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Higher oxides of chlorine: absorption cross-sections of Cl_2O_6 and Cl_2O_4, the decomposition of Cl_2O_6, and the reactions of OClO with O and O_3

T.J. Green, M. Islam[1], C. Canosa-Mas, G. Marston[2], R.P. Wayne*

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK

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Abstract

The absorption cross-sections of Cl_2O_6 and Cl_2O_4 have been obtained using a fast flow reactor with a diode array spectrometer (DAS) detection system. The absorption cross-sections at the wavelengths of maximum absorption (λ_{max}) determined in this study are those of Cl_2O_6: $(1.47 \pm 0.15) \times 10^{-17}$ cm^2 molecule^{-1}, at $\lambda_{max} = 276$ nm and $T = 298$ K; and Cl_2O_4: $(9.0 \pm 2.0) \times 10^{-19}$ cm^2 molecule^{-1}, at $\lambda_{max} = 234$ nm and $T = 298$ K. Errors quoted are two standard deviations together with estimates of the systematic error. The shapes of the absorption spectra were obtained over the wavelength range 200–450 nm for Cl_2O_6 and 200–350 nm for Cl_2O_4, and were normalized to the absolute cross-sections obtained at λ_{max} for each oxide, and are presented at 1 nm intervals. These data are discussed in relation to previous measurements.

The reaction of O with OClO has been investigated with the objective of observing transient spectroscopic absorptions. A transient absorption was seen, and the possibility is explored of identifying the species with the elusive *sym*-ClO_3 or ClO_4, both of which have been characterized in matrices, but not in the gas-phase.

The photolysis of OClO was also re-examined, with emphasis being placed on the products of reaction. UV absorptions attributable to one of the isomers of the ClO dimer, chloryl chloride ($ClClO_2$) were observed; some Cl_2O_4 was also found at long photolysis times, when much of the $ClClO_2$ had itself been photolysed. We suggest that reports of Cl_2O_6 formation in previous studies could be a consequence of a mistaken identification. At low temperatures, the photolysis of OClO leads to the formation of Cl_2O_3 as a result of the addition of the ClO primary product to OClO.

$ClClO_2$ also appears to be one product of the reaction between O_3 and OClO, especially when the reaction occurs under explosive conditions. We studied the kinetics of the non-explosive process using a stopped-flow technique, and suggest a value for the room-temperature rate coefficient of $(4.6 \pm 0.9) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} (limit quoted is 2σ random errors).

The photochemical and thermal decomposition of Cl_2O_6 is described in this paper. For photolysis at $\lambda = 254$ nm, the removal of Cl_2O_6 is not accompanied by the build up of any other strong absorber. The implications of the results are either that the photolysis of Cl_2O_6 produces Cl_2 directly, or that the initial photofragments are converted rapidly to Cl_2. In the thermal decomposition of Cl_2O_6, Cl_2O_4 was shown to be a product of reaction, although not necessarily the major one. The kinetics of decomposition were investigated using the stopped-flow technique. At relatively high [OClO] present in the system, the decay kinetics obeyed a first-order law, with a limiting first-order rate coefficient of 0.002 s^{-1}.

Keywords: Chlorine oxides; Absorption cross section; (Absorption) spectroscopy; Decomposition kinetics; Stratosphere ozone; ClO_3; Cl_2O_4; Cl_2O_6

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1. Introduction

The oxides of chlorine have been extensively studied in the laboratory for over 100 years, but our understanding of their complex chemistry is certainly not yet complete. The chemical instability of chlorine oxides was noted as early as 1823, when Michael Faraday observed a violent explosion while attempting to prepare chlorine dioxide [1] at the bidding of Humphry Davy (who first identified the gas in 1815); Faraday seems lucky not to have been seriously injured, and, indeed, appeared honoured to continue these dangerous experiments on Davy's behalf. The involvement of the oxides in catalytic removal of stratospheric ozone [2,3] has been a new stimulus to research on these species in the last few decades. The key chlorine species in ozone loss appear to be simple ones, Cl and ClO, with the dimer ClOOCl playing an important part at low temperatures in

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* Corresponding author. Tel.: +44-1865-275434; fax: +44-1865-275410.
E-mail address: wayne@physchem.ox.ac.uk (R.P. Wayne).

[1] Present address: School of Science and Technology, University of Teesside, Middlesbrough TS1 3BA, UK.

[2] Present address: School of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 6AD, UK.

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the polar ozone ‘hole’ phenomena: the photolysis of this species is of considerable interest in its own right [4]. OClO is present at relatively high concentrations, and is a marker for high bromine levels, since it is formed in the reaction

$$ClO + BrO \rightarrow OClO + Br \qquad (1)$$

but is probably only of minor significance itself in ozone removal. Nevertheless, the enhanced concentrations of both ClO and OClO clearly increase the possibility that higher oxides derived from these species, such as Cl_2O_3, Cl_2O_4 and Cl_2O_6, might play an atmospheric role, perhaps as reservoir species, and Cl_2O_6 itself has been implicated in a hypothetical cycle for ozone removal [5]. Cl_2O_6 may dissociate into $ClO_3 + ClO_3$ or $ClO_4 + OClO$, so that the transient species ClO_3 [6,7] and ClO_4 [8] are clearly of interest, and might conceivably even play some minor part in stratospheric chemistry. Regardless of the atmospheric impact of these oxides of chlorine, it is evident that they also pose fascinating questions about their structure, spectroscopy, and kinetics of formation and loss that may be addressed by appropriate laboratory and theoretical studies. The present paper describes some experimental investigations undertaken in an attempt to improve knowledge of some aspects of the properties and behaviour of this intriguing class of compound.

Any attempt to interpret the photochemistry of the several oxides of chlorine must naturally start with an investigation of the electronic spectroscopy, and a major theme of our study is a contribution to the quantitative spectroscopy of the oxides Cl_2O_4 and Cl_2O_6 in the ultraviolet region. Fig. 1 gives an overview of the absorption spectra of several of the most important oxides: the data for ClO, OClO and the three oxides just mentioned are a summary of the data determined by us, and described in the present paper for Cl_2O_4 and Cl_2O_6 and in [9] for Cl_2O_3; the spectra for $ClClO_2$ were obtained by Müller and Willner [10,11]. The similarity of the spectroscopy of the higher oxides of chlorine is unsurprising in view of their ubiquitous chlorine–oxygen bonds. The higher oxides were originally thought to have central Cl–Cl bonds with terminal oxygen atoms. However, sub-millimetre [12] and infrared [13–15] investigations in the gas-phase and in matrices have shown that Cl_2O_3, Cl_2O_4 and Cl_2O_6 all contain a bridged Cl–O–Cl bond. $ClClO_2$ is an exception in being the only higher chlorine oxide so far isolated that contains a Cl–Cl bond. $ClClO_2$ [10,11] is also unique in exhibiting considerable stability at room temperature—unlike its oxygen-bridged counterparts—and unlike the least thermally stable species Cl_2O_2, which has a peroxide ClOOCl structure. Computational studies have largely confirmed these experimental findings [5,16–22]. Further information on the bonding and structure of the oxides Cl_2O_n has come from photoionization spectroscopy [23], and on ClO_n from photoelectron spectroscopy with an electrospray source of the corresponding anions [24].

