Chlorine Nitrate Photochemistry. Photolysis Products and Kinetics of the Reaction CI + $CIONO_2 \rightarrow CI_2 + NO_3$

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The photolysis of chlorine nitrate was studied at 266 and 355 nm by using atomic resonance fluorescence detection of the primary products (O and Cl). The major photolysis route is to $Cl + NO_3$ ($\phi_1 = 0.90$) with the O + ClONO channel accounting for $\phi_2 = 0.10$. The kinetics of the reaction Cl + ClONO₂ \rightarrow Cl₂ + NO₃ (k₄) were studied over the temperature range 219–298 K. In Arrhenius form, $k_4(T) = 6.3 \times 10^{-12} \exp(150/T)$. The value $k_4(298)$ = 1.04×10^{-11} cm³ s⁻¹ is a factor of 50 faster than previously reported. A possible error in the prior kinetics study is identified, and the divergent results of earlier quantum yield studies are reconciled.

Introduction

Chlorine nitrate is a major reservoir for odd chlorine in the lower stratosphere where it is formed by the reaction

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

and removed chiefly by photolysis:¹

 $\begin{array}{c} \text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3 \\ \rightarrow 0 + \text{ClONO} \\ \rightarrow \text{ClO} + \text{NO}_2 \end{array}$ (ϕ_1) (ϕ_2) (ϕ_3)

A full assessment of the photochemical role played by chlorine nitrate requires a detailed knowledge of its photolytic decomposition channels. In three earlier studies of that photolysis, conflicting results were obtained. Two studies identified channel 2, O + ClONO, as the major photolysis route: Smith et al.² used steady-state photolysis and end-product analysis of mixtures with and without added ethane to infer that Cl atoms were not produced and on the basis of overall quantum yields, determined that channel 2 was dominant. Using flash photolysis-resonance absorption, Adler-Golden and Wiesenfeld³ saw definite (but unquantified) O-atom production and set an upper limit of <4% on Cl-atom yield, based on the lack of any Cl-atom appearance. In contradistinction, Chang et al.,⁴ using very low-pressure photolysis with mass spectrometric product detection, identified NO₃ (m/e 62) as the major product and inferred that channel 1, $Cl + NO_3$, was the dominant route with possibly $\sim 10\%$ of the photolysis yielding O + ClONO.

In this work, the $Cl + NO_3$ channel has been found to be the major route ($\sim 90\%$) for chlorine nitrate photolysis at 266 and 355 nm. In addition, the reaction of Cl with ClONO₂

$$Cl + ClONO_2 \xrightarrow{k_4} Cl_2 + NO_3$$

has been measured to be $\sim\!50$ times faster than reported previously.^{5,6} A possible source of error in that earlier kinetics study is identified later (see Discussion) and the divergent results for chlorine nitrate photolytic quantum yields are reconciled as a result of the new value obtained for k_4 .

Experimental Section

The photolysis of chlorine nitrate and kinetics of the Cl + $ClONO_2$ reaction were studied in the laser photolysisresonance fluorescence system shown in Figure 1. Chlorine nitrate, maintained in a bubbler in a low-temperature bath (methanol-dry ice, 195 K, or chloroform slush, 210 K), saturated a measured helium flow and entered a 30-cm long cell where its concentration was measured via absorption of 214-nm radiation from a Zn lamp. This flow (0-100 sccm) was diluted upon addition to the main cell by the major carrier gas flow (1000–5000 sccm), the flow rates being measured with calibrated Hastings mass flowmeters. Photolysis was achieved by using the frequency-tripled or -quadrupled (355 or 266 nm) output of a Quanta Ray Nd:YAG laser which was aligned along the flow axis of the photolysis cell. Mutually orthogonal axes contained O-ring ports used for the resonance fluorescence detection with Woods horn light traps opposite the detector (EMR 541G photomultiplier) and lamp, which was a standard microwave discharge of a flowing $\sim 0.1\%$ Cl₂ in He stream (for Cl atoms) or $\sim 1\%$ O₂ in He for O atoms. Cl atoms were usually detected by using resonance fluorescence in the 119-nm transition by flowing oxygen through an 0.8-cm filter between the lamp and cell to block residual 130-nm oxygen resonance emission and the 135-140-nm Cl lines. Some experiments utilized the 135-140-nm transitions by purging the filter with N_2 and inserting a BaF₂ window in front of the lamp to screen out the residual 130-nm O-atom radiation. O atoms were detected by using the 130-nm triplet in conjunction with the N_2 -purged filter. Experiments with and without a CaF_2 window inserted in front of the lamp to remove Lyman α (H-atom) emission were indistinguishable.

