Measurement of Relative Product Yields from the Photolysis of Dichlorine Monoxide (Cl_2O)

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The Cl and ClO quantum yields from the photodissociation of Cl_2O have been measured at 320, 360, 400, and 440 nm with the use of chemical ionization mass spectrometry (CIMS). All yields were measured at a pressure of 50 Torr and were normalized to a unit quantum yield at 255 nm. There is no evidence that either the Cl or ClO quantum yields deviate significantly from unity over the range of wavelengths employed. Comparison with other recent work on Cl_2O photolysis is made, and implications with respect to the understanding of the dissociation dynamics involved are discussed.

Introduction

Photodissociation represents an important loss mechanism for many temporary reservoir species in the stratosphere. Recently the photodissociation of chlorine oxides has attracted attention because of the role that they play in the catalytic depletion of stratospheric ozone. Although the chemistry of Cl_2O (dichlorine monoxide) is not of direct relevance to the stratosphere, an understanding of its photodissociation will further the understanding of the photochemistry of similar molecules. In addition, photodissociation of Cl_2O is often used to generate ClO radicals for use in laboratory studies

$$Cl_2O + h\nu \rightarrow Cl + ClO\ (\lambda_{thresh} = 840\ nm) \qquad (1)$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \qquad (2)$$

An accurate determination of the production of ClO depends on a knowledge of the quantum yields of reaction 1 at various wavelengths. Early studies of the photochemistry of Cl_2O[1−3] indicated that reaction 1 is the primary dissociation channel. In addition, it was believed that other dissociation channels are possible

$$Cl_2O + h\nu \rightarrow 2\,Cl + O(^3P)\ (\lambda_{thresh} = 292\ nm) \qquad (3)$$

$$Cl_2O + h\nu \rightarrow Cl_2 + O(^3P)\ (\lambda_{thresh} = 710\ nm) \qquad (4)$$

$$Cl_2O + h\nu \rightarrow Cl_2 + O(^1D)\ (\lambda_{thresh} = 335\ nm) \qquad (5)$$

More recently, Sander and Friedl[4] used broadband photolysis of Cl_2O to generate ClO in a study of the reaction of BrO with ClO. When Cl_2O was dissociated in the presence of Br_2 the production of BrO was observed. From the formation of BrO, they deduced a quantum yield of 0.25 ± 0.05 (integrated over the wavelengths of the arc lamp) for the production of $O(^3P)$ from reactions 3 and 4. Okumura and co-workers[5,6] were able to use photofragment translational energy spectroscopy to study the dissociation of Cl_2O at 308, 248, and 193 nm. From these studies, it was found that reaction 1 represents the only dissociation channel at 308 nm. In addition, $O(^3P)$ production was observed at 248 nm, but this is thought to have resulted from dissociation of vibrationally excited ClO. At 193 nm it is believed that dissociation takes place via reactions 4 and 5 but that subsequent dissociation of the excited Cl_2 yields Cl atoms. In a similar study, Tanaka et al.[7] employed photofragment ion imaging to characterize the angular distribution of Cl atoms produced from the photodissociation of Cl_2O at 235 nm. The observation of slow Cl atoms appeared to confirm that three-body dissociation (reaction 3) was occurring at this wavelength, though the yield for this channel was not quantified. Finally, Nickolaisen et al.[8] utilized broadband flash photolysis of Cl_2O with a series of filters to examine ClO yields in various regions of the spectrum. Though wavelength resolution was limited, they observed a decrease in ClO yield with increased pressure at wavelengths greater than about 300 nm.

To further resolve the nature of the photolysis of Cl_2O in this region of the spectrum, we have employed a broadband light source with a monochromator for wavelength discrimination. Detection and measurement of the yields of the photofragments are accomplished with chemical ionization mass spectrometry (CIMS). Use of the monochromator reduces the light flux available for photolysis, but it offers continuous wavelength selection. The corresponding reduction in photolysis is compensated for by the high sensitivity of the CIMS detection technique.

Experiment

Cl_2O was prepared using the method of Cady[9] by reacting an excess of Cl_2 with dried HgO. The Cl_2O was collected and Cl_2 removed in a series of vacuum distillations in 2-propanol/dry ice slush baths (196 K). The purity of the Cl_2O was checked with UV absorption spectroscopy and CIMS. It was determined that the Cl_2O sample was at least 99% pure. No OClO impurity was detected in the absorption measurements, but an upper limit of 1 ppm was estimated based on the detection limits of the spectrometer. Cl_2O mixtures were made with N_2 (UHP Matheson) which had been dried by passing it through a silica gel trap in liquid nitrogen (80 K). The Cl_2O mixtures were kept in glass bulbs and shielded from light to prevent decomposition through photolysis.