Chlorine dioxide OClO, is a widely used precursor in many of the syntheses of the higher chlorine oxides. Bowen [25] received the acclaim for the synthesis in 1923 of Cl_2O_6 from the photolysis of OClO, although Millon had reported [26] in 1843 the formation of Cl_2O_6 from OClO. Photolysis of OClO has been reported as producing numerous other chlorine oxides, including Cl_2O_7, Cl_2O_4, Cl_2O_3 and $ClClO_2$, depending on the experimental conditions chosen. Flash photolysis has been a widely used route in preparing precursors of chlorine oxides. In particular, the photolysis of OClO has been used to produce ClO—another widely used precursor. However, there is some doubt about the exact mechanism of OClO photolysis, which has been shown

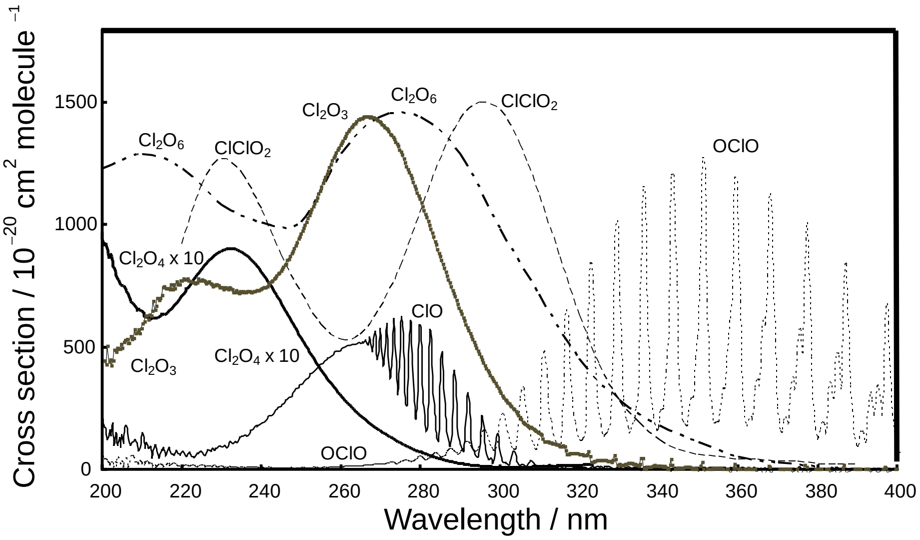

Fig. 1. Spectra of the oxides of chlorine discussed in this paper. The spectra for ClO, OClO, Cl_2O_4 and Cl_2O_6 are those determined in the research described here, and for Cl_2O_3 from our work to be published elsewhere [9]. For $ClClO_2$, the data are those published by Müller and Willner [10,11].

to be highly complex [27–34]. Two reaction channels are proposed

$$OClO + h\nu \rightarrow O + ClO \tag{2a}$$

$$OClO + h\nu \rightarrow Cl + O_2 \tag{2b}$$

The photofragments O, Cl and ClO are themselves highly reactive, necessitating considerable restrictions on experimental conditions to avoid undesirable complexity. It is easy to see how the variety of observed more complex end products could follow on from the initial photochemical steps represented by reaction (2).

Amongst the proposed reactions for the formation of the dichlorine oxides that are discussed in this work are

$$ClO + OClO + M \rightleftharpoons Cl_2O_3 + M \tag{3}$$

$$ClO_3 + ClO + M \rightarrow Cl_2O_4 + M \tag{4}$$

$$ClO_3 + ClO_3 + M \rightarrow Cl_2O_6 + M \tag{5}$$

$$ClO_4 + OClO \rightarrow Cl_2O_6 \tag{6}$$

The transient oxide ClO_3 has been intimately involved in the interpretation of the chemistry of the higher chlorine oxides ever since Goodeve and co-workers conducted an extensive study into Cl_2O_6, formed from the reaction of OClO with O_3 [35–37]. These workers concluded that Cl_2O_6 was in equilibrium with the monomer, ClO_3, with the equilibrium favouring ClO_3 in the vapour phase. Goodeve and Richardson also published [37] a UV spectrum of the monomer. Unfortunately, the identification of ClO_3 was shown to be erroneous by López and Sicre [38], but not until a considerable volume of knowledge had been built up around ClO_3/Cl_2O_6. Since ClO_3—as identified by Goodeve and Richardson—and Cl_2O_6 are the same molecule, making a positive identification of the real ClO_3 intermediate is imperative. The species has been identified positively in matrix experiments [7,15], and the ClO_3 must have been first formed in the gas-phase, from where it was deposited. Nevertheless, it has not yet proved possible to observe unequivocally a gas-phase spectrum, making the definitive mechanisms for the formation of both Cl_2O_6 and Cl_2O_4 somewhat uncertain. In our work, we have only been able to synthesize Cl_2O_6 from the reaction of OClO with O_3, a reaction that has been postulated to produce ClO_3

$$OClO + O_3 \rightarrow ClO_3 + O_2 \tag{7}$$

which could then dimerize to Cl_2O_6 in reaction (5).

Considerable insight into chlorine oxide chemistry was provided from laboratory studies conducted after it was found that catalytic ozone depletion by Cl atoms, involving the *sym*-ClO dimer [39] in polar latitudes, was at least partially responsible for the ozone 'holes' during springtime. The existence of O_3, OClO, ClO and Cl_2 in the polar stratosphere seemed to allow the possibility of complex atmospheric photochemistry involving the higher oxides of chlorine. Our improved understanding of stratospheric chemistry now indicates that the higher oxides of chlorine are unlikely to have a significant atmospheric role—with the exception of the ClO dimer [2]. However, while such a fundamental molecule as ClO_3 remains a mystery it is impossible to be sure that the higher oxides have no atmospheric role.

There exists only a single determination [40] of the absorption cross-sections for Cl_2O_4. For Cl_2O_6, the situation is even less straightforward. As long ago as 1937, Goodeve and Richardson [36,37] published a spectrum that they attributed to ClO_3, but which López and Sicre [38] have reassigned to Cl_2O_6. However, even accepting the new identification of the absorber, there remains a serious difference in the cross-sections derived by the two groups of workers, with those given by López and Sicre being several times larger than those of Goodeve and Richardson. The most recent data compilation from NASA/JPL [41] makes it clear that there remain uncertainties about the quantitative spectroscopy of the oxides Cl_2O_n. It has therefore seemed expedient for us to make new attempts to obtain quantitative absorption spectra for the molecules Cl_2O_3, Cl_2O_4 and Cl_2O_6, using somewhat different techniques from those adopted previously. In particular, we have used various implementations of the (discharge) flow method to examine the spectroscopy of the molecules to avoid problems associated with their decomposition. The avoidance of decomposition is especially important in the case of the short-lived Cl_2O_3, but is also a valuable improvement for the other two oxides. The absorption cross-sections of Cl_2O_3 are discussed in a separate paper [9], since the spectroscopy is more sensibly combined with our presentation of kinetic and thermodynamic studies that we have performed. To complement the spectroscopic investigations on the other oxides, we have also re-examined the thermal decomposition of Cl_2O_6, since the rates of that process are clearly directly related to the likely accuracy of the determinations of cross-section. In addition, we have made a further search for the elusive transient species ClO_3, since it is not only a potential product of the dissociation of Cl_2O_6, but also a hypothetical intermediate invoked in various aspects of the photochemistry and thermal chemistry of the oxides of chlorine. For these latter two investigations, we have employed a stopped-flow technique developed by us [42–44] for the investigation of reactions of this kind.

Overlapping absorptions occur in a chemical system containing more than one of the oxides simultaneously (see Fig. 1), and these absorptions may, over at least part of the spectral range, be structureless. The extraction of spectra unique to the individual oxides thus poses problems, which are compounded because of the difficulties inherent in generating well characterized, properly identified samples of the compounds of known purity. Such difficulties are probably responsible for the widely differing relative intensities reported for many chlorine oxide spectra. While the concurrent use of IR and UV spectroscopy has aided unequivocal identification of chlorine oxides, the difficulty of obtaining uncontaminated samples, and the variety of different conditions under which measurements have been made, still complicate the studies (see, for example [38,40,45,46]). Some workers have thus gone to great lengths to constrain the chemical system under study to avoid the contribution of unknown or mixed absorptions (see, for example [34,47]).

