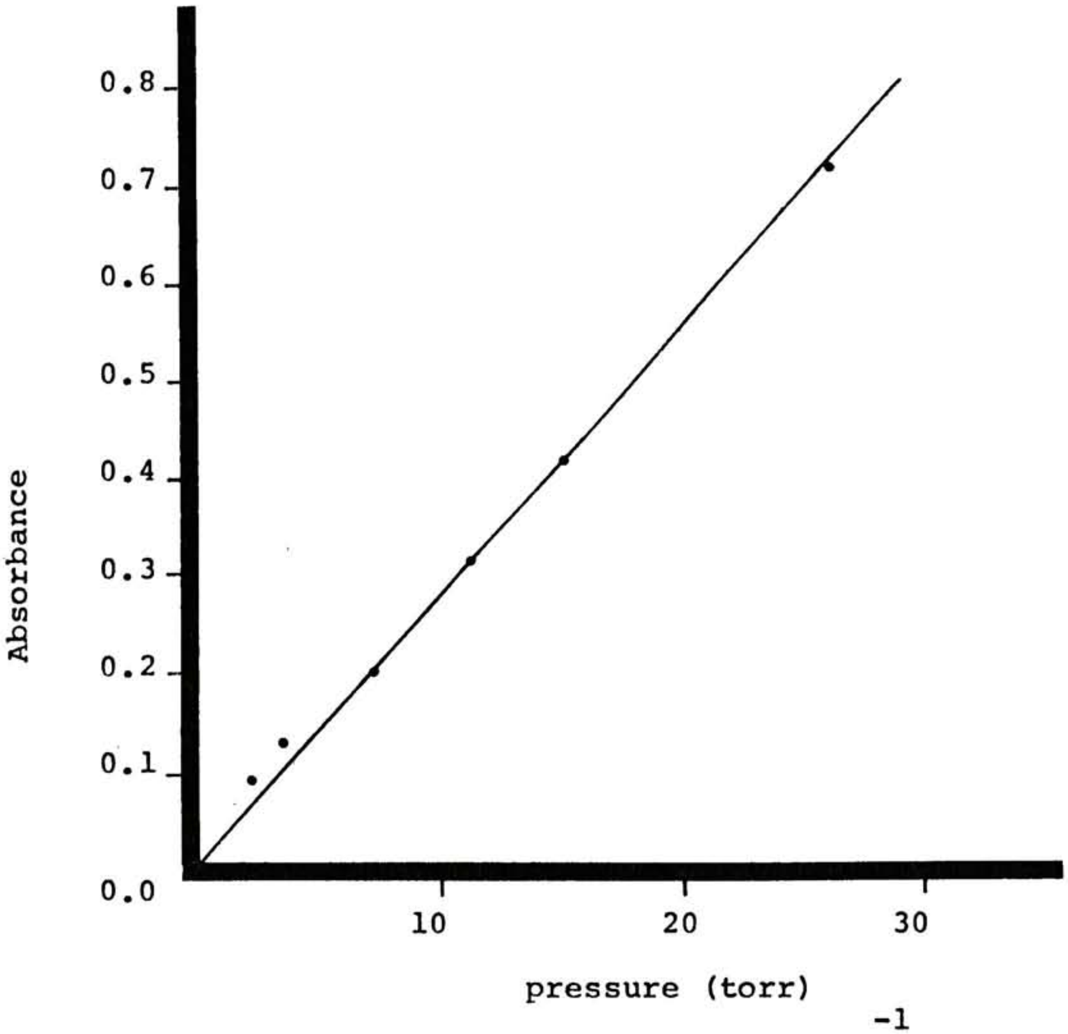


Figure 7. Beer's law plot for the 1600cm^{-1} absorption band of nitrogen dioxide.

coefficient of determination = 0.998

intercept = 0.011

slope = 0.0271

(mole cm).[49] The absorption coefficient of nitryl chloride was not known at the onset of this work. Therefore, it was assumed that the entire absorpiton at 3300A° was due to chlorine, and the maximum possible percent chlorine impurity was calculated from the total sample pressure and the extinction coefficient. The average result for the maximum chlorine impurity for all the samples prepared by the method of Volpe and Johnston[36] is 25.8%, with a percent standard deviation of 8.5%. The results and data for this determination are shown in Table 7.

In an attempt to remove any remaining chlorine, some purified nitryl chloride was distilled onto degassed deodorizing activated charcoal. Activated charcoal has been reported to have the ability to absorb 0.7 times its own weight of chlorine;[50] once the chlorine is in an absorbed state, it is difficult to remove, even by evacuation and heating.[50]

An ultraviolet spectrum was taken of the first portion of nitryl chloride, which was distilled off of the activated charcoal while the charcoal was maintained at -77° C, and compared to the ultraviolet spectrum taken of the same sample before it was distilled onto the activated charcoal. The ultraviolet spectra showed no change in the entire region 200-400 nm.

A mixture of nitryl chloride and chlorine was prepared

Table 7. % Chlorine in Nitryl Chloride by Ultraviolet Spectroscopy*

Pressure (torr)**	Path Length (cm)	Absorbance	% Chlorine*
89.9	10	0.721	22.4
103.3	2	0.178	26.7
37.8	2	0.065	26.3
16.0	2	0.031	28.6
9.6	2	0.017	26.7
39.0	2	0.071	28.2
95.0	2	0.160	25.6
16.5	2	0.027	25.6

Wavelength = 330 nm

Average = 25.8% chlorine

Standard deviation = 2.2

% standard deviation = 8.5

*These percentages are upper limits for the percent chlorine in the samples. See text for explanation.

**Pressure of nitryl chloride

and an ultraviolet spectrum taken. The mixture was then distilled onto more activated charcoal, and again the ultraviolet spectrum of the first portion of this sample was taken. A reduction in the amount of chlorine present in this sample was noted, the process was repeated, and again a reduction in the amount of chlorine was noted. This was not a quantitative experiment; however, it leads us to believe that the purified nitryl chloride samples contained little, if any, chlorine.

In another attempt to check the purity of the nitryl chloride, molecular weight determinations were made, using gas density measurements. The molecular weight of the samples was calculated from the ideal gas expression

$M = gRT/PV$.

The nitryl chloride was contained in a Pyrex bulb, which had a greaseless stopcock and a 10/30 inner glass standard taper joint. The volume of the bulb was determined from the weight of water it contained and the density of the water at 20° C. The weight of the gas was determined from the difference in weight of the bulb when it was filled and evacuated (less than 10^{-3} torr). The bulb was attached to the vacuum line through a viton "O" ring to a 20/30 outer glass standard taper joint to avoid errors in the weighings due to grease on the standard taper joint (see Figure 8). The weighings and pressure

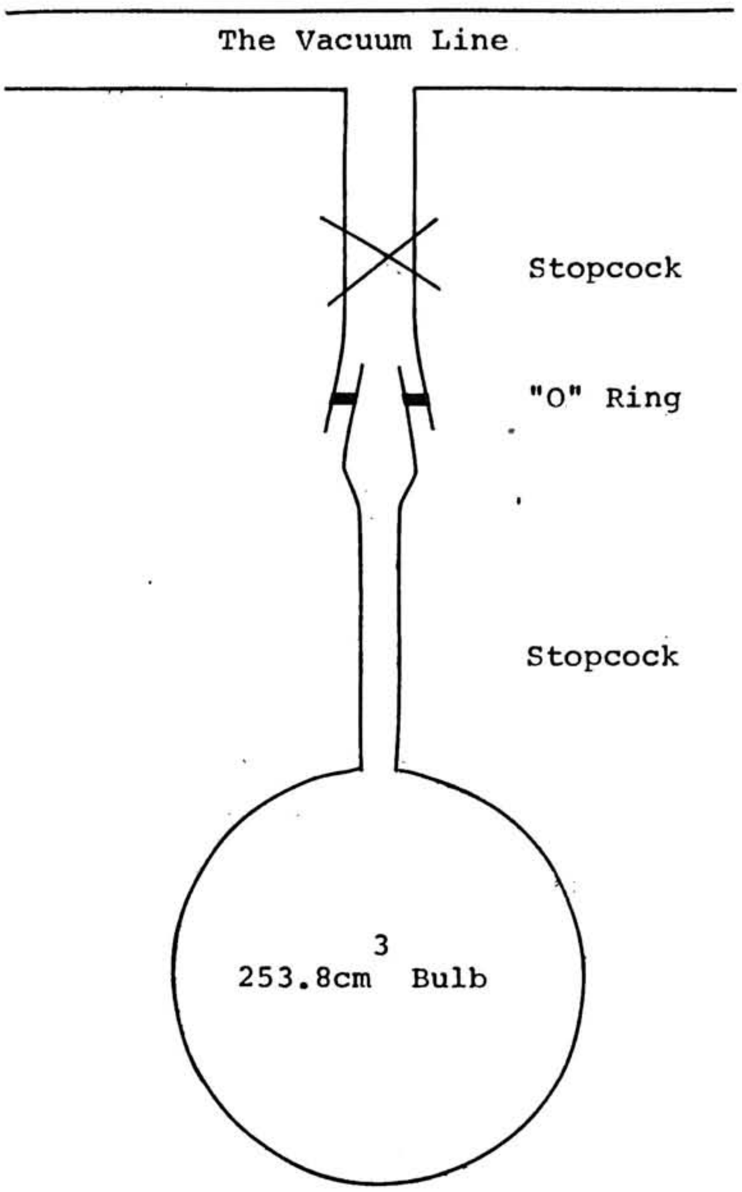


Figure 8. Molecular Weight Apparatus Showing "O" Ring Between the Inner and Outer Standard Taper Joints.

measurements were determined, using a Mettler analytical balance and a mercury manometer, respectively. As a check on the procedure, the molecular weight of air was also determined.