A schematic diagram of the Photo-CIMS experimental apparatus is shown in Figure 1 and has been described in detail

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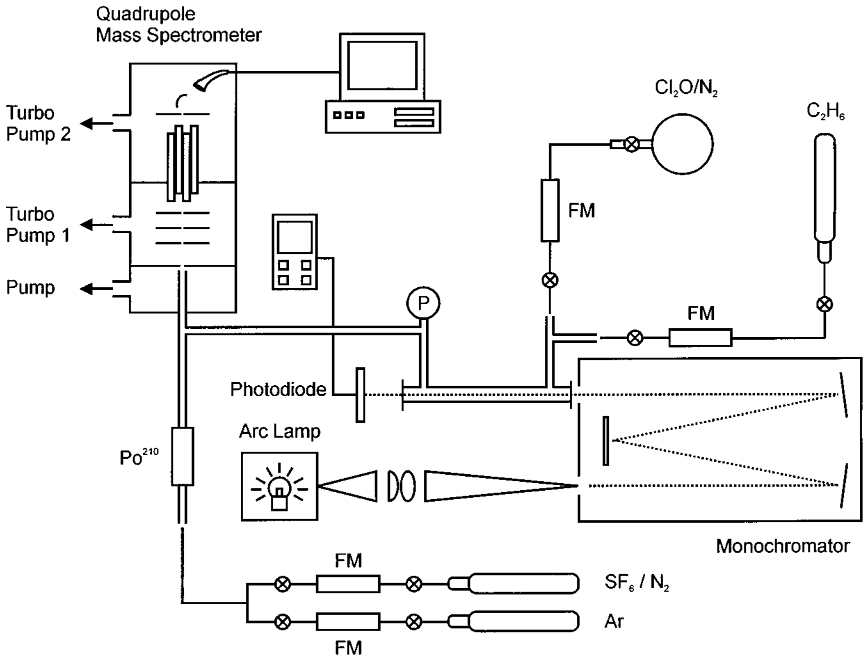

Figure 1. Schematic diagram of the apparatus used in this study.

in previous work.[10] A 75-W xenon arc lamp (Oriel 6137) produced white light that was focused into a monochromator (McKee-Pedersen Instruments 1018B) containing a diffraction grating (2360 lines/mm) to disperse the light and allow for wavelength selection. As in our previous work[10] the magnitude of any stray light (light of wavelength other than that selected with the monochromator) was measured with a second monochromator (ARC VM-503, 3600 lines/mm) coupled to the first one. It was found that the amount of this stray light was negligible in all of the experiments. The photolysis tube was positioned at the exit slit of the monochromator and was constructed from 1/4 in. o.d. (4 mm i.d.) Pyrex tubing 11 cm long with quartz windows at each end. The light flux was measured with a photodiode (Oriel 70282) whose response was calibrated as a function of wavelength.

The Cl_2O/N_2 flow (1−2 STP mL min^{-1}) and ethane (UHP Matheson) flow (1−2 STP mL min^{-1}) were introduced and mixed at the rear of the photolysis tube. The concentration of Cl_2O in the photolysis tube was typically $3-10 \times 10^{15}$ molecules cm^{-3}, and the residence time was about one second. The entire flow passed down the length of the tube and then entered the ion−molecule region where ionization was accomplished. A quadrupole mass spectrometer (ABB Extrel Merlin) was located at the end of the ion−molecule region. All gas flows were monitored with calibrated mass flow meters (Tylan). The pressures in the photolysis tube (~50 Torr) and the ion−molecule region (~25 Torr) were monitored using a 0−1000 Torr capacitance manometer (MKS Baratron).

The chemical ionization of the photolysis-titration products (ClO, HCl and Cl_2) was achieved as in some of our previous studies.[11] The reagent ion SF_6^- was generated by passing a 5 STP L min^{-1} flow of Ar with SF_6 (~1 ppm) through a Po(210) Nuclecel ionizer (NRD Inc.). In the ion−molecule region, the SF_6^- ionized the trace species through chemical reaction. The ClO and the Cl_2 were ionized via electron transfer, and the HCl was ionized via fluorine−chlorine exchange with the SF_6^- to yield SF_5Cl^-. The ions were detected with a quadrupole mass spectrometer housed in a two-stage differentially pumped vacuum chamber.

