

GAS PHASE ULTRA-VIOLET PHOTOABSORPTION CROSS-SECTIONS FOR NITROSYL CHLORIDE AND NITRYL CHLORIDE

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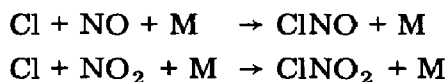
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Summary

The photoabsorption cross-sections for gaseous nitrosyl chloride and nitryl chloride have been determined from 190 to 400 nm at room temperature. The results for nitrosyl chloride differ from the work of Goodeve and Katz, especially at the shorter wavelengths, indicating that nitrosyl chloride is less of a chlorine atom sink in the stratosphere than previously thought. The nitryl chloride spectrum obeys Beer's law and is a continuum consisting of at least three excited electronic states. The absorption cross-section for nitryl chloride varies from 2.1×10^{-21} at 400 nm to 2.7×10^{-17} cm² molecule⁻¹ at 190 nm. No absorption for nitryl chloride (cross-sections less than 2×10^{-21}) was observed from 400 to 750 nm.

Introduction

Nitrosyl chloride (ClNO) and nitryl chloride (ClNO₂) are molecules of importance in the chemistry of the atmosphere [1]. In the stratosphere, these molecules may result from the termolecular reactions of chlorine atoms with nitric oxide and nitrogen dioxide where M is the third body in the reactions:



Photoabsorption cross-sections and quantum yields of photodissociation are of interest in the wavelength region above 190 nm for modelling the chemistry of the stratosphere. In the lower atmosphere, where wavelengths above 300 nm are important, their vapors are observed in the emissions from some

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chemical plants [2] and nitrosyl chloride is produced from the reaction of nitrogen dioxide with sodium chloride aerosols [3]. This paper reports on the photoabsorption cross-sections of nitrosyl chloride and nitryl chloride between 190 and 400 nm at room temperature.

Experimental

Absorption measurements were made with a Perkin-Elmer 450 double beam recording spectrophotometer which has a deuterium arc source, a photomultiplier detector, and a prism dispersing device. The spectral bandpass of the instrument is listed as 0.064, 0.054, 0.04, 0.019 and 0.017 nm at 400, 350, 300, 250 and 200 nm, respectively. The broad continuous absorption bands of Cl_2 , ClNO , and ClNO_2 were readily resolved and gave λ_{max} for Cl_2 [4] and ClNO [5] in agreement with those reported in the literature. The chart accuracy of the spectrophotometer is 0.9 and 0.1 nm at 400 and 200 nm, respectively, and the percentage transmittance accuracy is 0.5%. For measurements below 200 nm, the instrument was purged with nitrogen gas.

The absorption cells consisted of one and two (± 0.01) cm path length Pyrex cells with Suprasil windows and a 9.999 (± 0.001) cm path length cell with sapphire windows. Attached to each cell was a Pyrex tube containing a greaseless Teflon and Viton O-ring stopcock, and a standard taper joint for connection to the vacuum line.

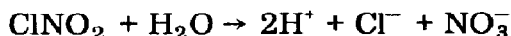
The vacuum system had a three-stage mercury diffusion pump and was evacuated to less than 10^{-3} Torr as indicated by a Bendix GTC-360 thermocouple gauge. In order to protect the manifold from mercury vapors, a liquid nitrogen trap separated the pump from the manifold. The connections between the vacuum manifold and the sample handling bulbs and gas cells were made through glass standard taper joints which were lightly greased with Dow Corning silicon high vacuum grease. All pressure measurements were taken with a dibutyl phthalate or mercury manometer in which the mercury was covered with six inches of dibutyl phthalate to prevent reaction between the gases and the mercury.

Nitrosyl chloride (Matheson Co., 97% minimum purity) was degassed at liquid nitrogen temperatures and distilled twice from -77°C to -196°C . During each distillation, the first and last one-quarter of the sample were discarded. Infra-red absorption spectroscopy showed no impurities in the nitrosyl chloride for pressures as high as 1/3 atm. and path lengths up to 10 cm.

Nitryl chloride was prepared using a modification of the Volpe and Johnston [6] method. A fine stream of anhydrous hydrogen chloride (M. G. Scientific) was passed through a porous glass bubbler into a nitric-sulfuric acid mixture which was vigorously stirred at 0°C with a magnetic stirring bar. The acid mixture contained 75 ml each of 20% fuming sulfuric acid and 98% sulfuric acid, 10 ml of 20% fuming nitric acid, and 40 ml of 69% nitric

acid. A calcium chloride drying tube prevented atmospheric water vapor from entering the apparatus. The nitryl chloride produced was trapped in a tube maintained at -77°C . After each of a number of thaw-freeze cycles the sample was degassed at -196°C , and then distilled twice by bulb-to-bulb distillation from -77° to -196°C , and then distilled portions ($\sim 1/8$ of the sample) of each distillation were discarded. After these distillations the sample was both pumped on and stored at -77°C .

