## Ultraviolet Absorption Cross Sections of Cl<sub>2</sub>O<sub>2</sub> between 210 and 410 nm

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The ultraviolet and infrared absorption cross sections of  $Cl_2O_2$  have been measured. The transient  $Cl_2O_2$  molecule was produced by using the gas-phase reaction  $ClO + ClO + M \rightarrow Cl_2O_2 + M$ . Three independent ClO radical source reactions were used in this study:  $Cl + O_3$ ,  $Cl + Cl_2O$ , and Cl + OClO. The  $Cl_2O_2$  UV absorption spectrum was recorded over the range 200-450 nm with a diode array spectrometer over the temperature range 205-250 K. The Cl<sub>2</sub>O<sub>2</sub> infrared absorption spectrum was recorded with a high-resolution Fourier transform spectrometer over the range 500-2000 cm<sup>-1</sup>. Both spectrometers were optically coupled to a fast flow multipass absorption cell. The UV absorption spectrum of Cl<sub>2</sub>O<sub>2</sub> is a structureless continuum with a peak at 245 nm. The measurable absorption extends out to 410 nm. The UV absorption cross section at the peak of the spectrum, 245 nm, was measured to be  $(6.5^{+0.8}_{-0.5}) \times 10^{-18}$  cm<sup>2</sup>. Infrared absorption features centered at 560, 653, and 750 cm<sup>-1</sup> have been assigned to the  $Cl_2O_2$  molecule. The present results are compared with other reported UV and IR measurements and the sources of discrepancies are discussed. The role of Cl<sub>2</sub>O<sub>2</sub> in atmospheric chemistry and in particular the Antarctic ozone "hole" are discussed.

#### Introduction

The cause and environmental implications of the large ozone loss, "ozone hole", observed in the Antarctic stratosphere during the springtime<sup>1</sup> over the past 10 years is a major concern of atmospheric scientists and society in general. The unusual combination of atmospheric conditions, low temperatures (<190 K), the presence of polar stratospheric clouds, and the presence of the polar vortex, which occur in the Antarctic stratosphere, leads to consideration of chemical mechanisms to explain the observed ozone losses. The following reaction mechanism<sup>2</sup>

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
 (1)

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$$
 (2)

$$ClOO + M \rightarrow Cl + O_2 + M$$
 (3)

$$2(Cl + O_3 \rightarrow ClO + O_2) \tag{4}$$

net: 
$$2O_3 \rightarrow 3O_2$$
 (5)

which under "normal" stratospheric conditions would not be significant is one of the mechanisms that has been proposed to account for the observed dramatic stratospheric ozone depletion.<sup>3</sup> This reaction mechanism was proposed because measurements in the ozone hole show greatly elevated levels of ClO<sup>4</sup> and OClO<sup>5</sup> which imply that chlorine chemistry plays a significant role in the ozone depletion. Evaluation of the significance of this reaction mechanism versus other possible chemical and/or dynamical processes which could contribute to the observed ozone depletion requires a detailed understanding of each of the elementary steps involved.

Until recently the spectroscopic and chemical properties of  $Cl_2O_2$  were not well understood and therefore represented a large uncertainty in interpreting the impact of the above reaction mechanism. Basco and Hunt<sup>6</sup> were the first to report spectroscopic measurements of the Cl<sub>2</sub>O<sub>2</sub> molecule by following the time-resolved flash photolysis of Cl<sub>2</sub>/OClO or Cl<sub>2</sub>/Cl<sub>2</sub>O mixtures at room temperature and over the pressure range 70-200 Torr. They measured UV absorption at six wavelengths over the range 232-292 nm and assigned the observed absorption spectrum to the Cl<sub>2</sub>O<sub>2</sub> molecule. They reported UV absorption cross sections that increased toward shorter wavelengths with a value of  $1.1 \times$ 10<sup>-17</sup> cm<sup>2</sup> at 232 nm.

Molina and Molina<sup>2</sup> have since reported UV absorption cross-section measurements of Cl<sub>2</sub>O<sub>2</sub> that differed significantly from those of Basco and Hunt.<sup>6</sup> Molina and Molina<sup>2</sup> studied reaction 1 in a flow reactor over the temperature range 240-298 K and over the pressure range 20-100 Torr. They monitored both UV and IR absorption. The following ClO radical source reactions were used in their study:

$$Cl + O_3 \rightarrow ClO + O_2$$
 (4)

$$Cl + OClO \rightarrow ClO + ClO$$
 (6)

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$
 (7)

They reported a broad UV absorption spectrum peaking at 265 nm which had a positive correlation with five IR absorption bands centered at 1225, 1057, 740, 653, and 562 cm<sup>-1</sup>. They report observing the same UV and IR bands with each of the three CIO radical sources used. The IR bands were assigned to two isomers of Cl<sub>2</sub>O<sub>2</sub> (ClOOCl and OClOCl). Their UV absorption spectrum had a measured peak cross section of  $6.5 \times 10^{-18}$  cm<sup>2</sup> at 265 nm.

Following the completion of recent measurements of the ClO IR line strengths in this laboratory,<sup>7</sup> we set out to observe the UV and IR absorption spectra of the  $Cl_2O_2$  molecule. These experiments produced a set of IR and UV spectra which we could not reconcile with the results of Molina and Molina.<sup>2</sup> Our measurements have led to a different interpretation of the spectra reported by Molina and Molina<sup>2</sup> as described below. Near the completion of our measurements we learned of the UV measurements of Cox and Hayman<sup>8</sup> who had independently reached conclusions similar to ours.

In this paper the UV and IR absorption spectra of  $Cl_2O_2$  are presented. The UV absorption cross sections of Cl<sub>2</sub>O<sub>2</sub> over the wavelength range 212-410 nm and the atmospheric photolysis rates calculated by using these data are reported. The sources of the discrepancies among the previous studies are discussed.

#### **Experimental Section**

The experimental apparatus is illustrated in Figure 1. Measurements were made using a discharge flow tube reactor coupled to a multipass absorption cell. Both a high-resolution Fourier transform spectrometer, FTS (Bomem DA3.002), operating in the IR region and a diode array spectrometer (EG&G PARC Model 1412) operating in the UV region were optically coupled to the absorption cell, allowing for the simultaneous measurement of IR and UV spectra of the gas sample.

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Figure 1. Schematic of high-resolution Fourier transform spectrometer, fast flow multipass absorption cell, and diode array spectrometer.

FTS Infrared Measurements. The FTS and multipass absorption cell are described in detail elsewhere<sup>7</sup> so only details pertaining to this study are presented here. The IR multipass optics of the absorption cell were adjusted to provide 62 passes over a base path of 1.57 m, yielding a geometrical path length of 97.3 m. A graphite light source, KBr beam splitter, and liquid He cooled Cu:Ge detector were used for all measurements. A 2250-cm<sup>-1</sup> long-pass filter was placed in the light source compartment to limit the bandwidth of the detector and hence reduce background noise. The majority of the measurements were made over the range of 500-2000 cm<sup>-1</sup> at a resolution of 1 cm<sup>-1</sup>. Higher resolution spectra were recorded over the observed Cl<sub>2</sub>O<sub>2</sub> IR absorption bands in an attempt to resolve rotational structure. A 0.02 cm<sup>-1</sup> resolution spectrum was recorded over the range 475-730 cm<sup>-1</sup>. For this measurement, a 735-cm<sup>-1</sup> long-pass filter mounted inside the Cu:Ge detector Dewar and cooled to liquid N<sub>2</sub> temperature was employed to further limit the band-pass. A 0.02 cm<sup>-1</sup> resolution measurement over the range 1100-1300 cm<sup>-1</sup> was also carried out. For this measurement, a wide-band-pass filter centered at 1050 cm<sup>-1</sup> was mounted inside the detector Dewar and cooled to liquid N<sub>2</sub> temperature.

