

UC Irvine

UC Irvine Previously Published Works

Title

Absorption cross sections for gaseous ClNO

²
and Cl

²
at 298 K: Potential organic oxidant source in the marine troposphere

Permalink

<https://escholarship.org/uc/item/49m9w8kj>

Journal

Journal of Geophysical Research, 97(D7)

ISSN

0148-0227

Authors

Ganske, J. A

Berko, H. N

Finlayson-Pitts, B. J

Publication Date

1992

DOI

10.1029/92JD00414

Peer reviewed

Absorption Cross Sections for Gaseous ClNO₂ and Cl₂ at 298 K: Potential Organic Oxidant Source in the Marine Troposphere

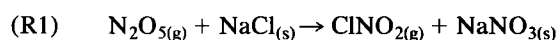
J. A. GANSKE, H. N. BERKO, AND B. J. FINLAYSON-PITTS

Department of Chemistry and Biochemistry, California State University, Fullerton

The absorption cross sections for gaseous ClNO₂ in the 200–370 nm region and for Cl₂ in the 270–400 nm region have been determined at 298 K. The cross sections for Cl₂ are in excellent agreement with the literature. At $\lambda < 300$ nm the absorption cross sections for ClNO₂ are in good agreement with those of Illies and Takacs (1976/1977) and Nelson and Johnston (1981) but are higher than those of Martin and Gareis (1956) from 220 to 240 nm. In the tropospheric region beyond 290 nm our results, which have been corrected for impurity Cl₂ using a combination of mass spectrometry and UV absorption, fall between those of Martin and Gareis (1956) and Illies and Takacs (1976/1977) and are in excellent agreement with the values of Nelson and Johnston (1981). Estimates of the photolysis rate constants and photolytic lifetimes for ClNO₂ for various solar zenith angles at the Earth's surface are reported. It is shown that atomic chlorine from ClNO₂ photolysis may be a significant initiator of organic photooxidation in both moderately polluted and remote marine atmospheres.

INTRODUCTION

The photochemistry of halogen-containing molecules in the atmosphere is currently a topic of vigorous research [World Meteorological Organization, 1990; Brune, 1991]. For example, recent laboratory studies have suggested that ClNO₂ may be formed in both the stratosphere and troposphere via heterogeneous reactions involving gaseous dinitrogen pentoxide. Tolbert *et al.* [1988] and Leu [1988] first reported the reaction of N₂O₅ with HCl/ice mixtures to form ClNO₂, indicating it could be produced by reactions on polar stratospheric clouds and hence play a role in the chemistry of the polar stratosphere. Similarly, the reaction of N₂O₅ with solid NaCl also produces nitryl chloride [Finlayson-Pitts *et al.*, 1989]:



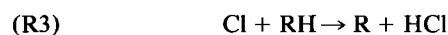
In the polluted marine troposphere, ClNO₂ may be formed from the reaction of NaCl in sea-salt particles with N₂O₅, produced by O₃-NO₂ reactions during nighttime hours [Finlayson-Pitts and Pitts, 1986; Atkinson *et al.*, 1986]. Michelangeli *et al.* [1991] have also suggested that this reaction may occur in the stratosphere after the injection of halide particles by alkaline volcanoes such as El Chichon.

Photolysis of ClNO₂ at 350 nm produces chlorine atoms with a quantum yield within experimental error of unity [Nelson and Johnston, 1981]:



While the reaction of Cl with O₃ is fast ($k^{298} = 1.2 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹) [DeMore *et al.*, 1990], atomic chlorine also reacts rapidly with organics, with rate constants for reaction with even the simple $\geq C_2$ alkanes approaching 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ [DeMore *et al.*, 1990]. Concentrations of total nonmethane organics vary from a few parts per billion (ppb) *C* or less in remote areas such as Mauna Loa [Greenberg *et al.*, 1992] up to parts per million (ppm) *C* in highly polluted urban areas [McElroy *et al.*, 1986]. Over

the Atlantic Ocean, off the coast of the United States, typical concentrations of ~50–100 ppb *C* have been measured recently (P. R. Zimmerman, personal communication, 1991). Thus, in the troposphere, where concentrations of O₃ typically range from 20 to 400 ppb from remote to highly polluted atmospheres respectively [Finlayson-Pitts and Pitts, 1986], chlorine atom reactions with organics may compete with that with O₃. In more polluted areas, they may actually predominate. This reaction, for example with alkanes,



generates free radicals and initiates photooxidation in the atmosphere in much the same manner as the hydroxyl (OH) free radical [Finlayson-Pitts and Pitts, 1986].

The rate of chlorine atom generation and hence its contribution to the oxidation of organics depends on both the rate of ClNO₂ formation and on its rate of photolysis, the latter determined in part by its absorption cross sections at wavelengths greater than 290 nm.