The results for nitryl chloride and air are shown in Tables 8 and 9. The average molecular weight of nitryl chloride was found to be 81.53 grams (standard deviation = 0.40), compared to the true molecular weight of nitryl chloride: 81.46. The average molecular weight of air was found to be 28.79 grams, with a standard deviation of 0.11.

The inherent errors in the molecular weight determinations were determined from the following expression:

$$\nabla M = \frac{M\nabla P}{P} + \frac{gR}{PV}\nabla T + \frac{gRT}{PV^2}\nabla V + \frac{RT}{PV}\nabla g$$

where ∇P, ∇T, ∇V, and ∇g are 1 torr, 1° C, 1 ml, and 0.0002 grams, respectively. The error for each determination is also shown in Table 8. Within experimental error, more than 5% chlorine could be detected, therefore we can conclude that the nitryl chloride was at least 95% pure.

The purity of nitryl chloride was also determined from the amount of chloride ion produced from the reaction of nitryl chloride with water. A known pressure of nitryl chloride was introduced into an evacuated bulb of known volume. The bulb opening was immersed under distilled

Table 8. Molecular Weight of Nitryl Chloride

Pressure, Atmospheres	Weight of Sample, grams	Molecular Weight, grams/mole	Inherent Error, grams/mole
0.631	0.5438	81.23	0.25
0.115	0.0994	81.46	0.95
0.125	0.1081	81.51	0.95
0.121	0.1052	81.94	0.95

Temperature = 23.55° C

Average molecular weight = 81.53

Standard deviation = 0.40

% standard deviation = 0.50

Table 9. Molecular Weight of Air

Pressure, Atmospheres	Weight of Sample, grams	Molecular Weight, grams/mole
0.9905	0.3033	28.76
0.9905	0.3037	28.80
0.9905	0.3039	28.82

Temperature = 22.55° C

Average molecular weight = 28.79

Standard deviation = 0.03

% standard deviation = 0.11

chloride-free water, and approximately 50 ml of water was introduced by opening the stopcock. The solution was shaken intermittently for 15 minutes to allow the nitryl chloride and water to react, and then it was transferred to a beaker, whereupon the bulb was rinsed twice with approximately 10 ml of water, which was also added to the contents of the beaker. The beaker and its contents were heated to near boiling for 30 minutes to remove any dissolved chlorine (see Discussion and Results section of this thesis). The chloride was then precipitated with silver nitrate.[51] The results of these determinations are shown in Table 10.

The nitryl chloride determined by this method showed an average purity of 99.6%, with a standard deviation of 0.14. Since nitrosyl chloride may also produce chloride upon reaction with water, this number must be corrected for the possible nitrosyl chloride impurity, giving 99.5% as the minimum purity of the nitryl chloride.

F. Constant Temperature Baths

During sample handling and the determination of the vapor pressure of nitryl chloride, the constant temperature baths listed in Table 11 were used.

Table 10. Gravimetric Determination of the Purity of Nitryl Chloride*

Gas Sample** atmospheres	Silver Chloride grams	Gas Sample** moles	Silver Chloride moles	% Nitryl Chloride
0.152	0.2311	1.62×10^{-3}	1.61×10^{-3}	99.5
0.170	0.2595	1.82×10^{-3}	1.81×10^{-3}	99.7

*Temperature = 22.2° C, Volume of bulb = 0.2583 liters

**Pressure of $ClNO_2$

Table 11. Constant Temperature Baths[52]

Slush Bath	Temperature° C[3, 7]
Methanol	-97.8
Ethyl acetate	-83.6
Chloroform	-66.0
Ethyl malonate	-56.0
Chlorobenzene	-45.2
Ethylene dichloride	-36.0
Carbon tetrachloride	-23.0

IV. RESULTS AND DISCUSSION

A. Preparation, Purification, and Purity of Nitryl Chloride

Nitryl chloride was synthesized by the two methods mentioned in Chapter III of this thesis. The modified Wise and Volpe[29] procedure proved to be superior, in that the nitryl chloride produced contained only small amounts of chlorine (less than 0.5%). The nitryl chloride produced from the Dachlauer[27] method contained approximately 10% chlorine, which it was never possible to remove totally. The percent chlorine was found by using the absorption cross section of nitryl chloride and chlorine at 330 nm (Section E of this Chapter).

Volpe and Johnston[36] have stated that nitryl chloride and chlorine form an azeotrope that can be removed by directly pumping on the sample. By use of ultraviolet spectrophotometry, changes in the extinction coefficient at the chlorine absorption maximum (330 nm) were never detected for purified nitryl chloride samples before and after they were pumped on. As the gravimetric determination of nitryl chloride showed, the samples were very pure (> 99.5%) and any changes from the removal of the azeotrope may not have been detectable.

The gravimetric method, which was developed for the determination of the purity of nitryl chloride proved to be very valuable. Nitryl chloride was allowed to react with water at 25° C.[42, 53]

$$ClNO_2 + H_2O \longrightarrow 2H^+ + Cl^- + NO_3^- \qquad (45)$$

to produce chloride ion, any chlorine present will be slightly soluble, as shown in Figure 9, where the solubility of chlorine is presented as a function of the partial pressure of chlorine at 20° and 80° C. The chlorine that is dissolved reacts reversibly with water:[54]

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl \qquad (46)$$

The equilibrium constant for the hydrolysis is given by:

$$K_{eq} = ((HOCl)(H^+)(Cl^-))/(Cl_2).$$

Table 12 shows the values for the equilibrium constant at various temperatures.[50]

The solubility of chlorine in water at 100° C is zero and, since the equilibrium is rapidly attained,[50] the dissolved chlorine was expelled by heating to near boiling for 30 minutes. The results were corrected for any chloride ion due to nitrosyl chloride (less than 0.1%), as determined by infrared spectrophotometry.

The nitryl chloride (greater than 99.5%) was a pale yellow-colorless liquid and a white solid. These properties are confirmed in the literature.[39] The infrared spectrum of our samples agreed with the results previously reported, which were presented in Chapter II. The spectrum