A typical mass spectrum collected using ethane to titrate the Cl atoms to HCl is shown in Figure 2. As observed by Huey et al.,[12] the SF_6^- reagent ion ionizes Cl_2O to produce Cl^- and Cl_2O^-. However, in these experiments Cl^- is observed with much larger intensity than is Cl_2O^-, whereas Huey et al. measured relative yields of 60% for Cl^- and 40% for Cl_2O^-. The sizable Cl^- signal does not complicate the ionization chemistry of the SF_6^- reagent ion because of the stability of the Cl^- ion. With a relatively large electron affinity of 3.615 eV,[13] Cl^- is not believed to ionize any of the photolysis-titration products, ClO, HCl and Cl_2, to a significant extent.

Results

Titration of Photofragments. The measurements of the yields of both of the photolysis products, Cl and ClO, were made with two different titration schemes. In the first titration scheme, an excess of ethane ($[C_2H_6] \sim 300 \cdot [Cl_2O]$) was added to the Cl_2O/N_2 flow in order to titrate nearly all of the reactive Cl to the more stable HCl:

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \tag{6}$$

It was then possible to detect both photolysis products with the ClO appearing as ClO^- and the Cl (titrated to HCl) as SF_5Cl^-

$$SF_6^- + ClO \rightarrow ClO^- + SF_6 \tag{7}$$

$$SF_6^- + HCl \rightarrow SF_5Cl^- + HF \tag{8}$$

To eliminate the possibility that the ethyl radical formed in reaction 6 may complicate the titration chemistry, a second titration scheme (with no ethane) was also used. In this scheme, the Cl formed from photolysis reacted with the Cl_2O:

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \tag{2}$$

The ClO yield was effectively amplified by a factor of 2 (with complete reaction of all Cl), and the Cl was titrated to the stable

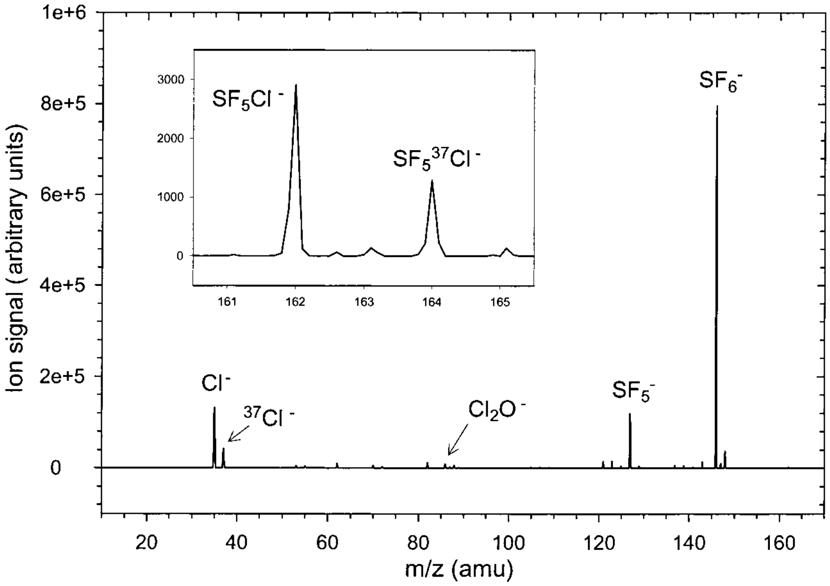

Figure 2. Sample mass spectrum with SF_6^- as the reagent ion. Ethane has been added to titrate the Cl photofragment to HCl which is detected as SF_5Cl^-, and the ClO photofragment is detected as ClO^-. The large Cl^- signal results from the ionization of Cl_2O.

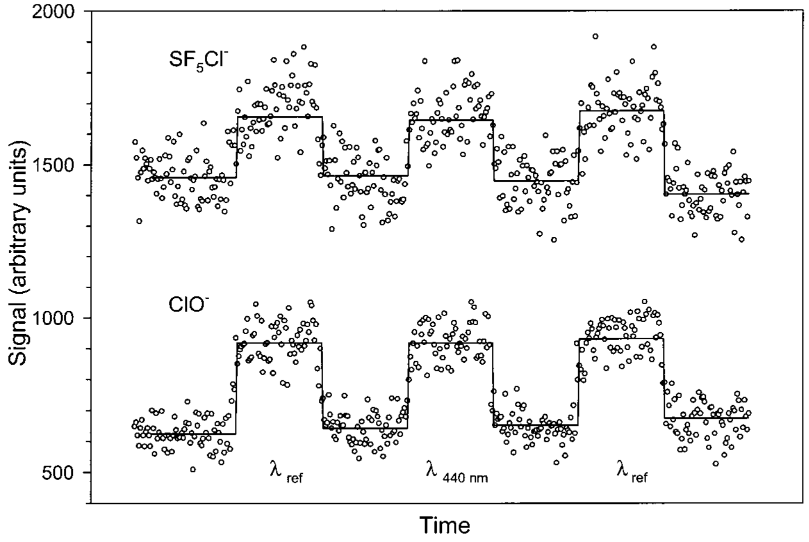

Figure 3. Sample signal rise for the detection of ClO as ClO^- and Cl as SF_5Cl^- at reference (255 nm) and measurement (440 nm) wavelengths. The solid line represents an average of the signal with and without the photolysis light.