Photolytic quantum yields were quantified by photolyzing known concentrations of a calibrating gas: NO_2 for O-atom yields, and Cl_2 or NOCl for Cl-atom yields. The Cl + ClONO₂ kinetics study utilized 355-nm photolysis of Cl_2 as the Cl-atom source, except for some experiments where 266-nm photolysis of ClONO₂ was used to provide the Cl atoms.

Temperatures were varied by circulating methanol from a Haake circulator through the jacketed cell and were measured with external thermocouples which had been cross-checked against an internal thermocouple probe which could be inserted into the gas stream in the center

⁽¹⁾ F. S. Rowland, J. E. Spencer, and M. J. Molina, J. Phys. Chem., 80, 2711-3, 2713-5 (1976).

⁽²⁾ W. S. Smith, C. C. Chou, and F. S. Rowland, Geophys. Res. Lett., 4, 517-9 (1977).

⁽³⁾ S. M. Adler-Golden and J. R. Wiesenfeld, Chem. Phys. Lett., 82, 281-4 (1981).

⁽⁴⁾ J. S. Chang, J. R. Barker, J. E. Davenport, and D. M. Golden, *Chem. Phys. Lett.*, 60, 385–90 (1979).
(5) M. J. Kurylo and R. G. Manning, *Chem. Phys. Lett.*, 48, 279–83

⁽¹⁹⁷⁷⁾

⁽⁶⁾ The value of k, mentioned in A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, *Geophys. Res. Lett.*, 4, 7-9 (1977), has not been published as the result from a detailed kinetics study and is not considered further in this paper.



Figure 1. Schematic diagram of the apparatus.

of the detection/reaction volume.

Chlorine nitrate used in this study was obtained from M. J. Molina and L. T. Molina at the University of California, Irvine,⁷ and was thoroughly degassed at 77 K. The vapor released upon warming to 195 K was used to acclimate the bubbler and handling line and then pumped away. A sample of ClONO₂ was then vacuum distilled from the storage vessel (195 K) to the bubbler (77 K). For experiments, the ClONO₂ was warmed to 195 or 210 K and flowed through the system for ~0.5 h before actual experiments were performed. This procedure purified the chlorine nitrate sample of more volatile impurities (it was, in essence, a distillation in which the initial fraction was discarded) and minimized contamination from the heterogeneous reaction⁸

$$2\text{ClONO}_2 + \text{H}_2\text{O}_{\text{adsorbed}} \rightarrow \text{Cl}_2\text{O} + 2\text{HNO}_3$$

The helium carrier gas was passed through a molecular sieve trap at 77 K immediately upstream of the bubbler to preclude contamination of the chlorine nitrate sample.

To verify the purity of the chlorine nitrate, samples were admitted to a 10-cm cell and analyzed on a Cary 14 spectrophotometer. The measured cross sections agreed within a few percent with the accepted values.⁹ The lack of enhanced absorption in the 280-nm region verified that the mole fraction of Cl_2O was <0.1%. The OClO impurity level was <0.01%, based upon the nonappearance of the 352-nm absorption peak. The NO₂ impurity level was <0.2%.

TABLE I: Cross Sections at 298 K

	$10^{20}\sigma$, cm ² molecule ⁻¹				
molecule	$\lambda = 355 \text{ nm}$	$\lambda = 266 \text{ nm}$	ref		
ClONO,	0.218	26	9		
Cl,	15.5	0.50	10		
NŐ,	51.3	2.2	9		
NOĈI	13.8	15.3	11		

Results

Quantum Yields. The quantum yields for production of Cl and O atoms in the photolysis of chlorine nitrate were obtained by comparing the atomic resonance fluorescence signal arising from photolysis of chlorine nitrate to that resulting from photolysis of a suitable precursor molecule whose absorption cross section and quantum yield were known: NO₂ photolysis for O-atom calibration and Cl₂ or NOCl photolysis for Cl-atom calibration.