The UV absorption cross sections of ClNO₂ have been reported by Martin and Gareis [1956] from 220 to 325 nm, Illies and Takacs [1976/1977] from 185 to 400 nm, and Nelson and Johnston [1981] from 270 to 370 nm. At the longer wavelengths ($\lambda \geq 290$ nm), which are important in tropospheric photochemistry [Finlayson-Pitts and Pitts, 1986], and particularly at $\lambda \geq 320$ nm, there are significant discrepancies in the reported cross sections, resulting in an uncertainty in the tropospheric rate of ClNO₂ photolysis and hence the rate of chlorine atom generation from this source of as much as ~30%.

In order to assess the potential rate of chlorine atom generation from ClNO₂ in the troposphere, we have remeasured the UV absorption cross sections of ClNO₂ with particular attention to the region $\lambda \geq 320$ nm. The absorption cross sections for Cl₂ have also been measured to correct for the small amounts of Cl₂ which are always present in ClNO₂; these chlorine cross sections are in excellent agreement with previous studies [Gibson and Bayliss, 1933; Fergusson *et al.*, 1936; Seery and Britton, 1964; Burkholder and Bair, 1983]. Finally, we show that initiation of tropospheric organic oxidation by atomic chlorine may be important in both remote and polluted marine atmospheres.

Copyright 1992 by the American Geophysical Union.

Paper number 92JD00414.
0148-0227/92/92JD-00414\$05.00

EXPERIMENTAL

Absorbance measurements were made with a Hewlett-Packard photodiode array ultraviolet-visible (UV-VIS) spectrophotometer (Model HP8452A) with 2 nm spectral bandwidth and 0.05 nm wavelength reproducibility. The absorption cell was a 10.0 cm pathlength pyrex cell with quartz windows and a Teflon stopcock. Pressures in the absorbance cell were measured using a capacitance pressure transducer (Datametrics, Type 570A 0–1000 torr) and electronic manometer (Datametrics Model 1174). Absorption cross sections for nitryl chloride were obtained from five different batches of ClNO₂ using sample pressures ranging from 0.117 to 97.4 torr. For Cl₂, spectra were obtained at pressures from 4.0 to 80.4 torr. All measurements were carried out at 298 K.

Nitryl chloride was prepared using the method of *Volpe and Johnston* [1956]. Briefly, anhydrous HCl (Union Carbide, 99%) was bubbled through a porous glass frit into a mixture of fuming nitric and fuming sulfuric acid which was stirred vigorously at 273 K. A calcium chloride drying tube prevented water from entering the apparatus. Ultrahigh purity He was passed through the reaction mixture immediately prior to, as well as after, the addition of HCl. The nitryl chloride was trapped at 196 K and then degassed by several freeze-pump-thaw cycles at 77 K. The crude product typically contained 92% ClNO₂, along with the impurities Cl₂, ClNO, and NO₂. The ClNO₂ was further purified as previously described [Ganske et al., 1991].

After purification the ClNO₂ used in these experiments was shown by Fourier transform infrared (FTIR) to contain less than 0.02% ClNO. However, despite repeated distillations and the use of a number of different batches of ClNO₂, Cl₂ could only be lowered to ~2%, which is still sufficient to contribute significantly to the absorption spectrum at the longer wavelengths. To correct for this, the impurity Cl₂ present in each ClNO₂ sample in this study was measured quantitatively using mass spectrometry (Extrel EMBA II system) immediately before and for some samples, immediately after the UV absorbance measurements. No increase in chlorine was noted after UV spectral analysis, indicating that insignificant thermal and photochemical decomposition occurred during the measurements. The ClNO₂ absorbances were corrected for the contribution from the Cl₂ impurity using the absorption cross sections for Cl₂ determined independently in these studies. The Cl₂ (Matheson, ≥99.5%) was degassed at 77 K before use.

RESULTS AND DISCUSSION

Figure 1 shows typical absorption spectra for both ClNO₂ and Cl₂. Clearly, even a small amount of Cl₂ can contribute significantly to the absorption at the longer wavelength end of the ClNO₂ absorption. Hence both the percent Cl₂ in the ClNO₂ and absorption cross sections for Cl₂ were determined independently.