UV Diode Array Spectrometer. Because the use of a UV diode array spectrometer is new to this experiment it will be described in more detail. Double-pass UV optics, probing the same volume of the absorption cell as the IR optics, were employed as shown in Figure 1. The quartz UV windows shown in Figure 1 are rotated 90° for clarity. The output of a D<sub>2</sub> lamp was collimated by using a 10 cm focal length quartz lens. The beam entered the cell via a 2.54 cm diameter quartz window. The beam was directed between the two "D" mirrors of the infrared multipass optics and traversed the length of the absorption cell. It then reflected off a spherical Al-coated mirror located just above and 2 cm in front of the IR Au-coated nesting mirror, again traversed the length of the cell, and exited through another 2.54 cm diameter quartz window located above the entrance window. The UV optical path was 330 cm long. However, this includes a 10 cm long stagnant volume located between the IR "D" mirrors and the UV windows. This volume was not temperature regulated. Because the stable species employed in this study (O<sub>3</sub>, Cl<sub>2</sub>O, and OClO) readily diffused behind the "D" mirrors, a path length of 330 cm was used in calculations for these species. For the transient species (ClO and Cl<sub>2</sub>O<sub>2</sub>) which did not significantly fill the stagnant volume, a path length of 310 cm was used. The 310 cm path length for transient species was tested by making UV absorption measurements of ClO with and without He flush gas added behind the "D" mirrors. The presence of flush gas had no affect on the observed CIO absorption, indicating CIO was not filling the volume behind the "D" mirrors. The exit beam was then focused by a 7.6 cm focal length quartz lens into a 0.25-m spectrograph (Jarrell Ash MonoSpec 27), equipped with a 100- $\mu$ m entrance slit and a 600 grooves/mm holographic grating, which dispersed the beam onto the 1024-element diode array detector. The UV spectral resolution was approximately 1.2 nm. The spectrograph was



Figure 2. Diagram of flow tube reactor and vacuum flange assembly.

calibrated by using emission lines from a Hg pen ray lamp and a 10- $\mu$ m entrance slit. The wavelength scale was accurate to  $\pm 0.2$ nm at 250 nm. For Cl<sub>2</sub>O<sub>2</sub> absorption cross section measurements near the peak of the spectrum, UV spectra were recorded over the range 200–340 nm. For the longer wavelength measurements, spectra were recorded over the range 310–450 nm. A Pyrex filter with a 300-nm cuttoff was placed in front of the entrance slit of the spectrometer for the longer wavelength measurements to limit interference from second-order reflection from the grating. Typically, each spectrum consisted of an average of 100 scans with an exposure time for each scan of 100 ms. Spectra were then transferred via the detector interface (EG&G PARC Model 1461) to an IBM PC for analysis.

Flow Tube Reactor. The flow tube reactor employed in this study is illustrated in Figure 2. The flow tube and the absorption cell were equipped with cooling jackets. Methanol was pumped rapidly from a temperature-regulated reservoir (Neslab, ULT-80DD) through the jackets maintaining gas temperatures as low as 200 K. The flow tube was attached to the multipass absorption cell by way of a flange/O-ring assembly, ensuring that the gases were maintained at a constant temperature throughout the entire apparatus. The flow tube was 150 cm in length and had an i.d. of 5.5 cm, except for the bottom 15 cm which was 3.5 cm i.d. This narrower portion of the flow tube was terminated with a piece of threaded glass. Any one of a number of Teflon plugs with a small orifice could then be threaded into the bottom of the flow tube. This enabled the flow tube reactor to be operated at high pressure (generally 25-35 Torr) and slow flow conditions (residence times between 3 and 10 s) while lower pressure measurements (5-10 Torr) and faster flow conditions could still be maintained in the absorption cell. Quantitative measurements were made using a Teflon plug with a 0.15 cm diameter hole. The expansion of the gases entering the absorption cell resulted in a concentration decrease of about a factor of 3-5 between the flow tube and the absorption cell. All concentrations reported in this paper are those in the absorption cell where the spectral measurements were made, unless otherwise noted.

 $Cl_2O_2$  was formed from the three body association of two ClO radicals

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
 (1)

where  $k_1 = 9 \times 10^{-33} (T/300)^{-3.6}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> for M = He.<sup>9</sup> The ClO radicals were generated by the reaction of Cl atoms with an excess of one of three precursor molecules

$$Cl + O_3 \rightarrow ClO + O_2$$
 (4)

$$Cl + OClO \rightarrow ClO + ClO \tag{6}$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \tag{7}$$

where  $k_4 = 2.9 \times 10^{-11} \exp(-260/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, <sup>10</sup>  $k_6 = 5.9 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> independent of temperature, <sup>11</sup> and  $k_7 = 9.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ independent of temperature}^{-12}$ For the majority of the measurements, Cl atoms were produced in a microwave discharge of 5% Cl<sub>2</sub> in He, which was further diluted with He. In a few experiments, Cl atoms were created in a microwave discharge of CCl<sub>4</sub> diluted in He. The initial Cl atom concentration,  $[Cl]_0$ , in the flow tube was in the range  $(1.5-6.0) \times 10^{14}$  atom cm<sup>-3</sup>. The ClO radical precursor (O<sub>3</sub>, Cl<sub>2</sub>O, or OCIO) was added through a moveable injector located at the top of the flow tube. For the quantitative measurements of the  $Cl_2O_2$  UV absorption cross sections, the injector was positioned about 3 cm below the Cl atom inlet, yielding a reaction distance in the flow tube of 135 cm. Precursor concentrations in the absorption cell were typically in the range of  $(1-5) \times 10^{14}$ molecules cm<sup>-3</sup>. He buffer gas with a total flow rate of about 40 STP cm<sup>3</sup> s<sup>-1</sup> (STP = 1 atm, 273 K) was added through the microwave discharge side arm and through the side arm located at the top of the flow tube. A small He flow,  $\sim 10$  STP cm<sup>3</sup> s<sup>-1</sup>, was also added to the absorption cell behind the nesting mirror to sweep out the dead volume behind the mirror. For a typical flow rate of 40 STP cm<sup>3</sup> s<sup>-1</sup> and a pressure of 25 Torr, the residence time in the flow tube was 3 s. Under these conditions the CIO formation reaction (reaction 4, 6, or 7) went to completion very rapidly (<1 ms) and there was sufficient time for reaction 1 to go to greater than 90% completion in the flow tube. CIO may also react with itself via the following bimolecular pathways

$$ClO + ClO \rightarrow Cl_2 + O_2$$
 (8a)

$$\rightarrow$$
 Cl + ClOO (8b)

$$\rightarrow$$
 Cl + OClO (8c

where  $k_{8a} = 3.4 \times 10^{-12} \exp(-1940/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,  $k_{8b} = 3.0 \times 10^{-12} \exp(-1940/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and  $k_{8c} = 5.7$  $\times 10^{-12} \exp(-2400/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>13</sup> However, because of the low temperatures (200-250 K) and high pressure (25-35 Torr) employed in this study, which favor reaction 1, loss of ClO via reactions (8a-c is insignificant (<1%). Loss of ClO via wall reaction has been shown to be insignificant.<sup>7</sup>

A loss process for  $Cl_2O_2$  is via its reaction with Cl atoms

$$Cl + Cl_2O_2 \rightarrow Cl_2 + ClOO$$
 (9)

which has been measured to be very fast  $(k_9 \simeq 10^{-10} \text{ cm}^3 \text{ mol-}$ ecule<sup>-1</sup> s<sup>-1</sup>).<sup>8</sup> Thus, if the ClO source reaction is sufficiently slow, some Cl atoms may remain after significant  $Cl_2O_2$  formation has occurred, leading to  $Cl_2O_2$  loss by reaction 9. Numerical model calculations were carried out for each of the CIO sources employed in this study to determine if  $Cl_2O_2$  loss via reaction 9 is likely to be significant. The model included the appropriate ClO source reaction, (4), (6), or (7); the bimolecular ClO self-reaction, (8); the termolecular ClO self-reaction, (1); reaction 3; and reaction 9. Cl<sub>2</sub>O<sub>2</sub> wall loss was not included in the model calculations because it was found to be insignificant in these experiments as will be discussed later. Because reaction 4,  $Cl + O_3$ , was the slowest ClO source reaction used in this study, it posed the most serious problem. The model calculations showed that, for an  $[O_3]_0$ to  $[Cl]_0$  ratio of 1.3, >20% loss of  $Cl_2O_2$  via reaction 9 was likely and that  $[O_3]_0/[Cl]_0$  of >4 was required before the contribution of reaction 9 becomes insignificant (<3%). Thus, accurate [Cl<sub>2</sub>O<sub>2</sub>] determinations could be made only under conditions of high  $[O_3]_0$ and low [Cl]<sub>0</sub>, which placed limitations on the usefulness of the O<sub>3</sub> source. First, because O<sub>3</sub> absorbs strongly in the same region as  $Cl_2O_2$  ( $\sigma_{O_3} = 1.15 \times 10^{-17} \text{ cm}^2$  at 253.7 nm),<sup>14</sup> high [O<sub>3</sub>]<sub>0</sub> led to saturated UV absorption, making quantitative analyses impossible. Also, since low [Cl]<sub>0</sub> had to be employed, only small [Cl<sub>2</sub>O<sub>2</sub>] could be produced, leading to large uncertainties in measuring absorption cross sections.

