Photolysis of Chlorine Nitrate at 254 nm

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The photolysis of ClONO₂ has been studied at 254 nm. The production of NO₃, NO₂, and ClONO and the removal of ClONO₂ have been observed directly, and the yield of $O({}^{3}P)$ has been inferred from the production of O₃. The production of Cl and NO₃ was found to be the dominant photolysis pathway. For ClONO₂ concentrations of $\leq 5 \times 10^{13}$ molecules cm⁻³, the values determined for the quantum yields for the removal of ClONO₂, $-\Phi_{ClONO_2}$, and the production of NO₃, Φ_{NO_3} , were 0.99 ± 0.1 and 1.04 ± 0.04 , respectively. However, these yields appear to be dependent on the ClONO₂ concentration and decrease as ClONO₂ concentration increases. For ClONO₂ concentrations in the range $(3-8) \times 10^{14}$ molecules cm⁻³, the yields, obtained for the formation of O, NO₂, and ClONO, are $\Phi_0 = 0.24$, $\Phi_{NO_2} = 0.25$, and $\Phi_{ClONO} \le 0.2$. No evidence was found for a significant production of NO. The observed behavior may be explained by the production of a long-lived excited state of $CIONO_2$. The results are discussed in relation to the stratospheric behavior of CIONO₂.

Introduction

ClONO₂ is thought to act as a temporary reservoir in the stratosphere for both NO_x (i.e., NO and NO₂) and ClO_x (i.e., Cl and ClO) species.^{1,2} The reactions of such compounds play an important role in determining the stratospheric O₃ abundance. Photolysis by ultraviolet radiation is an important loss process for ClONO₂ in the stratosphere. However, the precise effect of this process on the stratospheric O₃ budget depends on the nature of the products formed. Several photolysis pathways are available to CIONO₂:

> $CIONO_2 + h\nu \rightarrow CIO + NO_2$ $\lambda_1 \leq 1100 \text{ nm}$ (1)

> > \rightarrow Cl + NO₃ $\lambda_2 \leq 700 \text{ nm}$ (2)

 \rightarrow Cl + NO + O₂ $\lambda_3 \leq 652 \text{ nm}$ (3)

 \rightarrow ClONO + O(³P) $\lambda_4 \leq 391 \text{ nm}$ (4)

 \rightarrow Cl + NO₂ + O(³P) $\lambda_5 \leq 318$ nm (5)

 \rightarrow ClONO + O(¹D) $\lambda_6 \leq 241 \text{ nm}$ (6)

The gas-phase ultraviolet photolysis of ClONO₂ has been studied by a variety of techniques, of which two studies indicated evidence for channel 4. Smith et al.³ photolyzed ClONO₂ mixtures at 302.5 nm and used end product analysis to determine the dominant photochemical pathways. Adler-Golden and Wiesenfeld⁴ observed the production of O atoms in the flash photolysis of ClONO₂ mixtures but failed to observe Cl atoms and estimated an upper limit for the quantum yield of Cl to be 4%.

In contrast, four groups have found evidence for channel 2. Chang et al.⁵ used the technique of very low pressure photolysis to study the photochemical pathways 1 to 5, the light source used being a high-pressure xenon lamp. Detection of both products and reactants was made by mass spectrometry, and NO₃ was shown to be the major product of the reaction by the appearance of the m/e 62 peak. Cl atoms were identified by the observation of either Cl₂ in ClONO₂-N₂ mixtures or HCl in mixtures which contained added C_2H_6 . In addition, $O(^{3}P)$ yields were inferred by an NO₂ titration technique. Quantum yields for the production of Cl atoms, NO₃, and O(³P) of 1.0 ± 0.2 , 0.5 ± 0.3 , and ≤ 0.1 , respectively, were determined, and the authors concluded that channel 2 is the dominant photolysis channel. Marinelli and Johnston⁶ studied reactions 1-5 at 249 nm; the primary photolysis product NO₃ was detected by tunable dye-laser absorption spectroscopy at 662 nm. The primary quantum yield for NO₃ production was found to be (0.5(-0.1 + 0.3)). Margitan⁷ also studied the photolysis of ClONO₂ by laser flash photolysis, using a Nd:YAG laser at 266 and 355 nm. He observed the production of Cl and O atoms by resonance fluorescence and determined the quantum yields for Cl and O atom production to be 0.9 and 0.1.

Finally, Knauth and Schindler⁸ photolyzed ClONO₂ in the presence of NO₂ at 263 and 313 nm using a high-pressure Hg lamp and appropriate optical filters. Relatively high concentrations of ClONO₂ were used, and end product analysis was made by mass spectroscopic, ultraviolet, and infrared measurements. These authors found quantum yields for the removal of ClONO2 and production of N_2O_5 of 1.12 ± 0.2 and 0.96 ± 0.15, respectively.

The objective of this study was to investigate the primary products formed in the photolysis of ClONO₂ at 254 nm. A secondary aim was to understand the apparent discrepancy in the literature between the quantum yields for the production of NO₃ and Cl atoms.

Experimental Section

The photolysis of ClONO₂ at 254 nm has been investigated in the same apparatus in three ways. The first method employed continuous photolysis of flowing gas mixtures with reactant and product detection by matrix isolation Fourier transform infrared (FTIR) spectroscopy. In the second method the continuous photolysis of static gas mixtures was observed by UV-visible absorption measurements. The third approach employed the modulated photolysis of flowing gas mixtures (known as molecular modulation spectroscopy (MMS)), with detection of reactants and products by UV-visible absorption spectrometry.

The apparatus used in this study has been described in detail elsewhere^{9,10} and is shown schematically in Figure 1. The photolysis cell consisted of a jacketed quartz vessel, 148 cm long, whose end windows were inset yielding an optical path length of 114 cm. The photolysis cell was internally coated with a thin film of Teflon to minimize wall reactions.

The photolysis cell was surrounded by six low-pressure Hg lamps (Philips TUV lamps). More than 90% of the output intensity of these lamps is in the 253.7-nm emission; the rest of the power is distributed over the other Hg emission lines and a weak visible continuum. The photolysis lamps were powered by a

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Figure 1. Schematic diagram of the matrix isolation FTIR, UV-visible absorption, and modulated photolysis apparatus.

TABLE I: Ultraviolet Absorption Cross Sections Used in Th	is Study ^{a,o}
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gas	220 nm	235 nm	254 nm	313 nm	350 nm	400 nm	623 nm	ref
Cl ₂	c	_		1.9×10^{-19}	1.8 × 10 ⁻¹⁹	_	_	13
CIONO,	3.4×10^{-18}	1.5×10^{-18}	4.8×10^{-19}	1.3×10^{-20}	-	-	-	13
CIONO	?d	2.1×10^{-18}	7.5×10^{-19}	1.0×10^{-18}	2.7×10^{-19}	6×10^{-21}	-	22
CINO	9.0×10^{-18}	1.5×10^{-18}	2.4×10^{-19}	1.2×10^{-19}	1.4×10^{-19}	_	-	14
NO ₂	4.1×10^{-19}	1.5×10^{-19}	1.9×10^{-20}	2.0×10^{-19}	3.9×10^{-19}	6.1×10^{-19}	1.9×10^{-20}	15
NO	-	-	-	_	-	-	1.2×10^{-17}	10, 23
N_2O_5	2.2×10^{-18}	7.7×10^{-19}	3.4×10^{-19}	1.9×10^{-20}	2.3×10^{-21}	_	-	13

^a The units are cm² molecule⁻¹. ^b The resolution is 5 nm except for NO₃ where the resolution is 1 nm. ^c-denotes σ undetermined or anticipated small value (i.e., $\sigma \le 1 \times 10^{-19}$ cm² molecule⁻¹). ^d? denotes that σ is undetermined but its value estimated by extrapolation is large (i.e., $\sigma \approx 3 \times 10^{-18}$ cm² molecule⁻¹).