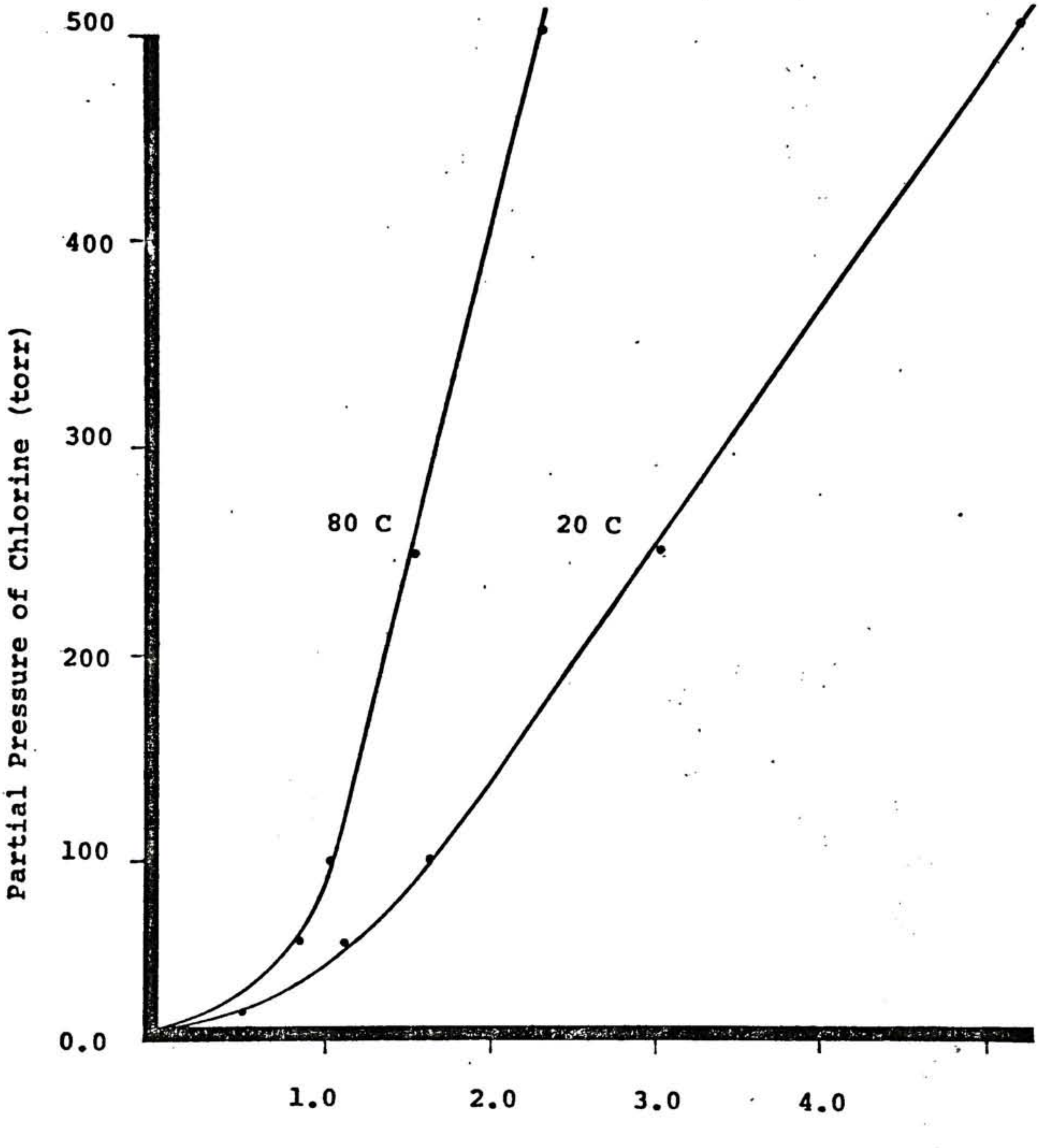


Figure 9. Solubility of Chlorine in Water at 20 C and 80 C.[48]

is shown in Figure 10 and Beer's Law data for the 1685 and 1310 cm^{-1} absorption bands are presented in Table 13. The Beer's Law plots are shown in Figure 11. These Beer's Law plots, which were used for quantitative determination, were frequently checked with different samples of nitryl chloride and found to be reproducible.

Table 12. Equilibrium Constants for the Hydrolysis of Chlorine

Temperature° C	K_{eq}
0	1.56×10^{-4}
1.2	1.64×10^{-4}
15	3.16×10^{-4}
17.6	3.63×10^{-4}
25	4.48×10^{-4}
70	10.0×10^{-4}

B. Vapor Pressure and Heat of Vaporization

The vapor pressure of nitryl chloride >99.5% was determined by measuring the pressure with a mercury manometer covered with dibutylphthalate as the temperature was controlled by use of constant temperature slush baths (Table 7). The results were shown in Table 11. A plot of the $\log_{10}$ of the vapor pressure versus $1/T(^{\circ}K)$ is plotted in Figure 12. A linear regression analysis on the data gives

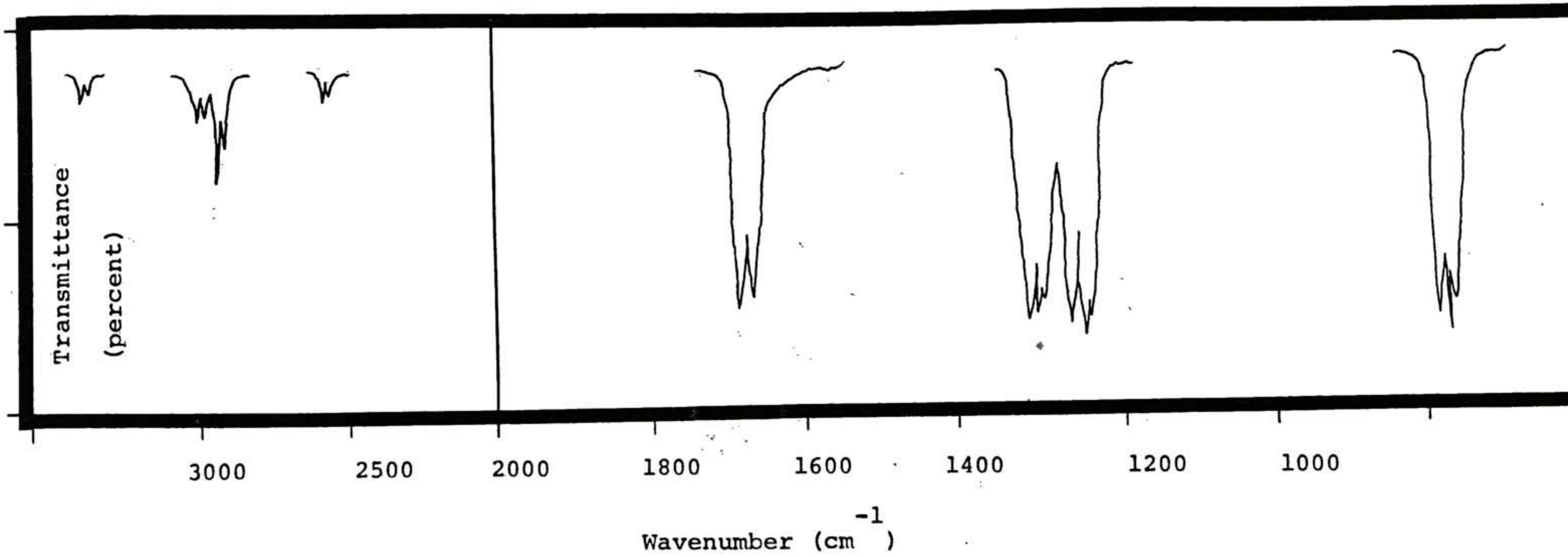


Figure 10. Infrared Spectrum of Nitryl Chloride.

Table 13. Beer's Law Data for the 1685 and 1310 cm^{-1} Absorption Bands of Nitryl Chloride

Absorbance at 1685 cm^{-1}	Absorbance at 1310 cm^{-1}	Pressure of $ClNO_2$, torr
1.38	.88	9.4
.93	.53	5.8
.13	--	0.58
.23	.10	1.08
1.24	.76	8.5
.77	.41	4.3
.39	.207	2.24

The coefficient of determination at 1685 cm^{-1} = 0.992, and at 1310 cm^{-1} = .998.