Reaction 9 is less significant with Cl<sub>2</sub>O as the ClO precursor, since reaction 6 is faster than reaction 4 by a factor of 11 at 210 K. Thus, smaller excesses of  $[Cl_2O]_0$  were required before reaction 9 became insignificant. Also, since the UV absorption cross section of  $Cl_2O$  (1.93 × 10<sup>-18</sup> at 255 nm)<sup>15</sup> is about 6 times smaller than that of O<sub>3</sub>, interference due to UV absorption by the excess Cl<sub>2</sub>O was less severe. For these reasons, using Cl<sub>2</sub>O as the ClO precursor led to more accurate Cl<sub>2</sub>O<sub>2</sub> UV absorption cross section determinations. The results from the Cl<sub>2</sub>O studies were therefore used in determining the reported Cl<sub>2</sub>O<sub>2</sub> absorption cross sections. Because of severe limitations imposed by secondary chemistry as discussed in the Results section, the OClO source was not used in determining the  $Cl_2O_2$  absorption cross sections.

In a typical  $Cl_2O_2$  absorption cross section determination, three spectra were recorded by using the diode array detector. Firstly a reference lamp spectrum  $(I_0)$  was recorded with only He flowing through the absorption cell. It was found by examining the ratio of successive measurements of  $I_0$  that the base line was stable to 0.05% for a period of 30 min. The precursor (O<sub>3</sub> or Cl<sub>2</sub>O) and  $Cl_2$  were then flowed through the cell and a second spectrum was recorded. For the third spectrum, the microwave discharge was turned on to initiate the formation of  $Cl_2O_2$ . This sequence of measurements took approximately 5 min. The second and third spectra were divided by  $I_0$  and converted into absorbance units, base e. The third spectrum typically contained the product molecule,  $Cl_2O_2$ , as well as unreacted ClO, trace amounts of OCIO, presumably formed from the bimolecular self-reaction of ClO (reaction 8c), Cl<sub>2</sub> not dissociated in the microwave discharge (which was approximately 75% of  $[Cl_2]_0$ ), and unreacted precursor. Thus, to obtain the Cl<sub>2</sub>O<sub>2</sub> spectrum, it was necessary to quantitatively subtract the spectrum of each of these unwanted species using previously recorded reference spectra. Reference spectra were recorded at the same temperature as the  $Cl_2O_2$  spectrum measurement.

ClO reference spectra were obtained by reacting an excess of Cl atoms with the precursor molecule ( $O_3$  or  $Cl_2O$ ) under fast flow conditions. A typical ClO reference absorption spectrum

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Figure 3. UV absorption reference spectra of O<sub>3</sub>, ClO, Cl<sub>2</sub>, Cl<sub>2</sub>O, and OCIO. The Cl<sub>2</sub> spectrum is multiplied by a factor of 10 for clarity.

is shown in Figure 3. The ClO reference spectra were quantified using an absorption cross section of  $4.35 \times 10^{-18}$  cm<sup>2</sup> at 253.7 nm.<sup>16</sup> This wavelength is in the continuum region of the ClO spectrum and therefore was insensitive to the resolution of the measurement. We also found the continuum to be insensitive to temperature, enabling us to use the same absorption cross section for all temperatures. The vibrational band structure of the ClO UV absorption spectrum provides a distinct spectral signature which enables accurate spectrum subtractions. Our UV detection limit for [ClO] was independent of the contents of the absorption cell in these experiments and was found to be  $4 \times 10^{11}$  molecules cm<sup>-3</sup>.

Reference spectra for O<sub>3</sub>, Cl<sub>2</sub>O, Cl<sub>2</sub>, and OClO were obtained by using the standard sources for these species. Typical reference spectra are shown in Figure 3. An absorption cross section of 1.15  $\times$  10<sup>-17</sup> cm<sup>2</sup> at 253.7 nm was used for quantitative determination of the [O<sub>3</sub>].<sup>14</sup> The O<sub>3</sub> absorption cross section at 253.7 nm has been shown<sup>14</sup> to vary less than 1% over the temperature range 225–298 K. The structure in the  $O_3$  absorption band around 260 nm provided the spectral signature used for accurate spectrum subtractions of O<sub>3</sub>. The detection limit for  $[O_3]$  was  $1.4 \times 10^{11}$ molecules cm<sup>-3</sup>.

The UV absorption cross sections reported by Lin<sup>15</sup> were used for quantitative determinations of  $[Cl_2O]$ . The relative shape of the Cl<sub>2</sub>O UV absorption spectrum we obtained agreed to within  $\pm 1\%$  of that reported by Lin.<sup>15</sup> The Cl<sub>2</sub>O spectrum consists of a broad continuum absorption peaking near 255 nm and containing a broad shoulder in the 270-290-nm region. The primary criterion used to perform Cl<sub>2</sub>O subtractions was to remove this shoulder from the observed spectrum which also contained  $Cl_2O_2$ , CIO, and Cl<sub>2</sub>. Because the Cl<sub>2</sub>O spectrum has no pronounced structure as in the  $O_3$  and ClO spectra,  $[Cl_2O]$  could not be determined as accurately. Our detection limit for  $[Cl_2O]$  was found to be 1  $\times$  $10^{12}$  molecules cm<sup>-3</sup> when Cl<sub>2</sub>O<sub>2</sub> was also present in the absorption cell

The OCIO absorption spectrum consists of a series of vibrational bands in the 260-475-nm region. The UV absorption cross sections of Wahner et al.<sup>17</sup> were employed for determination of [OCIO]. For experiments performed with OCIO as the CIO source, it was not possible to do the OClO subtractions accurately because the large [OClO] employed led to saturation on some of the stronger bands but not on the weaker bands. Thus, the shape of the reference spectrum did not match exactly with the experimental spectrum for all bands. For experiments in which  $Cl_2O$  or  $O_3$  was used as the ClO source, only trace amounts of OCIO were observed (<10<sup>11</sup> molecules cm<sup>-3</sup>). Because these levels of OCIO correspond to our detection limit, only an upper limit to [OClO] could be estimated.

The UV spectrum of Cl<sub>2</sub> has a peak cross section of  $2.56 \times 10^{-19}$ cm<sup>2</sup> near 330 nm.<sup>18</sup> The lack of structure in the Cl<sub>2</sub> spectrum makes it difficult to subtract quantitatively in the presence of other absorbing species. Therefore, the presence of Cl<sub>2</sub> was a main source of uncertainty in determining the shape of the  $Cl_2O_2$ spectrum at long wavelengths. The primary sources of Cl<sub>2</sub> in our experiments were from the undissociated Cl<sub>2</sub> in the microwave discharge source of Cl atoms and from the Cl<sub>2</sub> impurity in the  $Cl_2O$ . Depending on the ClO source used (reaction 4 or 7) it is possible to put limits on the amount of Cl<sub>2</sub> to be subtracted,  $[Cl_2]_{sub}$ . When reaction 4 is used as the ClO source  $[Cl_2]_{sub} \simeq$  $(1 - D)[Cl_2]_0$  and when reaction 7 is used  $[Cl_2]_{sub} \simeq (1 + D)[Cl_2]_0$ +  $[Cl_2]_{impurity}$ , where D is the microwave discharge efficiency. Typically  $D \simeq 0.25$  as determined from the observed  $\Delta[O_3]$  or  $\Delta$ [Cl<sub>2</sub>O] and the Cl<sub>2</sub> flow rate. We estimate a ±15% error in the subtraction of Cl<sub>2</sub>. Our detection limit for Cl<sub>2</sub> with no other absorbing species in the absorption cell was  $\simeq 6 \times 10^{12}$  molecules cm<sup>-3</sup>.

