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PRODUCTION OF ATOMIC OXYGEN FOLLOWING FLASH PHOTOLYSIS OF CIONO2

S.M. ADLER-GOLDEN * and J.R. WIESENFELD

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853, USA

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The photodissociation of CIONO₂ using a broad-band ultraviolet photolysis source has been investigated using time-resolved atomic absorption spectroscopy in the vacuum ultraviolet. The predominant atomic photolysis product is $O({}^{3}P_{J})$, the quantum yield for $Cl({}^{2}P_{J})$ production being less than 4%.

1. Introduction

The three-body reaction of ClO radicals with NO₂,

$$CIO + NO_2 + M \rightarrow CIONO_2 + M$$
,

has been shown to be sufficiently rapid [1-5] to make ClONO₂ a potential storage medium for ClO_x and NO_x in the stratosphere [6-8]. Because the reaction of ClONO₂ with oxygen atoms is relatively slow under stratospheric conditions [9-11], photodissociation of this molecule is believed to be primarily responsible for its atmospheric destruction [12].

Several possible routes are available for ClONO₂ photolysis in the middle ultraviolet,

$$CIONO_2 \rightarrow CIO + NO_2, \tag{1}$$

$$\rightarrow$$
 Cl + NO₃, (2)

$$\rightarrow \text{CIONO} + O(^{3}\text{P}). \tag{3}$$

Two experimental studies of ClONO₂ photodissociation are in disagreement over which mechanism is dominant. The first involved the analysis of a steadystate photolysis mixture [13] and concluded that process (3) was predominant. An elegant very-lowpressure photolysis (VLPP) study of ClONO₂ suggested [14], however, that Cl and NO₃ are the major products with $\approx 10\%$ of the dissociative events leading to formation of O(³P). Because of the potential significance of $CIONO_2$ in the chemistry of the stratosphere, the present work was undertaken in an attempt to resolve the discrepancy between the published results. Direct observation of the atomic products of $CIONO_2$ photolysis by a broad-band source suggests that oxygen atom formation is indeed predominant with relatively little direct production of atomic chlorine.

Experimental

The apparatus consisted of a standard flash photolysis source and room-temperature resonance absorption cell similar to others described previously [15], but modified [16] to be compatible with highly reactive ClONO₂. The flash photolysis circuit employed a krypton-filled lamp excited by a capacitor discharge, the input energy of which could be varied between 30 and 200 J. The spectral output was estimated to be that of a black body at ≈6500 K with a pulse width of $\approx 20 \,\mu$ s. The microwave-powered electrodeless discharge lamp for production of resonance emission was a slightly modified version of a standard design [16], and employed a flowing mixture of either 5% O_2 or 10% Cl_2 in Ar. In order to minimize CIONO₂ photolysis by the spectroscopic source, a vacuum insert was placed between the resonance lamp and the reaction vessel thereby shielding the source gas from the intense vacuum ultraviolet radiation at the lamp window. The photolysis cell was constructed

^{*} Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

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of 23 mm inner diameter Suprasil quartz. The reaction mixture, a dilute ($\approx 0.01\%$) solution of ClONO₂ in Ar buffer (total pressure 25–50 Torr) provided from a greaseless, mercury-free, vacuum manifold was continuously flowed through the cell. In a few instances where greased joints were unavoidable in the handling of ClONO₂, halocarbon grease was found to be suitably inert. The ClONO₂ sample, kindly donated by Dr. Louis Glasgow of E.I. DuPont, was purified by distillation from a CHCl₃ slush (209 K), followed by freeze-pumping from a C₂H₅Br slush (154 K), and stored in the dark under liquid N₂ prior to use.

Both the original sample and the effluent passing out of the photolysis cell were trapped out and analyzed by UV--visible absorption spectroscopy. These purity checks were essential because NO_2 or OCIO contaminants greatly enhance the decays of O and Cl atoms, respectively. Such impurities would also confound any attempt to study CIONO₂ photolysis, as they are easily photodissociated by the actinic radiation used here.

The concentration of chlorine nitrate in the photolysis cell was also monitored by vacuum UV absorption measurements. Mixtures flowed through the cell in the absence of flash-lamp operation had NO2 levels comparable to the initial solution, $\approx 0.3 - 0.5\%$ NO₂ in ClONO₂. However, it was found that flashlamp operation led to substantial ClONO₂ decomposition and consequent NO₂ formation. This required that the lowest practical photolysis input energy (50 J) be used for kinetic measurements; at this energy the $NO_2/CIONO_2$ ratio in the photolysis mixture was $\approx 0.6\%$. The kinetic results presented here are corrected for this impurity level. Resonance lamp operation without the vacuum insert also caused significant decomposition, products being OCIO and NO_2 .

The resonance radiation viewed down the length of the reaction cell was dispersed by a vacuum monochromator and detected by an EMI G-26E315 solar blind photomultiplier. For oxygen atom measurements the ${}^{3}S_{1} \leftarrow {}^{3}P_{2,1,0}$ transition at 131 nm was monitored, while for the chlorine atom measurements the $4s({}^{2}P_{3/2,1/2}) \leftarrow 3p({}^{2}P_{3/2,1/2})$ transition at 135 nm was monitored. Neither set of spin-orbit multiplets was resolved since at the argon pressure used the spin-orbit states of both Cl and O atoms are thermally equilibrated on the time scale of these experiments and hence kinetically coupled. The amplified photomultiplier output was digitized by a Biomation 802 transient recorder and fed to a PDP 11/03 computer for signal averaging and storage. Typically, \approx 50-200 shots (at a repetition rate of \approx 1 Hz) were averaged per experiment. The data were then analyzed on a Prime 400 computer using a nonlinear least-squares fitting procedure [17].