Absorption cross sections for Cl₂. Figure 2 gives Beer-Lambert plots of the measured absorbance (base 10) at various wavelengths as a function of the concentration of Cl₂ at 298 K. The plots were linear at all wavelengths, as expected for an unstructured absorption. The absorption cross section σ (cm² molecule⁻¹, base *e*), at a given wavelength is defined by

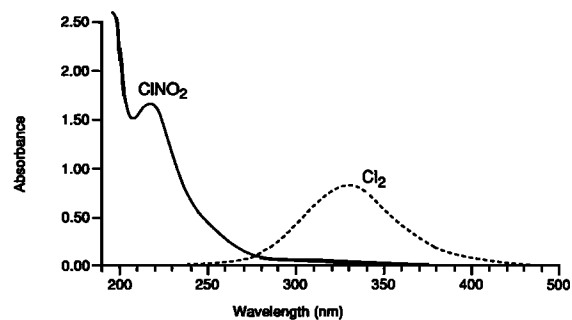


Fig. 1. Typical absorption spectra of gaseous ClNO₂ (3.63 torr) and Cl₂ (21.8 torr) in a 10-cm cell at 298 K.

$$\sigma(\lambda) = \frac{2.303 \log \{I_0(\lambda)/I(\lambda)\}}{[Cl_2] l} \quad (1)$$

where the path length $l = 10.0$ cm, $[Cl_2]$ is the concentration in molecules cm⁻³ and $\log \{I_0(\lambda)/I(\lambda)\}$ is the measured absorbance, base 10. From the slopes of plots such as Figure 2 the quantity $\log \{I_0(\lambda)/I(\lambda)\}/[Cl_2]$ was obtained and (1) then applied to obtain $\sigma(\lambda)$.

Table 1 shows the absorption cross sections for Cl₂ determined in this study as well as those reported earlier [Gibson and Bayless, 1933; Fergusson et al., 1936; Seery and Britton, 1964; Burkholder and Bair, 1983]. Our values are in excellent agreement with the previous studies.

Absorption cross sections for ClNO₂. Broad, unstructured ClNO₂ absorption bands and a λ^{\max} in agreement with previous studies [Nelson and Johnston, 1981; Martin and Gareis, 1956; Illies and Takacs, 1976/1977] were observed. Figure 3, the Beer-Lambert plot for several different wavelengths, is linear up to high absorbances with intercepts within experimental error of the origin. To derive the absorption cross sections, only the data with absorbance values in the range 0.05–1.0 were used to ensure that the data were not biased by small deviations from linearity at the higher pressures. Because of the wide range of absorption intensities from 200 to 370 nm, studies were carried out at

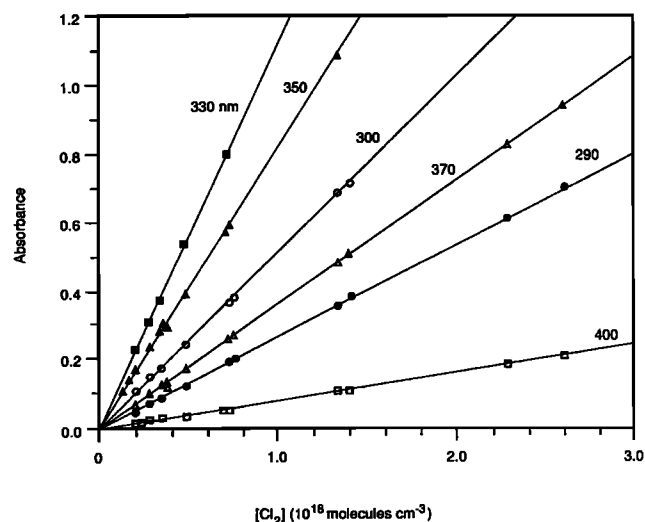


Fig. 2. Absorbance (base 10) as a function of pressure of gaseous Cl₂ at several different wavelengths at 298 K.

TABLE 1. Absorption Cross Sections for Gaseous Cl₂ at 298 K

λ, nm	10 ²⁰ σ, cm ² molecule ⁻¹ , base e*				
	This Work	Gibson and Bayliss [1933]†	Fergusson et al. [1936]‡	Seery and Britton [1964]	Burkholder and Bair [1983]
270	0.86	1.2	0.94	0.88	0.76
280	2.4	3.0	3.0	2.7	2.4
290	6.2	6.9	6.8	6.5	6.3
300	11.8	12.1	12.1	12.0	12.0
310	18.4	18.4	18.9	18.5	18.7
320	23.7	23.6	24.4	23.6	23.9
330	25.8	24.6	26.1	25.6	26.1
340	23.6	22.7	24.4	23.6	23.9
350	18.8	18.4	19.5	19.0	19.5
360	13.1	13.0	13.7	13.2	13.9
370	8.3	8.5	8.2	8.3	8.8
380	4.9	5.4	4.9	4.9	5.3
390	2.9	3.1	3.0	3.3	3.0
400	1.9	2.0	1.9	1.9	1.9

*The absorption cross section $\sigma = (\ln I_0/I)/Nl$, where N is the concentration in molecules cm⁻³ and the path length $l = 10.0$ cm.

†Interpolated from data at different wavelengths; experiments carried out at 291 K.