Performing the subtractions as described above yielded the spectrum of  $Cl_2O_2$  as well as a knowledge of the concentration of all the other species present in the absorption cell. The absorption cross section of Cl<sub>2</sub>O<sub>2</sub> was then obtained by mass balance. The [ClO]<sub>0</sub> was determined from the amount of precursor reacted, i.e., its concentration in spectrum 2 minus its concentration in spectrum 3. It is assumed that all of the [ClO]<sub>0</sub> was converted to the product,  $Cl_2O_2$ , via reaction 1 except the unreacted ClO remaining in spectrum 3, [ClO]<sub>f</sub>. The small amount of ClO converted to OClO, presumably via reaction 8c, was difficult to quantify because of the small absorbance but was always  $<10^{11}$ molecules cm<sup>-3</sup>. This unaccounted for loss of ClO leads to a maximum overestimation of the  $[Cl_2O_2]$  by about 2%, and thus a corresponding underestimation of the Cl<sub>2</sub>O<sub>2</sub> absorption cross section. The  $[Cl_2O_2]$ , by mass balance, was then obtained as follows:

$$[Cl_2O_2] = ([ClO]_0 - [ClO]_f)/2$$
(10)

It should be pointed out that, although the absorption cell was maintained at lower pressure than the flow tube, there is still sufficient time for some further conversion of the residual ClO to  $Cl_2O_2$  via reaction 1 in the absorption cell. The concentrations determined by our absorption measurements are averages along the length of the absorption cell. However, this should have no effect on our calculation of the  $[Cl_2O_2]$  since the mass balance, eq 10, still holds along the entire length of the cell.

*Error Analysis.* The errors in the determination of the  $Cl_2O_2$ absorption cross sections originate predominantly from uncertainties in the determination of the  $Cl_2O_2$  residual UV absorption spectrum and from the determination of the  $[Cl_2O_2]$  by mass balance, eq 10. These errors result from errors in our spectral subtractions, uncertainties in the available literature UV absorption cross sections of the species involved, and errors in the assumptions implicit in eq 10.

The accuracy of the Cl<sub>2</sub>O<sub>2</sub> UV absorption spectrum is determined solely by our ability to quantitatively subtract the absorptions of ClO, Cl<sub>2</sub>O, and Cl<sub>2</sub> from the spectrum. The uncertainty in the ClO spectrum subtraction has a negligible effect on the  $Cl_2O_2$  spectrum since these subtractions can be done very accurately. The uncertainty in the Cl<sub>2</sub>O spectrum subtraction contributes an error of  $\pm 5\%$  ( $\pm 15\%$ ) (all errors given as 1  $\sigma$ ) to the absorbance attributed to  $Cl_2O_2$  in the residual spectrum at 245 nm (280 nm). The uncertainty in the  $Cl_2$  spectrum subtraction contributes an error of  $\pm 15\%$  in the longer wavelength region of the spectrum (around 330 nm). However, we have reduced this source of error by performing some cross-section measurements using a nearly Cl<sub>2</sub>-free Cl atom source, namely a microwave discharge of  $CCl_4$ . A reasonable error estimate of the  $Cl_2O_2$ absorption cross section values due to unaccounted for absorption by Cl<sub>2</sub> near 330 nm is  $\pm 7\%$ 

Errors in calculating the  $[Cl_2O_2]$  by mass balance, eq 10, result from error in determining the  $[ClO]_f$  and  $[ClO]_0$ , where  $[ClO]_0$ 

<sup>(16)</sup> Wine, P. H.; Ravishankara, A. R.; Philen, D. L.; Davis, D. D.;
Watson, R. T. Chem. Phys. Lett. 1977, 50, 101.
(17) Wahner, A.; Tyndall, G. S.; Ravishankara, A. R. J. Phys. Chem.

<sup>1987, 91, 2734.</sup> 

<sup>(18)</sup> Burkholder, J. B.; Bair, E. J. J. Phys. Chem. 1983, 87, 1859.

## UV Absorption Cross Sections of Cl<sub>2</sub>O<sub>2</sub>

=  $\Delta([O_3] \text{ or } [Cl_2O])$ . Errors in determining  $[ClO]_f$  result from a  $\pm 10\%$  uncertainty in the literature cross section for this species and an uncertainty of  $\pm 1\%$  in the subtraction as discussed above. Error in determining  $\Delta[Cl_2O]$  results from an uncertainty of  $\pm 2\%$  in the literature absorption cross sections and from an uncertainty in our subtraction of  $\pm 5\%$ .

The absorption path length used for our UV concentration determinations was determined to be  $310 \pm 5$  cm, leading to an additional uncertainty of  $\pm 2\%$ .

In addition to the errors mentioned above, there is a possibility that a systematic error due to unaccounted for loss of ClO or  $Cl_2O_2$  could contribute. Any error of this nature would lead to an overestimation of the  $[Cl_2O_2]$ , and hence an underestimation of its absorption cross section provided species which absorb strongly in the same region are not produced as a result of the ClO or  $Cl_2O_2$  loss. It is difficult to estimate this uncertainty but it is probably <10%.

Combining these errors leads to an asymmetrical total uncertainty estimate of  $\pm 12\%/-8\%$  for the determination of the Cl<sub>2</sub>O<sub>2</sub> absorption cross section near the peak (245 nm), and an uncertainty of  $\pm 15\%/-10\%$  in the long-wavelength region around 330 nm. It should be pointed out, however, that the uncertainties in both the calculation of the [Cl<sub>2</sub>O<sub>2</sub>] and the Cl<sub>2</sub>O<sub>2</sub> UV absorption spectrum are not independent and tend to cancel. For example, an overestimate of  $\Delta$ [Cl<sub>2</sub>O] leads to both an overestimate of the [Cl<sub>2</sub>O<sub>2</sub>] and the residual absorption to Cl<sub>2</sub>O<sub>2</sub>.

*Materials and Calibrations.* He and  $Cl_2$  flow rates were measured with mass flowmeters calibrated by the rate of pressure change into a calibrated volume for flows <1 STP cm<sup>3</sup> s<sup>-1</sup> and with a wet test meter for flows >1 STP cm<sup>3</sup> s<sup>-1</sup>.

Ozone was generated by flowing O<sub>2</sub> through a commercial ozonizer and was collected on a silica gel trap cooled to 190 K. Excess O<sub>2</sub> was pumped off the trap, and the ozone was eluted as needed with a small flow (1 STP cm<sup>3</sup> s<sup>-1</sup>) of He. The ozone partial pressure,  $P_{O_3}$ , was measured by UV absorption at 253.7 nm by passing the O<sub>3</sub>-He mixture through a 10 cm long cell. The O<sub>3</sub> flow rate,  $F_{O_3}$ , was then calculated from the He flow rate,  $F_{He}$ , the total cell pressure,  $P_{T_1}$ , and  $P_{O_3}$  as follows:

$$F_{O_3} = F_{He} P_{O_3} / (P_T - P_{O_3})$$
(11)

The  $[O_3]$  in the main absorption cell was then obtained from  $F_{O_3}$ , the total gas flow rate, temperature, and pressure. The  $[O_3]$  obtained in this fashion was compared to that obtained from the two-pass UV optics in the absorption cell and the values were found to agree to within  $\pm 5\%$ .

OCIO was prepared by passing  $Cl_2$  through a tube packed with 50 g of NaClO<sub>2</sub> (Aldrich, 80% purity). Stable OCIO outputs could be obtained for about 15 min after which the output gradually decreased to zero and the NaClO<sub>2</sub> had to be replaced. The [OCIO] was determined by UV absorption in the main absorption cell with the diode array detector.

Cl<sub>2</sub>O was prepared by passing Cl<sub>2</sub> over glass beads coated with HgO, which was dried at 120 °C overnight before use. The product gas, containing mostly Cl<sub>2</sub>O and some unreacted Cl<sub>2</sub>, was trapped at 190 K, yielding a brown liquid. Some of the trapped Cl<sub>2</sub> was pumped off before use, yielding a final product which was approximately 80% Cl<sub>2</sub>O and 20% Cl<sub>2</sub>. Since the presence of Cl<sub>2</sub> did not affect any of our measurements, no further purification of the Cl<sub>2</sub>O was made. The [Cl<sub>2</sub>O] was determined by UV absorption in the absorption cell using the two-pass UV optics and the diode array spectrometer.