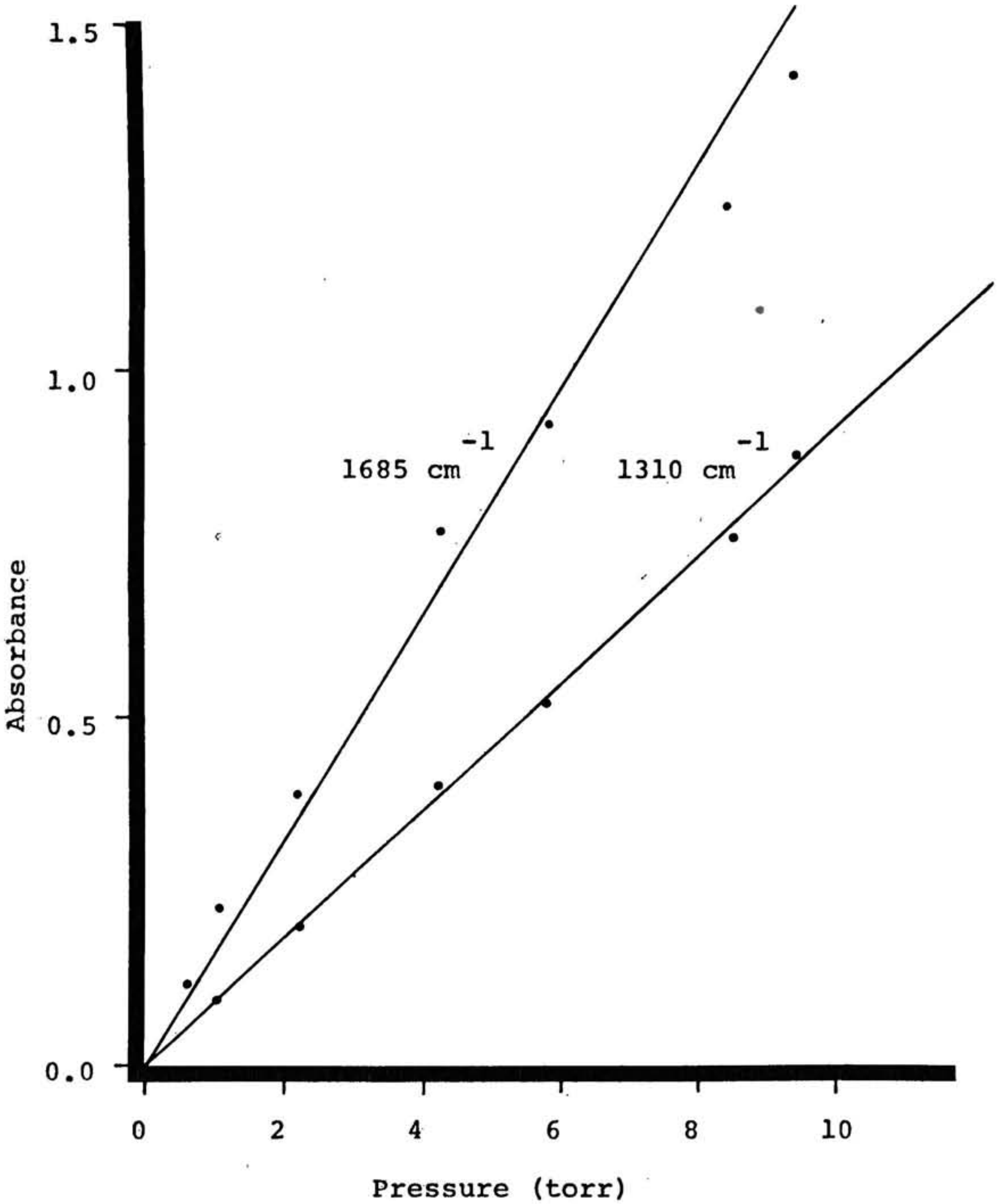


Figure 11. Beer's law plots for the 1685 and 1310 cm^{-1} absorption bands of nitryl chloride.

Table 14. Temperature Dependence of the Vapor Pressure of Nitryl Chloride

Temperature, °C	log P (torr)
-97.8	0.56
-83.6	1.10
-66.0	1.68
-56.0	1.94
-45.2	2.20
-36.0	2.50

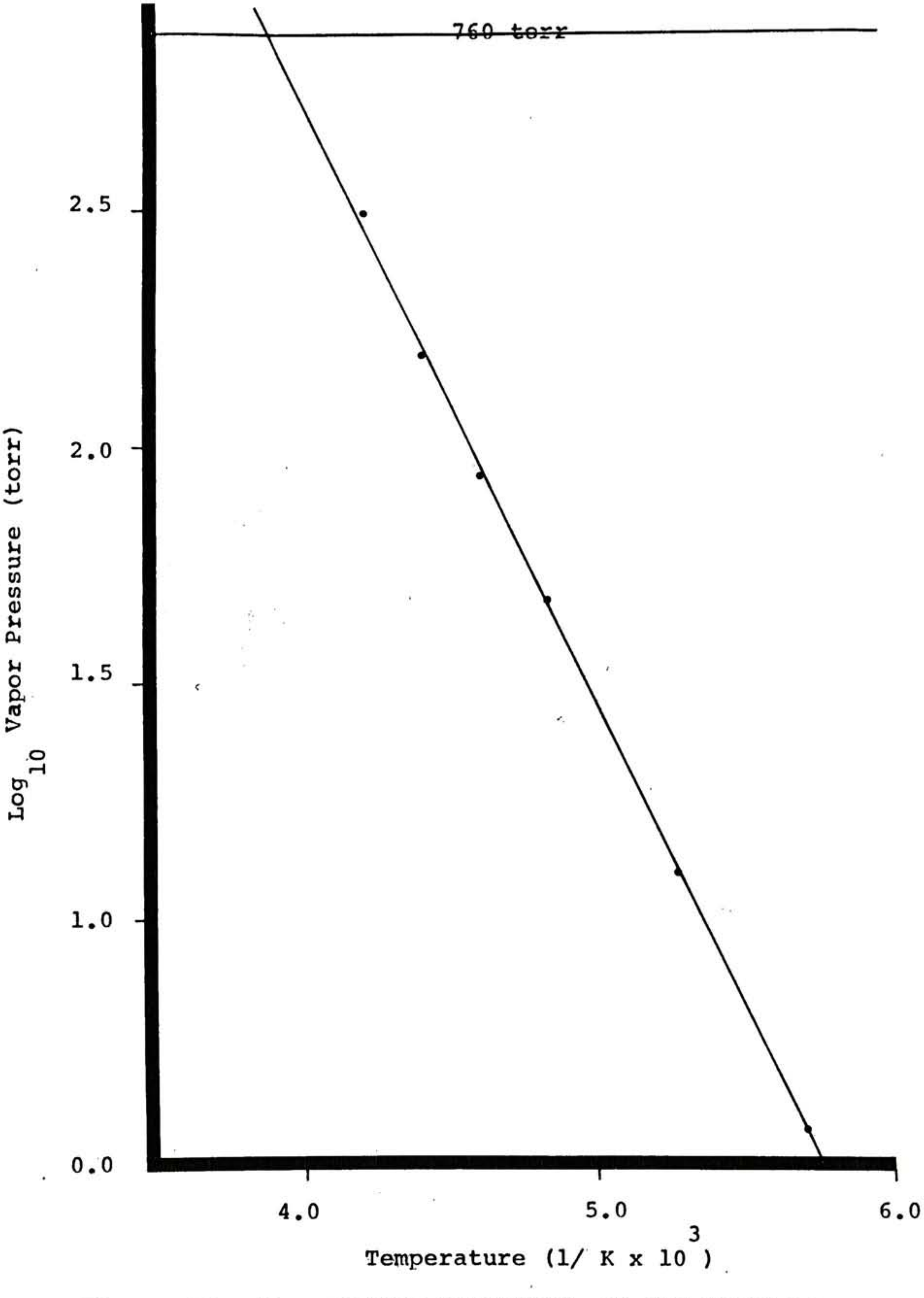


Figure 12. Temperature dependence of the vapor pressure of Nitryl Chloride.

the following equation for the straight line[56]

$$\log_{10} P\ (\text{torr}) = -1.28 \times 10^3 \frac{1}{T(^\circ K)} + 7.86.$$

The coefficient of determination (r^2) for the line is 0.998.

From the above equation, a boiling point of -16.1° C ± 0.1° was determined. The boiling point for nitryl chloride, as reported in the literature ranges from -5° to -15° C.[46, 57] Since boiling points are raised upon the introduction of impurities, these results may indicate that this nitryl chloride was purer than previous reported results in the literature.

Using these vapor pressure data, the heat of vaporization of nitryl chloride was determined to be 5.86 ± 0.11 kcal/mole from the Clausius-Clapeyron equation

$$\Delta H_{vap} = -2.303\ R\ \frac{d \log P}{d(1/T)}.$$

These results compare with the values of -14.9° C and 6.16 kcal/mole reported by Schumacher and Sprenger,[14] who prepared nitryl chloride by the reaction of ozone and nitrosyl chloride.

The vapor pressures of nitryl chloride, nitrosyl chloride, nitrogen dioxide, chlorine, and hydrogen chloride[58] are summarized in Figure 13. This information was useful in sample handling and sample purification.