In the absence of reabsorption of the emitted photons, the resonance fluorescence signal due to chlorine atoms produced from chlorine nitrate photolysis ($S_{\rm Cl}^{\rm CIONO_2}$) is proportional to the [Cl] which, in turn, is proportional to the [ClONO₂]

$$S_{Cl}^{ClONO_2} = C_{Cl}^{ClONO_2}[ClONO_2]$$
(I)

where $C_{\rm Cl}^{\rm ClONO_2}$ is the combined proportionality constant and is the product of several terms

$$C_{\rm Cl}^{\rm ClONO_2} = F_{\rm laser} \sigma_{\rm ClONO_2} \phi_{\rm Cl}^{\rm ClONO_2} D_{\rm Cl} \tag{II}$$

 F_{laser} is the laser flux, σ_{CIONO_2} is the absorption cross section of chlorine nitrate at the photolyzing wavelength, $\phi_{\text{Cl}}^{\text{CIONO}_2}$ is the quantum yield for production of Cl from ClONO₂ photolysis, and D_{Cl} is the resonance fluorescence detection constant for chlorine atoms and is a function of resonance lamp intensity and various geometry factors which are independent of the molecule being photolyzed. Thus, equations similar to eq I and II can be written for a reference compound (e.g., Cl₂) of known photolysis behavior and can be combined with I and II to give

$$\phi_{\mathrm{Cl}}^{\mathrm{CIONO}_2} = \frac{C_{\mathrm{Cl}}^{\mathrm{CIONO}_2}}{C_{\mathrm{Cl}}^{\mathrm{Cl}_2}} \frac{\sigma_{\mathrm{Cl}_2}}{\sigma_{\mathrm{CIONO}_2}} \phi_{\mathrm{Cl}}^{\mathrm{Cl}_2}$$

The known cross sections (and quantum yield for producing Cl from Cl₂) can then be combined with experimentally determined values of the two proportionality constants $C_{\rm Cl}^{\rm ClONO_2}$ and $C_{\rm Cl}^{\rm Cl_2}$ to obtain the quantum yield for production of Cl from ClONO₂. The C values are determined by measuring the fluorescence signals in the first MCA channel following the flash from several different concentrations of $ClONO_2$ or Cl_2 and plotting S vs. concentration to give C as the slope. Signals were generally accumulated over 1000-5000 laser flashes so that pulseto-pulse variations in laser flux were averaged out, but the overall experimental operating time was kept short (2-10 min per value) so that long-term laser drift ($\sim 5\%$) and resonance lamp drift (i.e., window transmission deterioration) were minimized. By alternately doing ClONO₂ runs and calibrating gas runs, we could further cancel experimental drift. Cross sections used in this work are listed in Table I. The quantum yield for production of Cl from Cl₂ is 2; $\phi_0^{NO_2}$ at 355 nm is 0.94.¹² All other calibrating gas quantum yields were taken to be unity.

⁽⁷⁾ Preparation of the chlorine nitrate is described in L. T. Molina, J.
E. Spencer, and M. J. Molina, *Chem. Phys. Lett.*, 45, 158-62 (1977).
(8) M. J. Molina, private communication, 1982.

^{(9) &}quot;Chemical Kinetics and Photochemical Data for Use in Atmospheric Modelling, Evaluation No. 4", NASA Panel for Data Evaluation, JPL 81-3, Jet Propulsion Laboratory, Pasadena, CA.

⁽¹⁰⁾ R. T. Watson, J. Phys. Chem. Ref. Data, 6, 871-917 (1977).
(11) NOCl cross sections were measured here and found to be identical

⁽¹¹⁾ Noci ross sections were measured nere and tould to be definition with those of N. M. Ballash and D. A. Armstrong (Spectrochim. Acta, Part A, 30, 941-4 (1974)) over the range 260-400 nm.

⁽¹²⁾ D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data, 9, 295-471 (1980).