The principle impurities which may be present in the nitryl chloride samples are ClNO, $\text{NO}_2/\text{N}_2\text{O}_4$, and Cl_2 [6]. Infra-red absorption spectroscopy showed no absorption by ClNO and $\text{NO}_2/\text{N}_2\text{O}_4$ in the nitryl chloride samples. Linear Beer's law plots for the infra-red absorption by ClNO [7] and $\text{NO}_2/\text{N}_2\text{O}_4$ [8] were used to fix upper limits of 0.1 and 2% by vol. respectively. A number of experiments were carried out which showed that the nitryl chloride contained little if any chlorine. Activated charcoal when added to nitryl chloride had no effect on the nitryl chloride absorption spectrum while the addition of charcoal to nitryl chloride-chlorine mixtures was found to reduce the ultra-violet absorption in the chlorine absorbing region [4] (240 - 450 nm). Activated charcoal has the ability to absorb 0.7 times its own weight of chlorine [9]. Gas density measurements of four samples ranging in pressure from 0.12 to 0.63 atm. gave a molecular weight of 81.53 ± 0.40 as compared to the true molecular weight of 81.46. The average inherent error was calculated to be 0.74 g/mol and within this error more than 5% chlorine could have been detected. The purity of nitryl chloride was also determined from the amount of chloride ion produced from the reaction [10] of nitryl chloride with water at 25°C :



Any dissolved chlorine which may be present in the sample reacts reversibly with water ($\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl}$). Since this equilibrium is rapidly attained [9] and chlorine is insoluble at 100°C [11], the solution was then boiled for 30 minutes to remove any chlorine gas. The chloride ion was precipitated as AgCl using AgNO_3 and the number of moles of AgCl, which were determined gravimetrically, were compared with the number expected from the pressure-volume measurements of the original gas sample. Two determinations gave a nitryl chloride purity of $99.6\% \pm 0.1\%$. Correcting for chloride ions resulting from the reaction [10] of the possible impurity ClNO with water gives 99.5% minimum purity.

Nitryl chloride was initially prepared by the reaction of chlorosulfonic acid with a fuming sulfuric acid-nitric acid mixture [2]. This synthesis, however, gave approximately 10% chlorine impurity and none of the results reported here used this method.

Nitryl chloride is a pale yellow-colorless liquid and a white solid and its vapor pressure fits the linear expression $\log_{10}P(\text{Torr}) = -1.28 \times 10^3 (1/T(\text{K})) + 7.86$ over the temperature range from 175.4 to 237.2 K. Extrapolation of these data gives a boiling point of 257.1 ± 0.5 K and use of the Clausius-Clapeyron equation results in a heat of vaporization of 5.86 ± 0.11 kcal/mol.

TABLE 1

Ultra-violet photoabsorption cross-sections for gaseous nitrosyl chloride

Wavelength (nm)	Cross-sections (σ) ^b (cm ² molecule ⁻¹)	± Inherent error (cm ² molecule ⁻¹)
400	5.15 (-20) ^a	1.80 (-21) ^a
390	6.10 (-20)	2.14 (-21)
380	7.78 (-20)	2.73 (-21)
370	9.43 (-20)	3.31 (-21)
360	1.13 (-19)	3.98 (-21)
350	1.19 (-19)	4.19 (-21)
340	1.24 (-19)	4.37 (-21)
330	1.20 (-19)	4.23 (-21)
320	1.08 (-19)	3.80 (-21)
310	1.05 (-19)	3.69 (-21)
300	8.67 (-20)	3.05 (-21)
290	8.47 (-20)	2.98 (-21)
280	9.35 (-20)	3.29 (-21)
270	1.15 (-19)	4.05 (-21)
260	1.61 (-19)	5.69 (-21)
250	2.99 (-19)	1.04 (-20)
240	7.68 (-19)	2.82 (-20)
235	1.77 (-18)	6.90 (-20)
230	3.17 (-18)	1.33 (-19)
225	6.00 (-18)	2.92 (-19)
220	1.07 (-17)	6.39 (-19)
215	1.80 (-17)	1.39 (-18)
210	2.99 (-17)	3.20 (-18)
205	4.70 (-17)	7.25 (-18)
200	6.74 (-17)	1.35 (-17)
195	7.58 (-17)	1.72 (-17)
190	5.20 (-17)	8.71 (-18)

^a 5.15 (-20) means 5.15×10^{-20} .