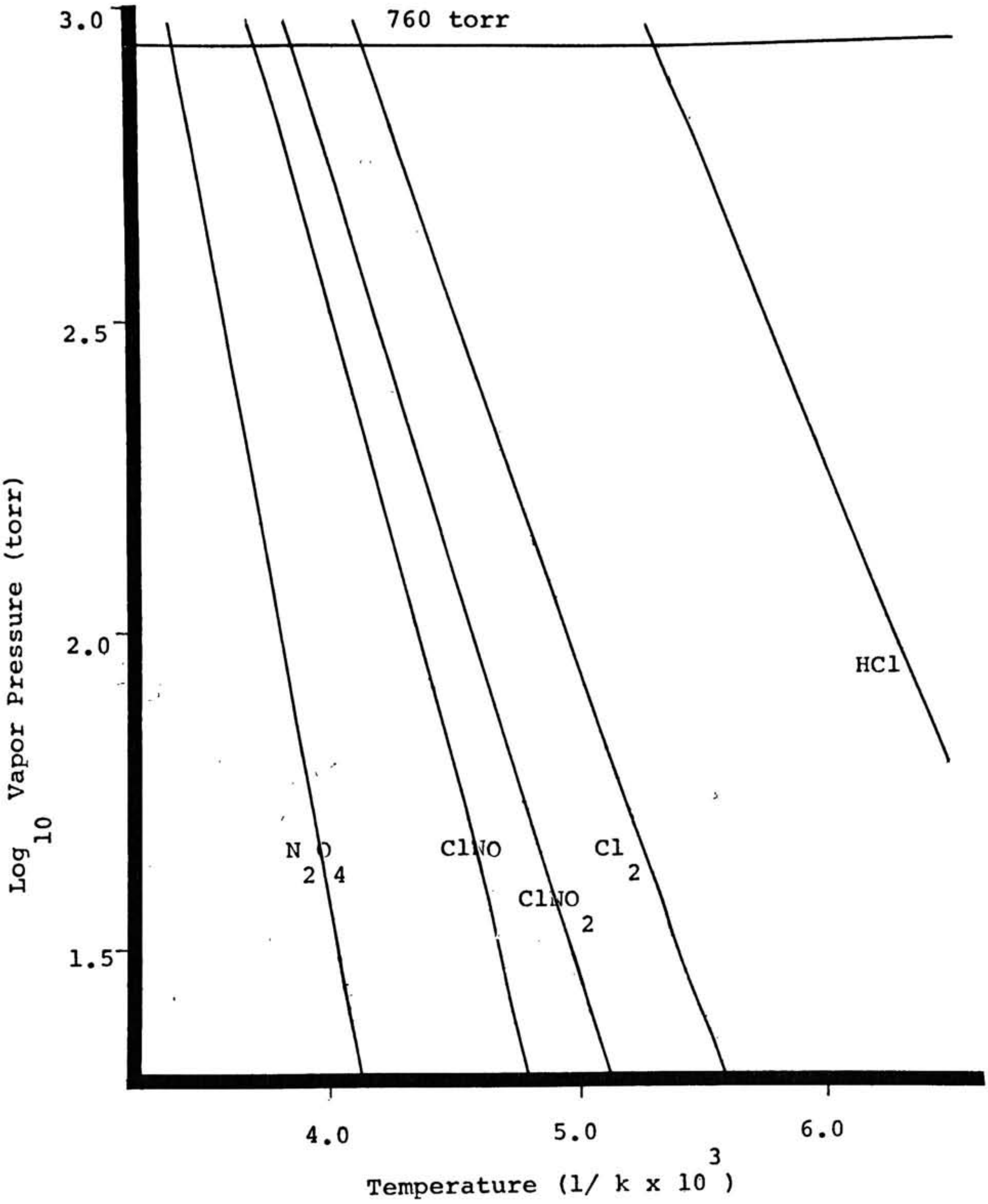


Figure 13. Temperature dependence of the vapor pressur of nitryl chloride, nitrosyl chloride, chlorine, nitrogen tetroxide, and hydrogen chloride.

C. Stability of Nitryl Chloride

The stability of nitryl chloride was investigated by storing some sample in a bulb, sealed from the atmosphere by a vacuum stopcock, at -77° C for one month. After the above time, the sample was cooled to -196° C. A small amount of non-condensible gas was detected on the thermocouple gauge. The ultraviolet and infrared spectra were taken. The infrared spectrum showed no nitrosyl chloride or nitrogen dioxide absorption bands. The ultraviolet spectrum of this sample agreed well with the spectra taken for the absorption cross sections of nitryl chloride (Section E of this Chapter).

The non-condensible gas probably came from leakage through the stopcock grease. The purity after one month was greater than 99.4%. In agreement with these results, Ray and Ogg[34] reported that their nitryl chloride could be stored at -77° C for periods greater than a month.

Nitryl chloride was also stored in an ultraviolet cell at room temperature in the dark. No change was noted in the spectrum until the fourth day. Quantitative measurements by ultraviolet spectroscopy are not feasible due to the similar spectra of nitrogen dioxide,[49] nitrosyl chloride, and nitryl chloride. After a month, infrared absorption spectroscopy showed that the major product was nitrogen dioxide; some nitrosyl chloride and nitryl chloride were also present.

Ray and Ogg studied the equilibrium

$$2ClNO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cl_2 + 2NO_2 \qquad (47)$$

from both directions, using silver chloride infrared windows, which do not react with nitrogen dioxide.[34] Precipitated silver chloride was used as a catalyst. The equilibrium constant was found to be less than 35.09 atm, which compares to the calculated equilibrium constant of 23.81 atm.[59] The "equilibrium" concentration of nitryl chloride was therefore greater than 2.7% of the total gases, which compares to 4.0% from the calculated equilibrium constant. The equilibrium was slowly attained, even with the catalyst and, after a week, the reactions were still incomplete.

Cordes and Johnston[38] studied the thermal decomposition of nitryl chloride and found the second order rate constant to be given by:

$k_{1obs} = 9.6 \times 10^{-8} cm^3 molecule^{-1} sec^{-1} exp(-27500/RT)$ between 100° and 250° C. The second order region was found to extend from 0 to 8 torr. Using this expression, the rate of decomposition of nitryl chloride at 25° C is calculated to be:

$k_{1calc} = 8.8 \times 10^{-28} cm^3 molecule^{-1} sec^{-1}$

By using the observed rate constant for the thermal decomposition, the percent decay of nitryl chloride can be calculated by calculating the pressure at the time t:

$$\frac{1}{P} = \frac{1}{P_o} + 2k_1t$$

For a 0.77 torr sample (the lowest pressure used in this work), the percent decay is 6.4×10^{-3}% after one hour. At higher pressures, there will be even less decomposition. The time required when using nitryl chloride as a gas was always less than an hour, therefore the thermal decomposition will be of no consequence.

The rate of the reverse reaction k_{-1}, the formation of nitryl chloride from chlorine and nitrogen dioxide, can also be calulated by using $k_{1(obs.)}$ (Cordes and Johnston[38]) and the calculated equilibrium constant. The value found is:

$$k_{-1(cal.)} = 2.7 \times 10^{-7} \text{atm}^{-2} \text{sec}^{-1}.$$

D. Mass Spectra of Some Reactive Gases

Attempts were made at obtaining the mass spectra of hydrogen chloride, chlorine, nitrogen dioxide, nitrosyl chloride, and nitryl chloride. Not all of these attempts were successful due to the reactivity of the gases in the mass spectrometer. The isotopic abundance of chlorine 35 and 37 was found to be in agreement with the literature[46] for all the chlorine-containing compounds.

Hydrogen chloride: The mass spectrum of hydrogen chloride is shown below.

m/e	assignment	relative intensity
35	Cl^{+35}	16.6 ± 0.1
36	HCl^{+35}	100
37	Cl^{+37}	5.4 ± 0.2
38	HCl^{+37}	31.5 ± 0.1

The mass spectrum was found to be reproducible.

Chlorine: The mass spectra taken of chlorine (>99%) all showed hydrogen chloride peaks. The relative intensities of the hydrogen chloride peaks varied with both pressure and exposure time of the sample to the mass spectrometer. The mass spectrum of chlorine was not reproducible.

Nitrogen dioxide: The mass spectrum of nitrogen dioxide became reproducible only after at least two hours of exposure of the gas to the mass spectrometer and inlet system. The only major peaks are shown below and are in agreement with the literature.[60]

m/e	assignment	relative intensity
30	NO^+	100
46	NO_2^+	36.2 ± 0.5

Nitrosyl chloride: The mass spectra taken of nitrosyl chloride (>97%) all contained chlorine and hydrogen chloride peaks. The spectrum never became reproducible, even after up to four hours of exposure of the gas to the spectrometer and inlet system.

Nitryl chloride: The mass spectra of nitryl chloride also contained chlorine and hydrogen chloride peaks that never became reproducible. The NO_2^+ and NO^+ peaks, however, did stabilize, allowing the determination of the relative peak intensities to ± 3%:

m/e	assignment	relative intensity
30	NO^+	100
46	NO_2^+	64 ± 3%

Determination of the percent chlorine in the nitryl chloride samples by mass spectrometry was not possible because the chlorine peaks varied in relative intensity with pressure. The spectrum of nitryl chloride did not show evidence of a parent peak. A search for the parent peak was carried out by varying the anode current from 5-80 microamps and by varying the ionization voltage from 5-70 eV.

Other workers[60, 61] have found that, in order to obtain reproducibility with reactive gases such as nitrogen dioxide and nitric acid, extensive conditioning of the mass spectrometer and inlet system of at least 8-10 hours was required. The irreproducibility of the spectra of reactive gases is due to reactions of the gases with trace compounds within the mass spectrometer, the inlet system, the metal walls of the spectrometer, or oil from the diffusion pump.

The experimental evidence suggests that mass spectrometry will not provide an acceptable method for detection of nitryl chloride without extensive conditioning of the spectrometer. The similarity of the intensities of the NO^+(m/e = 30) and NO_2^+(m/e = 46) peaks for nitryl chloride and nitrogen dioxide should make it difficult in determining these two compounds in mixtures.

E. The Absorption Cross Sections of Nitryl and Nitrosyl Chloride

The ultraviolet absorption cross sections of chlorine, nitryl chloride, and nitrosyl chloride were determined between 185 and 400 nm at room temperature. Such absorption cross sections of molecules important in the upper atmosphere may be used to calculate the intensity of radiation that penetrates the earth's atmosphere. Ultraviolet absorption cross sections (σ) are a measure of the extent to which molecules absorb ultraviolet radiation and are defined by the following expression:

$$\sigma = \ln(I_0/I)/CL$$

where C = concentration (molecules/cm^3)

I_0 = incident radiation

I = transmitted radiation

L = path length (cm)

The ultraviolet cross sections for chlorine are well known[4, 49, 62] and were determined as a control for our experiment. Results of this study for the chlorine maximum agreed with those reported in the references cited above, within 3%. The absorption cross sections of chlorine, as determined (Table 15, Figure 14), had a standard deviation below 3%. The maximum inherent error at the absorption maximum for chlorine was 7.0×10^{-21} cm^2 $molecule^{-1}$.