#### Results

During our UV and IR spectroscopic measurements we have used the following three CIO radical sources:

$$Cl + O_3 \rightarrow ClO + O_2$$
 (4)

$$Cl + OCIO \rightarrow CIO + CIO$$
 (6)

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$
 (7)

These sources are described in the Experimental Section. Due to the differences and limitations of each of the CIO radical sources we will present the results from each source separately.



Figure 4. (a) UV absorption spectrum recorded using  $Cl + O_3 \rightarrow ClO + O_2$  as the ClO radical source. The spectrum was recorded at 210 K. (b) Spectrum shown in frame a with O<sub>3</sub>, ClO, and Cl<sub>2</sub> absorptions subtracted quantitatively. (c) IR absorption spectrum recorded simultaneously with the UV absorption spectrum shown in frame a. The spectrum was recorded in 50 coadded scans at 1-cm<sup>-1</sup> resolution.

(A)  $Cl + O_3 \rightarrow ClO + O_2$ . Figure 4 shows typical UV and IR absorption spectra measured with the  $Cl + O_3$  reaction as the ClO radical source. Frame a shows the UV absorption spectrum recorded at a temperature of 210 K, a pressure in the flow tube of 25 Torr, and a pressure in the absorption cell of 5 Torr. The spectrum is a composite of absorptions by  $O_3$ , ClO, Cl<sub>2</sub>, and Cl<sub>2</sub>O<sub>2</sub>. O<sub>3</sub> accounts for approximately 75% of the total absorption at 250 nm. CIO is readily identified in the UV spectrum by the vibrational band progression observed between 270 and 310 nm. Cl<sub>2</sub> has a continuous absorption centered at 330 nm and accounts for approximately 1% absorption in this region. Frame b shows the spectrum obtained after the O<sub>3</sub>, ClO, and Cl<sub>2</sub> reference spectra have been subtracted quantitatively from frame a by using the procedures outlined in the Experimental Section. This residual spectrum, frame b, is the UV absorption spectrum of the  $Cl_2O_2$ molecule. The Cl<sub>2</sub>O<sub>2</sub> UV absorption spectrum is a broad structureless continuum with a peak at 245 nm. The measurable absorption extends out to  $\sim$ 410 nm. A residual absorption spectrum with the identical shape was observed at temperatures over the range 210-250 K, at flow tube pressures over the range 15-30 Torr, and at residence times in the absorption cell over the range 0.5-3 s.

The optimum conditions for accurate cross-section determinations with this source requires large excess amounts of  $O_3$ ,  $[O_3] > 10[Cl]_0$ . Under these conditions though UV absorption measurements are difficult because of the large  $O_3$  absorption cross section,  $1.15 \times 10^{-17}$  cm<sup>2</sup> at 253.7 nm. The cross-section measurements we have made with this source are consistent with those obtained with the Cl + Cl<sub>2</sub>O source, our primary method for absorption cross section determination, but are less precise. The quantitative absorption cross section measurements are given in subsection B. The reason for the decreased precision is that the absorption cross sections calculated from the mass balance decreased with increasing  $[Cl]_0$ , for a fixed  $[O_3]$ . The absorption cross sections decreased by as much as 50% when  $[O_3] = 2[Cl]_0$ . This result is consistent with the model calculations which include the rapid reaction

$$Cl + Cl_2O_2 \rightarrow Cl_2 + ClOO \tag{9}$$

Frame c shows the IR absorption spectrum, 1 cm<sup>-1</sup> resolution, which was recorded simultaneously with the UV spectrum shown in frame a. IR absorption bands centered at 560, 653, and 750 cm<sup>-1</sup> had a positive correlation with the UV absorption spectrum shown in frame b and are assigned to the  $Cl_2O_2$  molecule. The absorption band at 1040 cm<sup>-1</sup> and the band structure centered around 700 cm<sup>-1</sup> are due to residual O<sub>3</sub> precursor. The increased noise level near 500 cm<sup>-1</sup> is due to the decreased response of our FTS at long wavelengths. The relative intensities of the 560, 653, and 750  $\mbox{cm}^{-1}$  bands are 0.4, 1.0, and 0.2, respectively. The observed UV absorption by Cl<sub>2</sub>O<sub>2</sub> at 245 nm is 2.5 times greater than that of the strongest Cl<sub>2</sub>O<sub>2</sub> IR absorption band located at 653 cm<sup>-1</sup>. Therefore, we have a more sensitive detection of  $Cl_2O_2$ in the UV region than in the IR region. Given that the IR path length in our experiment is 33 times longer than the UV absorption path length, the IR peak cross section of the 653-cm<sup>-1</sup> band is  $\sim$ 83 times less than the UV absorption peak cross section. The  $Cl_2O_2$  IR bands were also recorded at higher resolution, 0.02 cm<sup>-1</sup>, in an attempt to resolve rotational structure which would aid in a determination of the geometry of this molecule. No rotational structure or partially resolved structure was observed. Because no change in the band shape was observed in going from 1 to 0.02 cm<sup>-1</sup> resolution, higher resolution spectra were not recorded.

At temperatures greater than 250 K secondary chemistry in the flow tube source becomes significant. This results from the decreased rate of formation of  $Cl_2O_2$  and in particular the increased rate of the bimolecular ClO + ClO reaction, (8). The presence of secondary chemistry is evident from the formation of OClO by reaction 8c. The OClO was observed by UV absorption and was present at the  $10^{12}$  molecules cm<sup>-3</sup> level. This would correspond to approximately 20% of the ClO radicals being lost through reaction 8. At these elevated temperatures the peak of the residual UV absorption spectrum, after O<sub>3</sub>, ClO, OClO, and Cl<sub>2</sub> subtraction, showed a shift toward longer wavelengths. As will be described in detail in subsection C this is due to the formation of  $Cl_2O_3$  by the reaction

$$ClO + OClO + M \rightarrow Cl_2O_3 + M$$
 (12)

The absorption spectrum of  $Cl_2O_3$  is shifted toward longer wavelengths relative to the spectrum of  $Cl_2O_2$ , causing the apparent shift in the residual spectrum. Also at T > 250 K, we observe  $Cl_2O_4$  in the IR absorption spectrum by its band at 1282 cm<sup>-1.19</sup> This indicates that other secondary reactions are occurring. The  $Cl_2O_4$  was not observed in the UV absorption spectrum, presumably because of its rather small UV absorption cross section, 9.4  $\times 10^{-19}$  cm<sup>2</sup> at 234 nm.<sup>20</sup>

(B)  $Cl + Cl_2O \rightarrow ClO + Cl_2$ . The residual UV absorption spectrum assigned to  $Cl_2O_2$  which was observed with the Cl + $Cl_2O$  source was identical with that recorded with the  $Cl + O_1$ source. Also, the same Cl<sub>2</sub>O<sub>2</sub> IR absorption bands were observed. The Cl<sub>2</sub>O<sub>2</sub> UV absorption cross sections as determined by mass balance were made for  $[ClO]_0$  over the range  $(1-5) \times 10^{14}$ molecules cm<sup>-3</sup>, temperature over the range 205-250 K, and residence time in the absorption cell from 1 to 3 s. Under conditions of high  $[Cl]_0$  and low  $[Cl_2O]$  such that  $[Cl_2O]/[Cl]_0 <$ 2 we observed a slight decrease,  $\sim 10\%$ , in the calculated Cl<sub>2</sub>O<sub>2</sub> absorption cross sections. We attribute this decrease to reaction 9, Cl + Cl<sub>2</sub>O<sub>2</sub>, which removes  $Cl_2O_2$  in the flow tube and causes us to overestimate  $[Cl_2O_2]$ . This decrease is twice as large as predicted by the chemical model and most likely results from the finite time required to mix the reactants (model calculations assume instantaneous mixing) in the flow tube at the high pressures used,  $\sim 25$  Torr. When  $[Cl_2O]/[Cl]_0$  was >2, the  $Cl_2O_2$ 