molecule Cl_2. The ClO was detected as ClO^- (again through reaction 7), and the Cl_2 was detected as Cl_2^-

$$SF_6^- + Cl_2 \rightarrow Cl_2^- + SF_6 \qquad (9)$$

With these two titration schemes it was possible to measure *both* of the photolysis product yields under the same conditions. This capability offered a consistency check between the two schemes as well as within each scheme.

Relative quantum yield calculations were made for each of the products at various wavelengths through comparison with product yields measured at a reference wavelength, 255 nm. This reference wavelength was chosen for a couple of reasons. First, Cl_2O possesses an absorption maximum very near to this wavelength. Second, the effect of pressure on the photodissociation of Cl_2O as reported by Nickolaisen et al.[8] is negligible in this region of the spectrum. The wavelength of the light in the photolysis tube was alternated between the reference and measurement wavelengths (see Figure 3) by changing the angle of the diffraction grating in the monochromator. Because only the wavelength of the light was changed, this procedure allowed other variables (including gas flows and concentrations) to be kept relatively constant between successive measurements.

Concentrations of some of the trace species in the flow system changed upon dissociation of Cl_2O. If the effective rate of photolysis of Cl_2O was different at the reference and measurement wavelengths, then the secondary chemistry involving these trace species would also be different. To minimize the effect of this difference on the concentrations of the species being measured, the ClO concentration (as measured by the ClO^- signal) was matched at the two wavelengths by attenuation of the light at the reference wavelength. Placement of a neutral density filter of appropriate optical density at the entrance slit of the monochromator allowed the light to be attenuated. Though reactions of the ClO radical with itself could decrease its concentration, typical ClO concentrations on the order of 10^{11} molecules cm^{-3} and a total residence time of about one second result in only approximately 1% of the ClO radicals being depleted. The ClO^- signal observed was then representative of the ClO concentration in the photolysis tube. With comparable

TABLE 1: Summary of the Quantum Yields Measured in This Study (relative to that at 255 nm)[a]

	with C_2H_6		without C_2H_6	
λ (nm)	Φ(ClO)	Φ(Cl)	Φ(ClO)	Φ(Cl)
320	0.98 ± 0.10	1.08 ± 0.16	0.95 ± 0.13	0.95 ± 0.18
360	1.04 ± 0.14	1.02 ± 0.19	1.06 ± 0.18	0.99 ± 0.15
400	1.02 ± 0.14	0.94 ± 0.16	1.06 ± 0.19	1.12 ± 0.16
440	1.06 ± 0.14	0.97 ± 0.13	1.17 ± 0.17	1.04 ± 0.17

[a] The quoted errors include estimated errors in the Cl_2O cross section[14] and represent 95% confidence limits

concentrations of all trace species at the two wavelengths similar detection sensitivities and secondary chemistry were ensured. This procedure allowed a direct comparison of photolysis-titration product yields at the two wavelengths.

Calculation of Quantum Yields. The quantum yield at the measurement wavelength (λ_2) was calculated relative to that at the reference wavelength (λ_1) through use of the following expression (derived in previous work[10])

$$\Phi_{\lambda_2} = \Phi_{\lambda_1} \frac{S_{\lambda_2}}{S_{\lambda_1}} \frac{I_{\lambda_1}}{I_{\lambda_2}} \frac{\lambda_1}{\lambda_2} \left[\frac{\exp(\sigma_{\lambda_1}[\mathrm{Cl_2O}]l) - 1}{\exp(\sigma_{\lambda_2}[\mathrm{Cl_2O}]l) - 1} \right] \qquad (10)$$

In this expression, S_λ is the signal rise of the corresponding species and I_λ is the light flux (in Watts) as measured by the wavelength-calibrated photodiode. Values for σ_λ represent the Cl_2O absorption cross section (taken from the literature[14]) weighted by the monochromator shape function. The shape function is determined by the slit geometry of the monochromator and in this case is triangular with maximum intensity at the central wavelength. The bracketed term at the end represents a correction for the attenuation of the light by Cl_2O, with l the length of the tube and the Cl_2O concentration determined through UV absorption. In using the above expression, it is assumed that both the Cl_2O concentration and the flow velocities of the gases remain constant between successive measurements, as is the case for all experiments presented here.