‡Obtained from Figure 2 (log₁₀ε versus wavelength) of Fergusson et al. [1936].

lower pressures of ClNO₂ (0.12–4.6 torr) to determine the absorption cross sections in the region $\lambda < 300$ nm and at higher pressures (to 97.4 torr) for the 300–370 nm region.

At wavelengths at and above 300 nm the ~2% impurity Cl₂ contributes more than 1% to the measured absorbances. Corrections for the Cl₂ contribution were made in the following manner. First, the slope (S) of the plot of absorbance versus total pressure was obtained at each wavelength. This slope is given by

$$S = l[f\epsilon_{\text{ClNO}_2} + (1-f)\epsilon_{\text{Cl}_2}] \quad (2)$$

where f is the fraction of ClNO₂ in the gas (0.98–0.99 in these studies), $(1-f)$ is the fraction of Cl₂, $l = 10.0$ cm, and ϵ_i are the absorption coefficients (units of torr⁻¹ cm⁻¹, base 10) of ClNO₂ and Cl₂ respectively. Since ϵ_{Cl_2} can be obtained from the absorption cross sections for Cl₂ as discussed above, and S , and $(1-f)$ are measured in these experiments, ϵ_{ClNO_2} can be determined and converted to the absorption cross section σ (cm² molecule⁻¹, base e) using

the appropriate conversion factors. The maximum correction to the total measured absorbance due to the Cl₂ impurity was 19% at 370 nm. Figure 4 and Table 2 summarize the absorption cross section data for ClNO₂ from this and previous studies.

The uncertainty in our cross sections from 200 to 290 nm, based on scatter in the absorbance-pressure plots such as Figures 2 and 3 (which includes different batches of ClNO₂), is $\pm 5\%$. From 300 to 370 nm there is an additional error associated with subtracting the contribution from Cl₂. This increases the uncertainty in the 300–360 nm region to $\pm 10\%$ and at 370 nm, to $\pm 20\%$.

Our absorption cross sections in the 200–300 nm region are within 5% of the data of Illies and Takacs [1976/1977] and Nelson and Johnston [1981], but are 8–24% higher than those of Martin and Gareis [1956] in the 220–240 nm region. In the 310–370 nm region our results are generally within ~5% of those of Nelson and Johnston [1981], except at 350 nm where our absorption cross section is 12.5% higher. Our values are significantly larger than those of Martin and Gareis [1956] from 310 to 325 nm, and lower than those of Illies and Takacs [1976/1977] from 310 to 370 nm. The reasons for these discrepancies are not clear. Nelson and Johnston [1981] suggest the presence of a 6% Cl₂ impurity would be consistent with the higher cross sections in the Illies and Takacs [1976/1977] study. The resolution used in our studies (2 nm) was lower than that used in earlier work. However, this is not expected to yield significantly different cross sections for unstructured absorptions such as Cl₂ and ClNO₂, which is confirmed by the excellent agreement between our cross sections for Cl₂ and the literature values.

Atmospheric implications. The implications of our absorption cross section data can be explored by using them to estimate photolysis rate constants (k_p) for ClNO₂ at the Earth's surface at various solar zenith angles. For illustrative purposes, the actinic flux recommendations of Peterson [1976] and Demerjian et al. [1980] can be used to obtain estimates of k_p . Table 3 summarizes these calculations, taking the quantum yield to be 1.0 as reported by Nelson and

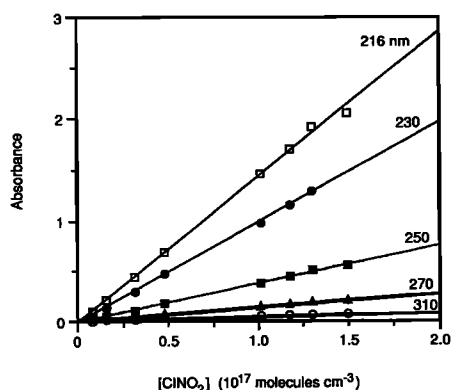


Fig. 3. Absorbance (base 10) as a function of concentration of gaseous ClNO₂ for several wavelengths. The absorbances have not been corrected for the small amount (2.2%) of Cl₂ present for which the largest correction is 19% at 370 nm.