TABLE I: Cl<sub>2</sub>O<sub>2</sub> Absorption Cross Sections (10<sup>-18</sup> cm<sup>2</sup>)

wavelength.	- 1	wavelength.		wavelength.	
nm	σ	nm	σ	nm	σ
212	2.18	280	2.27	346	0.13
214	2.15	282	2.11	348	0.12
216	2.12	284	1.96	350	0.11
218	2.12	286	1.82	352	0.10
220	2.15	288	1.68	354	0.10
222	2.29	290	1.53	356	0.092
224	2.49	292	1.40	358	0.087
226	2.78	294	1.28	360	0.078
228	3.14	296	1.17	362	0.074
230	3.56	298	1.05	364	0.070
232	4.05	300	0.94	366	0.065
234	4.60	302	0.84	368	0.054
236	5.10	304	0.75	370	0.052
238	5.58	306	0.67	372	0.048
240	5.99	308	0.60	374	0.045
242	6.29	310	0.52	376	0.043
244	6.47	312	0.46	378	0.038
246	6.49	314	0.40	380	0.037
248	6.43	316	0.35	382	0.032
250	6.22	318	0.31	384	0.033
252	5.97	320	0.29	386	0.026
254	5.64	322	0.27	388	0.030
256	5.28	324	0.25	390	0.026
258	4.91	326	0.24	392	0.026
260	4.54	328	0.22	394	0.019
262	4.22	330	0.20	396	0.021
264	3.90	332	0.19	398	0.017
266	3.60	334	0.18	400	0.021
268	3.36	336	0.17	402	0.017
270	3.15	338	0.16	404	0.018
272	2.94	340	0.16	406	0.013
274	2.76	342	0.15	408	0.013
276	2.58	344	0.14	410	0.009
278	2.41				

absorption cross sections and the shape of the spectrum were found to be invariant within experimental error,  $\pm 10\%$ , over the range of experimental conditions. We observed no systematic decrease in the calculated Cl<sub>2</sub>O<sub>2</sub> absorption cross sections when the residence time in the absorption cell was varied from 1 to 3 s. This indicates that there was no measurable Cl<sub>2</sub>O<sub>2</sub> wall loss in our experiment.

Particular attention was paid to determining precise absorption cross sections at wavelengths longer than 290 nm. Cross-section determinations in the range 270-380 nm are complicated by spectral interference from  $Cl_2$  which has a peak absorption at 330 nm. The Cl<sub>2</sub> spectrum has no distinct spectral signature which enables it to be subtracted unambiguously. The peak absorption cross section for Cl<sub>2</sub> is relatively small and under our experimental conditions the  $Cl_2$  absorption at 330 nm is about 1%. This is comparable to the magnitude of the Cl<sub>2</sub>O<sub>2</sub> absorption at 330 nm. To test that we are subtracting the residual Cl<sub>2</sub> correctly, we also used CCl<sub>4</sub> as a source of Cl atoms. This source has the advantage that the residual  $[Cl_2]$  is greatly reduced and therefore no spectral subtraction is required. The Cl<sub>2</sub>O<sub>2</sub> absorption cross sections obtained with the two Cl atom sources were identical,  $\pm 10\%$ , indicating that within our experimental uncertainty Cl<sub>2</sub> had been subtracted correctly.

The measured  $Cl_2O_2$  absorption cross sections are listed in Table I at 2-nm intervals over the range 212-410 nm. The spectrum has a peak absorption cross section of  $6.5 \times 10^{-18}$  cm<sup>2</sup> at 245 nm. The data listed in Table I represent an average of 20 separate quantitative measurements. The absorption cross section data are also displayed in Figure 5.

(C)  $Cl + OClO \rightarrow ClO + ClO$ . Under the experimental conditions used in this study, high pressure and low temperature, secondary chemistry is a major limitation in using this source to study  $Cl_2O_2$  either quantitatively or qualitatively. In the presence of excess OClO the reaction

$$ClO + OClO + M \rightarrow Cl_2O_3 + M$$
 (12)

was found to occur to an appreciable extent in the flow tube under

<sup>(19)</sup> Schell-Sorokin, A. J.; Bethune, D. S.; Lankord, J. R.; Loy, M. M. T.; Sorokin, P. P. J. Phys. Chem. 1982, 86, 4653.

<sup>(20)</sup> Lopez, M. I.; Sicre, J. E. J. Phys. Chem. 1988, 92, 563.





conditions that are optimum for producing Cl<sub>2</sub>O<sub>2</sub>. The Cl<sub>2</sub>O<sub>3</sub> molecule is a transient species for which there is little spectroscopic or kinetic information available.<sup>19,21,22</sup> To show that Cl<sub>2</sub>O<sub>3</sub> was indeed the interfering species, two other methods were used to react CIO with OCIO, both of which led to the observation of the same UV and IR spectra assigned to Cl<sub>2</sub>O<sub>3</sub>. In both methods we have used  $Cl + O_3$  as our ClO radical source. In the first method we added OClO to the flow tube downstream of the Cl atom microwave discharge port at a distance such that all Cl atoms had been converted to CIO but before there is sufficient time for CIO to be converted to  $Cl_2O_2$ . When OCIO is absent only spectra of  $Cl_2O_2$  are observed. When OCIO is added in large excess, [OCIO]  $\simeq 10^{16}$  molecules cm<sup>-3</sup>, we observe only the spectra of Cl<sub>2</sub>O<sub>3</sub>. In the second method the flow tube reactor was at room temperature while the absorption cell was at 210 K. This allows the ClO + ClO bimolecular reaction, (8), to proceed to an appreciable extent in the flow tube, producing OCIO through reaction 8c. Reactions 1 and 12 then take place primarily in the absorption cell and we observe spectra of both  $Cl_2O_2$  and  $Cl_2O_3$ .

Due to the competition between reactions 1 and 12 for ClO radicals, it is difficult to apply mass balance relationships with any confidence. For this reason we did not use the Cl + OClOsource for any quantitative measurements of the  $Cl_2O_2$  UV spectrum. Another major complication in using this source to study Cl<sub>2</sub>O<sub>2</sub> arises from the similarities between the UV and IR absorption spectra of  $Cl_2O_3$  and  $Cl_2O_2$ . The UV absorption spectrum of Cl<sub>2</sub>O<sub>3</sub> is shown in Figure 6a and a typical IR absorption spectrum is shown in Figure 6b. The UV spectrum peak is at 265 nm and extends toward longer wavelengths in a similar way to that of  $Cl_2O_2$ . We estimate the peak absorption cross section of Cl<sub>2</sub>O<sub>3</sub> to be  $\sim 1.8 \times 10^{-17}$  cm<sup>2</sup>, approximately 3 times that of Cl<sub>2</sub>O<sub>2</sub>. Only an estimate of the cross section was determined in this work, because we observed the Cl<sub>2</sub>O<sub>3</sub> absorption signal to decrease upon the increased addition of OCIO. This indicates that other unaccounted for chemistry such as

$$OClO + Cl_2O_3 \rightarrow products$$
 (13)

is occurring with the products likely being higher oxides of chlorine. Indirect evidence for this chemistry was obtained by operating the Cl + OCIO source at reduced temperature for 1 h, turning off the source, closing off the absorption cell from the vacuum pump, and allowing the cell to warm up to room temperature. When the temperature of the cell reached -15 °C, we observed UV absorption by unidentified species coming off the walls of the absorption cell. These species seemed to be unstable as the observed [OCIO] increased dramatically as the sample was allowed to stand for 1 h.

IR absorption bands were observed as shown in Figure 6b at 1225, 1057, 740, 653, and 560 cm<sup>-1</sup> when the Cl + OClO source was used. The weak band at  $653 \text{ cm}^{-1}$  is due to a small amount



Figure 6. (a) UV absorption spectrum of the transient  $Cl_2O_3$  molecule measured in this work (solid line) and the data taken from Molina and Molina (ref 2) (see text for details). (b) IR absorption spectrum recorded simultaneously with the UV absorption spectrum shown in frame a. The spectrum was recorded in 50 coadded scans at 1-cm<sup>-1</sup> resolution.