Table 15. Ultraviolet Absorption Cross Sections of Chlorine

Wavelength (nm)	Cross Sections ($cm^2 molecules^{-1}$)
400	1.3×10^{-20}
390	2.1×10^{-20}
380	3.4×10^{-20}
370	6.5×10^{-19}
360	1.1×10^{-19}
350	1.6×10^{-19}
340	2.2×10^{-19}
330	2.5×10^{-19}
320	2.5×10^{-19}
310	2.1×10^{-19}
300	1.4×10^{-19}
290	7.4×10^{-20}
280	3.4×10^{-20}
270	1.4×10^{-20}

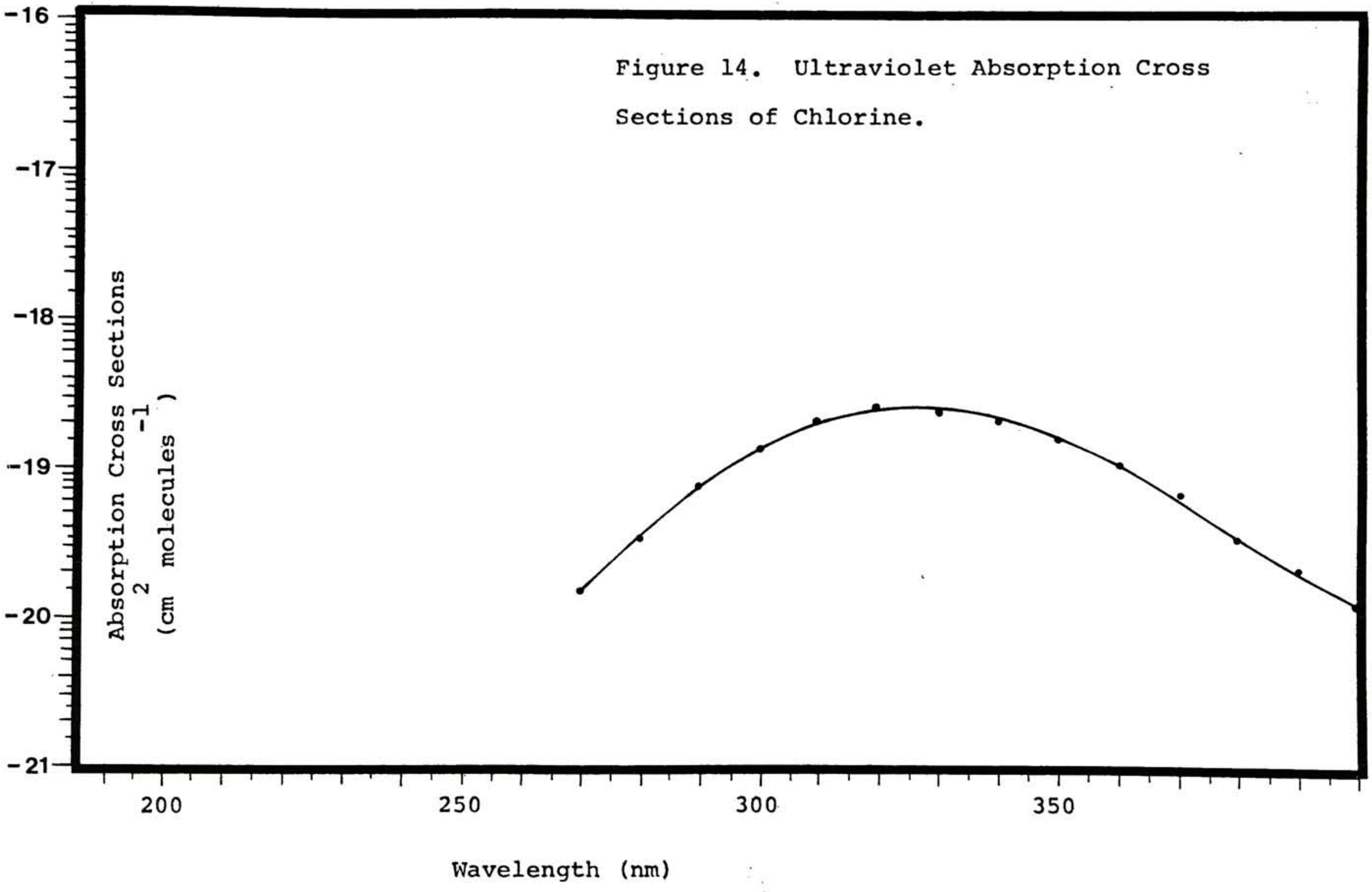


Figure 14. Ultraviolet Absorption Cross Sections of Chlorine.

The ultraviolet absorption cross sections of nitryl chloride (Table 16, Figure 15) were determined from 31 spectra coming from five different samples. The spectra were taken between 0.77 and 95 torr in 1, 2, or 10 cm path length cells. The absorption spectrum of nitryl chloride between the wavelengths 185 and 400 nm indicates that it consists of at least three different electronic excited states. The continuous nature of the spectrum suggests that photodissociation will occur. In Section F of this Chapter, six energetically possible reactions for the photodissociation of nitryl chloride are described, and the wavelength limits derived from thermodynamic data are presented. No aborption was found in the wavelength region between 400 and 750 nm, indicating absorption cross sections less than 2 x 10^{-21} $cm^2 molecule^{-1}$. There are no previous reports in the literature of the absorption cross sections of nitryl chloride.

The ultraviolet absorption cross sections of nitrosyl chloride (Table 17, Figure 16) were obtained between 190 and 400 nm from 29 spectra ranging in pressure from 0.72 to 52 torr. The results (solid line) differ from those reported by Goodeve and Katz[18] in 1939 (dotted line) as shown in Figure 16 and indicate that nitrosyl chloride is less of a sink for chlorine atoms than previously[6] anticipated. Goodeve and Katz'[18] results would agree with this

Table 16. Ultraviolet Absorption Cross Sections of Nitryl Chloride

Wavelength (nm)	Cross Sections (σ)[b], cm^{2}molecule^{-1}	± Inherent Error, cm^{2}molecule^{-1}	% Stan. Dev.
400	2.08 (-21)[a]	1.44 (-22)[a]	4
390	3.78 (-21)	2.62 (-22)	4
380	6.16 (-21)	4.28 (-22)	4
370	1.07 (-20)	7.44 (-22)	4
360	1.82 (-20)	1.28 (-21)	3
350	3.06 (-20)	1.42 (-21)	3
340	4.81 (-20)	1.69 (-21)	3
330	7.11 (-20)	2.49 (-21)	3
320	1.02 (-19)	3.59 (-21)	3
310	1.32 (-19)	4.66 (-21)	3
300	1.54 (-19)	5.44 (-21)	3
290	1.80 (-19)	6.37 (-21)	3
280	2.31 (-19)	8.20 (-21)	3
270	3.73 (-19)	1.33 (-20)	3
260	6.37 (-19)	2.32 (-20)	3.5
250	9.85 (-19)	3.66 (-20)	3.5
240	1.40 (-18)	5.34 (-20)	3.5
235	1.80 (-18)	7.03 (-20)	3.5
230	2.36 (-18)	9.52 (-20)	3.5
225	2.95 (-18)	1.22 (-19)	3.5
220	3.42 (-18)	1.46 (-19)	3.5

Table 16. (Cont.)

Wavelength, (nm)	Cross Sections $(\sigma)^b$, $cm^2molecule^{-1}$	± Inherent Error, $cm^2molecule^{-1}$	% Stan. Dev.
215	3.56 (-18)	1.53 (-19)	3.5
210	3.39 (-18)	1.45 (-19)	4
205	3.22 (-18)	1.36 (-19)	4
200	4.55 (-18)	2.06 (-19)	4
197.5	7.13 (-18)	3.66 (-19)	3.5
195	1.13 (-17)	8.53 (-19)	3.5
190	2.69 (-17)	2.53 (-18)	3
185	4.74 (-17)	5.09 (-18)	3

[a] 2.08 (-21) means 2.08×10^{-21}

[b] $(\sigma) = \ln(I_0/I)/([ClNO_2]L)$, where L is optical path length in cm and $[ClNO_2]$ is in molecules cm^{-3}.

