A Spectroscopic Study of Cl<sub>2</sub>O<sub>3</sub>

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The UV absorption spectrum of dichlorine trioxide,  $Cl_2O_3$  has been recorded in the wavelength range 220–340 nm and at 223 K using a recently developed flash photolysis–kinetic UV absorption spectroscopy apparatus.  $Cl_2O_3$  was generated in the reaction between CIO and OCIO following the partial photolysis of OCIO. The spectrum obtained is smooth, and shows a peak at 267 nm, where  $\sigma = 1.76 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> (base e). Results are broadly consistent with previous determinations of the spectrum, although we report higher crosssections in the long-wavelength tail of the absorption. The discrepancies between these and previous measurements are discussed, together with the atmospheric implications of this work.

The importance of the ClO radical in stratospheric ozone chemistry is well established (*e.g.* ref. 1) and OClO, produced predominantly in the reaction between ClO and BrO, has been regularly observed in the stratosphere (*e.g.* ref. 2). A reaction between ClO and OClO forming  $Cl_2O_3$  was suggested as early as 1956 in the laboratory studies of Lipscomb *et al.*<sup>3</sup> It has since been postulated<sup>4</sup> that this  $Cl_2O_3$  could act as a reservoir for atmospheric ClO.

$$ClO + OClO + M \rightleftharpoons Cl_2O_3 + M$$
 (1, -1)

The amount of  $Cl_2O_3$  formed in the atmosphere depends upon the concentrations of CIO and OCIO and the temperature, since the equilibrium constant for reaction (1) is extremely temperature dependent,  $Cl_2O_3$  being more stable at low temperatures.<sup>5,6</sup> In addition,  $Cl_2O_3$  is photolysed during daylight and its atmospheric lifetime is determined by its rates of photolytic and thermal removal. In order to define the atmospheric role of  $Cl_2O_3$ , it is therefore necessary to measure its absorption cross-sections and the rates of reactions (1) and (-1).

The UV–VIS absorption spectrum of  $Cl_2O_3$  is also required to ascertain its effect on other experimental studies of chlorine–oxygen systems. The photolysis of OCIO has been used extensively as a source of ClO in the laboratory and, in such systems, reaction (1) could produce  $Cl_2O_3$ . Some experimental studies (*e.g.* ref. 7) that used OCIO as a source of ClO have noted discrepancies at low temperatures which are consistent with  $Cl_2O_3$  formation. In addition, studies of the UV–VIS spectroscopy of other oxides of chlorine such as  $Cl_2O_4$  and  $Cl_2O_6$  (which have also been suggested as atmospheric ClO<sub>x</sub> reservoirs and which have absorption spectra in the same wavelength regions<sup>8,9</sup>) will require prior knowledge of the spectrum of  $Cl_2O_3$  which is often present in the same reaction systems.

The UV–VIS absorption of  $Cl_2O_3$  has been studied on several previous occasions. The first experiments to postulate the formation of this species, by Lipscomb *et al.*,<sup>3</sup> indicated a molar absorption coefficient for  $Cl_2O_3$  of 2700 l mol<sup>-1</sup> cm<sup>-1</sup> at 257.7 nm, equivalent to *ca.*  $1.0 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup>. The first measurement of the absorption spectrum of  $Cl_2O_3$ was published by Molina and Molina<sup>10</sup> who wrongly assigned the absorption to the CIO dimer,  $Cl_2O_2$ . Hayman and  $Cox^5$  and Burkholder *et al.*<sup>6</sup> have since published crosssection data for  $Cl_2O_3$  and also studied the equilibrium constant for reaction (1, -1) as a function of temperature. In a study of the kinetics of reaction (1) at low pressure, Parr *et al.*<sup>11</sup> measured the shape of the  $Cl_2O_3$  spectrum but did not report absolute cross-sections. While the relative shapes of the published spectra for  $Cl_2O_3$  are in reasonable agreement, the values for the absorption cross-sections are not: the values measured by Hayman and Cox are higher by *ca.* 30% at the peak of the spectrum and by a factor of 2–3 in the long-wavelength tail of the absorption spectrum near 330 nm. This paper describes a study of the absorption spectrum of  $Cl_2O_3$  in the wavelength range 220 to 340 nm and at a temperature of 223 K, which was carried out to resolve the discrepancies between the various spectroscopic measurements.