Figure 7. Comparison of the UV absorption cross section measurements from this work (solid line) with previously reported measurements: ( $\Delta$ ) Basco and Hunt (ref 6); (+) Molina and Molina (ref 2); and ( $\diamond$ ) Cox and Hayman (ref 8).

of  $Cl_2O_2$  formed in the source while the other four bands had a positive correlation with the UV absorption shown in Figure 6a which was have assigned to  $Cl_2O_3$ . The relative intensities of the Cl<sub>2</sub>O<sub>3</sub> IR bands are 1.0, 0.04, and 0.16 for the 1225-, 740-, and 560-cm<sup>-1</sup> bands, respectively. The IR band at 1057 cm<sup>-1</sup> is difficult to evaluate quantitatively because it is strongly overlapped by a band of OCIO, but it appears to be only slightly weaker than the band at 1225 cm<sup>-1</sup>. The band at 740 cm<sup>-1</sup> is similar to that observed for  $Cl_2O_2$  but is shifted 10 cm<sup>-1</sup> toward lower energy. The  $Cl_2O_3$  band we observe at 560 cm<sup>-1</sup> is indistinguishable from that observed from Cl<sub>2</sub>O<sub>2</sub> except for the relative intensity dependences. The relative absorbances observed for the UV band at 265 nm and the 1225-cm<sup>-1</sup> IR band of Cl<sub>2</sub>O<sub>3</sub> are in the ratio of 0.65,  $A_{\rm UV}/A_{\rm IR}$ . This means we have a greater sensitivity for detection of  $Cl_2O_3$  in the IR than in the UV region with our apparatus.

#### Discussion

Figure 7 shows a comparison of the  $Cl_2O_2$  UV absorption cross sections obtained in the present work with those of Basco and

<sup>(21)</sup> McHale, E. T.; von Elbe, G. J. Phys. Chem. 1968, 72, 1849.
(22) Molina, M. J.; Molina, L. T.; Ishiwata, T. J. Phys. Chem. 1980, 84, 3100.

Hunt,<sup>6</sup> Molina and Molina,<sup>2</sup> and Cox and Hayman.<sup>8</sup> Our absorption cross section results are in good general agreement with those of Cox and Hayman.<sup>8</sup> Cox and Hayman<sup>8</sup> studied reaction 1 at temperatures in the range 203-300 K using time-resolved UV absorption spectroscopy during the continuous photolysis of Cl<sub>2</sub>/O<sub>3</sub>, Cl<sub>2</sub>/OClO, or, Cl<sub>2</sub>/Cl<sub>2</sub>O mixtures. Their spectrum peaks at 245 nm with a measured absorption cross section of  $(6.4 \pm 0.6)$  $\times 10^{-18}$  cm<sup>2</sup> at the peak. The only significant difference between their absorption cross section results and ours lies in the region between 270 and 290 nm where our absorption cross section values are approximately 15-20% larger. However, this difference is within the combined uncertainties of the two measurements and most likely results from uncertainties in the spectral subtractions as outlined in the Experimental Section. Another possible source of this discrepancy could by the formation of Cl<sub>2</sub>O<sub>3</sub> during our Cl<sub>2</sub>O<sub>2</sub> UV absorption measurements. An upper limit to the contribution from Cl<sub>2</sub>O<sub>3</sub> to our UV absorption measurements can be obtained from our simultaneous IR absorption measurements. On the basis of the sensitivity of our IR absorption measurement for Cl<sub>2</sub>O<sub>3</sub> and a Cl<sub>2</sub>O<sub>3</sub> UV absorption cross section of  $1.8 \times 10^{-17}$ cm<sup>2</sup> at 265 nm we estimate that Cl<sub>2</sub>O<sub>3</sub> UV absorption could account for at most a 6% overestimation of the Cl<sub>2</sub>O<sub>2</sub> UV absorption cross section at 280 nm. The UV absorption spectra reported by both Basco and Hunt<sup>6</sup> and by Molina and Molina<sup>2</sup> are in very poor agreement with our measurements. Their measurements differ both in terms of the measured absorption cross sections and in terms of the relative shape of the spectrum.

We believe that the spectrum reported by Molina and Molina<sup>2</sup> for  $Cl_2O_2$  is in reality the spectrum of  $Cl_2O_3$ . The relative shape of the spectrum reported by Molina and Molina<sup>2</sup> and our measured  $Cl_2O_3$  spectrum are in good agreement. The Molina and Molina<sup>2</sup> data, normalized to our absorption spectrum at 270 nm, are plotted along with our Cl<sub>2</sub>O<sub>3</sub> absorption spectrum in Figure 6a for comparison. The IR absorption spectrum reported by Molina and Molina<sup>2</sup> also show the strong Cl<sub>2</sub>O<sub>3</sub> bands at 1225 and 1057 cm<sup>-1</sup>. The confusion between Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>3</sub> in the spectral identification arises from the manner in which the transient species were produced. In their study the same three ClO radical sources were used as in the present study namely,  $Cl + O_3$ ;  $Cl + Cl_2O$ ; and Cl + OClO. The complication arises because their ClO radicals were produced in a side-arm reactor at room temperature. Under the slow flow conditions used in their measurements the ClO radicals had sufficient time to react via the ClO + ClO bimolecular reaction, reaction 8, before entering the cooled UV and IR absorption cells. This allows a substantial amount of OCIO to be produced through reaction 8c. The presence of OCIO then leads to the formation of  $Cl_2O_3$  by reaction 12, ClO + OClO + M. We demonstrated this affect in our experiment by maintaining our flow tube at room temperature and the absorption cell at 210 K. We observed a combination of both Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>3</sub> being formed under these conditions. The UV and IR spectra Molina and Molina<sup>2</sup> recorded using the Cl +  $O_3$  and Cl + Cl<sub>2</sub>O sources therefore contained a combination of both the Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>3</sub> absorptions. Their spectra recorded by using the Cl + OClO source were primarily due to Cl<sub>2</sub>O<sub>3</sub> because of the large excess of OClO present in the source. Due to the similarities in the spectra of Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>3</sub> the ambiguity went undetected and Molina and Molina<sup>2</sup> reported spectra obtained with the Cl + OCIO source as due to Cl<sub>2</sub>O<sub>2</sub>. They also reported a peak absorption cross section of  $6.4 \times 10^{-18}$  cm<sup>2</sup> at 265 nm as determined by mass balance. Fortuitously their value is in good agreement with our value at the 245-nm peak of the  $Cl_2O_2$  spectrum. There is no apparent reason why their value is in agreement with ours. Considering the UV cross section of Cl<sub>2</sub>O<sub>3</sub> we have measured,  $\sim 1.8 \times 10^{-17}$  cm<sup>2</sup>, and the stoichiometry of reaction 12 compared to that of reaction 1, their reported cross section would have to be 9.0  $\times$  10<sup>-18</sup> cm<sup>2</sup> to be consistent with ours and Cox and Hayman's<sup>23</sup> absorption cross section measurements of Cl<sub>2</sub>O<sub>3</sub>.

The spectrum reported by Basco and Hunt<sup>6</sup> is more difficult to interpret. Although their measurements have the same source chemistry problems as in the work of Molina and Molina,<sup>2</sup> their spectrum resembles the spectrum of neither  $Cl_2O_2$  nor  $Cl_2O_3$ . Undoubtedly they produced some combination of Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>3</sub> as evidenced by the shoulder in their spectrum near 240 nm. However, a combination of Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>3</sub> spectra would not produce the linear increase in absorption cross section with decreasing wavelength below 240 nm. This feature may be evidence that there is yet another unidentified species absorbing strongly below 240 nm.

McGrath et al.<sup>24</sup> have performed ab initio molecular orbital calculations to determine the structures, relative energies, and vibrational spectra of the possible isomers of  $Cl_2O_2$ . The molecular structure of Cl<sub>2</sub>O<sub>2</sub> and the stability of isomers are important in assessing the likely photolysis products of Cl<sub>2</sub>O<sub>2</sub>, reaction 2, and their impact in the ozone destruction cycle. The calculations show the lowest energy isomer to have a ClOOCl, chlorine peroxide, structure:  $r_{CIO} = 1.741 \text{ Å}, r_{OO} = 1.420 \text{ Å}, \angle (CIOO) = 109^{\circ}, \text{ and}$  $\omega$ (ClOOCl) = 85°. Assuming the transition responsible for the UV absorption by  $Cl_2O_2$  promotes an electron on the Cl atom to a Cl-O  $\sigma^*$  orbital we expect a Cl-O bond to be broken in the dissociation process. Therefore, the photolysis products of a ClOOCl structure would be Cl + ClOO as written in reaction 2. This, however, is speculative and needs to be tested experimentally.