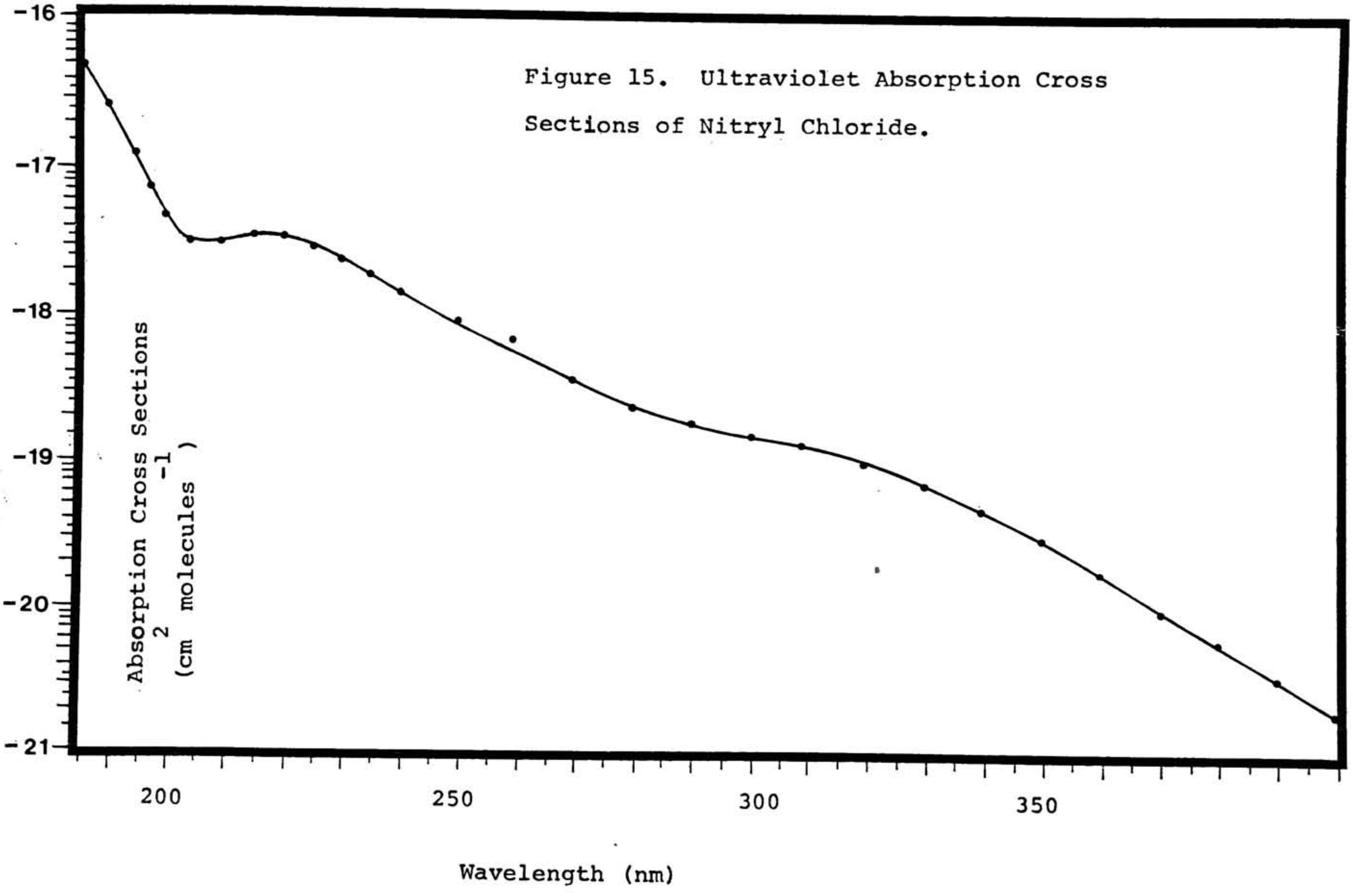


Figure 15. Ultraviolet Absorption Cross Sections of Nitryl Chloride.

Table 17. Ultraviolet Absorption Cross Sections of Nitrosyl Chloride

Wavelength, (nm)	Cross Sections (σ)^{b}, cm^{2}molecule^{-1}	± Inherent Error, cm^{2}molecule^{-1}	% Stan. Dev.
400	5.15 (-20)[a]	1.80 (-21)[a]	2.5
390	6.10 (-20)	2.14 (-21)	2.5
380	7.78 (-20)	2.73 (-21)	2.5
370	9.43 (-20)	3.31 (-21)	2.5
360	1.13 (-19)	3.98 (-21)	2.5
350	1.19 (-19)	4.19 (-21)	2.5
340	1.24 (-19)	4.37 (-21)	2.5
330	1.20 (-19)	4.23 (-21)	3
320	1.08 (-19)	3.80 (-21)	3
310	1.05 (-19)	3.69 (-21)	3
300	8.67 (-20)	3.05 (-21)	3.5
290	8.47 (-20)	2.98 (-21)	3
280	9.35 (-20)	3.29 (-21)	3
270	1.15 (-19)	4.05 (-21)	3
260	1.61 (-19)	1.04 (-21)	3
250	2.99 (-19)	1.04 (-20)	2.5
240	7.68 (-19)	2.82 (-20)	2.5
235	1.77 (-18)	6.90 (-20)	2
230	3.17 (-18)	1.33 (-19)	2
225	6.00 (-18)	2.92 (-19)	2
220	1.07 (-17)	6.39 (-19)	2

Table 17. (Cont.)

Wavelength, (nm)	Cross Sections (σ)[b], $cm^2 molecule^{-1}$	± Inherent Error, $cm^2 molecule^{-1}$	% Stan. Dev.
215	1.80 (-17)	1.39 (-18)	2
210	2.99 (-17)	3.20 (-18)	2
205	4.70 (-17)	7.25 (-18)	2
200	6.74 (-17)	1.35 (-17)	2
195	7.58 (-17)	1.72 (-17)	2
190	5.20 (-17)	8.71 (-18)	2

[a] 5.15 (-20) means 5.15 x 10^{-20}

[b] $\sigma = \ln(I_0/I)([ClNO_2]L)$, where L is optical pathlength in cm and $[ClNO_2]$ is in molecules cm^{-3}.

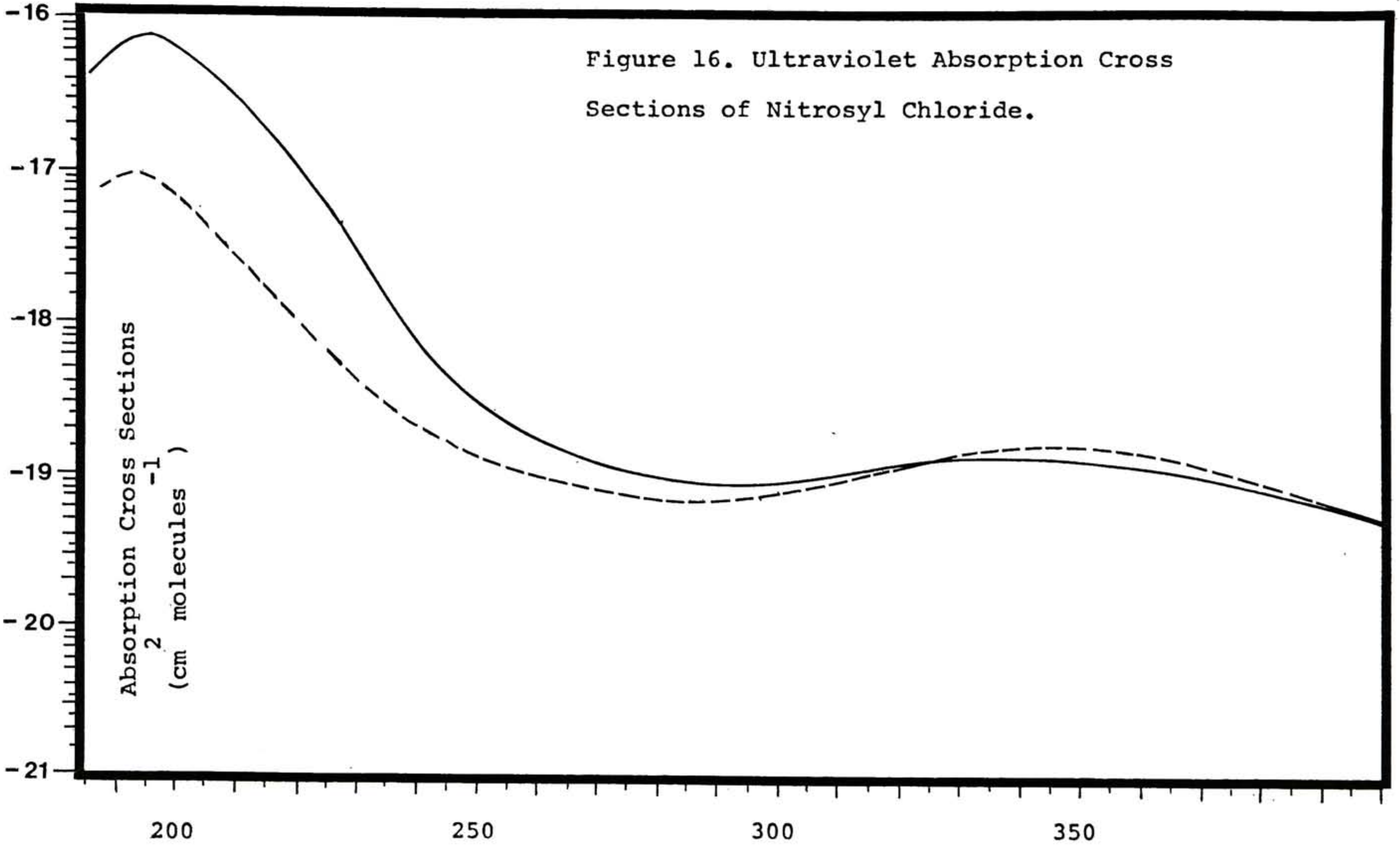


Figure 16. Ultraviolet Absorption Cross Sections of Nitrosyl Chloride.

study if their samples had contained 13% chlorine. The spectrum for nitrosyl chloride is also continuous in nature and indicates that at least two distinct electronic excited states exist in the wavelength region from 190 to 400 nm.