#### Experimental

#### Apparatus

The apparatus used for the study was a recently constructed flash photolysis-UV absorption spectroscopy system. This apparatus differs from conventional flash photolysis systems in the detection system used for monitoring the UV absorptions. In this experiment, a two-dimensional detector array: a charge-coupled device (CCD) is used. This detector enables monitoring of both spectrally and temporally resolved UV transmission from the reaction mixture by virtue of the ability to shift light-generated charge rapidly and efficiently from one row of detector elements (pixels) to the next along one of the axes of the two-dimensional array. Thus, by imaging spectrally resolved light from the reaction vessel across a small strip along the top of the CCD array (perpendicular to the axis of fast charge transfer), successive spectra can be recorded by repeated shifting (clocking) of charge generated in the illuminated region onto rows in the dark region of the device. Once the charge from the first row of pixels has traversed the entire device, readout of the signal can be done on a slower timescale.

The apparatus, together with a full description of the operation of the CCD is described fully in a separate publication.<sup>12</sup> Briefly, it consists of a gas handling system coupled to a 1 m long, cylindrical, quartz reaction vessel. The vessel is thermostatted using recirculating fluid, and can be maintained to  $\pm 0.5$  K at temperatures 193–373 K. Reactive species are generated by photolysis from a 1 m long xenon arc lamp, placed adjacent and parallel to the reaction vessel. This lamp emits pulsed broad-band radiation in the wavelength range 180–700 nm. A Pyrex filter can be placed around the lamp to prevent short wavelength (<280 nm) photolysis. The energy of the photolysis pulse, *ca.* 500 J, is completely discharged in *ca.* 20 µs.

As discussed above, photolytically produced species are detected in the reaction cell using UV-VIS absorption. The

source for this analysis light is a 30 W high-brightness deuterium lamp (for wavelengths 180-350 nm) or a 30 W continuous xenon arc lamp (for wavelengths 300-700 nm). The analysing radiation is collimated longitudinally through the reaction vessel (path length 98.2 cm) and focused onto a 550  $\mu m$  diameter fused silica optical fibre. Output from the optical fibre is f-matched and coupled to a 250 mm focal length imaging spectrograph. Spectrally resolved output from the spectrograph is then imaged across the top of a twodimensional CCD array and charge-transfer processes are used to shift spectra for storage out of the illuminated region of the device. The ultimate time resolution of spectral acquisition, governed by the image height on the device and the clocking frequency, is on the microsecond timescale and was not required for this experiment. The spectral coverage of the recordings in this work is 120 nm, using a 150 g mm<sup>-1</sup> grating. The spectral resolution used is 4.1 nm (FWHM), at a slit width of 150 µm, measured using emission lines from a medium pressure mercury lamp.

In a typical experiment, light from the reaction vessel is recorded by the CCD before, during and after the photolysis flash. Absorption spectra are then generated by ratioing each post flash recording  $(I_{t,\lambda})$  to an average preflash recording from pixels at the same wavelength  $(I_{0,\lambda})$ ,  $[A_{\lambda} = \ln (I_{0,\lambda})/I_{t,\lambda}]$ . These spectra therefore represent changes in absorption as a result of the flash.

#### **General Approach**

The  $Cl_2O_3$  cross-sections were measured in this work using a flash photolysis–UV absorption spectroscopy apparatus. Partial photolysis of OCIO in the presence of oxygen was used to produce CIO:

$$OCIO + hv \to O(^{3}P) + CIO$$
 (2)

 $Cl_2O_3$  was then rapidly generated by reaction (1). The photolytically produced O atoms underwent termolecular combination to form ozone:

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
(3)

Thus, the post-photolysis spectra recorded contained positive absorptions owing to the generation of  $Cl_2O_3$  and  $O_3$ products, and negative absorptions owing to the consumption of OCIO. The amount of OCIO consumed in the photolysis and subsequent reaction with CIO was then quantified and used to obtain the absolute absorption spectrum of  $Cl_2O_3$ .

#### **Preparation and Purity of OClO**

OCIO was produced by the oxidation of  $Cl_2$  by NaClO<sub>2</sub>. Chlorine (5% in N<sub>2</sub>, Distillers MG) was passed through a column packed with NaClO<sub>2</sub> (Aldrich) and glass beads and OCIO was formed in the reaction:

$$Cl_2 + 2NaClO_2 \rightarrow 2NaCl + 2OClO$$
 (4)

The explosive hazards associated with large concentrations of OClO are well documented (*e.g.* Lopez *et al.*<sup>13</sup>) and to avoid these dangers, OClO was prepared *in situ*. The gases leaving the NaClO<sub>2</sub> column were passed directly into the reaction cell.