20-kHz signal of up to 1 kV and were switched on and off at frequencies between 0.01 Hz and 5 kHz or run continuously. The ratio of light-on to light-off time could be varied between 0.1 and 9.

Collimated light from either a D_2 lamp or a quartz halogen lamp passed once through the cell before being focused onto the entrance slit of a 0.3-m monochromator. The wavelength calibration of the monochromator was checked at 254, 313, 404, and 632.8 nm with the emission from a low-pressure Hg lamp and a HeNe laser. The current from the photomultiplier was converted to a voltage, V. In the absence of photolysis this voltage was then offset by an equal and constant voltage, V_0 . The residual signal, $\Delta \nu = V - V_0$, was sent to a 1024-channel 9-bit averager. In this manner small modulated absorptions produced in the cell can be measured with increased sensitivity. A photodiode which observed the photolysis lamps provided the trigger for the averager. The optical density, OD, for small absorptions is given by

$OD = \Delta v / V_0$

After an experiment, the signal from the averager and the voltage V_0 were sent to a microcomputer for mathematical manipulation. Modulated absorptions of both products and reactants were recorded at different wavelengths (e.g., NO₃ at 623 nm, NO₂ at 400 nm), and the absorption cross sections used are listed in Table I. The initial gas-phase concentration of ClONO₂ was determined from optical density measurements at 220 nm on its addition to and removal from the cell.

Matrices were grown in a microsampling cryostat which was connected to the photolysis cell through a Teflon solenoid valve. Typically, matrices were grown at 10 K by opening the solenoid valve in five 0.15-s pulses. The cryostat chamber was mounted permanently to the FTIR spectrometer, Model BOMEM DA03.01. Matrix isolation FTIR spectra were usually recorded from 400 to 3900 cm^{-1} at 0.5-cm⁻¹ resolution.

ClONO₂ was synthesized by mixing freshly prepared Cl₂O with N_2O_5 at 195 K and allowing the contents to warm slowly to 273 K.¹¹ The resulting mixture was purified by trap-to-trap distillation at 195, 155, and 77 K. The fraction which collects at 155 K contains ClONO₂. The distillation was repeated several times to ensure high purity.

Experiments were performed on both static and flowing mixtures of ClONO₂ in N₂ or O₂. Flows of ClONO₂ were obtained by passing dry N₂ through ClONO₂ held at 195 K. As shown in Figure 1, the gas mixtures are flowed transversely through the photolysis cell to ensure thorough mixing. At 195 K the vapor pressures of the solids N₂O₅ and N₂O₄ are much lower than that of the liquid ClONO₂. Consequently, any impurities in the ClONO₂ do not enter the flow. The purity of ClONO₂ in the photolysis cell was investigated by both its UV absorption and matrix isolation FTIR spectra. Small amounts of NO₂ and HNO₃ were observed. The source of the HNO₃ is probably heterogeneous reaction of ClONO₂ and H₂O at the wall of the cell. The source of NO₂ may well be decomposition of ClONO₂ and HNO₃ on the walls of the cell.

The decay of static mixtures of $ClONO_2$ in the cell was monitored both by matrix isolation FTIR and UV absorption. It was essential to condition the photolysis cell to minimize wall losses:

$$ClONO_2 \rightarrow products$$
 (7)

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Figure 2. FTIR matrix isolation spectrum of a photolyzed (310 $\leq \lambda \leq$ 400 nm) gas-phase mixture of Cl_2 (1.0 × 10¹⁶ molecules cm⁻³) and NO₂ $(7.0 \times 10^{14} \text{ molecules cm}^{-3})$ in N₂ (90 Torr) at 298 K.

TABLE II: Matrix Isolation FTIR Band Strengths

molecule	absorption, cm ⁻¹	assignt	S_{ν}/S_{ν_3}
CIONO ₂	778	VA	0.41
-	809	V ₃	0.30
	1292	v2	0.73
	1730	$v_1, (v_2 + v_6)$	1.09
CIONO	1717	ν_1	≈0.25
CINO ₂	1269	ν_{1}	≈0.13
-	1674	V4	≈0.3
N_2O_5	1245	ν_{12}	1.0
	1704	ν_{11}	1.0
	1745	ν_1	1.5
NO ₂	1616	ν_3	0.59
HNO ₃	902	ν ₅	≈0.2

After this conditioning of the cell, the rate of loss of ClONO₂ at the wall, k_7 , was determined to be $k_7 \leq 1.0 \times 10^{-4} \text{ s}^{-1}$.

In the experiments using matrix isolation, the bulk flow of N_2 contained 10 vppm of N_2O which was used as a reference gas of known mixing ratio in the N_2 matrix. The absorption due to the v_3 band of N₂O was used to calculate the relative band strength $S_{\nu}^{X}/S_{\nu_{1}}^{N_{2}O}$ of absorption features due to other species. Calibration was achieved by flowing mixtures of the species, X, in the N_2O-N_2 bulk gas through the photolysis cell and depositing a matrix. The gas-phase concentration of the species was determined from optical density changes in the UV or visible spectrum. It is assumed that mixing ratios in the matrix are the same as those in the gas phase. The relative band strengths, $S_{\nu}^{X}/S_{\nu_{3}}^{N_{2}O}$, were calculated and the values obtained are listed in Table II.

A CIONO matrix isolation FTIR reference spectrum was obtained by deposition of gas-phase mixtures of Cl_2 and NO_2 in N_2 , photolyzed by black lamps ($310 \le \lambda \le 400$ nm). An example of the spectrum obtained is shown in Figure 2. The photolysis of such mixtures proceeds via the reactions

$$Cl_2 + h\nu \rightarrow Cl + Cl$$
 (8)

$$Cl + NO_2 + M \rightarrow ClONO + M$$
 (9a)

$$\rightarrow \text{CINO}_2 + \text{M}$$
 (9b)

Niki et al.¹² have estimated the branching ratio k_{9a}/k_9 to be 0.8 at 700-Torr total pressure. The infrared band strengths of the absorption features of ClNO2 and ClONO relative to the band strength of the v_3 band of N₂O were calculated from an estimate of the ClONO and ClNO₂ gas-phase concentrations and the matrix isolation FTIR absorptions. The concentrations of ClONO and CINO₂ were estimated from optical density measurements around 220 nm, assuming that $\sigma_{220}^{\text{CINO}} \approx \sigma_{220}^{\text{CINO}_2}$ and using the recommended branching ratio k_{9a}/k_{9b} .¹³ The relative band Burrows et al.

strengths obtained are listed in Table II.

The intensity of the photolysis lamps at 254 nm was measured by using the rate of photolysis of CINO as an actinometer. CINO was prepared by mixing pure Cl₂ with an excess of NO and allowing the equilibrium to establish itself. Subsequently, the ClNO was frozen at 195 K and the excess NO pumped away. This procedure was repeated several times to ensure high purity. The photolysis rate of ClNO at 254 nm, k_{10} , was determined from measurement of the decay of pure ClNO:

$$CINO + h\nu (\lambda = 254 \text{ nm}) \rightarrow CI + NO$$
 (10)

$$Cl + ClNO \rightarrow Cl_2 + NO$$
 (11)

The decay of CINO concentration is related to k_{10} by the expression

$$2k_{10} = -d \ln (\text{ClNO})/dt$$

The value of k_{10} was determined to be $(8.3 \pm 0.5) \times 10^{-4}$ s⁻¹ per lamp.