The inherent errors in the absorption cross sections were found by use of the following expression.

$$\Delta\sigma = \left|\frac{\partial(\ln(I_0/I)/LC)}{\partial I_0}\Delta I_0\right| + \left|\frac{\partial(\ln(I_0/I)/LC)}{\partial I}\Delta I\right| + \left|\frac{\partial(\ln(I_0/I)/LC)}{\partial C}\Delta C\right| + \left|\frac{\partial(\ln(I_0/I)/LC)}{\partial L}\Delta L\right|$$

where   represents the error in the measurement. The error in the measurements are:

$C = 1 \times 10^{15}$ molecules/cm^3

L_o = 0.05 cm (on chart)

I = 0.05 cm (on chart)

L   given in the experimental section

The maximum inherent errors are reported along with the absorption cross sections in Tables 16 and 17.

The absorption cross sections of molecules of atmospheric interest, such as nitryl chloride and nitrosyl chloride that we have studied, are necessary in order to perform modelling calculations that estimate the perturbations upon the ozone belt. Absorption cross sections have been used for the kinetic monitoring of reactions that may occur in the stratosphere.[4]

F. Photochemistry of Nitryl Chloride

The continuous nature of the absorption spectrum of nitryl chloride suggests that photodissociation will occur. The following preliminary photochemical steps involving C-N and O-N bond breakage are energetically possible. The wavelengths at which the onset of these processes occur have been calculated from the C-N and O-N bond disociation energies,[32] atomic energy levels for chlorine,[63] and oxygen,[64] and the electronic energy levels for nitrogen dioxide.[55]

$$ClNO_2 + h\nu \longrightarrow Cl(^2P_{3/2}) + NO_2(^2A_1) \quad \lambda \leqslant 852nm \quad (48)$$

$$ClNO_2 + h\nu \longrightarrow Cl(^2P_{1/2}) + NO_2(^2A_1) \quad \lambda \leqslant 792nm \quad (49)$$

$$ClNO_2 + h\nu \longrightarrow Cl(^2P_{3/2}) + NO_2(^2B_1) \quad \lambda \leqslant 349nm \quad (50)$$

$$ClNO_2 + h\nu \longrightarrow Cl(^2P_{1/2}) + NO_2(^2B_1) \quad \lambda \leqslant 338nm \quad (51)$$

$$ClNO_2 + h\nu \longrightarrow O(^3P_0) + ClNO \quad \lambda \leqslant 415nm \quad (52)$$

$$ClNO_2 + h\nu \longrightarrow O(^1D) + ClNO \quad \lambda \leqslant 250nm \quad (53)$$

The dissociation of nitryl chloride may prove to be a very important sink for the compound in the stratosphere. Some preliminary experiments were carried out to determine the products of the gas phase photolysis of nitryl chloride at two wavelengths, 253.7 nm and 350 nm between 2 and 8 torr. The infrared and ultraviolet spectra before and after photolysis were studied. After photolysis at 253.7 nm in a 2-cm ultraviolet cell for 10 minutes in the Rayonet Photochemical Reactor, nitrogen dioxide/nitrogen tetroxide and a small amount of nitryl chloride were observed. These samples contained no non-condensible gases.

Nitryl chloride was also photolyzed for 5 minutes at wavelengths longer than 350 nm, where the absorption cross sections of nitryl chloride are rather small, $\sigma < 3.06 \times 10^{-20} cm^2 molecule^{-1}$. The ultraviolet absorption spectrum after photolysis showed the presence of nitrogen dioxide/ nitrogen tetroxide, nitryl chloride and, possibly, nitrosyl chloride. After exposure to the radiation, the spectrum continued to change for two days. Upon transferal of the sample to an infrared cell, some non-condensible gas was present, presumably oxygen. The major product after two days was nitrosyl chloride.

The change in the spectrum after the photolysis could be accounted for by the formation of a catalyst at the longer wavelengths, which would aid in the formation of nitrosyl chloride from nitryl chloride or from nitrogen dioxide and chlorine. The nitryl chloride that was photolyzed at the shorter wavelength did not exhibit any changes after the photolysis.

Dahner and Wilson[66] photolyzed nitryl chloride in a Pyrex bulb ($\lambda > 275$ nm). They followed the reaction by measuring the pressure with a Bourdon gauge. The products, chlorine and nitrogen dioxide, were formed after an induction period. The authors found that the color of nitrosyl chloride was absent in the products, and the amount of non-condensible gas was negligible. (Nitrosyl chloride is a yellow gas and a yellow-red liquid, while nitrogen dioxide is a yellow-brown gas and a brown liquid.[46] We would not attempt to distinguish them by color.) Dahner and Wilson "presumed" that the occurrence of the photochemical reaction was due to trace amounts of "sensitizing" impurities, probably chlorine, and that the mechanism could be:

$$Cl_2 + h\nu \longrightarrow 2Cl \qquad (54)$$

$$Cl + Cl + M \longrightarrow Cl_2 + M \qquad (55)$$

$$Cl + ClNO_2 \longrightarrow Cl_2 + NO_2 \qquad (56).$$

G. Photochemistry of Nitrosyl Chloride

The photochemistry of nitrosyl chloride has been studied throughout the visible and ultraviolet regions (185 to 750 nm).[49] The compound has been found to dissociate at wavelengths below 750 nm according to the following reactions:

$$ClNO + h\nu \longrightarrow NO(^2\Pi) + Cl(^2P_{3/2}) \quad \lambda \leq 753 \text{ nm} \quad (57)$$

$$ClNO + h\nu \longrightarrow NO(^2\Pi) + Cl(^2P_{1/2}) \quad \lambda \leq 706 \text{ nm} \quad (58)$$

Two reactant molecules are consumed for every photon according to:[63]

$$ClNO + h\nu \longrightarrow Cl + NO \qquad (59)$$

$$Cl + ClNO \longrightarrow Cl_2 + NO \qquad (60).$$

APPENDIX I

Thermal Decomposition of Nitrosyl Chloride

The thermal decomposition of nitrosyl chloride proceeds according to the reversible reaction:

$$2ClNO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2NO + Cl_2.$$

Waddington and Tolman[67] studied the thermal decomposition as well as the equilibrium between 150° and 250° C and found the rate constants to be given by:

$$k_1 = 4.3 \times 10^{11} T^{\frac{1}{2}} \exp(-24000/RT) \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

$$k_2 = 3.15 \times 10^{10} T^{\frac{1}{2}} \exp(-6860/RT) \text{ cm}^6\text{mole}^{-2}\text{sec}^{-1}$$

By using the calculated rate at 300° C from the above data, the percent decay of nitrosyl chloride at some time t may be calculated. Initially, the rate of decomposition will be:

$$-d(ClNO)/dt = k_1(ClNO)^2$$

and the pressure will be given by:

$$1/A - 1/A_0 = k_1 t.$$

Using these relations, the present decay of a sample at 0.72 torr would be 1×10^{-4} percent after one hour. At higher pressures, there will be even less decomposition, therefore, since nitrosyl chloride was never kept in the gaseous state for more than an hour, this decomposition will be inconsequential.

APPENDIX II

Dissociation of Nitrogen Tetroxide

In determining the percent nitrogen dioxide/nitrogen tetroxide detectable in a 20-torr sample of nitryl chloride, the following equilibrium must be taken into account:

$$N_2O_4 + xClNO_2 \rightleftharpoons 2NO_2 + xClNO_2$$

The fraction of N_2O_4 that is dissociated (αe) can be calculated by:

$$\alpha e = \frac{-K_pn_f \pm ((K_pn_f)^2 + 4(4nP + K_pn)K_p(n_f + n))^{\frac{1}{2}}}{2(4nP + K_pn)}$$

where:

K_p = equilibrium constant = 0.134 at 25° C

n_f = moles of $ClNO_2$

n = initial moles of N_2O_4

P = total pressure

Since trace impurities of nitrogen dioxide/nitrogen tetroxide were being sought, it was assumed that the sample purity was greater than 99%. Under these conditions, the fraction of nitrogen tetroxide that is dissociated is greater than 0.09. Therefore it can be assumed that the impurity would be nitrogen dioxide.

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