To maximise the conversion of  $Cl_2$  to OCIO, the column length of NaClO<sub>2</sub> was long (50 cm) and flow rates of  $Cl_2$ mixture were kept low (<20 sccm). The gas flow was thoroughly dried before and after conversion by passing the gas through P<sub>2</sub>O<sub>5</sub> traps. In addition, the OCIO preparation line was shielded to avoid OCIO photolysis by ambient light. Any Cl<sub>2</sub> not converted to OCIO in the column would be subject

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to photolysis in the flash, and the Cl atoms thus produced could interfere with the predicted chemistry, for example through their fast reaction with OCIO. Careful checks were therefore made to determine the purity of the OCIO produced in the NaClO<sub>2</sub> column, as described below.

## Determination of OClO Purity by Measurement of Flow Rates

Flows of  $Cl_2$ -mixture (through the NaClO<sub>2</sub> column) and O<sub>2</sub> (carrier gas) were directed through calibrated mass-flow controllers (MKS 100 series) and the flow rates recorded. With a knowledge of these flows, the  $Cl_2$ -mixture composition, the total pressure and the stoichiometry of reaction (4), the expected OClO concentration assuming complete conversion of  $Cl_2$  to OClO, was calculated. The spectrum of OClO was then recorded in the range 220 to 340 nm and the absorption cross-sections were determined from the calculated OClO concentration and the absorbance, using the Beer–Lambert Law. The cross-sections were found to be significantly lower (by *ca.* 30%) than the literature values,<sup>14</sup> suggesting incomplete conversion of  $Cl_2$  to OClO. Thus, to determine the actual concentrations of OClO in the cell, a gas phase titration with NO was carried out.

### Determination of OClO Concentrations by NO Titration

Known flows of  $Cl_2$ -mixture were passed through the NaClO<sub>2</sub> column and into the cell as described above and UV absorption spectra were recorded in the region 250 to 350 nm. Flows of NO were then mixed with the OClO flow before entering the cell and the quantity of NO<sub>2</sub> formed in reactions (5) and (6) was measured by recording the visible absorption spectrum of NO<sub>2</sub> between 400 and 500 nm. Similar spectra were recorded in the absence of OClO.

$$NO + OCIO \rightarrow NO_2 + CIO$$
 (5)

$$NO + ClO \rightarrow NO_2 + Cl$$
 (6)

The NO<sub>2</sub> cross-sections from Harwood and Jones<sup>15</sup> were used to calculate  $\Delta$ [NO<sub>2</sub>], the change in the NO<sub>2</sub> concentration on adding the OCIO.  $\Delta$ [NO<sub>2</sub>] was used because the NO gas had a slight NO<sub>2</sub> impurity. The Cl atoms produced in reaction (6) were also expected to react with NO which was in large excess. Thus, from the reaction stoichiometry, two NO<sub>2</sub> molecules were expected from every OCIO molecule consumed. The measured  $\Delta$ [NO<sub>2</sub>] for a variety of Cl<sub>2</sub> flows was plotted as a function of the theoretical [OCIO] (calculated from the flow rates as described above).

The relationship between  $\Delta[NO_2]$  and the predicted concentration of OCIO was found to deviate from linearity at high Cl<sub>2</sub> flows. This was attributed to the fact that at high [OCIO], Cl and ClO also react with the NO<sub>2</sub> formed, reducing its concentration. To test this hypothesis, the titration was modelled using the FACSIMILE numerical integration software package.<sup>16</sup> The reactions (5), (6) and those between (Cl + NO), (Cl + NO<sub>2</sub>) and (ClO + NO<sub>2</sub>) were included in the model with rate constants taken from DeMore *et al.*<sup>17</sup> The actual concentrations of OCIO that would produce the measured values of  $\Delta[NO_2]$  were then calculated. Fig. 1 shows the [OCIO] determined in this way plotted against the [OCIO] calculated from the flow rates used.

The gradient of the titration plot was found to be less than unity, suggesting that there was indeed less OCIO present than expected on the basis of the flow rates used. Approximately 30% of the Cl<sub>2</sub> entering the NaClO<sub>2</sub> was not converted into OCIO. It was necessary to determine whether molecular chlorine (which could interfere with the production of Cl<sub>2</sub>O<sub>3</sub>) was present in the OCIO flow and thus a careful assessment of the quantity of Cl<sub>2</sub> impurity was undertaken.