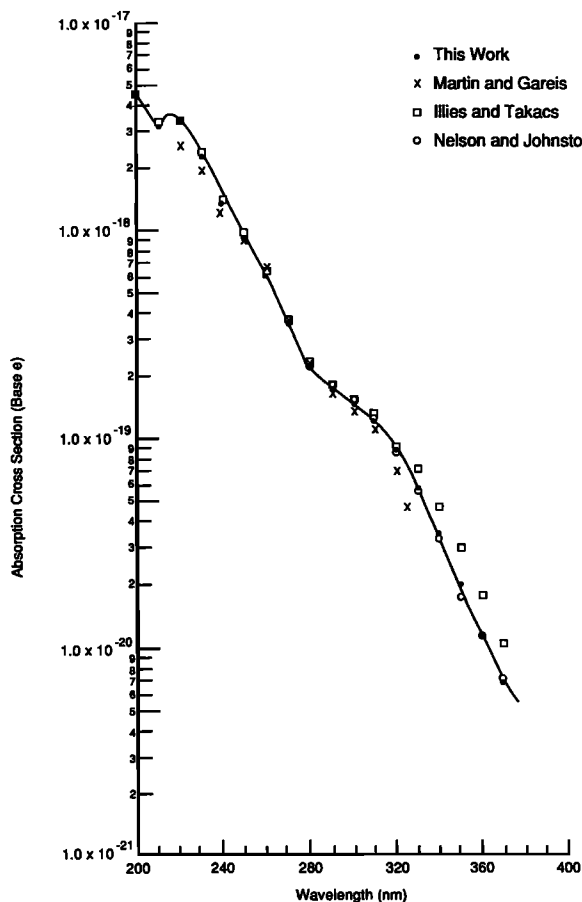
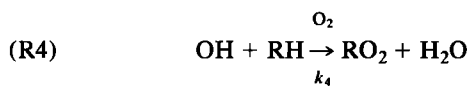


Fig. 4. Absorption cross sections for gaseous ClNO₂ as a function of wavelength at 298 K. Solid circles: this study; crosses: *Martin and Gareis* [1956]; open squares: *Illies and Takacs* [1976/1977]; open circles: *Nelson and Johnston* [1981].

Johnston [1981] at 350 nm. Also shown are the corresponding lifetimes of ClNO₂ with respect to photolysis ($\tau^{\text{ClNO}_2} = 1/k_p$), and the photolysis rate constants calculated using the higher-absorption cross sections of *Illies and Takacs* [1976/1977]. It can be seen that the smaller-absorption cross sections lead to photolysis rate constants and hence rates of chlorine atom generation from ClNO₂, which are ~75% of those predicted using the data of *Illies and Takacs* [1976/1977]. It should be noted that these photolysis rate constants are likely to be upper limits, and hence the lifetimes lower limits, to the effective tropospheric values; thus the average tropospheric temperature is less than 298 K and the absorption cross sections are expected to fall with decreasing temperature.

In the troposphere the major initiator of organic oxidation is the OH radical [*Finlayson-Pitts and Pitts*, 1986]:



However, because chlorine atoms also react rapidly with organics,

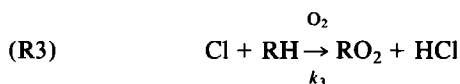


TABLE 2. Absorption Cross Sections of Gaseous ClNO₂ at 298 K

λ , nm	$10^{20} \sigma$, cm ² molecule ⁻¹ , base e*			
	This Study	<i>Martin and Gareis</i> [1956]†	<i>Illies and Takacs</i> [1976/1977]	<i>Nelson and Johnston</i> [1981]
200	468		455	
210	320		339	
216	348		356‡	
220	339	2.6×10^2	342	
230	226	1.9×10^2	236	
240	133	1.2×10^2	140	
250	90.6	90	98.5	
260	61.3	66	63.7	
270	35.3	36	37.3	37.2
280	22.0	23	23.1	22.3
290	17.3	17	18.0	18.1
300	14.9	14	15.4	15.5
310	12.1	11	13.2	12.5
320	8.87	6.7	10.2	8.70
330	5.84		7.11	5.58
340	3.54		4.81	3.33
350	2.04		3.06	1.78
360	1.15		1.82	1.14
370	0.69		1.07	0.72

*The absorption cross section $\sigma = (\ln I_0/I)/Nl$, where N is the concentration in molecules cm⁻³ and the path length $l = 10.0$ cm.

†Obtained from Figure 3 ($\log_{10} e$ versus wavelength) of *Martin and Gareis* [1956].

‡Peak value at 215 nm is reported.

they too can initiate photooxidation if produced in sufficient quantities. Steady state concentrations of OH and Cl can be estimated from their rate of production by photolysis of precursors (such as HONO, O₃, and HCHO in the case of OH, and ClNO₂ in the case of Cl), and their rate of removal. For example, if (R3) with organics were the sole removal process, the steady state concentration of atomic chlorine

TABLE 3. Calculated Photolysis Rate Constants and Photolytic Lifetimes for ClNO₂ at the Earth's Surface at Various Solar Zenith Angles

Solar Zenith Angle, deg	$10^4 k_p$ (s ⁻¹)*		τ , ‡ hours
	This Study	<i>Illies and Takacs</i> [1976/1977]†	
0	3.82	4.87	0.73
10	3.77	4.81	0.74
20	3.62	4.62	0.77
30	3.35	4.29	0.83
40	2.96	3.81	0.94
50	2.44	3.16	1.1
60	1.77	2.32	1.6
70	1.00	1.33	2.8
78	0.44	0.59	6.3
86	0.088	0.12	31

*Calculated from $k_p = \sum \phi \sigma J$, where J are the actinic irradiance values (photons cm⁻² s⁻¹) from *Peterson* [1976] and *Demerjian et al.* [1980]. Quantum yield assumed to be 1.0 at all wavelengths, based on measurement of *Nelson and Johnston* [1981] at 350 nm.