Multiplex spectroscopy, in which many or all wavelength points are probed simultaneously, is clearly virtually essential. We have deployed diode array spectroscopy for the purpose, so that the complete spectral range under study is recorded at the same time. One great advantage of using such multiplex spectroscopy is that errors resulting from long-term baseline drifts can be substantially diminished. In addition, the structured regions of the $A^2A_2 \leftarrow X^2B_1$ transition of OClO and $A^2II \leftarrow X^2II$ transition in ClO allow removal of the spectral contribution of these species by scaling reference spectra and subtracting them from the mixed spectrum to reveal underlying broad band features.

2. Experimental

2.1. Apparatus

The diode array spectrometer (DAS) used was a Jobin-Yvon CP200, operated by QUIK-VIEW software installed on a 486-SX PC. A 360 groove mm^{-1} holographically etched grating was employed in the attached spectrograph which yielded a resolution of ca. 1.5 nm (FWHM) when coupled with an entrance slit width of 50 μm. The UV light source was a 50 W deuterium lamp (Hamamatsu) mounted in lamp housing (Oriel) fitted with a rear reflector. The output from the lamphouse was partially collimated by passing it through two plano-convex quartz lenses. The light beam passed through an iris before entering the collimation system of the DAS.

Most experiments were conducted using a conventional flow-tube constructed of quartz (38 mm i.d.), and fitted with a sliding injector. A schematic diagram of the experimental set up is shown in Fig. 2. A path length of 10.5 cm was obtained from a single pass through a quartz cross-piece (30 mm i.d.) attached at right-angles to the direction of flow. Quartz discs (Suprasil-A, 3 mm thick, 35 mm diameter) were attached to the ends of the cross-piece as optical windows. A rotary vacuum pump (Leybold), fitted with a Roots blower, was used to provide a flow down the flow-tube, which was attached to a conventional gas-handling manifold to allow manipulation of gases. A capacitance manometer (MKS Baratron, 0–10 Torr) was used to record the pressure in the flow-tube. It was situated as close to the cell as possible (ca. 15 cm downstream).

Some experiments employed a stopped-flow apparatus as described by Biggs et al. [42] and Boyd et al. [43,44]. A cylindrical cell of quartz, or of Pyrex capped with Suprasil windows, formed the absorption cell (optical path = 23.5 cm, cell diameter = 6 cm). A flow of carrier gas containing the reactants of interest could be passed through the cell. The flow could be interrupted by the simultaneous actuation of three valves that diverted the carrier flow to the pump, and isolated the contents of the reaction cell. A pressure transducer (MKS Baratron, range 0–10 or 0–100 Torr) provided a measurement of the gas pressure in the reaction cell. The contents of the cell were probed using the DAS as previously described, and the time evolution of the absorption features provided the data needed for analysis of the kinetics.

2.2. Reagents and syntheses

Precursor reagents were manipulated using the gas-handling manifold. Chlorine was used as supplied by BDH (99.99%) with freeze–pump–thaw cycles used for further

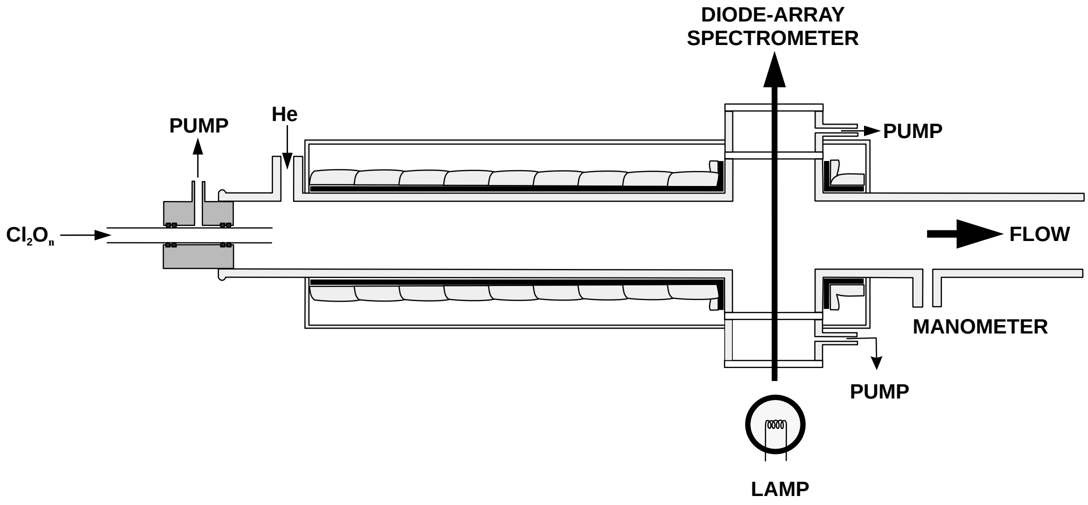

Fig. 2. Diagrammatic representation of the key parts of the flow-tube used in the determination of cross-sections. A path length of 10.5 cm was obtained from a single pass through a quartz cross-piece (30 mm i.d.) attached at right-angles to the direction of flow down a conventional quartz flow-tube (38 mm i.d.).

purification. OClO was made as required in a purpose-built synthesis rig using the method of Derby and Hutchison [48] in a reaction formally represented by the equation

$$\tfrac{1}{2}Cl_2 + NaClO_2 \rightarrow OClO + NaCl \qquad (8)$$

The effluent from the $NaClO_2$ (BDH, 'technical grade') was dried by passing the gas over a bed of P_2O_5. No evidence for contamination by CO_2 or H_2O was found when analysing an OClO sample by FTIR spectroscopy. However, quantitative conversion of Cl_2 to OClO could not be achieved.[3]

Ozone was synthesized as required using a commercial corona-discharge ozonizer (Argentox) which produced approximately 3% O_3 in O_2. The effluent gas from the ozonizer was first passed through a trap held at 196 K to remove oxides of nitrogen before being passed to a second trap containing silica gel, also held at 196 K, on which the O_3 was adsorbed. The adsorbed ozone was desorbed into a 6 l Pyrex bulb as required. Up to approximately 250 Torr of ozone with a purity of >80% was readily produced by this method. The entire system used for synthesis was enclosed in a purpose-built polycarbonate/aluminium protective shield, with sliding hatches allowing access to the experiment. Wooden boxes, lined with wire mesh and filled with vermiculite, were used to protect the bulbs from light and mechanical shock, and provide some protection against explosion. A greaseless cone and tap (Young's) facilitated removal and connection of the storage bulbs to the ozone synthesis rig and the experimental gas-handling manifold.