Quantum yields were determined for photolysis at both 266 and 355 nm, with no discernible difference. The average value obtained for $\phi_{Cl}^{ClONO_2}$ was 0.93 ± 0.09 (single standard deviation) for eight determinations at 298 K. A set of three experiments at 238 K (with $\lambda = 355$ nm) yielded a quantum yield of 0.80 ± 0.05 . In view of the difficulties inherent in the quantum yield measurements and the overlap of the individual experimental values, the differences between the 298 and 238 K yields may not be real, and an overall average of 0.90 ± 0.10 would be reasonable for modeling purposes. A quantum yield determination involves ratioing two separate C-value measurements, each accurate to $\pm 10-15\%$ at best. The 355-nm experiments are particularly difficult since the peak signal observe for ClONO₂ photolysis is 50-100 counts in 5000 flashes.

The quantum yields for production of O atoms varied from 0.08 to 0.25, with no apparent dependence on wavelength or temperature. Undoubtedly, some of this variation was due to residual Cl in the resonance lamp, which excited the dominant product, Cl and contributed slightly to the apparent O-atom fluorescence signal. The Cl interference was minimized in one set of measurements by flowing only He through the lamp for several days and making a $\phi_0^{\text{ClONO}_2}$ determination without having added any Cl₂ to the lamp. That determination gave $\phi_0^{\text{ClONO}_2} = 0.10$. Additional verification that the signal was truly due to O-atom fluorescence was obtained by measuring the rate of that O-atom disappearance due to reaction with ClONO₂ and obtaining values consistent with the known⁹ rate constant for O + ClONO₂ (nearly 2 orders of magnitude slower than Cl + ClONO₂). A value of 0.10 for $\phi_0^{\text{ClONO}_2}$ would be consistent with the measured $\phi_{\rm Cl} = 0.90$ and lies nearer the lower end of the observed range of ϕ_0 values, which is reasonable in view of the potential chlorine interference. All quantum yields represent primary photolysis since they were observed to be independent of laser power for factors of 2 or 3 variations in that photolysis flux.

An attempt was made to identify possible production of ClO (ϕ_3) by adding NO to the photolysis mixture and looking for additional Cl atoms from

 $ClO + NO \rightarrow Cl + NO_2$

The results were indistinguishable from photolysis without NO, giving an upper limit of $\phi_{ClO} < 0.2$. Kinetics of $Cl + ClONO_2 \rightarrow Cl_2 + NO_3$. The chlorine-

Kinetics of $Cl + ClONO_2 \rightarrow Cl_2 + NO_3$. The chlorineatom fluorescence signal resulting from $ClONO_2$ photolysis was observed to decay at a rate nearly 50 times faster than that expected from the literature value⁵ for the process

$$Cl + ClONO_2 \rightarrow products$$

where k_4 had been reported to be 2.2×10^{-13} cm³ s⁻¹ at 298 K. Since the apparent value of $k_4 = 1 \times 10^{-11}$ cm³ s⁻¹ was independent of laser power, residence time, pressure, and number of flashes, reactions with impurities and photolysis products seemed unlikely to account for a value of that magnitude. A detailed investigation was therefore undertaken.

Molecular chlorine was photolyzed at 355 nm to provide chlorine atoms, which were monitored by resonance fluorescence at 119 nm. A typical semilogarithmic plot of the decay of that signal as a function of time is shown in Figure 2. The slope of that plot gives directly $k_{obsd}^{I} = k_4[ClONO_2] + k_d^{I}$, where k_d^{I} comprises mostly diffusive loss of Cl atoms out of the formation/detection region. The linearity of the decay plots over 2 orders of magnitude change in [Cl] verifies that secondary reactions are unimportant. A plot of k_{obsd}^{I} vs. [ClONO₂] gives k_4 as the slope (Figure 3). The [ClONO₂] in the photolysis cell was de-



Figure 2. Typical In S CI vs. t decay plot.



Figure 3. Typical k¹_{obsd} vs. [CIONO₂] plot.

termined by absorption in the 30-cm cell and the ratio of flow rate through the cell $(0-100 \text{ cm}^3 \text{ min}^{-1})$ divided by total flow $(1000-5000 \text{ cm}^3 \text{ min}^{-1})$:

$$[\text{ClONO}_2] = \frac{\ln I / I_0}{(30)(3.5 \times 10^{-18})} \frac{F_{\text{cell}}}{F_{\text{total}}}$$

For a given low-temperature slush bath, I/I_0 was constant, and the [ClONO₂] was changed by varying the flow rate. A different range of concentrations was obtained for the same flow rates by changing the slush bath. Either dry ice-methanol (195 K) or a chloroform slush (210 K) was used. In addition to expanding the range of concentrations



Figure 4. k_{0bbd}^{1} vs. [CIONO₂] plot showing independence of results on [CI]₀.