The rate of absorption of photons by ClONO₂ at 254 nm, k_{phot} , was calculated from a knowledge of k_{10} and the absorption cross sections of ClNO and ClONO₂ at 254 nm, $\sigma_{254}^{\text{ClNO}}$ and $\sigma_{254}^{\text{ClONO}_2}$:

$$k_{\text{phot}} = \sum_{i=1}^{5} k_i = k_{10} \sigma_{254}^{\text{CIONO}_2} / \sigma_{254}^{\text{CINO}_2}$$

The value of $\sigma_{254}^{\text{CIONO}_2}$ is taken from an evaluation of photochemical data for use in stratospheric modeling.¹³ At 253.7 nm $\sigma_{254}^{\text{CINO}}$ was measured to be 2.6 \times 10⁻¹⁹ cm² molecule⁻¹ in this work and is in agreement with a recent study of the UV spectrum of ClNO.14 A value of $(1.5 \pm 0.09) \times 10^{-3} \text{ s}^{-1}$ per lamp for k_{phot} was obtained.

NO₂ has a minimum in its UV absorption around 250 nm.¹⁵ Due to the small emission at 313 nm from the photolysis lamps and subsequent photolysis of NO2, it was necessary to measure the photolysis rate of NO2. This was readily achieved by observation of the photolysis of pure NO₂, which proceeds via the reactions

$$NO_2 + h\nu \rightarrow NO + O$$
 (12)

$$O + NO_2 \rightarrow NO + O_2 \tag{13}$$

The NO₂ decay is given by

$$-\frac{d \ln [NO_2]}{dt} = \frac{d[NO]}{dt} \frac{1}{[NO_2]_0} = 2k_{12}$$

Both the decay of NO₂ and the production of NO were monitored. The NO was measured by resonance absorption of the $\gamma(0,0)$ band of NO at 226 nm emitted from a microwave lamp, through which a flow of air at low pressure passed. The value of k_{12} was determined to be $(1.22 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ per lamp.

Results

(a) Matrix Isolation FTIR Studies. ClONO₂ in N₂ was flowed through the cell, and matrix isolation FTIR spectra of both the initial mixture and the photolyzed mixture were recorded. Two concentrations of ClONO₂, 3×10^{14} and 7×10^{14} molecules cm⁻³, were photolyzed, and the residence times, t_{res} , in the cell were 45 and 3 s, respectively. In both cases the total pressure in the cell was maintained at 20 Torr and the temperature was 298 K.

An example of the FTIR spectrum obtained is shown in Figure 3. As well as the precursor $CIONO_2$ and impurities HNO_3 , NO_2 , and H_2O , the end products N_2O_5 and ClONO are identifiable, N_2O_5 by its characteristic 1704- and 1745-cm⁻¹ absorptions and ClONO by its weak absorption at 1717 cm⁻¹. The ratio of

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Figure 3. FTIR matrix isolation spectra of gas-phase mixtures of ClO-NO₂ (3.0 × 10¹⁴ molecules cm⁻³) in N₂ (20 Torr) at 298 K: (a) unphotolyzed and (b) photolyzed ($\lambda = 254$ nm).

[ClONO]/[N₂O₅] changed from 0.5 to 1.2 as the ClONO₂ concentration was increased from 3×10^{14} to 7×10^{14} molecules cm⁻³.

The formation of ClONO may be interpreted as evidence for the occurrence of pathway 4. The appearance of N_2O_5 is explained by reaction of NO_3 with impurity NO_2 :

$$NO_2 + NO_3 + M = N_2O_5 + M$$
 (14)

 NO_3 is generated directly by channel 2 and also by reaction of the Cl or O atom products with excess $CIONO_2$ via reactions 15 and 16:

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$$
 (15)

$$O + ClONO_2 \rightarrow ClO + NO_3$$
 (16)

As the ratio k_{16} [ClONO₂]/ k_{13} [NO₂] was about 0.4 in these experiments (no added O₂), the majority of O atoms reacted with NO₂ via reaction 13.

In Figure 3 the amount of NO_2 also increases on photolysis of $ClONO_2$. This could possibly indicate that a photolysis pathway such as reaction 5 is present. However, it may also result from secondary chemical reactions.

Provided pathway 2 dominates, the amount of N_2O_5 observed should be approximately the same as the amount of $ClONO_2$ photolyzed, namely, $2t_{res}k_{phot}[ClONO_2]_0$ (assuming that the NO₃ formed reacts with the NO₂ impurity). However, the amount of N_2O_5 observed was less than that expected.

An upper limit for the yield of ClONO can be estimated assuming the ClONO to be in a stationary state determined by production via ClONO₂ photolysis (i.e., k_{phot} [ClONO₂]₀) and flow out of the cell. Φ_{ClONO} was found to be ≤ 0.2 at the concentrations of ClONO₂ used.

(b) UV-Visible Studies. In order to quantify the somewhat qualitative observations from the matrix isolation FTIR studies, experiments were performed on *static* and *flowing* mixtures with detection of products and reactants by UV-visible absorption spectrometry. The bulk gas was either N_2 or O_2 at a pressure of 20 Torr, and the cell was normally held at 298 K.

(i) Photolysis of Static Mixtures of ClONO₂ in N₂. In one set of experiments static mixtures of ClONO₂ in N₂ were photolyzed. The ClONO₂ concentration was varied from 8×10^{12} to 1.0×10^{16} molecules cm⁻³, and the initial decay of optical density at 220 nm for each concentration was recorded.

The rate of change of optical density, $d(OD_{220})/dt$, is related to the path length, *l*, absorption cross sections at 220 nm, σ'_{220} , and concentrations of absorbing species, c_i (e.g., *i* are ClONO₂, NO₃, NO₂, N₂O₅, and ClONO), by the equation

$$d(OD_{220})/dt = l(\sum_{i=1}^{n} \sigma_{220}^{i} dc_{i}/dt)$$

Since ClONO₂ has the largest absorption cross section at 220 nm



Figure 4. Plot of Φ_{OD} versus ClONO₂ concentration.



Figure 5. Plot of the NO₃ concentration versus time in the modulated photolysis ($\lambda = 254$ nm) of ClONO₂ (8.0×10^{14} molecules cm⁻³) in N₂ (23 Torr) at 313 K.

of all reactants and products, then, to a first approximation as $t \rightarrow 0$ (i.e., at times less than the induction period for secondary products), this yields

$$(d(OD_{220})/dt)_0 = l\sigma_{220}^{CIONO_2}(d[CIONO_2]/dt)_0$$

In excess ClONO₂ every Cl atom produced by channels 2, 3, and 5 reacts rapidly via reaction 15 to remove a ClONO₂ and generates an NO₃. In this way the Cl concentration rapidly reaches a small stationary state. This implies that, under the conditions used, every photon which produces a Cl atom removes two ClONO₂ molecules. Therefore, the yield for the removal of ClONO₂, determined from the changes in OD at 220 nm, Φ_{OD} , may be defined by the relationship

$$\Phi_{\rm OD} = -\frac{(d(\rm OD_{220})/dt)_0}{2k_{\rm phot}[\rm ClONO_2]_0/\sigma_{220}^{\rm ClONO_2}}$$

where $[ClONO_2]_0$ is the initial concentration of $ClONO_2$. If every photon absorbed by $ClONO_2$ produces a Cl atom, then the value of Φ_{OD} is 1. If other processes take place, then the value will be less than 1.

A plot of Φ_{OD} versus initial ClONO₂ concentration is shown in Figure 4. For ClONO₂ concentrations of $\leq 5 \times 10^{13}$ molecules cm⁻³, Φ_{OD} values lie close to 1 (mean $\Phi_{OD} = 0.99 \pm 0.1$), but for ClONO₂ concentrations of $\geq 5 \times 10^{13}$ molecules cm⁻³, Φ_{OD} decreases toward a mean value of 0.31 ± 0.05 above 1 × 10¹⁵ molecules cm⁻³.

The influence of photolysis lamp intensity on Φ_{OD} was investigated by varying the number of lamps and/or reducing their output intensity. No strong dependence of the quantum yield on light intensity was observed.