Fig. 1 Yield of OClO from the NaClO<sub>2</sub> column. [OClO] inferred from gas-phase titration with NO (after correction for secondary chemistry) vs. the expected [OClO] assuming full conversion of chlorine.

## Determination of the Quantity of Cl<sub>2</sub> in the OCIO Flow

A liquid-phase double-titration<sup>18</sup> was performed to determine the  $Cl_2$  concentration quantitatively. A flow of OCIO mixture was bubbled through 10% KI(aq) and the dissolved OCIO and  $Cl_2$  oxidised I<sup>-</sup> to I<sub>2</sub>:

$$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$$
 (7)

$$2OClO(aq) + 2KI(aq) \rightarrow 2KClO_2(aq) + I_2(aq)$$
(8)

The quantity of iodine released was then measured by titration with  $Na_2S_2O_3$  solution with a suitable indicator. The addition of excess glacial acetic acid to the mixture then selectively reduced the  $CIO_2^-$  (from the OCIO):

$$KClO_2 + 4CH_3COOH + 4KI$$

$$\rightarrow \text{KCl} + 2\text{I}_2 + 4\text{CH}_3\text{COOK} + 2\text{H}_2\text{O} \quad (9)$$

The extra iodine released was again titrated with sodium thiosulfate. The quantities of iodine released at each stage allowed the calculation of the dissolved concentrations of OCIO and Cl<sub>2</sub>. The average proportion of Cl<sub>2</sub> in the OCIO flow calculated from these measurements was 2.8 ( $\pm 0.7$ )% where the error is 1  $\sigma$ .

Suspecting that this result might have been due to a low solubility of  $Cl_2$  in the KI solution, we passed the  $Cl_2$  mixture (without conversion to OCIO) through the KI solution at a known flow rate for a measured time. The total amount of  $Cl_2$  dissolved was then measured using the titration technique described above and compared with the quantity passed through the solution, calculated from the flow rate used. It was found that more than 97% of the expected  $Cl_2$  was accounted for in the titration and thus low  $Cl_2$  solubility was not expected to affect the results.

These results suggest that although *ca.* 30% of the  $Cl_2$  entering the NaClO<sub>2</sub> was not converted to OClO, the quantity of chlorine in the OClO was less than 3%. The effect of Cl atoms photolytically released from this  $Cl_2$  impurity was expected to be small, especially given the low absorption cross-sections of  $Cl_2$ . A FACSIMILE model showed that even if all the  $Cl_2$  impurity was photolysed, the post flash OClO concentrations would be affected by less than 1%. The  $Cl_2$  impurity was therefore expected to have a negligible effect on the measurement of the  $Cl_2O_3$  cross-sections.

A possible explanation for the 'missing' chlorine was found by considering the impurities in the NaClO<sub>2</sub>. The highest grade NaClO<sub>2</sub> available was 80% pure with Na<sub>2</sub>CO<sub>3</sub> as the major impurity. It has been suggested<sup>18</sup> that some of the Cl<sub>2</sub> reacts with Na<sub>2</sub>CO<sub>3</sub> to give inert products:

$$Na_2CO_3(s) + Cl_2(g) \rightarrow 2NaCl(s) + CO_2(g) + \frac{1}{2}O_2(g)$$
 (10)

It was assumed that the small concentrations of  $CO_2$  formed played no role in the chemistry and thus the OClO flow was used directly without further purification.

## Method

## UV Spectroscopy of OClO

In order to determine the quantity of photolytically produced  $Cl_2O_3$ , cross-sections for OCIO were required. Absorption cross-sections for OCIO were determined at a variety of temperatures by measuring the absorbance of the OCIO produced as described above in the wavelength range 250 to 350 nm and using the NO titration described above to measure the OCIO concentration. The NO titration was used only at room temperature because at lower temperatures the titration chemistry is complicated by the formation of  $N_2O_4$ ,  $N_2O_3$  and  $Cl_2O_3$ . To assess the OCIO concentrations for the measurement of cross-sections at lower temperatures, the NO titration was performed before cooling the reaction cell and an ideal gas correction applied.

A comparison between the room-temperature OClO crosssections measured here with those of Wahner *et al.*<sup>14</sup> is shown in Fig. 2. In this plot, the absorption cross-sections of Wahner *et al.*<sup>14</sup> have been smoothed<sup>19</sup> to match the lower instrument resolution used in this study. The excellent agreement between the two sets of cross-sections at room temperature gives confidence in the NO titration technique.