Synthesis of Cl_2O_6 was achieved using the method described by Goodeve and Richardson [36,37]. Ozone and OClO were introduced into a mixing volume via two needle-valves. The approximate flow rates of the two reactants could be monitored using ruby-float ball flow-meters (Jenson, RS-1). A yellow–brown vapour, clearly distinct in colouration to the green–yellow appearance of OClO, could be observed in the mixing volume. The yellow–brown vapour is believed to be Cl_2O_6, since the shape of the absorption spectrum of the vapour closely matches that published in the literature for Cl_2O_6 [41]. The presumed reaction sequence leading to the formation of Cl_2O_6 is reaction (7) followed by the dimerization process (5), although alternative schemes involving the intermediate ClO_4 are also possible [22,46]. Optimum conditions for the synthesis involved roughly equivalent concentrations of OClO and O_3, together with a comparatively high pressure in the reaction chamber (in the range 150–200 Torr). A flow through the mixing vessel was achieved by connecting the outlet to a rotary vacuum pump. A greaseless tap (Young's) was used as a crude valve to regulate the flow through the mixing chamber. A Pyrex trap, downstream of the mixing vessel and upstream of the outlet tap, was kept at 253 K (glycol–solid CO_2 slush) to trap out Cl_2O_6 in the liquid phase. Some experimentation with the conditions of the synthesis was required. If the reactant concentrations were too low, no Cl_2O_6 was formed. If reactant concentrations (or pressure) were allowed to rise too high, an explosion resulted. The explosion was accompanied by an audible 'ting' like a glass rod striking glass tubing, and a flash of light. Under some conditions, the explosions were periodic, presumably as the concentration of the chain propagator increased, before being depleted in the explosion. In the explosions, the yellow–brown vapour in the mixing vessel would disappear, the material in the chamber becoming colourless. No explosions occurred without significant concentrations of the yellow–brown vapour having been present, and we observed a memory effect in the apparatus—once an explosion had occurred, it was harder to achieve stable conditions for synthesis again. We found that liquid Cl_2O_6 was unaffected by the explosions, indicating some considerable stability. It did explode on accidental exposure to ethyne, however, and has been reported as unstable by other workers, notably Goodeve and Richardson [36]. While synthesized Cl_2O_6 was unaffected by the explosions, OClO and O_3 were themselves destroyed, presumably by the shock-front generated in the explosion. Glass sinters placed subsequently in the delivery lines succeeded in preventing explosion fronts from travelling back to destroy any reservoirs of the reactants. Considerable precautions were taken to avoid personal injury, including encasing the entire Cl_2O_6 synthesis rig in polycarbonate shielding and wearing protective clothing. Goodeve and Richardson [36] remarked over 65 years ago that "... the authors' experience with [Cl_2O_6] and other oxides of chlorine have shown that *there are no safe conditions* under which they can be handled. Elaborate precautions against harm arising from explosions have only partly succeeded in preventing personal injuries". So far, in our own experiments on the oxides of chlorine, we have avoided even partial injury (from explosions of Cl_2O_6, but not, unfortunately, from all causes).

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[3] While some workers have reported quantitative conversion of Cl_2 to OClO in the effluent from the $NaClO_2$ beds, we were unable to achieve high yields, in spite of using long residence times to maximize conversion of Cl_2 to OClO. We found no evidence, using FTIR spectroscopy, of H_2O or CO_2 contamination of the OClO after drying with P_2O_5. Using calibrated flow meters to control the delivery of Cl_2 through the $NaClO_2$ beds allows prediction of the OClO concentration, assuming 100% conversion of Cl_2 and the stoicheiometry of reaction (8) implied by the equation. Even at the smallest Cl_2 flows possible, and with additional $NaClO_2$ beds attached in-line, we were unable to achieve better than 85% conversion of Cl_2 to OClO—well outside the errors associated with our determination of the absorption cross-section of OClO and the calibration of the flow meter. We found, as have others, that moist $NaClO_2$ is required to generate OClO. If the $NaClO_2$ was used dry from the container, OClO production ceased after a few minutes, but could be restarted by lightly moistening the $NaClO_2$. Additionally, OClO production was not possible if the $NaClO_2$ beds had been subjected to a vacuum for any length of time. It seems that moisture is an essential component of reaction (8), which indicates considerably more complexity than the reaction 'as written' would suggest. We suspect that some Cl_2 and or OClO is lost from our system heterogeneously on the moist $NaClO_2$ beds. This conclusion is given additional credence by the fact that the $NaClO_2$ beds always showed a yellow–green discolouration after long periods of operation. The $NaClO_2$ used in the beds was therefore changed regularly—typically before each day's experiments.

We found Cl_2O_6 to have a melting point (ca. 3 °C) consistent with the measurements of Goodeve and Richardson [36,37]. It was found to be a dark red substance and formed acicular red crystals if transferred under vacuum to a trap at 77 K. The excellent morphology of the crystals was taken to indicate good purity of the sample. OClO seemed to be the only impurity in samples collected at 253 K and not purified further. After pumping (rotary pump) on such samples, we could discern no difference in the UV spectra compared with Cl_2O_6 that had been purified by recrystallization at 77 K.

The oxide Cl_2O_4 was synthesized by allowing a cold finger containing ∼2 ml of Cl_2O_6 to decompose in the dark at room temperature for ∼48 h. The mixture was cooled to 77 K using liquid N_2, and connected to the flow-tube system in order to analyse mixtures resulting from the decomposition. A colourless gas, presumably O_2, was pumped off. By replacing the liquid–N_2 trap with one of solid CO_2, Cl_2 was observed to evaporate from the trap. OClO and Cl_2O_4 have similar vapour pressures, so that it was not possible to achieve any significant removal of OClO from the Cl_2O_4 sample. The contamination was not a problem, since the optical absorption due to OClO could be quantitatively removed by spectral stripping. A trap at 253 K was used to allow the mixture of Cl_2O_4 and OClO vapours to be released from the cold-trap whilst keeping unreacted Cl_2O_6 in the cold finger.

All syntheses were carried out in a laboratory from which sunlight was excluded. Experiments were originally carried out in darkened conditions until we found that laboratory light (standard fluorescent tubes) had no noticeable effect.

2.3. Measurements of absorption cross-sections

The determinations of the absorption cross-sections of Cl_2O_6 and Cl_2O_4 followed identical methods, a sample of each oxide being introduced separately into the flow-tube. For each oxide, the measurements were made by connecting a cold-trap containing the species of interest to the upstream end of the flow-tube. A greaseless tap (Young's) could be opened and closed to allow a constant flow of either Cl_2O_6 or Cl_2O_4 to travel down the flow-tube to the detection region. Measurements were made in pairs, one with a high concentration of the species of interest, the other with a low concentration. The two spectra were then subtracted from each other, as were the corresponding pressures. This procedure reduces low-frequency baseline excursions, as well as reducing errors associated with any zero-offsets in the pressure measurements. Maximum pressures of Cl_2O_4 and Cl_2O_6 used in the spectroscopic experiments were ca. 0.6 Torr, and the gases were assumed to be ideal, allowing a calculation of the number density in the sample from the difference in pressures. Absorbances were measured in this way for several concentrations of absorber, and the cross-sections calculated using the known optical path. The experimental method was verified using a flow of Cl_2, regulated with a flow-meter and needle-valve. The resulting cross-section determination is shown in Fig. 3, which also displays the values currently recommended [41].

The only impurity in the samples of Cl_2O_6 and Cl_2O_4 was assumed to be OClO. The contribution of OClO to each difference spectrum could be quantified by applying the Beer–Lambert law to its absorbance, and then stripped out from the difference spectrum using scaled reference spectra (described in [9]). The effect of OClO on the Cl_2O_6 difference spectra was small, but was rather larger on the Cl_2O_4 difference spectra because of our inability to easily purify the Cl_2O_4. Determination, in each case, of σ at λ_{max} allows the entire spectrum to be placed on a scale of absolute absorption cross-section.

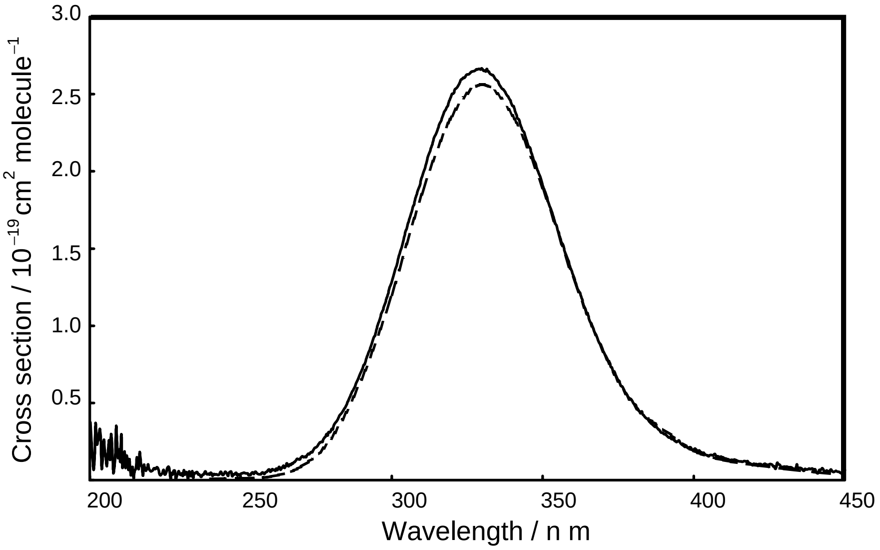

Fig. 3. Absorption cross-section of Cl_2 determined in the discharge-flow system for validation of the technique adopted: (—) this work; (- - -) current NASA/JPL recommendation [41].