(ii) Modulated Photolysis of Flowing Mixtures of $ClONO_2$ in N_2 . A second set of experiments were performed on flowing $ClONO_2$ mixtures. The NO₃ produced by modulated photolysis of these mixtures was monitored by optical density measurements



Figure 6. Plot of Φ_{NO_3} versus ClONO₂ concentration.

at 623 nm. An example of the production of NO_3 as a function of time is shown in Figure 5.

 NO_3 is produced by both channel 2 and reactions 15 and 16. Provided that $CIONO_2$ is in excess, the initial rate of increase of NO_3 concentration, $(d[NO_3]/dt)_0$, is given by

$$(d[NO_3]/dt)_0 = k_2[CIONO_2]_0 + k_{15}[CI][CIONO_2] + k_{16}[O][CIONO_2]$$

The production of NO₃ by reaction 16 is small as the majority of O atoms react with impurity NO₂. The parameter Φ_{NO_3} may be considered as the yield of NO₃ and is defined by the relationship

$$\Phi_{\rm NO_3} = \frac{(d[\rm NO_3]/dt)_0}{2k_{\rm phot}[\rm ClONO_2]_0}$$

 $(d[NO_3]/dt)_0$ is the initial rate of increase of $[NO_3]$, and $[ClO-NO_2]_0$ is the initial concentration of $ClONO_2$. If every photon absorbed by $ClONO_2$ produces a Cl atom and an NO₃ via channel 2, then the value of Φ_{NO_3} is 1. If other photolysis pathways are present, then Φ_{NO_3} is less than 1.

 Φ_{NO_3} was determined as a function of [ClONO₂]₀, and a plot is shown in Figure 6. This curve is similar in appearance to that obtained for Φ_{OD} . For ClONO₂ concentrations of $\leq 5 \times 10^{13}$ molecules cm⁻³, Φ_{NO_3} is close to 1 (mean $\Phi_{NO_3} = 1.04 \pm 0.05$). At higher concentrations Φ_{NO_3} decreases. At the highest flowing concentrations of ClONO₂ used, 8×10^{14} molecules cm⁻³, the mean value of Φ_{NO_3} is 0.44 ± 0.09.

mean value of Φ_{NO_3} is 0.44 ± 0.09 . The influence of photolysis light intensity on Φ_{NO_3} was investigated by varying the number of photolysis lamps. No significant dependence of Φ_{NO_3} on photolysis light intensity was noted. To reduce the yield of N_2O_5 , several experiments were undertaken at 313 K. N_2O_5 dissociates approximately 10 times faster at 313 K than at 298 K, regenerating NO_2 and NO_3 . No significant changes in Φ_{NO_3} were observed at this temperature.

To obtain values of Φ_{OD} in the modulated photolysis of ClONO₂ mixtures, the absorption at 220 nm was monitored. In this case the photolysis of relatively high concentrations of ClONO₂ (4.8 × 10¹⁴ and 8.5 × 10¹⁴ molecules cm⁻³) were studied at 313 K. The values of Φ_{OD} were in agreement with those obtained in the investigations of static mixtures.

In a further set of measurements the modulation of optical density at both 350 and 400 nm was monitored during the photolysis of flowing ClONO₂ mixtures in N₂ at 313 K. The modulated absorption at 400 nm is attributed to NO₂. For concentrations of ClONO₂ around 8×10^{14} molecules cm⁻³ in 20 Torr of N₂ the yield of NO₂, determined from the relationship

$$\Phi_{\rm NO_2} = \frac{(d[\rm NO_2]/dt)_0}{k_{\rm phot}[\rm ClONO_2]_0}$$

was found to be approximately 0.25.

When O_2 replaced N_2 as the bulk gas, a decrease in absorption at 400 nm was observed. These observations may be qualitatively explained as follows. Any O atoms generated react with NO_2 via reaction 13 in the absence of O_2 to form NO, which subsequently reacts with NO₃ to produce NO₂:

$$NO + NO_3 \rightarrow NO_2 + NO_2 \tag{17}$$

When O_2 is present in excess, the majority of O atoms generated react with O_2 to form O_3 and the amount of NO produced is diminished. As a result, no net production of NO₂ is observed but rather an overall removal of NO₂ via its reaction with NO₃. Conversely, this implies that in the N₂ carrier gas experiment Φ_{NO_2} is approximately the same as Φ_0 .

The modulated absorptions observed at 350 nm in the photolysis of CIONO₂ mixtures may be due to NO₂, Cl₂, or CIONO. After subtraction of the NO₂ contribution at 350 nm, a residual modulated signal was present. As Cl₂ and CIONO have similar absorption cross sections at 350 nm, it is not possible to deconvolute their individual contributions from this modulated absorption signal. However, the absorption at 350 nm is consistent with an initial rate of increase of Cl₂ concentration, $(d[Cl_2]/dt)_0$, which is approximately half of $(d[NO_3]/dt)_0$.

In order to investigate the production of O atoms in the photolysis of ClONO₂, experiments were carried out using ClONO₂ and O₂ mixtures. O atoms were converted to O₃, and this was monitored at 270 nm. The concentrations of reactants in this set of experiments were as follows: [ClONO₂] = 3.0×10^{14} , [NO₂] = 1.7×10^{13} , and [O₂] = 7.5×10^{18} (the units are molecules cm⁻³). Any O atoms generated on photolysis of these mixtures will either react with NO₂ or form O₃ via

$$O + O_2 + M \rightarrow O_3 + M \tag{18}$$

The absorption at 270 nm was observed to increase and that at 400 nm to decrease on photolysis of these mixtures. This is consistent with the production of O_3 via reaction 17 and the removal of NO_2 by reaction 14. The rate of production of O_3 , $d[O_3]/dt$, is much larger than that expected from photolysis of NO_2 in the system and is approximately 18% of the observed $(d[NO_3]/dt)_0$. Assuming that the O atoms are produced in a primary step, then the quantum yield for production of O atoms, Φ_0 , is given by

$$\Phi_{\rm O} = \frac{\rm d[O_3]}{\rm dt} \frac{1}{k_{\rm phot}[\rm CIONO_2]_0} \frac{k_{18}[O_2][M] + k_{13}[\rm NO_2]}{k_{18}[O_2][M]}$$

and was estimated to be approximately 0.24.

Finally, any production of NO in the system was investigated by using resonance absorption as the detection technique. Due to the presence of a 50-Hz modulation in the resonance lamp, the minimum detectable absorption (3×10^{-5}) was higher than for the D₂ and quartz halogen lamps. Such an absorption corresponds to an NO concentration of 3.3×10^{10} molecules cm⁻³. No signal attributable to NO was detected in a modulated photolysis experiment using a ClONO₂ concentration of 1.5×10^{14} molecules cm⁻³, which implies that the initial rate of increase of NO was less than 2×10^{11} molecules cm⁻³ s⁻¹. For the same mixture the initial rate of increase of NO₃ was determined to be 6.0×10^{11} molecules cm⁻³ s⁻¹. This indicates that the production of NO from the photolysis of ClONO₂ is less and possibly very much less than the production of NO₃. As NO and NO₃ react rapidly together, a small production of NO in the photolysis of ClONO₂ at 254 nm cannot be excluded from these observations.

Discussion

The direct observation of NO₃ by its visible absorption spectrum and the observation of N₂O₅ as an end product in the 254-nm photolysis of ClONO₂ indicate that pathway 2 occurs. Comparison of the Φ_{OD} and Φ_{NO_3} values shows that this pathway is the dominant channel in the photolysis of ClONO₂ by 254-nm radiation. However, both Φ_{OD} and Φ_{NO_3} appear to be dependent on the concentration of ClONO₂. The maximum values of both Φ_{OD} and Φ_{NO_3} tend to a value of 1 at low ClONO₂ concentration.