## Production and Spectroscopy of Cl<sub>2</sub>O<sub>3</sub>

#### Modelling the System

To test the validity of the OCIO photolysis method for  $Cl_2O_3$ , production, and to quantify the conversion of CIO to  $Cl_2O_3$ , FACSIMILE was used to model the chemical system. The quantity of photolytically generated CIO converted into  $Cl_2O_3$  increases as the temperature decreases and thus a low temperature of 223 K was selected for the measurements. The values of the rate constants used in this numerical simulation are shown in Table 1. The initial values of the reactant species used in the simulation were typical of those used in the experiments:  $[OCIO] = 5.5 \times 10^{14}$  molecules cm<sup>-3</sup>,  $[O_2] = 3 \times 10^{18}$  molecules cm<sup>-3</sup>,  $[N_2] = 2.2 \times 10^{19}$  molecules cm<sup>-3</sup>. For the simulation, 10% of the OCIO was assumed to be photolysed in the flash.

In the reaction simulation, the value of the equilibrium constant for reaction (1)  $(K_p^1)$  was taken from the recommendation of Burkholder *et al.*<sup>6</sup> which used all values of  $K_p^1$  from ref. 6 and all but the lowest-temperature value from ref. 5, in a Van't Hoff plot of ln  $(K_p)$  vs. (1/T). The bimolecular reac-



Fig. 2 Comparison of OCIO cross-sections obtained. Bold line: this work; faint line: Wahner *et al.*<sup>14</sup> Cross-sections from Wahner *et al.* are offset by  $+1 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> for clarity.

 Table 1
 Summary of reactions included in the FACSIMILE simulation of the OCIO photolysis system

| reaction  | rate coefficient at 223 K and 760 Torr /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> | ref. |
|---|--|------|
| $O + O_2 + M \rightarrow O_3 + M$                       | $3.9 \times 10^{-14}$  | 17   |
| $ClO + OClO + M \rightarrow Cl_2O_3 + M$                | $4.02 \times 10^{-12}$   | 6    |
| $Cl_2O_3 + M \rightarrow ClO + OClO + M$                | 84.9 <sup>a</sup>  | 6    |
| $CIO + CIO + M \rightarrow CI_2O_2 + M$                 | $1.04 \times 10^{-12}$   | 17   |
| $Cl_2O_2 + M \rightarrow ClO + \tilde{C}l\tilde{O} + M$ | 0.012ª   | 17   |

<sup>a</sup> Units are s<sup>-1</sup>.

tion rate for reaction (1), was calculated from the Troe parametrisation given in ref. 6. The bimolecular channels of the CIO self reaction were not considered because the CIO dimer formation dominates at 223 K. The results of the simulation are shown in Table 2 and verify that  $Cl_2O_3$  is expected to be the dominant product.

Under close scrutiny, the simulation shows that the greater thermodynamic stability of  $Cl_2O_2$  over  $Cl_2O_3$  results in the slow build up of  $Cl_2O_2$  at the expense of  $Cl_2O_3$  at long reaction times. After a reaction time of 0.2 s the UV absorption due to ClO is expected to be less than 0.2% of that of  $Cl_2O_3$ , whereas that due to  $Cl_2O_2$  is expected to contribute 3%. Thus, in order to minimise the contribution of  $Cl_2O_2$ , only the spectral information gathered up to 0.2 s after the flash was used for the measurement of the  $Cl_2O_3$  cross-sections.

## Determination of the Cl<sub>2</sub>O<sub>3</sub> Absorption Cross-sections

Flows of OCIO in  $O_2$  were directed into the cell at 223 K and 760 Torr. Using a CCD clocking speed of 1 ms per shift, photolysis experiments were performed in order to obtain 1000 sequential spectra from *ca*. 0.4 s before the flash until *ca*. 0.6 s after it. The absorbance for each post-flash row was then calculated relative to the pre-flash intensity values and all the post-flash spectra up to 0.2 s after the flash were averaged. An example of a spectrum obtained in this way is displayed as spectrum (a) in Fig. 3.