Use of eq 10 is valid for the determination of quantum yields using any of the photolysis-titration products. Table 1 lists the quantum yields (relative to that at the reference wavelength of 255 nm) as measured for both dissociation products with each of the two titration schemes using a bandwidth of ± 1.80 nm (fwhm) and a pressure of 50 Torr. Figure 4 shows these relative quantum yields at the four measurement wavelengths: 320, 360, 400, and 440 nm. The uncertainties listed represent 95% confidence limits and include estimated uncertainties in the measurement of the light flux (± 5%) as well as estimated uncertainties in the Cl_2O absorption cross sections as published in the literature.[14] It should be noted that the uncertainties in the published cross section data contribute a significant amount to the overall uncertainties in the determination of the relative quantum yields.

Absorption Spectrum. To identify and quantify impurities which may be present in the Cl_2O mixtures, UV−visible absorption spectra were taken using a commercial spectrometer (Cary) with a path length of 10.5 cm. A typical spectrum of a mixture of 5 Torr of Cl_2O in 995 Torr of N_2 is shown in Figure 5. Also shown for comparison are the cross section data of Lin.[14] The lack of any structure to the long-wavelength side of the peak near 255 nm is significant in the interpretation of the nature of the excited state and is discussed in more detail in the next section.

Discussion

The measured quantum yields for production of both Cl and ClO from the photodissociation of Cl_2O are essentially constant at all wavelengths. The yields at the various measurement wavelengths agree well with the yield at the reference wavelength as well as with each other. In addition, the yields calculated from the measurements of the Cl and ClO fragments are consistent with one another indicating that there is no unaccounted for secondary chemistry present.

Comparison with Flash Photolysis Experiments. In the broadband flash photolysis experiments conducted by Nickolaisen et al.[8] ClO yields were observed to decrease with increasing pressure. In fact, the yields reported decreased by more than an order of magnitude from 5 Torr to 100 Torr in some of the measurements. The decrease appeared to be more pronounced at longer wavelengths, and it was proposed that this trend is evidence of intersystem crossing from an excited singlet state ($1\ ^1B_1$) to an excited triplet state ($1\ ^3A_2$) with which it is in near resonance (Figure 6a). The $1\ ^3A_2$ state can be collisionally quenched to a lower energy triplet state ($1\ ^3B_1$), and this lower energy state could either be quenched to the ground singlet state, $1\ ^1A_1$, or dissociate to Cl and ClO. Higher pressures would result in more efficient quenching to the metastable $1\ ^3B_1$ state (and eventually the $1\ ^1A_1$ state) leading to less efficient production of the ClO photofragment. It was argued that light of wavelength shorter than about 300 nm would not result in appreciable coupling between the $1\ ^1B_1$ state and the triplet manifold. Thus, the competition between dissociation and pressure-dependent quenching would not be expected at those wavelengths. With this mechanism, Nickolaisen et al. were able to explain the long-wavelength pressure dependence that they observed in the ClO product yield.

The mechanism outlined above requires that intersystem crossing from the singlet manifold to the triplet manifold ($1\ ^3A_2 \leftarrow 1\ ^1B_1$) be efficient enough to compete with both quenching and dissociation of the initial excited state, $1\ ^1B_1$. Subsequently, this $1\ ^1B_1$ dissociative state would be required to be sufficiently long-lived to allow for such efficient crossing to the $1\ ^3A_2$ state. Evidence of such a quasi-bound state would be expected to appear in the form of vibrational structure in the absorption spectrum of Cl_2O near the initial excitation to the $1\ ^1B_1$ state (~364 nm[8]). However, in absorption measurements that we made at wavelengths from 190 to 400 nm (Figure 5), no such vibrational structure was observed at a resolution of 0.1 nm. It therefore seems unlikely that Cl_2O possesses a bound excited-state accessible at wavelengths shorter than 400 nm and that intersystem crossing from the $1\ ^1B_1$ state would be inefficient. These findings do not seem to be consistent with the mechanism proposed by Nickolaisen et al.