The identification of ClONO and the indirect observation of O atoms suggest that pathway 4 may also occur at 254 nm. This observation of ClONO, although somewhat tentative due to its

 TABLE III: Chemical System Used for Simulation of ClONO2

 Photolysis

reaction	k ^a	comment ^l
$\overline{\text{ClONO}_2 + h\nu} \rightarrow \text{ClO} + \text{NO}_2$	$\Phi_1 k_{nhot}^c$	N
$ClONO_2 + h\nu \rightarrow Cl + NO_3$	$\Phi_2 k_{\rm phot}^c$	Ι
$ClONO_2 + h\nu \rightarrow Cl + NO + O_2$	$\Phi_{3}k_{\rm phot}^{c}$	Ι
$CIONO_2 + h\nu \rightarrow CIONO + O$	$\Phi_4 k_{\rm phot}^{c}$	I
$ClONO_2 + h\nu \rightarrow Cl + NO_2 + O$	$\Phi_5 k_{\rm phot}^{d}$	I
$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	$0.4(\sigma_{254}^{N_2O_5}/\sigma_{254}^{CINO})k_{10}^{d}$	NN
$N_2O_5 + h\nu \rightarrow NO_3 + NO + O$	$0.6(\sigma_{254}^{N_2O_5}/\sigma_{254}^{CINO})k_{10}^{c}$	NN
$NO_2 + h\nu \rightarrow NO + O$	<i>k</i> ₁₂	NN
$O_3 + h\nu \rightarrow O(1D) + O_2$	$0.9(\sigma_{254}^{O_3}/\sigma_{254}^{CINO})k_{10}$	Ν
$O_3 + h\nu \rightarrow O + O_2$	$0.1(\sigma_{254}^{O_3}/\sigma_{254}^{ClNO})k_{10}$	Ν
$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	1.0×10^{-11}	Ι
$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}	N
$Cl + NO_2 + M \rightarrow ClONO + M$	1.3×10^{-30}	N
$Cl + NO_2 + M \rightarrow ClNO_2 + M$	1.8×10^{-31}	N
$Cl + NO_3 \rightarrow ClO + NO_2$	2.7×10^{-11}	I
$ClO + NO_2 \rightarrow Cl + NO_2 + O_2$	4.0×10^{-13}	Ν
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.8×10^{-31}	Ν
$ClO + O \rightarrow Cl + O_2$	4.0×10^{-11}	N
$ClO + NO \rightarrow Cl + NO_2$	1.8×10^{-11}	N
$NO_3 + NO_2 \rightarrow N_2O_5$	4.0×10^{-13f}	I
$N_2O_5 \rightarrow NO_2 + NO_3$	0.016 ^f	I
$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$	5.6×10^{-16}	N
$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$	3.4×10^{-16}	N
$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34}	I
$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	I
$O + NO_3 \rightarrow NO_2 + O_2$	1.0×10^{-11}	NN
$O + CIONO_2 \rightarrow CIO + NO_3$	2.0×10^{-13}	NN
$NO + NO_3 \rightarrow NO_2 + NO_2$	3.0×10^{-11}	I
$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}	Ν
$O(^{1}D) + M \rightarrow O + M$	4.0×10^{-11}	Ν
$O(^{1}D) + CIONO_{2} \rightarrow CIO + NO_{3}$	2.0×10^{-10e}	Ν

^a Units; s⁻¹, cm³ molecule⁻¹ s⁻¹, and cm⁶ molecule⁻² s⁻¹ for first-order, second-order, and third-order rate coefficients, respectively. The pressure of N₂ in the simulation is 20 Torr and the temperature 298 K. ^b The comment column in the table assigns to each reaction a qualitative assessment of its importance to the simulated fit of the observed NO₃ behavior: I implies important; NN, nonnegligible; and N, negligible. ^c Φ₁ was assumed to be 0.0 in these simulations; Φ₂, Φ₃, Φ₄, and Φ₅ were varied. ^d The values for the yields of the N₂O₅ photolysis routes are taken from work in this laboratory²⁴ and by Ravishankara et al.²⁵ ^e The values for $k_{O(^{1}D)+ClONO_{2}}$ is assumed to be gas kinetic. ^fAt 20-Torr total pressure the rate coefficients for the formation and decomposition of N₂O₅ are no longer linearly dependent on pressure. Consequently, the values listed are the effective values of the rate coefficients at 20-Torr total pressure obtained by using the recent measurements of the rate coefficient for the reaction of NO₂ with NO₃¹⁰ and the N₂O₅ equilibrium constant.²⁶

weak infrared absorption, is the first direct observation of this species in the photolysis of ClONO₂.

Possible explanations of the observed Φ_{NO_3} and Φ_{OD} behavior are considered in the following section.

(i) N_2O_5 Formation. The first potential explanation of the observed decrease of Φ_{OD} and Φ_{NO_3} with increasing ClONO₂ concentration is the formation of end product N_2O_5 in the system. Absorption at 220 nm due to N_2O_5 formation may lead to an underestimate of the ClONO₂ removal yield, Φ_{OD} . However, any underestimate is unlikely to be ClONO₂ concentration dependent. Therefore, the production of N_2O_5 does not explain the observed behavior of Φ_{OD} . Similarly, provided the quantity $(d[NO_3]/dt)_0$ is correctly estimated, formation of N_2O_5 does not explain the observed trend in Φ_{NO_3} data as a function of ClONO₂ concentration. The lack of a significant increase in Φ_{OD} and Φ_{NO_3} at elevated temperatures is further evidence against the formation of N_2O_5 providing the explanation for the decrease in Φ_{OD} and Φ_{NO_3} .

(ii) Secondary Chemistry. In an effort to fully understand the production and removal of NO_3 in the photolysis cell, selected data sets at high and low concentrations of ClONO₂ were modeled by computer simulation using the FACSIMILE program.¹⁶

The chemical system used to simulate the data is listed in Table III. Flow in and out of the photolysis cell was modeled assuming that the cell corresponds to a stirred flow reactor, i.e., $k_{\text{flow out}} =$ $1/t_{\rm res}$. At the residence times used in these experiments $k_{\rm flow out}$ is larger than the rate coefficient for the decomposition of N_2O_5 . In order to facilitate analysis of the chemical mechanism, a qualitative assignment of the importance of each reaction to the simulation of the NO₃ behavior is given in Table III (I, important; NN, nonnegligible; and N, negligible). NO_3 is produced in the system by the photolysis of ClONO₂ via channel 2 and the reaction of Cl with $CIONO_2$. NO₃ is removed primarily by reaction with NO_2 and by flow out. The initial increase of NO_3 concentration is defined by the value of Φ_2 . Any production of O, NO, or NO₂ in the photolysis of ClONO₂ should be noticeable in the shape of the NO_3 concentration time profile as it approaches its stationary-state value.

The NO₃ concentration modulation was simulated allowing the value of Φ_2 to be least squares fitted to its optimum value. At the low concentration of ClONO₂ (2 × 10¹³ molecules cm⁻³), the chemical model described the NO₃ modulation well over the whole modulation cycle and the value for the channel 2 yield was approximately 1, in agreement with Φ_{NO_2} .

proximately 1, in agreement with Φ_{NO_3} . For mixtures with concentrations of 8×10^{14} and 1.5×10^{14} molecules cm⁻³ of ClONO₂, the initial rate of increase of NO₃ concentration is best fit to the model with values for Φ_2 of 0.3 and 0.7, respectively. This agrees with the values of Φ_{NO_3} obtained. At the highest ClONO₂ concentration (8.0 × 10¹⁴ molecules

At the highest ClONO₂ concentration $(8.0 \times 10^{14} \text{ molecules} \text{ cm}^{-3})$, the NO₃ behavior as it approached steady state was not well described by this model. NO₃ in the model approaches steady state more slowly than in the experiment. This indicates that some small loss of NO₃ is missing from the model. Any photolysis of NO₃ by the photolysis lamps is insufficient to explain this loss. This effect can qualitatively be explained by the buildup due to secondary chemistry of some species which reacts with NO₃ (e.g., O or NO). The high-concentration data were simulated by using the reactions listed in Table III. The values of the ClONO₂ photolysis yields Φ_2/Φ_5 were varied and their optimum values found by a least-squares method. No significant values were obtained for $\Phi_3-\Phi_5$, and the simulation failed to fit well the stationary-state NO₃ concentration.