Differential spectral fitting techniques were used to fit the measured OCIO cross-sections to this post-flash spectrum. In the 300 to 340 nm wavelength region OClO has a strong and structured absorption spectrum. The other species produced in the flash have smooth (or very weak) absorptions in this region and thus the OClO concentrations were determined in the presence of other absorbers using the OCIO vibrational structure. The smooth spectral shape was filtered out from both the post-flash spectrum and the OClO reference spectrum to give structured differential spectra. The differential OCIO reference spectrum was then fitted to the differential post-flash spectrum using a linear least-squares technique.<sup>19</sup> The least-squares coefficient from the fitting process, divided by the optical pathlength, gave the change in the concentration of OCIO produced by the flash and in the subsequent reactions ( $\Delta [OClO]$ ).

The absorbance due to the OCIO destroyed [spectrum (b) in Fig. 3] was then added to the post-flash spectrum. The



Fig. 3 Decomposition of the post-flash spectrum. The post-flash spectrum (a) contains a negative absorption due to OCIO consumption (b) and a positive absorption due to ozone formation (c). The residual spectrum (bold line) after adding in the OCIO contribution and subtracting the  $O_3$  contribution [(a) + (b) - (c)] is attributed to  $Cl_2O_3$ .

quantity of ozone produced by the reaction of  $O({}^{3}P)$  with  $O_{2}$ (3) was calculated from the stoichiometry of reactions (1), (2) and (3) and was expected to be determined by:

$$-\Delta[\text{OClO}] = 2\Delta[\text{O}_3] = 2\Delta[\text{Cl}_2\text{O}_3] \tag{I}$$

The absorbance due to the ozone formed in the experiment [spectrum (c) in Fig. 3] was calculated (from this  $\Delta$ [O<sub>3</sub>] and appropriately smoothed cross-sections taken from Daumont *et al.*,<sup>20</sup> using the Beer-Lambert Law) and subtracted from the post-flash spectrum. The residual absorbance (bold line in Fig. 3) was attributed to the Cl<sub>2</sub>O<sub>3</sub> formed in reaction (1) and the cross-sections were calculated from this absorption and the Cl<sub>2</sub>O<sub>3</sub> concentration.

As described above, the ClO dimer  $(Cl_2O_2)$  was expected to be present in small quantities after the flash. The FAC-SIMILE model allowed the estimation of an upper limit of the contribution to the post-flash absorption due to  $Cl_2O_2$ . The maximum optical depth due to  $Cl_2O_2$ , calculated using the  $Cl_2O_2$  cross-sections from Burkholder *et al.*,<sup>21</sup> was expected to be less than 1.5% of that due to  $Cl_2O_3$  at 265 nm and its influence was therefore assumed to be negligible. FACSIMILE was also used to check the reaction stoichiometry [eqn. (I)] and small changes (<4%) to the concentrations of  $Cl_2O_3$  calculated from  $\Delta$ [OCIO] were made on the basis of these simulations before the calculation of the  $Cl_2O_3$ cross-sections.

#### Results

#### Cl<sub>2</sub>O<sub>3</sub> Cross-sections

The cross-sections measured for  $Cl_2O_3$  at 223 K (averaged over 5 nm intervals) are shown in Table 3. Fig. 4 shows the cross-sections as a function of wavelength and the cross-section values from previous measurements. Burkholder *et al.*<sup>6</sup> found that the absorption spectrum of  $Cl_2O_3$  shows no temperature dependence. Thus the values from the different

Table 2 FACSIMILE simulation of the OCIO photolysis system: predicted temporal variation of OCIO, Clo, Clo, O<sub>2</sub>O<sub>3</sub> and Cl<sub>2</sub>O<sub>2</sub>

| time after flash/s | [OClO]/molecules cm <sup>-3</sup>                | [ClO]/molecules cm <sup>-3</sup>             | $[Cl_2O_3]/molecules \text{ cm}^{-3}$            | $[Cl_2O_2]/molecules \text{ cm}^{-3}$ |
|--------------------|--|--|--|---------------------------------------|
| before flash       | $5.5 \times 10^{14}$<br>5 × 10^{14}              | $0 \\ 5 \times 10^{13}$                      | 0  | 0                                     |
| 0.1                | $4.553 \times 10^{14}$                           | $2.1 \times 10^{11}$                         | $4.471 \times 10^{13}$                           | $1.6 \times 10^{12}$                  |
| 0.4<br>0.6         | $4.569 \times 10^{14}$<br>$4.583 \times 10^{14}$ | $2.0 \times 10^{11}$<br>$1.9 \times 10^{11}$ | $4.311 \times 10^{13}$<br>$4.160 \times 10^{13}$ | $3.2 \times 10^{12}$                  |



Fig. 4 Cl<sub>2</sub>O<sub>3</sub> cross-sections and comparison with previous determinations. Bold line: this work; normal lines: error limits  $(\pm 1 \sigma, \text{see} \text{text for details})$  for this work;  $\textcircled{\bullet}$ , Lipscomb *et al.*<sup>3</sup>;  $\textcircled{\bullet}$ , Hayman and Cox;<sup>5</sup>  $\diamondsuit$ , Burkholder *et al.*,<sup>6</sup>  $\Box$ , Burkholder *et al.*<sup>21</sup>

studies, which were measured at different temperatures, are compared directly.