^b $\sigma = \ln(I_0/I)/([ClNO]L)$ where L is optical path length in cm and $[ClNO]$ is in molecules/cm³.

These results compare with the values of 258.2 K and 6.14 kcal/mol reported by Schumacher and Sprenger [12] who prepared nitryl chloride by the reaction of ozone with nitrosyl chloride. These two sets of data give entropies of vaporization for nitryl chloride of 22.79 and 23.78 e.u./mol, respectively.

Results and discussion

The ultra-violet photoabsorption cross-sections for nitrosyl chloride were obtained from 29 spectra with sample pressures varying from 0.72 to 52 Torr. The absorption spectra obeyed Beer's law and each cross-section reported in Table 1 had a percentage standard deviation of $3 \pm 1\%$. Table 1 also includes our

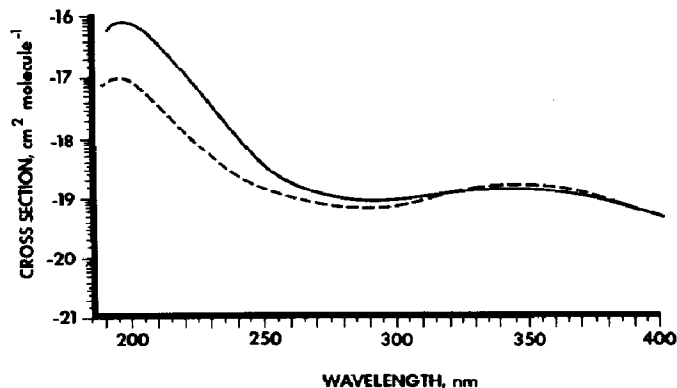


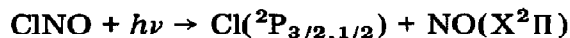
Fig. 1. The ultra-violet photoabsorption spectrum of gaseous nitrosyl chloride at room temperature. This work (—); Goodeve and Katz (- - -).

calculated maximum inherent error for each cross-section. Error treatment for cross-section measurements has been discussed in detail by Hudson [13].

A comparison of our results with those of the work of Goodeve and Katz [5] in 1939 is shown on the semilogarithmic plot in Fig. 1. Our results are significantly higher at the shorter wavelengths (about a factor of 8 at 195 nm) and lower at wavelengths above 325 nm. This disagreement could be due to the presence of chlorine in their nitrosyl chloride. In addition, since this earlier work [5] employed several single beam optical systems with photographic detection, errors may arise due to short term fluctuations in the transmitted radiation intensity, I , or long term drifts of the incident intensity, I_0 . Photographic detection has the advantage of allowing the entire absorption spectrum to be recorded simultaneously, but the disadvantage that calibration is not simple and photographic density is not a linear function of the incident photon flux. Errors in determination of I_0/I can occur because of non-uniformity of the emulsion over the plate or film, incorrect development procedures, and uneven shrinkage on drying [13]. Goodeve and Katz [5] listed no error limits with their cross-sections.

The absorption spectrum of nitrosyl chloride has eleven maxima from 185 to 670 nm [5]. The short wavelength band in Fig. 1 has been labelled A while the long wavelength band was designated B. Photofragment spectroscopy studies [14] of ClNO at 347 nm, which lies predominately in the B band, indicate that this transition is to a state of A' symmetry. A strong diffuse system has also been observed in the vacuum ultra-violet region from 135 to 160 nm [15].

Photolysis studies [14, 16] have shown that the breakage of the Cl-N bond for nitrosyl chloride occurs with a quantum yield of unity over the visible and near ultra-violet bands:



Combining the known photochemistry with our photoabsorption cross-sections and the intense solar radiation fluxes, we predict that stratospheric ClNO is less of a sink for chlorine atoms than previously [17] anticipated.