The results of our photolysis experiments indicate that there is no change in the quantum yield for reaction 1 from 255 to 440 nm at a pressure of 50 Torr (at which quenching should be significant). Employing the transition energies as calculated by Nickolaisen et al., absorption of 255 nm light should excite to the $1\ ^1B_2$ state (with intersystem crossing to the triplet manifold assumed nonexistent). However, absorption of 440 nm light should excite directly to the $1\ ^3B_1$ state as it is the only state indicated which is accessible at this energy. The fact that the quantum yields that we measured are identical (within error) at these two wavelengths indicates that quenching of the $1\ ^3B_1$ state (at 440 nm) is no more efficient than of the $1\ ^1B_2$ state (at 255 nm). Likewise, the quantum yields that we measured at 320 and 360 nm indicate that quenching of the $1\ ^1B_1$ state and of the $1\ ^3A_2$ state (via the $1\ ^3B_1$ state) is no more efficient than

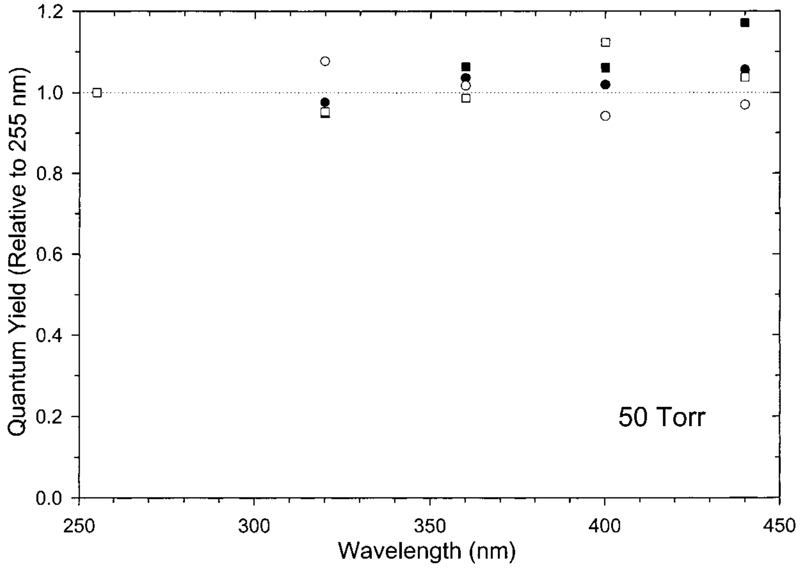

Figure 4. Quantum yields (relative to that at 255 nm) for the Cl and ClO products at 320 nm, 360, 400, and 440 nm: ●: ClO yield (with ethane), ○: Cl yield (with ethane), ■: ClO yield (no ethane), □: Cl yield (no ethane). The dashed line represents the quantum yield at the reference wavelength (255 nm).

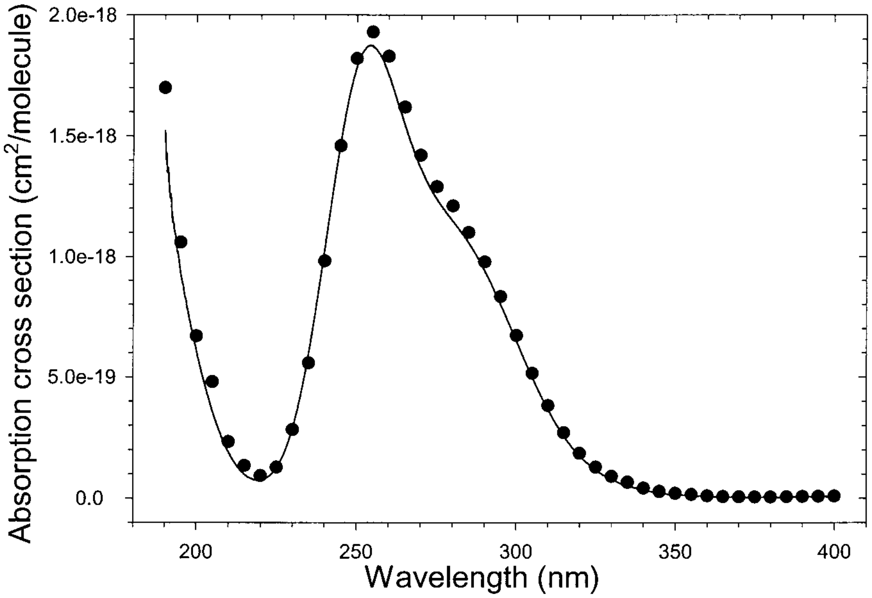

Figure 5. Absorption cross section of Cl_2O (—) measured every 0.1 nm from 190 to 400 nm. The data of Lin[14] (●) are shown for comparison.

quenching of the 1 $^1B_2$ state. The quantum yields measured in our experiments, therefore, do not appear to be consistent with the findings, calculated transition energies and proposed mechanism of Nickolaisen et al.