The possibility of a reaction between NO₃ and ClONO₂ reducing the value obtained for Φ_2 was also investigated by simulation. At the lower ClONO₂ concentrations such a reaction had no effect, but at higher concentrations the addition of such a reaction leads to an increase in the predicted yield of Φ_2 in the computer fit. Of the possible bimolecular NO₃ reactions with ClONO₂ only the production of ClNO₂ is exothermic:

$$NO_3 + CIONO_2 \rightarrow CIO + N_2O_5$$
 $\Delta H_{19a} = 13.9 \text{ kJ mol}^{-1}$
(19a)

 $\rightarrow \text{ClONO} + \text{NO}_2 + \text{O}_2 \qquad \Delta H_{19b} = 16.8 \text{ kJ mol}^{-1} \qquad (19b)$

$$\rightarrow \text{ClNO}_2 + \text{NO}_2 + \text{O}_2 \qquad \Delta H_{19c} = -53.6 \text{ kJ mol}^{-1} \quad (19c)$$

As $ClNO_2$ was not observed in the matrix isolation studies of this system, this reaction does not provide an explanation of the NO_3 behavior.

If a reaction between NO₃ and ClONO₂ takes place, it might occur at the walls of the cell. However, the behavior of Φ_{OD} indicates that such a wall reaction must regenerate ClONO₂. This seems improbable.

In summary, computer simulation of the system including all known chemical reactions yielded values of Φ_2 similar to the experimentally determined parameters Φ_{NO_3} and Φ_{OD} . However, the reaction mechanism did not simulate well the NO₃ concentration approach to its stationary state for high ClONO₂ concentrations.

(iii) Quenching of a ClONO₂ State. Addition of Φ_{NO_3} (\approx 0.4) and the upper limit for Φ_0 together, at a ClONO₂ concentration

⁽¹⁷⁾ Marinelli, W. J. Ph.D. Thesis, University of California, Berkeley, 1981.

of 3×10^{14} molecules cm⁻³, implies that at least 36% of photons absorbed remain unaccounted for. This suggests that one explanation of the above observations might be self-quenching of a ClONO₂ excited state.

If self-quenching occurs, a plot of Φ^{-1} versus [ClONO₂]₀ is predicted to be linear when only one excited state is generated. However, this plot is curved, which indicates that more than one excited ClONO₂ molecule is generated. The data may be analyzed assuming that two excited states of ClONO₂ are generated which both lead to Cl and NO₃ but that one of these states is quenched by or reacts with ClONO₂. This behavior is described in the following chemical scheme:

$$\text{ClONO}_2 + h\nu \ (\lambda = 254 \text{ nm}) \rightarrow \text{ClONO}_2^*$$
 (I)

$$\rightarrow \text{ClONO}_2^{**} \tag{II}$$

$$\rightarrow$$
 O + ClONO (III)

$$ClONO_2^* \rightarrow products$$
 (IV)

$$ClONO_2^{**} + ClONO_2 \rightarrow ClONO_2 + ClONO_2$$
 (Va)

$$\rightarrow$$
 products + ClONO₂ (Vb)

$$\text{ClONO}_2^{**} \rightarrow \text{products}$$
 (VI)

The products of reactions IV and VI are assumed to be Cl and NO₃ in this analysis, and reaction V may quench or produce other products. The Cl produced reacts rapidly with the excess ClONO₂ present via reaction 15 to generate NO₃. Assuming that ClONO₂*, ClONO₂**, and Cl achieve stationary-state concentrations, then the observed parameters Φ_{OD} and Φ_{NO_2} may be related to the primary quantum yields Φ_0^I , Φ_0^{II} , and Φ_0^{III} by the relationships

$$\Phi_{\rm NO_3} - \Phi_0^{\rm I} = \Phi_0^{\rm II} k_{\rm VI} / (k_{\rm V} [{\rm ClONO_2}]_0 + k_{\rm VI})$$
(A)

$$\Phi_{\rm OD} - (\Phi_0^{\rm I} + \Phi_0^{\rm III}/2) = \Phi_0^{\rm II} \left(\frac{2k_{\rm VI} + k_{\rm Vb} [\rm ClONO_2]_0}{2(k_{\rm VI} + k_{\rm V} [\rm ClONO_2]_0)} \right)$$
(B)

The averaged value for Φ_{OD} at ClONO₂ concentrations of $\geq 1.0 \times 10^{15}$ molecules cm⁻³ is 0.31. In this analysis this is assumed to be the value of the quantum yield, Φ_0^I , for the nonquenching route (I) and (IV). The maximum value of the quantum yield for the quenching pathway (II), (V), and (VI), Φ_0^{II} , is therefore 0.69. $\Phi_{NO_1}^{II}$ is defined by

and Φ_{OD}^{II} by

$$\Phi_{\rm OD}^{\rm II} = \Phi_{\rm OD} - \Phi_0^{\rm I}$$

 $\Phi_{\mathrm{NO}_3}^{\mathrm{II}} = \Phi_{\mathrm{NO}_3} - \Phi_0^{\mathrm{I}}$

Rearrangement of eq A and B, assuming that Φ_3 is small, leads to the relationships

$$\frac{\Phi_0^{\rm II}}{\Phi_{\rm NO_1}^{\rm II}} = 1 + \frac{k_{\rm V} [{\rm CIONO_2}]_0}{k_{\rm VI}} \tag{C}$$

$$\frac{\Phi_0^{\rm II}}{\Phi_{0}^{\rm II}} = \frac{2(k_{\rm VI} + k_{\rm V}[{\rm ClONO}_2]_0)}{(2k_{\rm VI} + k_{\rm VF}[{\rm ClONO}_2]_0)} \tag{D}$$

Plots of $\Phi_0^{\rm II}/\Phi^{\rm II}$ versus [ClONO₂]₀ for $\Phi_{\rm OD}$ and $\Phi_{\rm NO_3}$ data are shown in Figure 7. The plot of eq C should be linear whereas the plot of eq D is expected to exhibit some curvature. $\Phi_{\rm NO_3}$ data appear to fall on a reasonable straight line; however, the $\Phi_{\rm OD}$ data is so scattered that it could be linear or curved. The slope of the line drawn through the $\Phi_{\rm NO_3}$ data shown in Figure 7 is (1.8 ± 0.2) $\times 10^{-14}$ cm³ molecule⁻¹. This implies that the ratio $k_{\rm V}/k_{\rm VI}$ is about 1.8×10^{-14} cm³ molecule⁻¹.

Division of eq C by eq D leads to the relationship

$$2k_{\rm VI}\left(\frac{\Phi_{\rm DD}^{\rm II}}{\Phi_{\rm NO_3}^{\rm II}}\right) = 2k_{\rm VI} + k_{\rm Vb}[{\rm ClONO_2}]_0 \tag{E}$$

Taking the values of $\Phi_{NO_1}^{II}$ and Φ_{OD}^{II} for concentrations of ClONO₂



Figure 7. Plot of Φ_0^{II}/Φ^{II} versus ClONO₂ concentration.

of 3×10^{14} and 8×10^{14} molecules cm⁻³ enables the ratio of $k_{\rm Vb}/k_{\rm VI}$ to be calculated from relationship E. This ratio was estimated to be approximately 2.8×10^{-15} cm³ molecule⁻¹. Combining this result with the value for the ratio $k_{\rm V}/k_{\rm VI}$ implies that the ratio of $k_{\rm Va}/k_{\rm Vb}$ is approximately 5.5.