Figure 5. Arrhenius plot of ln k_4 vs. 1/T.

available, the change in the baths varied the residence times of the chlorine nitrate within the handling system. The independence of k_4 with regard to slush bath (Figure 3) thus provides evidence that decomposition of CIONO_2 in the handling lines was unimportant.

To further verify the lack of secondary chemistry, we varied $[Cl]_0$ over nearly 1 order of magnitude by varying $[Cl_2] \times 11 \times 10^{13}$ cm⁻³) and laser power (10–40 mJ), with no effect on the observed decay rates as seen in Figure 4. Additionally, the rate was observed to be independent of the number of flashes per sample (varied from 3 to 1 by varying the flow velocity).

Experiments were performed over the temperature range 219–298 K at pressures of He and Ar of 20–100 torr. The results are summarized in Table II and plotted in Arrhenius form in Figure 5. The average of 10 independent k_4 values at 298 K (comprising 79 individual experiments) is $k_4(298) = (1.04 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The Arrhenius expression for the line in Figure 5 is

$$k(T) = 6.3 \times 10^{-12} \exp(150/T)$$

The 4% uncertainty quoted for k(298) is the 1σ standard deviation and indicates the precision (reproducibility) of the measurement; overall experimental accuracy is estimated to be $\pm 15\%$.

Because of the great disparity between this study and the previous Kurylo and Manning⁵ work on Cl + ClONO₂, extensive experimental checks were performed. The excellent linearity of the semilogarithmic decay plots coupled with the independence of the rate constant upon changes in [Cl]₀, Cl₂, laser power, and number of flashes precludes interference from secondary reactions.

The most fundamental point to verify was that the fluorescence signal resulted from Cl atoms. The resonance

TABLE II: Summary of Results for k_4

<i>Т</i> , К	М	P, torr	pow- er, mJ	10^{-13} . [Cl ₂] ₀ , cm ⁻³	no. of expts	notes	$10^{11} \cdot k^{\Pi}, \ cm^3 \ s^{-1}$
298	He	40	30	4.7	15	а	1.01
	He	80	30	4.7	7	а	1.06
	He	40	30	4.7	8	ь	1.02
	He	46	30	1.5	5	b,c	1.02
	Ar	40	40	4.6	7	а	1.06
	Ar	40	40	2.0	5	а	1.06
	Ar	40	40	10.6	5	а	1.10
	Ar	40	10	4.6	7	а	1.10
	Ar	20	40	4.6	10	b	0.97
	Ar	100	40	4.0	10	b	1.00
273	He	40	30	5.0	7	а	1.14
258	He	40	30	5.3	10	а	1.20
249	\mathbf{He}	40	30	5.5	7	а	1.16
248	He	40	40	4.4	10	а	1.10
238	He	40	30	5.8	12	а	1.20
	He	80	30	5.8	9	а	1.27
223	He	40	30	6.1	7	а	1.19
219	He	40	40	4.8	9	а	1.24
	He	40	10	4.8	9	а	1.24
	He	80	40	5.0	6	а	1.25

^a ClONO₂ bath at -78 °C. ^b ClONO₂ bath at -63 °C. ^c Increased velocity; 1 flash/sample.

fluorescence detection at 119 nm used an 0.8 cm atm O_2 filter which blocked out all vacuum-UV lamp emission except for the 119-nm Cl line and the hydrogen Lyman α line at 121.6 nm. Some experiments were also performed by using the Cl multiplet near 135 nm (no O_2 filter) with a BaF₂ window inserted to block all radiation shorter than 132 nm (i.e., blocking O at 130 nm and H at 121.6 nm). Additionally, experiments were conducted by using 266-nm photolysis of ClONO₂ as the Cl-atom source. All cases yielded identical results. Further confirmation of the experimental reliability was obtained by measuring the rate constant for the reaction

$$Cl + CH_4 \rightarrow CH_3 + HCl$$

The value measured $(k = 0.95 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1})$ is in excellent agreement with the recommended⁹ $k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