†Using absorption cross sections out to 370 nm only; including their values reported out to 400 nm increases k_p by 6–12%.

‡Lifetime of ClNO₂ with respect to photolysis using absorption cross sections from this study.

would be given by $[Cl]_{ss} = k_p[ClNO_2]/k_3[RH]$. The rate of reaction of the organic, $d[RH]/dt$, in (R3) is then given by

$$\frac{d[RH]}{dt} = k_3[RH][Cl]_{ss} = k_p[ClNO_2] \quad (3)$$

A similar approach applies to the reaction of organics with OH. Thus a rough semiquantitative assessment of the relative importance of chlorine atoms and the hydroxyl radical in organic oxidations can be obtained by comparing the rates of generation of Cl and OH, respectively.

For comparison, in polluted urban atmospheres, HONO acts as a significant source of OH at dawn [Finlayson-Pitts and Pitts, 1986]. Using the recommended absorption cross sections [DeMore et al., 1990] and actinic irradiance values at the Earth's surface [Peterson, 1976; Demerjian et al., 1980] the rate of generation of OH from 3 ppb HONO at a solar zenith angle of 86° is approximately 5×10^6 radicals $cm^{-3} s^{-1}$.

The rate of chlorine atom generation depends on the ambient concentration of ClNO₂, which has not been measured. However, an estimate of potential concentrations in polluted marine areas can be obtained from the collision rate of N₂O₅ with NaCl particles and the reaction probability ϕ for this gas-solid reaction [Finlayson-Pitts and Pitts, 1986]. From gas-kinetic molecular theory the rate of collisions (C) of the gas at concentration $[N_2O_5]$ with a surface of area A is given by

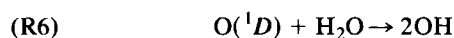
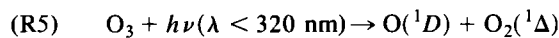
$$C = [N_2O_5]A(RT/2\pi M)^{1/2} \quad (4)$$

where R is the gas constant, T the temperature, and M the molecular weight of N₂O₅. The available surface area per cubic centimeter of air for suspended NaCl particles at a concentration of 30 particles cm^{-3} and radius 1 μm is $4 \times 10^{-6} cm^2$. At an N₂O₅ concentration [Atkinson et al., 1986] of 1 ppb (1 ppb = 2.5×10^{10} molecules cm^{-3} at 298 K), the gas-solid collision rate is 6×10^8 collisions $cm^{-3} s^{-1}$.

The rate of production of ClNO₂ is then given by ϕC . In separate experiments [Livingston and Finlayson-Pitts, 1991] a lower limit to ϕ has been shown to be $>2.5 \times 10^{-3}$ for the reaction of N₂O₅ with dry NaCl at 298 K. The most recent study of the reaction probability [Hanson and Ravishankara, 1991] for the analogous reaction of N₂O₅ with HCl/ice reports $\phi = 0.024$ at 200 K, suggesting that the N₂O₅-NaCl reaction could be at least an order of magnitude faster than the lower limit. Taking $\phi = 0.024$ for an NaCl surface, the rate of generation of ClNO₂ is 1.4×10^7 molecules $cm^{-3} s^{-1}$, or ~ 0.6 ppt s^{-1} . In 10 hours of darkness, for example, overnight, 5×10^{11} ClNO₂ cm^{-3} , or ~ 20 ppb could be formed. This is likely an overestimate, as it assumes constant availability of N₂O₅ and salt surface, and in addition assumes the reaction is not limited by diffusion to the surface which becomes increasingly important at $\phi > 10^{-3}$ [Schwartz and Freiberg, 1981]. However, it does provide an order-of-magnitude approach.

At a solar zenith angle of 86°, characteristic of early morning, the rate of chlorine atom generation, given by $k_p[ClNO_2]$, is approximately 4×10^6 atoms $cm^{-3} s^{-1}$, comparable to that for OH generation from 3 ppb HONO. Thus, even given the relatively small absorption cross sections for ClNO₂ in the actinic region, it may well be responsible for significant amounts of organic photooxidation in polluted marine urban areas.