#### Errors in the Cross-sections

The errors displayed in Fig. 4 as plain lines are the statistical errors  $(1\sigma)$  on the cross-sections taken from six determinations. The main systematic errors involved in this work arise from the determination of  $\Delta$ [OClO]. The error on the differential spectral fitting of OCIO was estimated to be  $\pm 10\%$  which comprises the errors estimated from the differential cross-sections for OCIO and the error in the fitting process. This error directly affects the optical depth of OCIO and ozone stripped from the post-flash spectrum and, therefore, the calculated concentration of Cl<sub>2</sub>O<sub>3</sub>. At the longwavelength end of the spectrum, the errors arising from baseline accuracy become more significant because a small absorption due to Cl<sub>2</sub>O<sub>3</sub> was being measured under a large negative OClO absorption. The systematic errors on the cross-sections estimated from all these factors (including the influence of  $Cl_2O_2$ ) are 15% at 260 nm, 20% at 310 nm increasing to 40% at 340 nm.

Table 3 Cross-sections for  $Cl_2O_3$  at 223 K (averaged over 5 nm intervals)

| wavelength/nm<br>(centre of averaging interval) | cross-section $/10^{-17}$ cm <sup>2</sup> molecule <sup>-1</sup> |
|---|--|
| 220   | 1.44   |
| 225   | 1.33   |
| 230   | 1.22   |
| 235   | 1.14   |
| 240   | 1.14   |
| 245   | 1.25   |
| 250   | 1.38   |
| 255   | 1.55   |
| 260   | 1.70   |
| 265   | 1.76   |
| 270   | 1.71   |
| 275   | 1.56   |
| 280   | 1.34   |
| 285   | 1.09   |
| 290   | 0.87   |
| 295   | 0.68   |
| 300   | 0.51   |
| 305   | 0.40   |
| 310   | 0.32   |
| 315   | 0.27   |
| 320   | 0.24   |
| 325   | 0.21   |
| 330   | 0.20   |

### Discussion

Below 310 nm, the cross-sections for  $Cl_2O_3$  measured in this study lie in between the values given by Hayman and Cox<sup>5</sup> and Burkholder *et al.*<sup>6</sup> The value of  $\sigma(Cl_2O_3)$  at the peak of the absorption spectrum measured by Burkholder *et al.*<sup>21</sup> (an earlier study) is, however, in excellent agreement with the peak cross-section measured here. The value of  $\sigma(Cl_2O_3) =$  $1.03 \times 10^{-17}$  measured at 257.7 nm by Lipscomb *et al.*<sup>3</sup> is *ca.* 30% lower than the present study, but not inconsistent, given the uncertainties incurred in using photographic plates for quantification of absorption.

The general shapes of the absorption spectra are similar, though this study records a slightly deeper trough at 240 nm than the previous studies. This study also records slightly higher cross-sections in the long wavelength tail than the previous measurements. The cross-sections in the tail of the absorption are subject to the largest errors due to the small absorption of  $Cl_2O_3$  at these wavelengths. However, repeated measurements were in good agreement in the tail, and no residual OCIO structure can be seen in the spectra, giving confidence in these data.

While the cross-sections measured by Burkholder *et al.*<sup>6</sup> are in agreement with those measured here at the peak (267 nm) within the error limits in both studies, their values are systematically lower than those of this study. As pointed out in their work, the reaction between O and OClO<sup>22</sup> may have led to an overestimation of the concentrations of  $Cl_2O_3$  present and a consequent underestimation of the absorption cross-sections. The cross-sections measured by Hayman and Cox<sup>5</sup> are in closer agreement with the present values, but there are differences in the shapes of the spectra, especially between 230 and 270 nm.