TABLE 2

Ultra-violet photoabsorption cross-sections for gaseous nitryl chloride

Wavelength (nm)	Cross-sections (σ) ^b (cm ² molecule ⁻¹)	\pm Inherent error (cm ² molecule ⁻¹)
400	2.08 (-21) ^a	1.44 (-22) ^a
390	3.78 (-21)	2.62 (-22)
380	6.16 (-21)	4.28 (-22)
370	1.07 (-20)	7.44 (-22)
360	1.82 (-20)	1.28 (-21)
350	3.06 (-20)	1.42 (-21)
340	4.81 (-20)	1.69 (-21)
330	7.11 (-20)	2.49 (-21)
320	1.02 (-19)	3.59 (-21)
310	1.32 (-19)	4.66 (-21)
300	1.54 (-19)	5.44 (-21)
290	1.80 (-19)	6.37 (-21)
280	2.31 (-19)	8.20 (-21)
270	3.73 (-19)	1.33 (-20)
260	6.37 (-19)	2.32 (-20)
250	9.85 (-19)	3.66 (-20)
240	1.40 (-18)	5.34 (-20)
235	1.80 (-18)	7.03 (-20)
230	2.36 (-18)	9.52 (-20)
225	2.95 (-18)	1.22 (-19)
220	3.42 (-18)	1.46 (-19)
215	3.56 (-18)	1.53 (-19)
210	3.39 (-18)	1.45 (-19)
205	3.22 (-18)	1.36 (-19)
200	4.55 (-18)	2.06 (-19)
197.5	7.13 (-18)	3.66 (-19)
195	1.13 (-17)	8.53 (-19)
190	2.69 (-17)	2.53 (-18)
185	4.74 (-17)	5.09 (-18)

^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/cm³.

Thirty-one spectra were taken of nitryl chloride with pressures from 0.77 to 95 Torr. The spectra obeyed Beer's law and the photoabsorption cross-sections listed in Table 2 had percentage standard deviations of between 3 and 4%. The absorption spectrum (Fig. 2) suggests that at least three electronically excited states are accessible in the region from 185 to 400 nm. No absorption was found ($\sigma < 2 \times 10^{-21}$ cm² molecule⁻¹) in the visible region between 400 and 750 nm. Muller [18] in 1862 had reported that the visible absorption spectrum of nitryl chloride was identical with that of nitrosyl chloride; however, subsequent work had shown that ClNO₂ is a colorless gas. No change was observed in the ultra-violet spectrum of nitryl chloride when a sample was stored for three days at room temperature in the dark indicating little thermal decomposition.

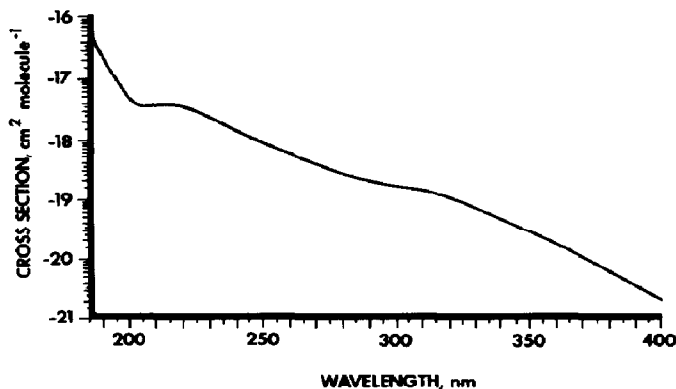
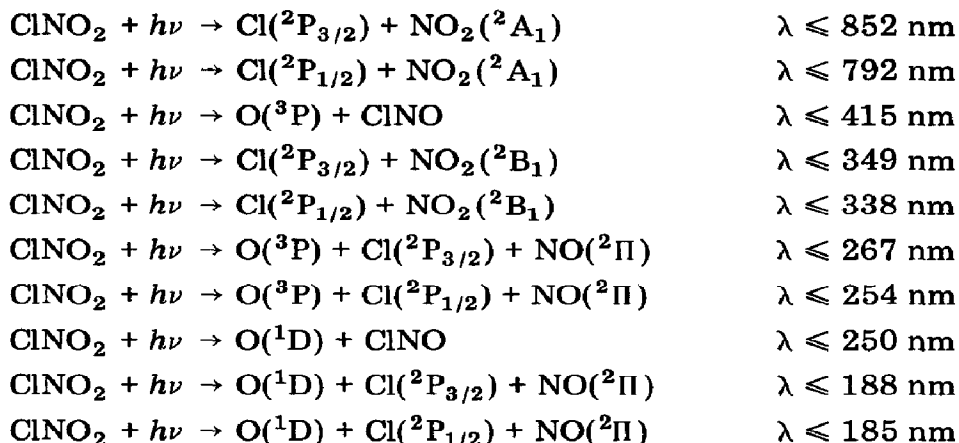


Fig. 2. The ultra-violet photoabsorption spectrum of gaseous nitryl chloride at room temperature.

The continuous shape of the absorption spectrum indicates that photo-dissociation can occur. Some of the energetically possible dissociation steps are listed below with their wavelength limits which were calculated from the Cl-N and O-N bond dissociation energies [19], the atomic energy levels for chlorine [20] and oxygen [21], and the electronic energy levels for nitrogen dioxide [22].



Studies investigating the primary products and their quantum yields from the photolysis of nitryl chloride are in progress.

Acknowledgement

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