In more remote marine areas the photolysis of O₃, followed by the reaction of electronically excited O(¹D) with water, is a major source of OH:



$$k_6 = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

O(¹D) can also be deactivated to the ground state by air ($k_{N_2} = 2.6 \times 10^{-11}$, $k_{O_2} = 4.0 \times 10^{-11}$ $cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [DeMore et al., 1990]. At a relative humidity of 50% at 298 K, approximately 10% of the O(¹D) reacts with water, the rest being deactivated. Using the recommended [DeMore et al., 1990] absorption cross sections and quantum yields for O₃, the rate of OH generation from (R5) and (R6) at a solar zenith angle of 86° and an O₃ concentration of 40 ppb is $\sim 8 \times 10^3$ radicals $cm^{-3} s^{-1}$.

The concentration of N₂O₅ has not been measured in remote marine areas. It will depend on the concentrations of NO₃ and NO₂ from which it is formed, as well as the temperature, since the equilibrium constant for the NO₂-NO₃-N₂O₅ system is very temperature-sensitive [DeMore et al., 1990]. Taking a constant N₂O₅ concentration of 1 ppt (2.5×10^7 molecules cm^{-3}), which seems reasonable [Finlayson-Pitts et al., 1990] based on NO₂ and O₃ concentrations, and the same NaCl concentration as above, a ClNO₂ concentration of 5×10^8 molecules cm^{-3} (~ 20 ppt) could be formed in 10 hours of darkness. At a solar zenith angle of 86° the rate of chlorine atom generation would then be $\sim 4 \times 10^3$ atoms $cm^{-3} s^{-1}$, again comparable to the OH generation by ozone photolysis.

Clearly, these calculations are approximate in nature and have a number of uncertainties associated with them, in addition to those discussed above. For example, the effects of varying amounts of water on the NaCl particle surface on the ClNO₂ yield is not known so that these estimates are most relevant to dry particles below the deliquescence point of NaCl, $\sim 76\%$. In addition, the sea-salt particles are not distributed evenly throughout the troposphere but are found primarily in the tropospheric boundary layer. Hence the potential for a significant contribution of chlorine atoms to volatile organic compound oxidation is greatest in the marine boundary layer impacted by NO_x emissions.

However, given the potential importance of chlorine atom chemistry in marine areas, it is important that a search for such species as ClNO₂ be undertaken, for example using infrared spectroscopy, in both polluted and remote areas. In addition, it is important to simultaneously measure NO₃ and NO₂ concentrations in these areas so that concentrations of N₂O₅ can be calculated. Furthermore, obtaining the gas-solid reaction efficiency for the N₂O₅-NaCl reaction, as well as for other potential chlorine sources such as the NO₂-NaCl reaction [Schroeder and Urone, 1974; Finlayson-Pitts, 1983] is important; such studies are currently underway in this laboratory.

Finally, if chlorine atoms are significant contributors to organic photooxidation in marine areas, the relative rates of decay of the organics should reflect the relative rate constants for reaction with Cl, which are different from those for reaction with OH. It might therefore be productive to follow the relative rates of loss in a mixture of organics after sunrise

in marine air masses where fresh injections of the organics into the air mass are minimal.

Acknowledgments. We are grateful to the National Science Foundation for support of this work (grant ATM 9005321). We thank M. J. Ezell and T. Jayaweera for technical assistance, C. Lai for review of the manuscript, and P. R. Zimmerman for providing data prior to publication.