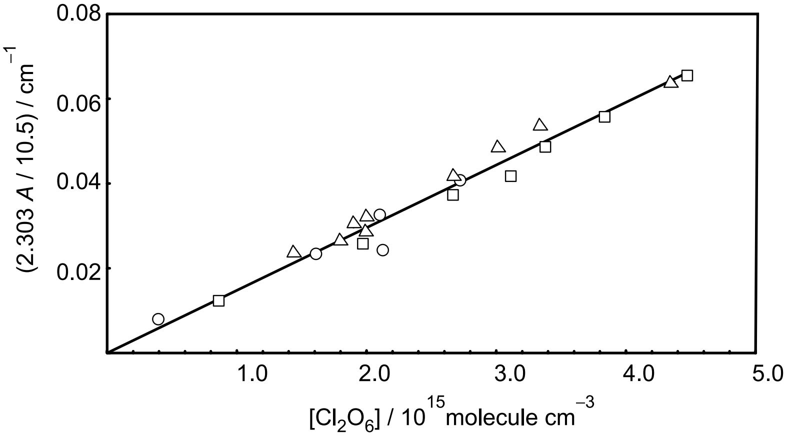

Fig. 4. Scaled absorbance of Cl_2O_6 as a function of concentration. The different symbols represent experiments performed on different days, but have no other significance.

3. Results and discussion

3.1. Absorption cross-sections

Fig. 4 illustrates the type of data obtained in the experiments on Cl_2O_4 and Cl_2O_6: it shows absorbance measured at $\lambda = 276\,\text{nm}$ as a function of $[Cl_2O_6]$ in this case. The ordinate is scaled by $(\ln 10)/(\text{pathlength}) = 2.303/10.5$, so that the slope of this plot gives the absorption cross-section at the stated wavelength. The three different symbols represent experiments performed on three separate days, but are in other respects the same. Similar results were obtained in the case of Cl_2O_4.

The use of a DAS coupled to a spectrograph allows rapid acquisition of a spectrum over the wavelength range covered by the spectrograph. The values of the absorption cross-sections obtained at one wavelength (λ_{max} is the obvious choice) can therefore be used to place a spectrum of the chlorine oxide on a scale of absolute cross-section, so long as the spectrum is free of absorbing impurities. Any errors associated with the absorption cross-section obtained at λ_{max} scale linearly over the rest of the spectrum, which allows determination of the absorption cross-sections over the entire wavelength range of the spectrograph with a high degree of precision. The results are shown in Figs. 5 and 6 for Cl_2O_6 and Cl_2O_4, respectively. The shaded area in Fig. 5 corresponds to twice the standard deviation of the slope of Fig. 4; the error bar at λ_{max} in Fig. 6 includes estimates of the systematic error as well, as discussed later.

Table 1 summarizes the absorption cross-sections obtained in the present work at the wavelength of maximum absorption, and also lists for comparison the values adopted

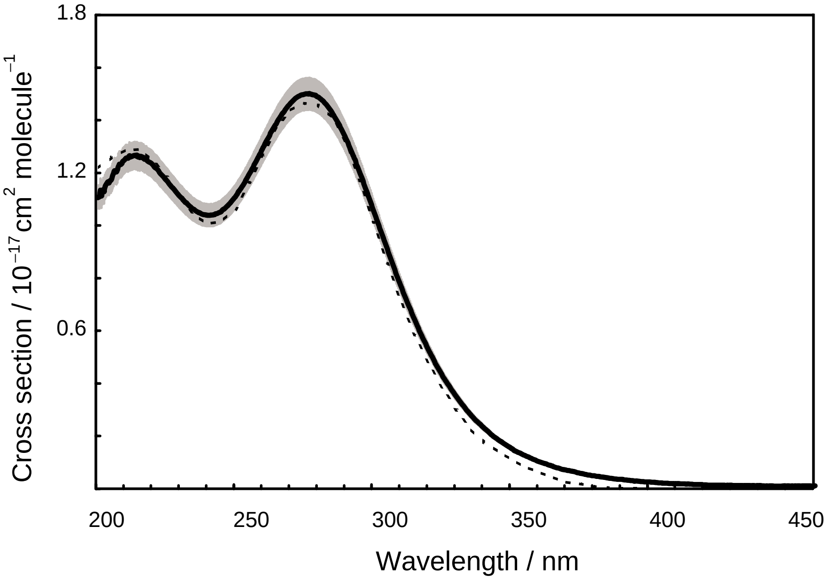

Fig. 5. Absorption spectrum of Cl_2O_6: (—) this work; (- - -) López and Sicre [38].

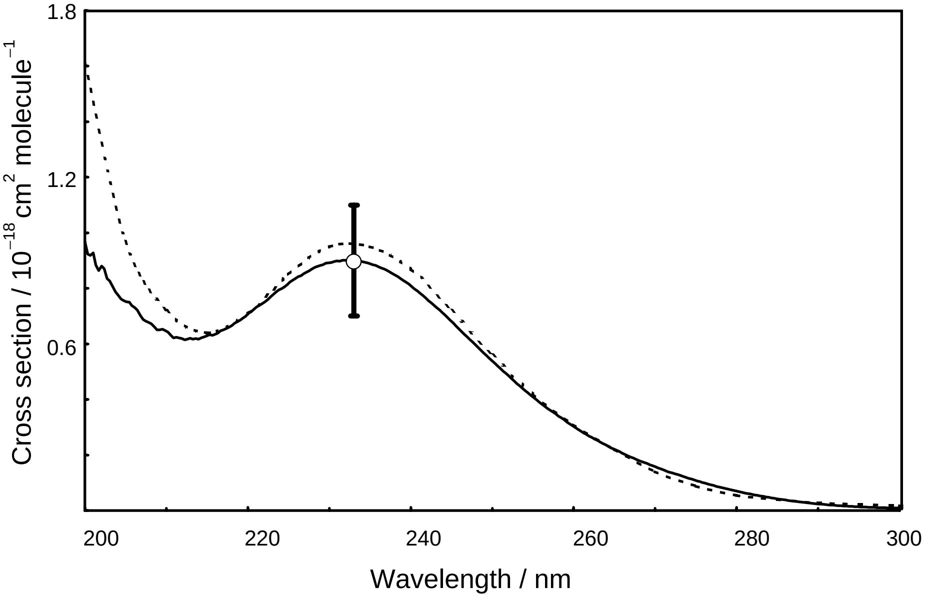

Fig. 6. Absorption spectrum of Cl_2O_4: (—) this work; (- - -) López and Sicre [40].

in recent data compilations [41]. For convenience, this table also includes the cross-section for Cl_2O_3, the determination of which is described elsewhere [9].