Comparison with Calculated Transition Energies. Recent ab initio calculations reported by Del Bene et al.[15] and Toniolo et al.[16] have also indicated that the singlet Cl_2O transition energies calculated by Nickolaisen et al.[8] may be overestimated by as much as 1 eV for some transitions. In their work, Nickolaisen et al. calculated the vertical excitation energy to the lowest singlet state (1 $^1B_1$) at 3.41 eV (364 nm). This assignment would require absorption of photons of significantly lower energies (such as the 400 and 440 nm used in our experiments) to be attributed to excitation to a triplet state (1 $^3B_1$ at 2.63 eV, or 471 nm). On the other hand, Toniolo et al.[12] have calculated excitation to the 1 $^1B_1$ state to be at 2.68 eV (463 nm) and to the 1 $^1B_2$ state to be at 4.39 eV (282 nm), shown for comparison in Figure 6b. With these transition energies, it is possible to interpret the data of our experiments entirely in terms of excitation to singlet states, each of which dissociates with unit quantum yield at the wavelengths employed (and at 50 Torr).

Interestingly, the identity of the metastable 1 $^3B_1$ state by Nickolaisen et al. was made based in part on an absorption spectrum (from approximately 400 nm to 550 nm) which was attributed to the 2 $^3A_2 \leftarrow 1\ ^3B_1$ excitation. The observation of structure in this spectrum near the calculated transition energy of 3 eV (415 nm) for this 2 $^3A_2 \leftarrow 1\ ^3B_1$ excitation appeared to confirm the metastable nature of the 1 $^3B_1$ state. However, they pointed out that singlet−singlet transitions could not be ruled out as the source of the metastable spectrum. In fact, the work of Toniolo et al.[16] indicates the presence of a singlet state, 3 $^1A_1$, with a transition energy of 2.67 eV (465 nm) above the first excited state, 1 $^1B_1$ (see Figure 6b). This calculated transition energy falls well within the metastable spectrum observed by Nickolaisen et al. and may constitute a plausible

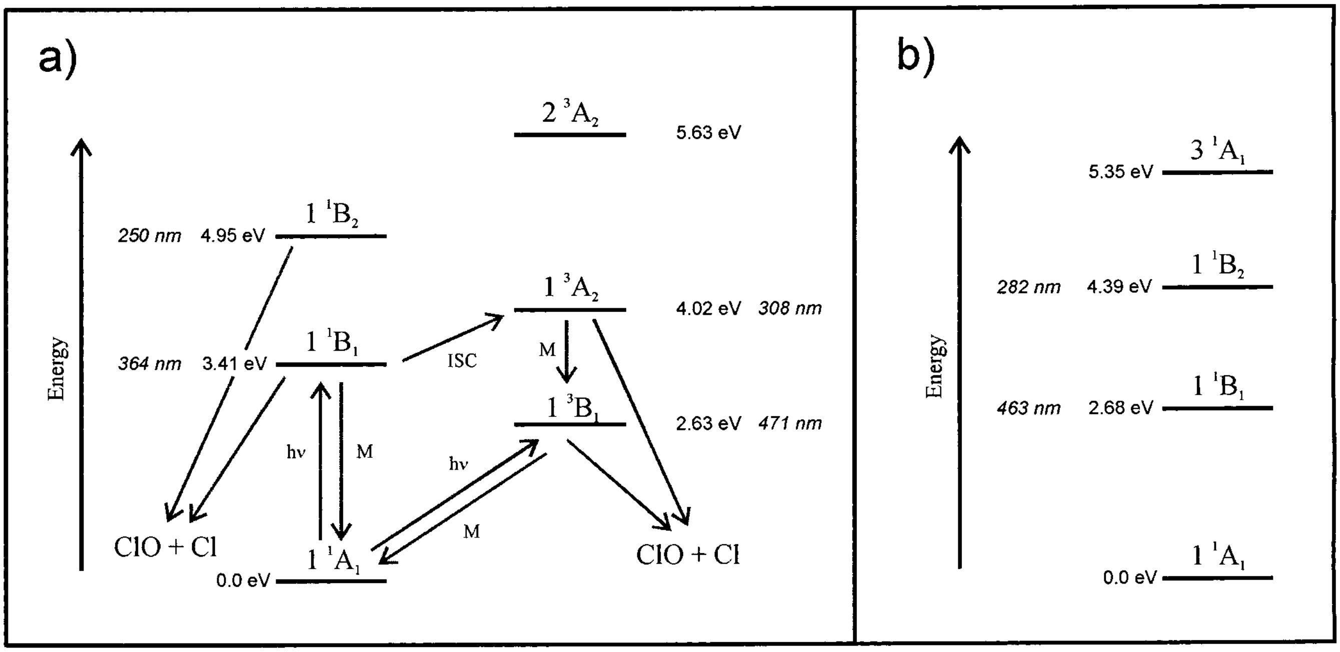

Figure 6. Energy diagrams of Cl_2O electronic states with vertical excitation energies (and corresponding wavelengths). (a) Adapted from diagram and calculations of Nickolaisen et al.[8] Here, *hν* represents absorption of a photon, M represents collisional quenching and ISC indicates intersystem crossing. (b) Singlet transition energies calculated by Toniolo et al.[16]