The possibility that the Cl disappearance might be due to reaction with an impurity was carefully investigated. Because the measured rate constant was 1×10^{-11} cm³ s⁻¹, assuming that the reactant was ClONO₂, any impurity reaction would have to be extremely fast to account for the observed rate. A reasonable candidate is

$$Cl + Cl_2O \xrightarrow{\kappa_5} Cl_2 + ClO$$

which, since $k_5 = 1 \times 10^{-10}$ cm³ s⁻¹, requires a 10% Cl₂O in ClONO₂ impurity level. Since the ClONO₂ itself was known to contain <0.1% impurity (see Experimental Section), the Cl₂O would have had to arise from heterogeneous decomposition

$$2\text{ClONO}_2 + \text{H}_2\text{O}_{\text{adsorbed}} \xrightarrow{\text{surface}} \text{Cl}_2\text{O} + 2\text{HNO}_3$$

This process could be ruled out by the observation that k_4 was independent of residence times in either the handling lines or main photolysis system, since there is no obvious mechanism which could account for 10% conversion of ClONO₂ into Cl₂O independent of [ClONO₂] and time. Nonetheless, an in situ absorption analysis was carried out.

At the low concentrations of chlorine nitrate used in the experiments, it was not possible to perform in situ absorption analysis. By lowering the flow velocity by 1 order of magnitude and increasing [ClONO₂] by a factor of 10, we could obtain concentrations that were high enough to permit spectroscopic observation in a 20-cm long cell downstream of the photolysis cell. Absorption was measured at 241 and 283 nm and yielded an upper limit for Cl_2O of <3%, which excludes $Cl + Cl_2O$ as the source of the Cl loss.

Adler-Golden and Wiesenfeld³ encountered difficulties in their measurement of the $O + ClONO_2$ rate constant due to impurities (OClO and NO₂) resulting from photodecomposition of the $ClONO_2$ by their resonance lamp. Such interferences were insignificant in this study. The fluorescence lamp and detector optical axes were orthogonal to the flow axis, so that the residence time of $ClONO_2$ in the lamp beam was ~ 30 ms. Since the Cl + OClO rate constant is only a factor of 6 faster than the $Cl + ClONO_2$ rate constant being measured, an OClO/ClONO₂ impurity level of $\sim 15\%$ would have been required for the observed rate constant to be explained by Cl + OClO. This would require a resonance-lamp-induced photolysis of ClONO₂ of ~5 s⁻¹ which, if $\sigma \sim 10^{-17}$ cm², requires a lamp flux of 5×10^{17} photons cm⁻² s⁻¹ which is about 2 orders of magnitude greater than normally expected. The Adler-Golden and Wiesenfeld study of $O + ClONO_2$ was much more sensitive to contamination due to the slower rates being observed, and the absorption detection technique which increases exposure of $CIONO_2$ to the analysis lamp. Empirical evidence that the kinetic results here are not complicated by impurities from such resonance lamp photodecomposition consists of the following: (1) Rate constants are independent of flow velocity, i.e., residence time in the lamp beam. (2) Cl detection at 119 and 135 nm yielded identical rate constants, even though the total lamp fluxes were very different. (3) Resonance lamp intensity was varied by 1 order of magnitude (window transmission deterioration) with no effect on observed rate constants. In addition, the rates of O-atom disappearance were observed to be consistent with the literature O + $ClONO_2$ rate constant, indicating a lack of interference from impurities.

Semiquantitative confirmation of the kinetics was obtained in a discharge flow-mass spectrometric apparatus. The disappearance of Cl atoms upon addition of $\sim 10^{13}$ cm⁻³ ClONO₂ was observed to be in good agreement with $k_4 = 1 \times 10^{-11}$ cm³ s⁻¹. Also, by monitoring ClONO₂ via its fragment peak at m/e 46 (NO₂), we observed the disappearance of ClONO₂ upon addition of excess Cl atoms ($\sim 10^{13}$ cm⁻³), along with the appearance of a small peak at m/e 62, which would correspond to the NO₃ product (the m/e 62 peak disappeared quickly upon addition of NO, consistent with NO₃ behavior). The products of the Cl + ClONO₂ reaction were iden-