If reaction V occurs at every collision, then $k_{\rm V}$ is probably in the range (6–9) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (cf. other large molecules such as CH₃S* quenched by CH₃SSCH₃, $k \approx 7 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹¹⁸), then the value of $k_{\rm VI}$ is approximately 7 × 10⁴ s⁻¹. This implies a lifetime of the order of 20 μ s for this excited state of ClONO₂. This lifetime is long for an excited state, which is subsequently supposed to fall apart to generate Cl and NO₃. It implies that this molecule, if formed, is metastable (e.g., a bound excited state or an isomer of ClONO₂).

Although the behavior of Φ_{OD} and Φ_{NO_3} is reasonably well described by the above mechanism, it is necessary to consider whether the difference between these two parameters might be explained by other effects such as end product formation. For example, formation of N₂O₅ and ClONO, which absorb at 220 nm, would lead to an underestimation of Φ_{OD} . This means that the left-hand side of eq D would be overestimated. This effect does not explain the difference between the plots of Φ_{OD} and Φ_{NO_3} data shown in Figure 7.

The above mechanism invoking the formation of two excited states of $ClONO_2$ is appealing in that it correctly predicts the observed trends of both Φ_{NO_3} and Φ_{OD} . However, it necessitates the production of a metastable form of $ClONO_2$, which at best seems improbable.

(iv) Unidentified Secondary Chemistry. Finally, the observed behavior may be explained by invoking some, as yet unidentified, chemistry, which increases in importance as the $ClONO_2$ concentration increases.

It is now necessary to compare the results of this study with those obtained in other investigations. The end product analyses of both Smith et al.³ and Knauth and Schindler⁸ are qualitatively in agreement in that N_2O_5 is the main nitrogen-containing product. The limitations of the mechanism proposed by Smith et al.³ have been described recently by Margitan⁷ and will not be discussed further. At the $ClONO_2$ concentrations used by Knauth and Schindler,⁸ considerable quenching is predicted from the results obtained here. Quantum yields of 0.8 for the removal of NO_2 , 1.12 for the removal of $ClONO_2$, and 0.96 for the production of N_2O_5 are reported, although considerable internal discrepancies exist in the definitions of the quantum yields used. Similarly, the concentration range $(1.2-80) \times 10^{14}$ molecules cm⁻³, used by Adler-Golden and Wiesenfeld⁴ in their flash photolysis experiment, is such that a reduction in the apparent photolysis rate of ClONO₂ would be predicted from our work. The O atoms observed may arise as a product of reaction Vb. Reasons for the failure of these workers to observe Cl atoms have been discussed by Margitan.⁷

(18) Black, G.; Jusinski, L. E. J. Chem. Phys. 1986, 85, 5379.

λ, nm	technique ^a	Φ_{Cl}	Φ_{NO_3}	Φ _{O(³P)}	Φ_{ClO}	Φ_{NO_2}	Φ_{CIONO}	-Φ _{CINO3}	ref
302.5	CP FPA GC			1.0		0.1	1.0	4.0	3
260380	CP VLPP MS	1.0 ± 0.2	0.8-0.4	≤0.1	≤0.04				5
200-900	FP RT RA	≤0.04		В					4
249	LFP RT LA		0.85-0.45						6
266	LFP PT PF	0.9 ± 0.1		0.1					7
265			0.96 ± 0.2	0.1 ± 0.02		0.05		1.12 ± 0.2	8
254	CP MIFTIR						≤0.2		this work
254	MMS RT UV-VisA		1.0-0.4	≤0.24				1.0-0.3	this work

^aCP, continuous photolysis; FP, flash photolysis; LFP, laser flash photolysis; MMS, molecular modulation spectrometry; FPA, final product analysis; GC, gas chromatography; VLPP, very low pressure photolysis; MS, mas spectroscopy; RT, real time; LA, laser absorption; RA, resonance absorption; RF, resonance fluorescence; UV-IRA, ultraviolet and infrared absorption; UV-VisA, ultraviolet and visible absorption; MIFTIR, matrix isolation Fourier transform infrared spectroscopy.

Chang et al.⁵ were the first to obtain direct evidence for the formation of NO_3 in the photolysis of $ClONO_2$. Their mass spectroscopic identification of NO₃ led to quantum yields which varied as a function of ClONO₂ concentration. The NO₃ quantum yield was determined by a calibration of the NO₃ m/e 62 peak and the measured amount of CIONO₂ lost. This is the first evidence for the reduction of the NO3 yield as ClONO2 concentration increases. However, the amount of NO3 produced is less than the amount of ClONO₂ removed, whereas in our work the amount of NO₃ produced was equal to the amount of ClONO₂ removed. In their ClONO₂ concentration range $(2-35) \times 10^{12}$ molecules cm⁻³, Φ_{NO_3} varied continuously from 0.8 to 0.4. These authors interpreted this result as being most likely due to secondary chemistry. Such variations were not reported in the other quantum yields determined, but the concentration ranges used in the determination of the Cl quantum yield, $\Phi_{Cl} = 1 \pm 0.2$, and the O quantum yield, $\Phi_0 \approx 0.1$, are not stated.

Marinelli and Johnston⁶ in their study varied the concentration of ClONO₂ in the range $(3-8) \times 10^{14}$ molecules cm⁻³. In this laser flash photolysis experiment, no significant variation in Φ_{NO_3} was observed, as estimated from the initial amount of NO₃ formed. The authors obtained a value of 0.55 ± 0.1 and considered that some of the secondary growth of NO₃ might be due to a long-lived excited state of NO₃. Since this work was performed, the accepted value of the rate coefficient for the reaction of Cl with ClONO2 has increased by 2 orders of magnitude. The secondary growth of NO₃ is therefore almost certainly due to reaction of Cl with $ClONO_2$, which implies that 0.55 is the primary yield of NO₃. The absorption cross section of ClNO at 249 nm,¹⁷ used to determine the fluence by these authors, was 7.5×10^{-19} cm² molecule⁻¹ compared with the value of $3.48 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ recently measured in our laboratory.14 Recalculation of the fluence leads to a value for Φ_{NO_3} of approximately 0.25 instead of 0.55. This value is a little lower than that obtained in our study over the same concentration range.

In another laser flash photolysis study Margitan⁷ measured the Cl atom yield in ClONO₂ photolysis at 266 and 355 nm. In the majority of the experiments the reactant mixture contained relatively small concentrations of ClONO₂ ($\leq 7 \times 10^{13}$ molecules cm⁻³), in an excess of argon, 10–40 Torr. A few experiments were performed with concentrations as large as 2×10^{14} molecules cm⁻³. $\Phi_{\rm Cl}$ was determined to be 0.93 ± 0.09 at 266 nm and 298 K and 0.8 ± 0.05 at 355 nm and 238 K. $\Phi_{\rm O}$ varied from 0.08 to 0.25. This variation was not wavelength or temperature dependent but was attributed in part to residual Cl emission from the resonance lamp. After attempts to remove Cl₂, a value for $\Phi_{\rm O}$ of 0.1 was obtained in one set of experiments. The values obtained for $\Phi_{\rm Cl}^{\rm Cl}$ at ClONO₂ concentrations below 7 × 10¹³ molecules cm⁻³ are in good agreement with our work. The values of $\Phi_{\rm Cl}$ for both 266 and 355 nm at higher concentrations are a little lower (e.g., 0.8

instead of 0.9) but agree within experimental uncertainty with the lower concentration values. The variability of Φ_0 in this work would be explained if O atoms were a product of reaction Vb. However, the discrepancy between the results of Margitan and those obtained here at concentrations of ClONO₂ of about 2 × 10^{14} molecules cm⁻³ is not simply explained. Margitan also investigated any production of ClO by addition of NO to the reactant mixture. No evidence was found for the existence of reaction 1.