An additional explanation for the discrepancies between the various studies lies in the influence of  $Cl_2O_2$ . In the previous studies<sup>5,6</sup> it is conceivable that significant concentrations of Cl<sub>2</sub>O<sub>2</sub> were formed due to its greater thermodynamic stability over Cl<sub>2</sub>O<sub>3</sub>. Cl<sub>2</sub>O<sub>2</sub> absorbs strongly in the UV with a spectral peak at ca. 246 nm (e.g. Burkholder et al.<sup>21</sup>), the spectral region in which the cross-sections from ref. 5 and 6 differ in shape from those measured here. In order to test the potential influence of Cl<sub>2</sub>O<sub>2</sub>, linear combinations of the cross-sections for Cl<sub>2</sub>O<sub>3</sub> measured in the present study, and the Cl<sub>2</sub>O<sub>2</sub> cross-sections from ref. 21 were produced and the resulting spectra were found to have similar shapes to those spectra assigned to pure  $Cl_2O_3$  in ref. 5 and 6. Thus, the differences in shapes between the Cl<sub>2</sub>O<sub>3</sub> spectra measured here with previous studies are consistent with the presence of  $Cl_2O_2$  in the previous studies.

In this study, the concentrations of molecular oxygen were kept sufficiently high so that the interference of the O + OCIO reaction was negligible. In addition, the ability to select the times at which post-flash spectra are recorded using the CCD detection technique allowed the measurement of the spectrum of  $Cl_2O_3$  before it had significantly decomposed. We conclude that the discrepancies in spectral shape between this and previous studies are due to the presence of other UV-absorbing species in these studies which were not present in our study.

## **Atmospheric Implications**

The cross-sections measured for  $Cl_2O_3$  were included in the one-dimensional photochemical model of  $Lary^{23}$  and the atmospheric photolysis rates of  $Cl_2O_3$  were calculated as a function of solar zenith angle. The absence of any vibrational fine structure in the  $Cl_2O_3$  absorption spectrum suggests that the electronic transitions involved are dissociative and thus

the quantum yield for Cl<sub>2</sub>O<sub>3</sub> photolysis was assumed to be unity throughout the wavelength region studied here. The photolysis rate calculations were performed at a variety of altitudes for a standard atmosphere† in March. The photolysis rate for an overhead sun at an altitude of 20 km was calculated to be 0.0045 s<sup>-1</sup>. At the lowest atmospheric temperatures (ca. 180 K) and at pressures typical of the stratosphere, the rate constant for thermal decomposition  $(k_{-1})$  will be ca. 0.1 s<sup>-1</sup>. It is clear, therefore, that typical atmospheric photolysis rates of Cl<sub>2</sub>O<sub>3</sub> are significantly lower than rates of its thermal decomposition. Thus, the lifetime of Cl<sub>2</sub>O<sub>3</sub> is likely to be determined by its thermal decomposition rather than its photolysis. Since the atmospheric lifetime of  $Cl_2O_3$  is never likely to be greater than a few tenths of a second,  $Cl_2O_3$  is unlikely to be an important reservoir for atmospheric  $ClO_x$ .

## Conclusions

This spectroscopic study of Cl<sub>2</sub>O<sub>3</sub> has demonstrated the capability of this new flash photolysis technique for performing spectroscopic studies of photolytically generated species. In particular, the ability to make repeated spectral measurements at short times after the flash in a single experiment allows the spectroscopy of unstable species, in this system permitting the recording of the spectrum of Cl<sub>2</sub>O<sub>3</sub> before it has been significantly converted to the thermodynamically more stable  $Cl_2O_2$ . The differences in the crosssections determined here for  $Cl_2O_3$  with previous studies are attributed to the influences of other UV-absorbing species (notably  $Cl_2O_2$ ). Our cross-sections have been used to determine the atmospheric photolysis rate of Cl<sub>2</sub>O<sub>3</sub>. The thermal decomposition of Cl<sub>2</sub>O<sub>3</sub> in the atmosphere is the dominant loss process and, given its short lifetime, Cl<sub>2</sub>O<sub>3</sub> is unlikely to be an important reservoir for  $ClO_x$ .

This work continues to highlight the importance of the flash photolysis technique which was developed in Cambridge in the 1950s. Professor Thrush played a major role in these developments and it is remarkable that the absorption coefficients published by him and his co-workers in 1955 lie within 30% of those published here, considering the difficulty in making spectroscopic measurements using photographic plates and taking into account the great advances in technology that have come about since this original work was undertaken.

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<sup>†</sup> US standard atmosphere (1976).