alternative to its assignment as a triplet−triplet transition and its interpretation as evidence of a metastable triplet state. It is clear that further research is required to elucidate the nature of the excited states accessible in the UV as well as the possibility of intersystem crossing from singlet to triplet states.

Possible Impurities and Secondary Chemistry. Impurities in the Cl_2O gas mixtures which absorb in the UV region of the spectrum could complicate the measurement of the Cl_2O photofragment yields. In particular, OClO, a common chlorine oxide impurity, possesses a highly structured spectrum with large cross section values at wavelengths from 300 to 450 nm. To ascertain the overall purity of the Cl_2O gas mixture and possibly to identify the presence of any impurities, UV−visible absorption spectra were taken from 190 to 400 nm. Figure 5 shows a typical spectrum taken using a Cary UV−vis spectrometer with the measurements of Lin[14] shown for comparison. The very good agreement with the data of Lin and the lack of any structure in the recorded spectrum indicate that if OClO is present at all it must be so at insignificant amounts. The lack of OClO absorption features make it difficult to confirm or to quantify its presence in the Cl_2O mixture, but an upper limit of 1 ppm on the OClO concentration is estimated based on the recorded absorption measurements.

Photolysis via the alternate dissociation reactions 3−5 could also complicate the chemistry through the production of O atoms. These O atoms could react with the large concentration of Cl_2O present leading to the creation of ClO radicals

$$O(^3P)/O(^1D) + Cl_2O \rightarrow 2\,ClO \qquad (11)$$

We are not able to distinguish ClO radicals produced in this manner from those produced directly by dissociation of Cl_2O in reaction 1. However, the dissociation reactions 4 and 5 create a Cl_2 molecule in addition to the O atom, and the Cl_2 would be detected as Cl_2^-. In the experiments in which the Cl atoms were titrated by an excess of ethane, reactions 4 and 5 would be the only source of Cl_2 molecules and the quantum yield for these two channels could be measured from the Cl_2^- signal. No Cl_2^- signal rise was observed with the light, and thus, we conclude that the total quantum yield for channels 4 and 5 is negligible at the wavelengths studied. In addition, the three-body dissociation to yield Cl + Cl + O (reaction 3) is not thermodynamically accessible at the measurement wavelengths. Therefore, the yields measured at 320, 360, 400, and 440 nm represent dissociation via reaction 1 only.

At the reference wavelength of 255 nm reaction 3 is energetically accessible, though, and this must be taken into account when the measurements are normalized to the quantum yield at this wavelength. Assuming a dissociation quantum yield of unity, if the quantum yield for dissociation via reaction 3 (Cl + Cl + O) is *f*, then the quantum yield for reaction 1 (Cl + ClO) is $(1 - f)$. In the experiments in which the Cl was titrated with ethane, for example, a quantum yield of $(1 + f)$ can be expected for HCl as well as ClO because the O atoms react with Cl_2O (reaction 11). This factor of $(1 + f)$ is the effective quantum yield for the production of HCl or ClO products, and it must be included in eq 10 (in $\Phi_{\lambda 1}$) when measurements at the longer wavelengths are normalized to those at 255 nm. This normalization results in quantum yields which are larger by the factor of $(1 + f)$. The only dissociation channel at the longer wavelengths is reaction 1, so quantum yields greater than unity are not possible for either product. Because the measured quantum yields at these wavelengths are already unity (within error), they cannot be scaled by the factor of $(1 + f)$, and the quantum yield for channel 3, *f*, must be negligible at 255 nm. However, it is possible that *f* is larger at shorter wavelengths (as observed by Tanaka et al.[7] at 235 nm and Moore et al.[6] at 248 nm).

Conclusion

The results of our experiments with Cl_2O photolysis suggest that there is no change in the quantum yields of Cl and ClO from 255 to 440 nm at a pressure of 50 Torr. These results are not consistent with the long-wavelength pressure dependence observed by Nickolaisen et al.[8] or with their proposed mechanism of Cl_2O excitation and dissociation. On the basis of our measurements and the work of Nelson et al.[5] it is recommended that the quantum yield for reaction 1 be taken as unity (within experimental error) over this wavelength range.

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