The products of the Cl + ClONO₂ reaction were identified by performing photolysis experiments with varying amounts of NO present $(1.5 \times 10^{14}-50 \times 10^{14} \text{ cm}^{-3})$. If the reaction proceeded through O-atom abstraction to form ClO + ClONO, the added NO would have regenerated Cl atoms via

$$ClO + NO \rightarrow Cl + NO_2$$

resulting in curved decay plots and lower k^{I}_{obsd} values. In contrast, the observed effect of added NO was to increase k^{I}_{obsd} in a manner consistent with the rate constant for

$$Cl + NO + Ar \xrightarrow{k_6} ClNO + Ar$$

(The observed k_6 was ~20% lower than the literature value.⁹)

Discussion

This study clearly establishes that $k_4 \sim 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 298 K. The disparity between this work and the

earlier Kurylo and Manning study⁵ must therefore be a result of a systematic error in that investigation. The most reasonable explanation is that they were observing the disappearance of O atoms via the $O + ClONO_2$ reaction and that, at their concentrations of ClONO₂, virtually all the Cl had disappeared before their observations began. This explanation is based on the observation in this study that a Cl lamp emits O resonance radiation with about 10-30% of the intensity of an optimized O lamp, and it is supported by the following observations regarding the Kurylo and Manning work: (1) Their k^{I}_{obsd} vs. [ClONO₂] data clearly show that some reaction involving ClONO₂ was being studied. (2) Their reported results for $Cl + ClONO_2$ are consistently $\sim 20\%$ higher than their O + ClONO₂ results. (3) The resonance fluorescence was performed "without wavelength resolution", and no mention is made of the use of a BaF_2 window to screen out lamp H and O resonance lines, as was done in other Cl kinetic studies in that laboratory.¹³ (4) Observation of the fluorescence was begun 350 μ s after the flash due to what was ascribed to a flash-lamp tail; this is a significantly longer decay than they normally used. Similar results could be obtained here by operating the lamp as a combined O and Cl lamp.

These new results for k_4 are in much better agreement with those expected based on other Cl-atom reactions: the previous A factor of 2×10^{-12} cm³ s⁻¹ was low compared to normal A factors of $\sim 1 \times 10^{-11}$ cm³ s⁻¹ for most Cl reactions. Additionally, the old $k(298) = 2.2 \times 10^{-13}$ cm³ s⁻¹ was unusually low compared to the rate constants for Cl + ClNO (3 × 10⁻¹¹) and Cl + Cl₂O (9.8 × 10⁻¹¹).

The results for the ClONO₂ quantum yields obtained here are in excellent agreement with the study of Chang et al.⁴ The determination that photolysis at 355 nm is not markedly different from that at 266 nm indicates that the shoulder appearing on the ClONO₂ absorption curve for $\lambda > 350$ nm does not correspond to a major change in the photolysis route.

The disagreement between this work (and Chang et al.⁴) and the Adler-Golden and Wiesenfeld³ study, which did not observe Cl atoms, can be ascribed to the rapid removal of the photolytically formed Cl by reaction with ClONO₂. The new value for k_4 measured here indicates that, for their typical [ClONO₂] $\sim 5 \times 10^{14}$ cm⁻³, the Cl lifetime for disappearance would have been $\sim 200 \ \mu$ s, comparable to their delay time. Since they did not attempt to quantify their observed O-atom yield, they were unaware that it only accounted for $\sim 10\%$ of the photolysis. The Smith et al.² quantum yield determination was

The Smith et al.² quantum yield determination was based on the nonappearance of additional HNO₃ when $ClONO_2$ was photolyzed with C_2H_6 present:

$$ClONO_{2} \rightarrow Cl + NO_{3}$$
$$Cl + C_{2}H_{6} \rightarrow HCl + C_{2}H_{5}$$
$$HCl + ClONO_{2} \xrightarrow{\text{surface}} Cl_{2} + HNO_{3}$$

The lack of HNO_3 was taken to mean that Cl was not a primary product. The final products and quantum yields are consistent with photolysis to either Cl + NO_3 or O + ClONO. Although the Smith et al. work cannot be particularly faulted, the complex heterogeneous chemistry required for inferring the results makes it less reliable than the direct observations of the present study and that of Chang et al.