The errors quoted in the table are twice the standard deviations of the slope of the absorbance–concentration plots used to derive the cross-sections, taken together with estimates of systematic errors. The most significant components in the cases of Cl_2O_6 and Cl_2O_4 come from uncertainties in the small contributions to absorption at the longer wavelengths of contaminant OClO, and, to a lesser extent, from uncertainties in the measurements of pressure. Thus, in the determination of the cross-section for Cl_2O_6, fluctuations in the baseline resulting from subtraction of the OClO spectrum at $\lambda > 400$ nm can become significant, and the true error in this spectral region probably approached 10%. The same arguments hold for Cl_2O_4, although the effect of OClO, which was always present, is larger, and much more had to be stripped out at the longer wavelengths, adding to the uncertainty at $\lambda > 290$ nm. The pressure correction for OClO is also larger in this case, so that a total uncertainty of about 22% is suggested for $\lambda > 290$ nm. At the position of λ_{max} for each of these oxides, the errors resulting from the spectral stripping procedure will be substantially smaller, but we think it wise to quote errors based on the worst-case scenarios.

The comparison presented in the table shows that there is good agreement within the limits of errors that we have quoted with existing published cross-sections. However, we would humbly suggest that our central values from the new determination could more closely approach the true ones because the methodology that we have adopted has been designed to reduce contributions from species adventitiously present and to minimize spectral contamination by use of the possibilities for stripping and manipulation afforded by the use of the DAS.

Tables 2 and 3 present the detailed absorption cross-sections measured as a function of wavelength for Cl_2O_6 and Cl_2O_4. The values are presented for 1 nm wavelength intervals, and are obtained from a cubic-spline interpolation of the individual array-element data that possess a nominal spacing of 0.34 nm.

Despite the reasonably good agreement of our results with the older values of the cross-sections at λ_{max}, in each case there are potentially significant differences in the shapes of the spectra, as is indicated in Figs. 5 and 6 for Cl_2O_6 and Cl_2O_4. We regard it as an important point of our experiments

Table 1
Absorption cross-sections at the peak of the UV spectra

Absorber	σ (cm^2 molecule^{-1})	T (K)	λ_{max} (nm)	σ (cm^2 molecule^1)	λ_{max} (nm)
Cl_2O_3	$(1.44 \pm 0.72) \times 10^{-17}$[a]	243	267	1.68×10^{-17}[c]	265
Cl_2O_4	$(9.0 \pm 2.0) \times 10^{-19}$[b]	298	234	9.5×10^{-19}[c]	230–235
Cl_2O_6	$(1.47 \pm 0.15) \times 10^{-17}$[b]	298	276	1.44×10^{-17}[c]	270–280

[a] Green et al. [9].
[b] This work.
[c] Sander et al. [41]; temperature not specified.

Table 2
Absorption cross-sections of Cl_2O_6 at $T = 298\,K$

λ (nm)	σ (10^{-17} cm^2)	λ (nm)	σ (10^{-17} cm^2)	λ (nm)	σ (10^{-17} cm^2)	λ (nm)	σ (10^{-17} cm^2)
200	1.104	263	1.357	326	0.412	389	0.036
201	1.132	264	1.375	327	0.396	390	0.036
202	1.135	265	1.393	328	0.380	391	0.034
203	1.155	266	1.410	329	0.365	392	0.033
204	1.161	267	1.426	330	0.350	393	0.031
205	1.178	268	1.440	331	0.337	394	0.031
206	1.208	269	1.454	332	0.322	395	0.029
207	1.208	270	1.466	333	0.309	396	0.029
208	1.233	271	1.476	334	0.296	397	0.028
209	1.242	272	1.485	335	0.284	398	0.026
210	1.254	273	1.492	336	0.271	399	0.026
211	1.254	274	1.496	337	0.261	400	0.026
212	1.261	275	1.499	338	0.251	401	0.025
213	1.266	276	1.500	339	0.241	402	0.024
214	1.266	277	1.500	340	0.231	403	0.024
215	1.262	278	1.497	341	0.222	404	0.022
216	1.260	279	1.494	342	0.212	405	0.021
217	1.251	280	1.488	343	0.203	406	0.021
218	1.245	281	1.479	344	0.195	407	0.020
219	1.239	282	1.469	345	0.188	408	0.020
220	1.230	283	1.458	346	0.180	409	0.019
221	1.219	284	1.444	347	0.174	410	0.019
222	1.207	285	1.428	348	0.167	411	0.019
223	1.194	286	1.411	349	0.160	412	0.018
224	1.182	287	1.392	350	0.153	413	0.018
225	1.170	288	1.373	351	0.146	414	0.018
226	1.156	289	1.352	352	0.141	415	0.018
227	1.144	290	1.329	353	0.136	416	0.016
228	1.132	291	1.306	354	0.130	417	0.016
229	1.120	292	1.281	355	0.126	418	0.016
230	1.108	293	1.255	356	0.121	419	0.015
231	1.097	294	1.229	357	0.117	420	0.015
232	1.086	295	1.201	358	0.111	421	0.014
233	1.076	296	1.173	359	0.107	422	0.014
234	1.066	297	1.144	360	0.103	423	0.014
235	1.060	298	1.115	361	0.099	424	0.013
236	1.052	299	1.086	362	0.096	425	0.014
237	1.048	300	1.056	363	0.092	426	0.014
238	1.042	301	1.027	364	0.089	427	0.014
239	1.040	302	0.997	365	0.085	428	0.013
240	1.039	303	0.968	366	0.081	429	0.013
241	1.040	304	0.939	367	0.078	430	0.013
242	1.041	305	0.910	368	0.075	431	0.012
243	1.044	306	0.880	369	0.073	432	0.012
244	1.049	307	0.851	370	0.071	433	0.013
245	1.056	308	0.822	371	0.069	434	0.012
246	1.065	309	0.794	372	0.066	435	0.012
247	1.074	310	0.767	373	0.064	436	0.012
248	1.085	311	0.740	374	0.061	437	0.012
249	1.098	312	0.714	375	0.058	438	0.012
250	1.111	313	0.689	376	0.057	439	0.011
251	1.127	314	0.664	377	0.054	440	0.012
252	1.142	315	0.639	378	0.052	441	0.011
253	1.160	316	0.615	379	0.050	442	0.010
254	1.177	317	0.592	380	0.049	443	0.010
255	1.197	318	0.569	381	0.047	444	0.011
256	1.217	319	0.547	382	0.046	445	0.010
257	1.236	320	0.526	383	0.044	446	0.010
258	1.256	321	0.506	384	0.043	447	0.010
259	1.276	322	0.485	385	0.041	448	0.010
260	1.297	323	0.465	386	0.040	449	0.011
261	1.317	324	0.447	387	0.038	450	0.011
262	1.337	325	0.429	388	0.037		

Table 3
Absorption cross-sections of Cl_2O_4 at $T = 298$ K

λ (nm)	σ (10^{-19} cm^2)	λ (nm)	σ (10^{-19} cm^2)	λ (nm)	σ (10^{-19} cm^2)
200	9.681	251	5.112	302	0.083
201	9.282	252	4.855	303	0.083
202	8.788	253	4.583	304	0.083
203	8.286	254	4.330	305	0.085
204	7.784	255	4.094	306	0.088
205	7.522	256	3.852	307	0.092
206	7.324	257	3.635	308	0.097
207	6.928	258	3.433	309	0.102
208	6.751	259	3.228	310	0.108
209	6.495	260	3.028	311	0.114
210	6.462	261	2.836	312	0.121
211	6.217	262	2.663	313	0.128
212	6.179	263	2.512	314	0.135
213	6.197	264	2.355	315	0.142
214	6.174	265	2.207	316	0.149
215	6.294	266	2.058	317	0.155
216	6.346	267	1.925	318	0.162
217	6.506	268	1.797	319	0.168
218	6.658	269	1.694	320	0.174
219	6.847	270	1.581	321	0.179
220	7.082	271	1.468	322	0.183
221	7.310	272	1.362	323	0.188
222	7.495	273	1.280	324	0.191
223	7.747	274	1.177	325	0.194
224	7.970	275	1.083	326	0.196
225	8.177	276	0.995	327	0.197
226	8.384	277	0.914	328	0.198
227	8.552	278	0.838	329	0.197
228	8.721	279	0.766	330	0.196
229	8.833	280	0.698	331	0.195
230	8.919	281	0.635	332	0.192
231	8.986	282	0.576	333	0.189
232	9.006	283	0.521	334	0.185
233	9.010	284	0.470	335	0.180
234	8.967	285	0.422	336	0.175
235	8.889	286	0.379	337	0.170
236	8.786	287	0.339	338	0.163
237	8.660	288	0.303	339	0.157
238	8.494	289	0.270	340	0.150
239	8.306	290	0.240	341	0.143
240	8.097	291	0.213	342	0.136
241	7.865	292	0.189	343	0.130
242	7.605	293	0.168	344	0.123
243	7.358	294	0.150	345	0.117
244	7.095	295	0.134	346	0.111
245	6.810	296	0.121	347	0.106
246	6.517	297	0.110	348	0.102
247	6.230	298	0.101	349	0.099
248	5.953	299	0.094	350	0.098
249	5.663	300	0.088		
250	5.384	301	0.085		