REFERENCES

- Atkinson, R., A. M. Winer, and J. N. Pitts, Jr., Estimation of night-time N₂O₅ concentrations from ambient NO₂ and NO₃ radical concentrations and the role of N₂O₅ in night-time chemistry, *Atmos. Environ.*, **20**, 331–339, 1986.
- Brune, W. H., Stratospheric chemistry, *Rev. Geophys.*, suppl., **29**, 12–24, 1991.
- Burkholder, J. B., and E. J. Bair, Potential energy parameters and shapes of the vibrational components of the 345-nm system of chlorine, *J. Phys. Chem.*, **87**, 1859–1863, 1983.
- Demerjian, K. L., K. L. Schere, and J. T. Peterson, Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants of atmospheric species in the lower troposphere, *Adv. Environ. Sci. Technol.*, **10**, 369–459, 1980.
- DeMore, W. B., S. P. Sander, D. M. Golden, M. J. Molina, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ.*, **90-1**, Jan. 1, 1990.
- Fergusson, W. C., L. Slotkin, and D. W. G. Style, The absorption spectrum of aqueous chlorine and hydrogen peroxide vapour, *Trans. Faraday Soc.*, **32**, 956–962, 1936.
- Finlayson-Pitts, B. J., Reaction of NO₂ with NaCl and atmospheric implications of NOCl formation, *Nature*, **306**, 676–677, 1983.
- Finlayson-Pitts, B. J., and J. N. Pitts, Jr., *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, John Wiley, New York, 1986.
- Finlayson-Pitts, B. J., M. J. Ezell, and J. N. Pitts Jr., Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N₂O₅ and ClONO₂, *Nature*, **337**, 241–244, 1989.
- Finlayson-Pitts, B. J., F. E. Livingston, and H. N. Berko, Ozone destruction and bromine photochemistry at ground level in the Arctic spring, *Nature*, **343**, 622–625, 1990.
- Ganske, J. A., M. J. Ezell, H. N. Berko, and B. J. Finlayson-Pitts, The reaction of OH with ClNO₂ at 298 K: Kinetics and mechanisms, *Chem. Phys. Lett.*, **179**, 204–210, 1991.
- Gibson, G. E., and N. S. Bayliss, Variation with temperature of the continuous absorption spectrum of diatomic molecules, Part I, Experimental, the absorption spectrum of chlorine, *Phys. Rev.*, **44**, 188–192, 1933.
- Greenberg, J. P., P. R. Zimmerman, W. H. Pollock, R. Lueb, and L. E. Heidt, Diurnal Variability of atmospheric methane, non-methane hydrocarbons and carbon monoxide at Mauna Loa, *J. Geophys. Res.*, in press, 1992.
- Hanson, D. R., and A. R. Ravishankara, The reaction probabilities of ClONO₂ and N₂O₅ on polar stratospheric cloud materials, *J. Geophys. Res.*, **96**, 5081–5090, 1991.
- Illies, A. J., and G. A. Takacs, Gas phase ultra-violet photoabsorption cross-sections for nitrosyl chloride and nitryl chloride, *J. Photochem.*, **6**, 35–42, 1976/1977.
- Leu, M. T., Heterogeneous reactions of N₂O₅ with H₂O and HCl on ice surfaces, *Geophys. Res. Lett.*, **15**, 851–854, 1988.
- Livingston, F. E., and B. J. Finlayson-Pitts, The reaction of gaseous N₂O₅ with solid NaCl at 298 K: Estimated lower limit to the reaction probability and its potential role in tropospheric and stratospheric chemistry, *Geophys. Res. Lett.*, **18**, 17–20, 1991.
- Martin, H., and R. Gareis, Die kinetik der reaktion von ClO₂ mit NO₂ in der Losungsphase, *Z. Elektrochem.*, **60**, 959–964, 1956.
- McElroy, F. F., V. L. Thompson, D. M. Holland, W. A. Lonnenman, and R. L. Seila, Cryogenic preconcentration-direct FID method for measurement of ambient NMOC: Refinement and comparison with GC speciation, *J. Air Pollut. Control Assoc.*, **36**, 710–714, 1986.
- Michelangeli, D. V., M. Allen, and Y. L. Yung, Heterogeneous reactions with NaCl in the El Chichon volcanic aerosols, *Geophys. Res. Lett.*, **18**, 673–676, 1991.
- Nelson, H. H., and H. S. Johnston, Kinetics of the reaction of Cl with ClNO and ClNO₂ and the photochemistry of ClNO₂, *J. Phys. Chem.*, **85**, 3891–3896, 1981.
- Peterson, J. T., Calculated actinic fluxes (290–700 nm) for air pollution photochemistry, *Rep. EPA-600/4-76-025*, U.S. Environ. Protect. Agency, Washington, D. C., June 1976.
- Schroeder, W. H., and P. Urone, Formation of nitrosyl chloride from salt particles in air, *Environ. Sci. Technol.*, **8**, 756–758, 1974.
- Schwartz, S. E., and J. E. Freiberg, Mass-transport limitation to the rate of reaction of gases in liquid droplets: Application to oxidation of SO₂ in aqueous solutions, *Atmos. Environ.*, **15**, 1129–1144, 1981.
- Seery, D. J., and D. Britton, The continuous absorption spectrum of chlorine, bromine, bromine chloride, iodine chloride and iodine bromide, *J. Phys. Chem.*, **68**, 2263–2266, 1964.
- Tolbert, M. A., M. J. Rossi, and D. M. Golden, Antarctic ozone depletion chemistry: Reactions of N₂O₅ with H₂O and HCl on ice surfaces, *Science*, **240**, 1018–1021, 1988.
- Volpe, M., and H. S. Johnston, Energy transfer processes in the unimolecular decomposition of nitryl chloride, *J. Am. Chem. Soc.*, **78**, 3903–3910, 1956.
- World Meteorological Organization, Scientific Assessment of Stratospheric Ozone: 1989, *Rep. 20*, vol. 1, Global Res. and Monit. Proj., World Meteorol. Org., Geneva, 1990.

H. N. Berko, B. J. Finlayson-Pitts, and J. A. Ganske, Department of Chemistry and Biochemistry, California State University, Fullerton, CA 92634.

(Received September 9, 1991;
revised February 13, 1992;
accepted February 13, 1992.)