The results of this study will not seriously impact current stratospheric models. Those models are presently using $Cl + NO_3$ as the major products of $ClONO_2$ photo-

⁽¹³⁾ M. J. Kurylo and W. Braun, Chem. Phys. Lett., 37, 323-5 (1976).

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lysis, which is consistent with this work. Even with the much faster value for k_4 , the low concentration of Cl throughout the stratosphere precludes $Cl + ClONO_2$ being a significant loss of $ClONO_2$, relative to the much faster photolysis.

Finally, these results may indicate a useful source of NO₃ for kinetic studies:

$$ClONO_{2} + h\nu \rightarrow Cl + NO_{3}$$

$$Cl + ClONO_{2} \rightarrow Cl_{2} + NO_{3}$$
net
$$2ClONO_{2} + h\nu \rightarrow Cl_{2} + 2NO_{3}$$

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Note Added in Proof. Kurylo et al.¹⁴ have recently remeasured k_4 and obtain $k_4 = 7.3 \times 10^{-12} \exp(165/T) \text{ cm}^3$ s⁻¹ in excellent agreement with the results reported here.

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Studies of the Protein–Protein Interaction of Lysozyme in Dimethyl Sulfoxide–Water Solutions by Quasielastic Light Scattering

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The mean relaxation time of lysozyme due to translational diffusion in the Me_2SO-H_2O solution has been measured with the laser light beating spectroscopic technique. The effective hydrodynamic radius is determined as a function of the Me₂SO concentration and as a function of the concentration of lysozyme. A reversible polymerization process associated with the Me₂SO-induced protein-protein interaction has been observed. Extensive polymerization occurs at the mole fraction of Me_2SO in the range of 0.17–0.32.

Introduction

Studies of the protein-protein interaction and protein denaturation phenomena in the presence of chemical agents are of great research interest. In the aqueous protein solution, the presence of dimethyl sulfoxide (Me₂SO) is known to be capable of causing a reversible conformational change of the protein because of the substitution of the water molecules by Me₂SO.¹ If Me₂SO is added to an aqueous solution of lysozyme, significant conformational change can occur when the Me₂SO concentration is between 60 to 70 vol % (corresponding approximately to a 2:1 Me₂SO hydrate, $(CH_3)_2SO \cdot 2H_2O$. This result was obtained on the basis of the change in the optical rotation and intrinsic viscosity data of the lysozyme molecules in Me_2SO-H_2O solution.² Since the optical rotation technique measures the amount of helical (coiled) structure present in the distribution of the protein conformation, it does not directly provide information about the actual size change as the protein molecule undergoes the conformational change. In contrast, the quasielastic light scattering technique has the advantage of being able to directly determine the actual average size of the macromolecule in the solution. Several review articles concerning the theory of optical mixing spectroscopy as applied to the study of motion of macromolecules in a solution can be found in literature.³⁻⁵ Thus, only a brief description of this technique is required here.

For a monodisperse macromolecular sample in a solution, the time correlation function g(t) associated with the translational diffusion of macromolecules is given by

$$g(t) = \exp(-t/\tau) \tag{1}$$

where τ is the relaxation time due to translation diffusion and is related to the translation diffusion coefficient D by $\tau = (Dq^2)^{-1}$. The quantity q is the amplitude of the scattering vector given by

$$q = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2} \tag{2}$$

where n is the index of refraction of the scattering medium; λ_0 is the wavelength of the excitation light in vacuo; θ is the scattering angle.

According to the simple Stokes-Einstein formula, the diffusion coefficient D is related to the effective hydrodynamic radius R by

$$D = kT/(6\pi\eta R) \tag{3}$$

where η is the viscosity of the solvent.

On the basis of eq 1 and 3, it is quite clear that quasielastic light scattering is an effective method for a direct determination of the size change of the macromolecule in a solution. This optical mixing technique has been used

⁽¹⁾ S. J. Singer, "Advances in Protein Chemistry", Vol. 1, Academic Press, New York, 1962

⁽²⁾ K. Hamaguchi, J. Biochem. (Jpn.), 56, 441 (1964).

R. Pecora, Annu. Rev. Biophys. Bioeng., 1, 257 (1972).
 S. Fujime, Adv. Biophys., 3, 1 (1972).
 B. Chu, "Laser Light Scattering", Academic Press, New York, 1974.