that the use of the multiplex DAS means that the *relative* spectrum obtained is likely to be of high precision, regardless of the assumptions made about absolute concentrations, and the only likely cause of errors in the shape of the spectrum would be the presence of unknown absorbers for which allowance had not been made.

Our identification of Cl_2O_6 is based on the experience of previous workers who have used the reaction of $OClO + O_3$ to prepare samples in the past. The possible contributions of other species to the absorption spectrum of Cl_2O_6, and the measured pressure within the flow-tube, would be sources f error in our measurements. All known possible impurities (OClO, Cl_2O_4, Cl_2, O_2, $ClClO_2$) have sufficiently high vapour pressure that they will have been largely removed in the purification process. Since our spectra of Cl_2O_6 were highly self-consistent with the relative intensities of their peaks, any strongly absorbing chromophore would have had to have a similar vapour pressure to remain undetected. This seems unlikely in view of our current knowledge of chlorine oxide species and the use of FTIR spectroscopy in other workers' studies of Cl_2O_6 [2,11]. Nonetheless, any future identification of a suitable candidate species would have a strong impact on the absorption cross-section measurement of Cl_2O_6 presented here.

In the case of Cl_2O_4, our method of preparing the oxide is based on that of López and Sicre [40], who (to our knowledge) have published the only other spectrum. It is thus perhaps not surprising that there is a good general agreement between our results and theirs both for the general shape of the spectrum and for the value of the absorption cross-section at the absorption peak. The divergence between the results is greatest at shorter wavelengths (approaching $\lambda = 200$ nm), where the radiation is attenuated significantly by the quartz windows. However, we are confident in the accuracy of our measurements even at $\lambda = 200$ nm because of the multiplex nature of our detection system: the simultaneous acquisition of the spectrum over the entire wavelength range allows us to scale the shape of the whole spectrum using the absorption cross-section obtained at the wavelength of the peak absorption.

3.2. *ClO_3 and the absorber in the reaction of O with OClO*

For some time, there has been indirect evidence of an unknown absorber formed in the flash photolysis of OClO [49], and Mauldin et al. [34] were able to show directly the presence of such an absorber in the photochemical system. We therefore thought it desirable to search for such a species in the reaction of O with OClO in systems where ultraviolet radiation was *not* present. We adapted our flow experiments accordingly. In fact, our prime motivation was to try to produce and identify positively the intermediate, *sym*-ClO_3, which has been implicated in the formation of Cl_2O_6 (reaction (5)) and Cl_2O_4 (reaction (4)). Although ClO_3 is well known in solution chemistry [50] and has been characterized by infrared spectroscopy in matrices [7,15], no gas-phase spectrum has yet been published.

We utilized the flow system described earlier to allow OClO to react with O-atoms generated by a microwave discharge passed through O_2/He. It has been postulated [31,51] that this reation should form *sym*-ClO_3

$$O + OClO + M \rightarrow sym\text{-}ClO_3 + M \qquad (9)$$

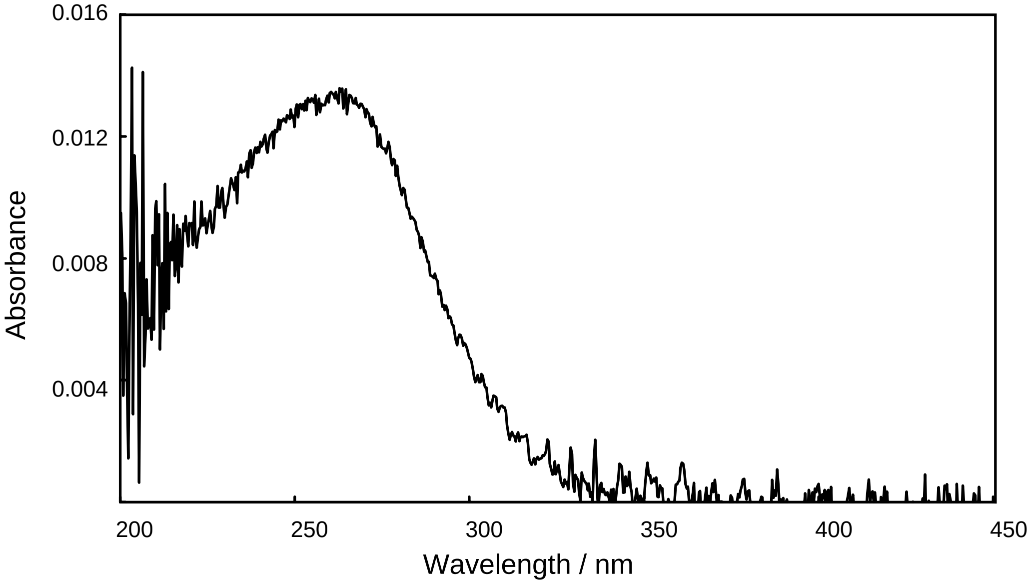

Fig. 7. Absorbance as a function of wavelength for the unidentified absorber produced in the interaction of O with OClO.

We, did, indeed, observe a transient absorption at millisecond timescales of reaction that decayed away as the reaction time was increased. By subtracting the spectral contribution of OClO, the spectrum shown in Fig. 7 was revealed, which shows a broad, featureless absorption with $\lambda_{max} \simeq 265\,nm$. The wavelength of this peak seems too far removed from that of O_3 [41] for ozone to be responsible for the absorption; in any case, the estimated rate of production from traces of O_2 in the system is much too small for enough O_3 to be formed. It would obviously be tempting to ascribe the absorption to ClO_3. However, the matrix spectrum appears to be in conflict with such an identification. Kopitsky et al. have published an improved spectrum [15] in which they generated ClO_3 by the low-pressure thermolysis of $FOClO_3$ with subsequent quenching of the gaseous products in a neon matrix. The electronic absorption consists of two overlapping bands, with the stronger having a peak at $\lambda \simeq 320\,nm$ and the weaker at $\lambda \simeq 450\,nm$. Thus, if our unidentified gas-phase band is, indeed, ClO_3, the matrix shift must be surprisingly large.

Kopitsky et al. [15] examined the photochemistry of the matrix-trapped ClO_3. In the context of the present studies, one interesting observation was that irradiation by visible light led to the formation of Cl_2O_6. These workers suggest that a small fraction of $(ClO_3)_2$ van der Waals dimers are activated so that they can undergo asymmetric bond linking to $O_2ClOClO_3$. This process would thus be the matrix equivalent of the hypothetical gas-phase process represented by reaction (5).