A comparison of the results from different groups is shown in Table IV. Note that Φ_{OD} values from the present work are listed as Φ_{CINO_2} .

Conclusions and Atmospheric Implications

The dominant pathway in the photolysis of ClONO₂ by 254-nm radiation generates Cl and NO₃. In addition, evidence has been found for the production of both O and ClONO. The observed decrease in Φ_{OD} and Φ_{NO_3} with increasing ClONO₂ concentration may be explained by the formation of molecules in two excited states of ClONO₂, one of which is metastable in character and strongly interacts with ground-state ClONO₂. However, the lifetime of this metastable ClONO₂ appears to be anomalously large. Interaction between this proposed metastable CIONO₂ and ground-state ClONO₂ would lead either to regeneration of ClO-NO2 or to the formation of other products. Consequently, O and ClONO may be formed either in this reaction or directly by channel 4. The only other plausible explanation of the observations invokes as yet unidentified chemical reactions, e.g., heterogeneous chemistry. It is interesting to note that Molina and Molina¹⁹ in their investigation of the temperature dependence of the CIONO₂ absorption cross section between 220 and 360 nm suggested the existence of more than one ClONO₂ excited state.

The results presented here appear to be in reasonable agreement with the recent laser flash photolysis studies of Marinelli and Johnston⁶ and of Margitan,⁷ which are in apparent disagreement. The time scale of measurement of both these experiments is small compared to that described here. Marinelli and Johnston⁶ observed the production of NO₃ within 10 μ s of the laser flash. The decay of any metastable ClONO₂ to produce Cl and NO₃ would not be observed at such short time scales because the concentrations used by these authors are such that any metastable ClONO₂ reacts with ClONO₂. The time resolution of Margitan's experiment appears to be of the order of 100 μ s,⁷ and the concentrations of ClONO₂ used such that the majority of metastable ClONO₂ prefer to dissociate rather than react with ground-state ClONO2. Based on our estimate of its lifetime, any metastable ClONO₂ will have decayed in 60 μ s to Cl and NO₃ (i.e., during the first observation point). This elegantly explains the difference between the yield of Cl atoms observed by Margitan⁷ and the NO₃ yield observed

⁽¹⁹⁾ Molina, L. T.; Molina, M. J. J. Photochem. 1979, 11, 139.

by Marinelli and Johnston.⁶ However, as mentioned above, the probability that such a metastable $CIONO_2$ state exists is considered to be small.

In the stratosphere the products NO_3 and ClONO will both be rapidly photolyzed:

 $NO_3 + h\nu \rightarrow NO + O_2$ $\lambda_{20a} \le 620 \text{ nm}$ (20a)

$$\rightarrow NO_2 + O(^{3}P) \qquad \lambda_{20b} \le 590 \text{ nm} \qquad (20b)$$

 $CIONO + h\nu \rightarrow Cl + NO_2 \qquad \lambda_{21a} \leq 1670 \text{ nm} \quad (21a)$

 \rightarrow ClO + NO $\lambda_{21b} \leq 1093 \text{ nm}$ (21b)

Uncertainties in the NO yield in the NO₃ photolysis exist,¹³ but in the atmosphere channel 20b, which generates O atoms, dominates. Provided that reaction 21a dominates over reaction 21b, the photolyses of ClONO₂ via pathways 2 and 4 followed by that of NO₃ and ClONO are equivalent in the stratosphere. If reaction 21b occurs, then the products ClO and NO are generated instead of Cl and NO₂. As all these radicals react to remove odd oxygen (O and O₃) in the stratosphere, to a first approximation the photolysis of ClONO₂ via channel 2 or channel 4 has the same effect.

Due to the low concentrations of ClONO₂, any interaction between the proposed metastable state of ClONO₂ and ClONO₂ cannot be of stratospheric importance. However, N₂ or O₂ might also react with such a species. It appears from this work that any metastable state of ClONO₂ formed by absorption of 254-nm photons at 298 K does not react significantly with 20 Torr of N₂ or O₂.

In the stratosphere ClONO₂ absorbs radiation at wavelengths which are longer than 254 nm. Production of a metastable ClONO₂ is presumably wavelength and/or temperature dependent. At wavelengths closer to the threshold of production, the lifetime of such a molecule might be longer. It is interesting in this respect to note that Margitan⁷ found Φ_{Cl} to be 0.8 ± 0.05 at 238 K in the 355-nm photolysis of ClONO₂ using argon as buffer gas.

 $ClONO_2$ is generated in the stratosphere by the pressure-dependent reaction between ClO and NO₂. Its maximum concentration is observed at about 30 km.²⁰ In the MPI-Mainz two-dimensional model the two principal loss mechanisms considered for $ClONO_2$ in the stratosphere are photolysis and reaction of O atoms with $ClONO_2$.²¹ The reaction of OH with $ClONO_2$,

although its products are uncertain, can be considered as the next most significant loss process:

$$OH + ClONO_2 \rightarrow products$$
 (22)

The majority of the ClONO₂ in the stratsophere lies between 12 and 30 km. At 55° N the model values for the photolysis rate of ClONO₂, J_{ClONO_2} , and the first-order removal of ClONO₂ by reactions 16 and 22, k_{16} [O] and k_{22} [OH], are 6.8 × 10⁻⁵, 6.2 × 10⁻⁶, and 1.5 × 10⁻⁶ s⁻¹ at 30 km and 3.5 × 10⁻⁵, 2.6 × 10⁻⁹, and 2.6 × 10⁻⁷ s⁻¹ at 12 km, respectively. Production of metastable ClONO₂, which re-forms ClONO₂, in the photolysis of ClONO₂ will reduce J_{ClONO_2} , which in turn will lead to a corresponding increase in the stratospheric concentration of ClONO₂.

Higher concentrations of ClONO₂ in the stratosphere than currently predicted imply that less Cl is present as ClO_x. Lower concentrations of ClO_x in the stratosphere should reduce the predicted O₃ depletion by the tropospheric release of chlorofluorocarbon compounds. However, as NO_x would also be somewhat reduced by an increase in ClONO₂, detailed computer simulations need to be performed to take into account the coupled nature of stratospheric chemistry, before predicting such effects. Although the uncertainty in the recent ClONO₂ concentration profile measurement is in the range 30–45%, it is interesting to note that this profile is approximately 25% higher than model predictions.²⁰

In conclusion, for a better understanding of the atmospheric behavior of $ClONO_2$, it is necessary to investigate the photolysis of $ClONO_2$ molecules generated by absorption between 280 and 360 nm over temperature and pressure ranges of relevance to the upper atmosphere.

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Registry No. ClONO₂, 14545-72-3; NO₃, 12033-49-7; NO₂, 10102-44-0; ClONO, 65283-98-9; O₃, 10028-15-6; Cl, 22537-15-1; O, 17778-80-2; N₂O₅, 10102-03-1.

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Control of the Yield of Competing Unimolecular Reactions through Double-Resonance Coherent Trapping

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It is shown that simultaneous irradiation by two laser frequencies can be used to control the relative yields of products for a certain class of unimolecular reactions. These must involve a "doorway state", which can decay either directly or indirectly (i.e., after transferring energy to other intermediate states). The infrared photopredissociation of the complex H-F-Li to give H-F + Li or H + Li-F is studied as an example, on the basis of a simple model.

Introduction

A certain number of processes in physics and chemistry can be schematized as in Figure 1. Starting from the ground state $|g\rangle$, the quantum system under study can be excited to state $|1\rangle$ by absorption of a photon ω_1 . Two channels are then open: (i) the direct decay into the continuum $\{|\epsilon_1\rangle\}$ (process A₁); (ii) the indirect (i.e., via the state $|2\rangle$) decay into the continuum $\{|\epsilon_2\rangle\}$ (process A₂).

In this paper we show how it is possible to achieve some control on the relative yields of processes A_1 and A_2 by using another laser

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