The calculated<sup>24</sup> vibrational frequencies for ClOOCl are 119 (torsion), 328 (ClOO symmetric bend), 446 (ClOO asymmetric bend), 633 (ClO symmetric stretch), 679 (ClO asymmetric stretch), and 765 (OO stretch) cm<sup>-1</sup> which have relative intensities of 0.019,  $4 \times 10^{-7}$ , 0.06, 0.67, 1.0, and 0.31, respectively. Our measurements are limited to >500  $cm^{-1}$  and, therefore, we can only compare our results with the calculated bands at 633, 679, and 765 cm<sup>-1</sup>. We observed band centers at 560, 653, and 750 cm<sup>-1</sup>. The O-O stretch band at 750 cm<sup>-1</sup> is in good agreement with the calculated value of 765 cm<sup>-1</sup>. We observed just one band centered at 653  $\text{cm}^{-1}$  while the calculations predict two bands at 633 and 679 cm<sup>-1</sup>. The calculated bands at 633 and 679 cm<sup>-1</sup> have only slightly different intensities. A matrix isolation study of reaction 1 by Cheng and Lee<sup>25</sup> led to the observation of two peaks located at 647.6 and 649.8 cm<sup>-1</sup>. Due to the width of our 653-cm<sup>-1</sup> band, 25 cm<sup>-1</sup>, we cannot distinguish between just one or possibly two closely spaced bands. The intensity ratio of the 750-cm<sup>-1</sup> band to the 653-cm<sup>-1</sup> band is in excellent agreement with that observed by Cheng and Lee25 and the calculated values assuming that our 653-cm<sup>-1</sup> band intensity is due to both CIO stretch vibrations. This implies there are two closely spaced bands in our observations. The third band we observe is centered at 560 cm<sup>-1</sup> and is approximately 50 cm<sup>-1</sup> wide. This band position does not agree with any of the calculated frequencies, the nearest calculated bands being either the ClO symmetric stretch which lies 70 cm<sup>-1</sup> higher or the CIOO asymmetric bend which lies 120  $cm^{-1}$  lower. It is not likely to be due to the ClO stretch band because of the intensity arguments given above. Another possibility is that it is a combination band of the 119-cm<sup>-1</sup> torsion and the 446-cm<sup>-1</sup> ClOO asymmetric bend. The observed intensity ratio,  $A_{560}/A_{653}$ , of 0.4 does not agree with the calculated intensity ratios of the combination band or that of the ClOO asymmetric bend. A band centered at 545 cm<sup>-1</sup> was observed in the matrix isolation measurements<sup>25</sup> but was assigned to Cl<sub>2</sub> absorption activated by a  $Cl_2/O_3$  complex in the matrix. The assignment of the band we observe at 560 cm<sup>-1</sup> is at present not clearly understood.

The present work extends the Cl<sub>2</sub>O<sub>2</sub> UV absorption cross section measurements to 410 nm which enables an accurate calculation of the atmospheric photolysis rate, J value. The region of the  $Cl_2O_2$  spectrum from 290 to 410 nm has the greatest impact in determining the stratospheric photolysis rates because O<sub>3</sub> in the atmosphere attenuates solar radiation at wavelengths <290 nm. Solomon<sup>26</sup> calculated the atmospheric photolysis rate of  $Cl_2O_2$ 

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for the springtime Antarctic stratosphere using our absorption cross section data. The photolysis rate calculations are dependent on both the solar zenith angle and altitude. Due primarily to the long-wavelength data the calculated photolysis rate is approximately a factor of 3 greater than the values based on the data of Molina and Molina.<sup>2</sup> Solomon<sup>26</sup> calculated  $J = 1.5 \times 10^{-3} \text{ s}^{-1}$  for solar zenith angles between 80° and 88° at an altitude of 25 km. With the thermal dissociation rate constant for Cl<sub>2</sub>O<sub>2</sub> measured by Cox and Hayman,<sup>8</sup> the photolysis rate at 25 km, T= 190 K, is approximately 50 times faster than thermal dissociation. Therefore, the primary loss process for Cl<sub>2</sub>O<sub>2</sub> in the Antarctic stratosphere is by photolysis. These results indicate that the rate-limiting step in the  $Cl_2O_2$  ozone destruction cycle is reaction 1, ClO + ClO + M, as reactions 3 and 4 are known to be fast.

An interesting uncertainty in the photochemistry of  $Cl_2O_2$  is the possibility of photodissociation in the visible region. Due to the larger solar flux in the visible compared to the UV region, it would require a  $Cl_2O_2$  absorption cross section of only  $\sim 10^{-21}$  $\mathrm{cm}^2$  in the visible region for photolysis to be significant. An increased rate of photolysis yielding the same products as reaction 2, Cl + ClOO, would not alter the interpretation of the ozone depletion cycle. However, if different photolysis products were formed such as CIO + CIO it would have a significant effect. In the present experiments we did not attempt to measure the  $Cl_2O_2$ absorption cross sections in the visible region of the spectrum.

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# Laser Photolysis of Carboxylic Acids in the Gas Phase. Direct Determination of the OH Quantum Yield at 222 nm<sup>†</sup>

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The primary quantum yields for formation of OH radicals in the photolysis of the monomer and dimer of formic, acetic, and propionic acid vapor at 222 nm have been determined at two temperatures for the first time. The absorption cross sections of the monomer and dimer of each acid were also determined at 222 nm. The quantum yield measurements were made by using a laser photolysis-resonance absorption technique and are relative to the quantum yield of OH from the photolysis of nitric acid, which was taken as unity. The OH quantum yields from the monomers were found to be the following: formic, 0.70-0.80; acetic, 0.55-0.70; propionic, 0.15-0.35. The quantum yields from the dimers were 0.15 for formic acid and near zero for the other acids. The differences in OH quantum yields for the monomer and dimer are interpreted in terms of the reaction pathway imposed by the structure of the dimer.

#### Introduction

Recent experiments using expanded beam techniques have provided the opportunity to study the photolytic behavior of clustered species. By comparison of the results with those of the corresponding monomeric species, it was possible to determine the constraints on the photolytic pathways imposed by the geometry of the weakly bonded complex. For example, in the photodissociation of  $CO_2$ ·HBr and  $(N_2O)_2$  complexes, reactions of hot H atoms and of  $O(^{1}D)$  along specific channels were observed, which were determined by the alignment of the two molecules in the complex.<sup>1,2</sup> Other examples are photochemical studies of  $(OCS)_2$  and  $(CS_2)_2$ .<sup>3</sup> The expanded beam technique is extremely useful for generating such otherwise unstable dimers. In the case of carboxylic acids, however, although hydrogenbonded dimers are readily formed and make up a significant fraction of the vapor composition at pressures of a few Torr at room temperature, there has been very little quantitative study of the photolytic channels either of the dimers or of the monomers. In part, the lack of information is due to the complexity of interpreting results of experiments where comparable amounts of both monomer and dimer are present. However, as demonstrated in the present work, it is possible to separate certain aspects of the photochemistry of the monomer and dimer of carboxylic acids in bulk experiments and to interpret the results in terms of constrained reaction geometry of the hydrogen-bonded dimer.

The first absorption band of the acids lies below  $\sim 250-260$ nm and is associated with the  $n \rightarrow \pi^*$  transition of the carbonyl

group.<sup>4</sup> The stable products observed on photolysis of formic acid in this spectral region were CO,  $H_2O$ ,  $CO_2$ , and  $H_2$ .<sup>5-7</sup> Of the decomposition channels 1-5, early work<sup>5,6</sup> favored a molecular

- HCOOH +  $h\nu \rightarrow H_2 + CO_2$ (1)
  - $\rightarrow$  H<sub>2</sub>O + CO (2)

$$\rightarrow$$
 HCO + OH (3)

$$\rightarrow$$
 H + COOH (4)

$$\rightarrow$$
 HCOO + H (5)

mechanism (channels 1 and 2), on the basis of the stable product analysis, parahydrogen experiments,6 and antimony mirror experiments.<sup>8</sup> The latter indicated that H atoms were not formed at wavelengths greater than 190 nm. In subsequent work Gorden and Ausloos<sup>7</sup> photolyzed formic and formic- $d_1$  acid alone and in

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