3. Results and discussion

Resonance absorption transients were analyzed in the usual manner. The oxygen atom concentration decays exponentially from the value initially measured $\approx 200 \,\mu s$ after the flash according to pseudofirst-order kinetics, $[O] = [O]_0 \exp(-k_1 t)$, where $k_1 = k_O [CIONO_2] + k_D$ and k_O is the second-order rate constant for reaction of oxygen atoms with $CIONO_2$. The value, k_D , represents the first-order rate for diffusive removal of atoms through the Ar buffer gas. The oxygen atom concentration is empirically related to absorbance at 131 nm, A, via the modified Beer-Lambert law [18],

 $A = (\epsilon l[0])^{\gamma},$

yielding

 $A_t = A_0 \exp(-k_1 \gamma t)$

as the expression describing the time-dependent absorbance. The value of k_0 is determined from the slope of a plot of k_1 versus [ClONO₂], while γ is determined from the slope of a plot of $\ln A_0$ versus $\ln [ClONO_2]$. For oxygen atoms, the value of γ was found to be 0.8 ± 0.10 (1 standard deviation).

A typical determination of the bimolecular rate constant for reaction of O with ClONO₂ is displayed in fig. 1. Including a small correction for the NO₂ impurity, the rate constant for oxygen atom decay, k_0 , was found to be $(2.3 \pm 0.6) \times 10^{-13}$ cm³ molecule⁻¹. This compares favorably with the room-temperature literature value [11] of 2.0×10^{-13} and thus supports the applicability of the experimental method as well as the analysis of impurities in the photolysis mixture.

Oxygen atoms produced in the photolysis of $CIONO_2$ might result from the secondary photolysis





of a primary photoproduct such as NO3. It may readily be shown that at the photon flux characteristic of the current apparatus, photolysis of either ClONO₂ or a photoproduct such as NO_3 (which has a very high absorption cross section [19]) will occur to the extent of less than 5%. Thus, if the observed oxygen atoms were produced by a secondary photolysis, their yield would follow a quadratic dependence upon photolysis energy. On the other hand, if oxygen atoms were a primary product of ClONO₂ photolysis, their yield would be linearly dependent upon photolysis energy. To test for the photolysis mechanism, the input flash energy was varied over the range 30-100 J. A linearly proportional dependence of oxygen atom yield upon input energy was observed to within experimental uncertainty. It may therefore be concluded that the observed oxygen atoms are a direct photolysis product of ClONO₂. Photolysis of the low concentrations of NO_2 and OClO present are estimated to yield at most 10% of the oxygen atoms observed in these experiments.

Next, an attempt was made to observe chlorine atoms following $ClONO_2$ photolysis using the same apparatus and experimental conditions. No absorption of the chlorine atom resonance line at 135 nm was observed. With the same set up, it was possible to observe substantial yields of chlorine atoms from the photolysis of both PCl₃ and CCl₄. It may be concluded that the quantum yield of chlorine atoms from ClONO₂ photolysis is very low. While it is difficult to quantify the relative sensitivity of oxygen and chlorine atom detection in the present apparatus, a rough estimate of an upper limit on the yield of Cl from ClONO₂ photodissociation may be estimated by comparison with the experiments on CCl₄. Assuming at least a 5:1 ratio in chorine atom production for equal initial concentrations of CCl₄ and ClONO₂ and taking into account the relative UV absorption cross sections of CCl₄ [20] and ClONO₂ [12] (in a ratio of less than or equal to 0.2 above 200 nm) along with a unit quantum yield of Cl from CCl₄ photolysis [20], we estimate the quantum yield for chlorine atoms from ClONO₂ photolysis to be less than 4%.

The current results may be compared with previous studies on ClONO₂ photoproducts. This work most closely resembles the flash photolysis—resonance fluorescence experiments of Kurylo and Manning [11,21]. In those studies, the photolyzing radiation extended into the vacuum UV whereas in this work actinic radiation was above ≈ 200 nm. Both O and Cl were observed in the earlier work [11,21] but the relative yields were not reported. The fact that it was found necessary to augment the chlorine atom yield by the addition of CCl₄ to the photolysis mixture in order to measure the rate of chlorine atom reaction with ClONO₂ does suggest a low efficiency for (2) with respect to (3).

The present experiment is also in agreement with the earlier study of $ClONO_2$ photodissociation in a static system [13]. The discrepancy between these experiments and the VLPP study [14] remains a puzzle. It is unclear whether they arise from a fundamental and unrecognized difference between the detection methods used or merely from a wavelength dependence of the $ClONO_2$ photodissociation mechanism which then makes the experimental results sensitive to the output spectrum of the light sources used. Investigation of $ClONO_2$ photolysis using monochromatic laser sources might be useful in reconciling this outstanding discrepancy.

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