Another conceivable identification of the unknown gas-phase absorber would be ClO_4, produced in a matrix by Kopitsky et al. by flash pyrolysis of highly diluted Cl_2O_6. The proposed pathways for pyrolysis of the hexoxide are

$$O_2Cl\text{–}OClO_3 \rightarrow ClO_2 + ClO_4 \quad \text{major path} \qquad (10a)$$

$$O_2ClO\text{–}ClO_3 \rightarrow ClO_3 + ClO_3 \quad \text{minor path} \qquad (10b)$$

where the key Cl–O bonds are emphasized to show how the products are formed. Note, incidentally, that reaction (10b) is the reverse of reaction (6), invoked, for example, by López et al. [46] to account for the formation of Cl_2O_6 when Cl_2 is photolysed in the presence of Cl_2O_4. Since the sequence of reactions

$$O + OClO + M \rightarrow sym\text{-}ClO_3 + M \qquad (9)$$

$$ClO_3 + ClO_3 + M \rightarrow Cl_2O_6 + M \qquad (5)$$

could also generate Cl_2O_6 in the interaction of O with OClO, generation of some ClO_4 in the gas-phase system cannot be discounted. However, the matrix-isolation spectrum has λ_{max} lying at ca. 420 nm, which does seem too remote from our gas-phase feature for the latter to be the same form of ClO_4 as that observed in matrices.

Willner (private communication) has suggested that the absorption closely resembles that of *asym*-ClO_3 ($ClO\cdot O_2$) observed by his group [15], but without the fine structure observed in the matrix experiments. This species was obtained in the matrix by photolysis ($\lambda > 455\,nm$) of *sym*-ClO_3.

Whatever the molecular formula and structure of the absorber is, it is undoubtedly an oxide of chlorine, since without OClO present we were unable to observe any attenuation of light from $\lambda = 200$ to 450 nm. The absorber is almost certainly also the same as the one observed in the photochemical systems [34,49]. For example, Mauldin et al. [34] present a spectrum which consists of a broad feature with $\lambda_{max} = 260$ nm that flattens out at shorter wavelengths to reach about 60% of its maximum absorption at $\lambda = 220$ nm. Our spectrum has closely similar characteristics, with $\lambda_{max} = 265$ nm.

3.3. *Photolysis of OClO–Cl_2 mixtures: the formation of $ClClO_2$ and Cl_2O_3*

During the course of our experiments, we discovered that a small amount of OClO could be photolysed by the spectroscopic probe beam from the 30 W deuterium lamp when working at high [OClO]. Since López and Sicre [40] report the formation of Cl_2O_4, and Zabel [52] indicated that Cl_2O_6 could be formed by UV irradiation, we made a brief investigation of the photochemical system in which OClO and Cl_2 were present. Of course, photochemical studies of OClO have a long and distinguished history, but the aim of our experiments was specifically to see if absorbing species could be formed that might interfere with our determinations of the absorption cross-sections using the DAS. The results somewhat surprised us.

The experiments were all static ones, using either the stopped-flow system described in Section 2, or with an off-line cell whose contents were subsequently examined spectroscopically by expansion into the flow-tube (but used without flow). We employed as light sources the probe lamp (30 W, deuterium) and an arc lamp (75 W, Xe) with a quartz cell at room temperature, an excimer laser at $\lambda = 308$ nm (XeCl, 50 mJ pulse^{-1}, pulse length 20 ns) with an off-line Pyrex cell, and the 75 W Xe-arc lamp with a Pyrex cell in the stopped-flow system cooled to 228 K.

In the room-temperature experiments using the broad-band sources (and using a long-pass filter, $\lambda > 495$ nm, with the Xe-arc), an absorber was observed to build up in the system. The absorption matched well that presented for chloryl chloride, $ClClO_2$, by Müller and Willner [10,11]. Fig. 8 shows a comparison between our spectrum and that of Müller and Willner, and also displays our spectrum of Cl_2O_6. The figure makes it clear that the absorber in our photochemical system is $ClClO_2$ and not Cl_2O_6. Entirely similar results were obtained with the probe lamp, only the build up of $ClClO_2$ was much slower. Ultimately, the absorption due to $ClClO_2$ reached a steady-state, suggesting that the species is also being consumed, presumably by thermal decomposition or by photolysis. Using off-line photolysis at $\lambda = 308$ nm, after 100 flashes Cl_2 was observed as the main product, but some $ClClO_2$ was also present. After a longer photolysis time (12,000 flashes), some Cl_2O_4 was formed together with traces of $ClClO_2$.

Reasonable reaction schemes that account for the observed products start, for the longer wavelength photolysis, with the production of atomic Cl, followed by addition to OClO to form $ClClO_2$.

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{11}$$

$$Cl + OClO + M \rightarrow ClClO_2 + M \tag{12}$$

although alternatives involving excited OClO are also plausible, given that the filtered radiation, at least, is only just capable of dissociating Cl_2. For the laser photolysis at $\lambda = 308$ nm, the sequence

$$OClO + h\nu \rightarrow O + ClO \tag{2a}$$

$$O + OClO + M \rightarrow sym\text{-}ClO_3 + M \tag{9}$$

$$ClO_3 + ClO + M \rightarrow Cl_2O_4 + M \tag{4}$$

provides a route to Cl_2O_4. Since Cl_2O_4 is stable at room temperature [52], and does not absorb significantly at $\lambda = 308$ nm, it will be favoured over $ClClO_2$, which has a strong absorption and is probably photolysed efficiently.

The most obvious criticism of the proposed schemes is that the reaction between Cl and OClO has been widely studied before and chloryl chloride has apparently not been seen. We suggest that the explanation is the similarity of the UV absorption spectra of $ClClO_2$ and Cl_2O_6. The formation

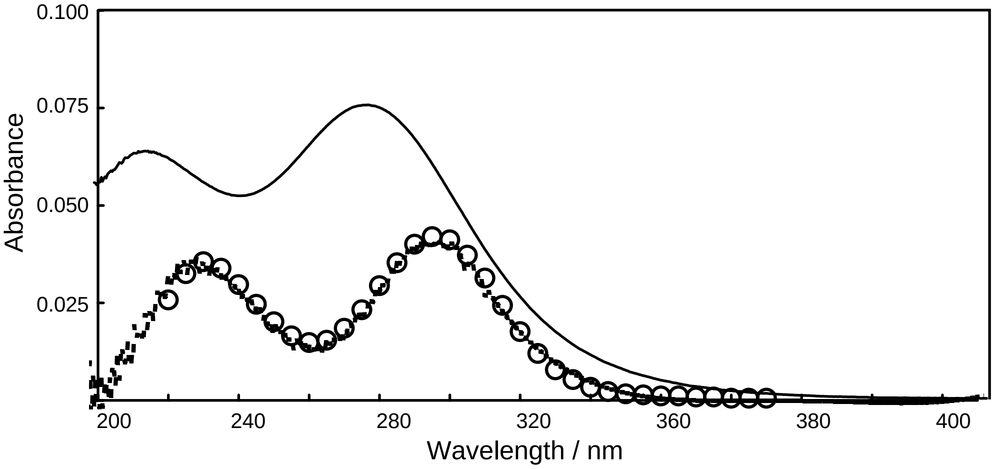

Fig. 8. Comparison of the absorption spectra of $ClClO_2$ and Cl_2O_6: (—) Cl_2O_6; (- - -) $ClClO_2$, both present work; (○) $ClClO_2$ [10,11].

of Cl_2O_6 from the photolysis of OClO has been suggested several times [38,45,52]. We have found no evidence to support this hypothesis, and have never been able to detect significant quantities of Cl_2O_6 in the products of the photolysis of OClO or OClO/Cl_2 mixtures. The hypothesis is, in any case, surprising given the instability of Cl_2O_6 at room temperature in the gas-phase (discussed later in this paper, and in [38]). It seems possible, in view of the often reported discrepancies in UV absorption spectra, that $ClClO_2$ has been mistakenly identified as Cl_2O_6 (see Fig. 8). Zabel [53] has now also seen $ClClO_2$ in his more recent work with chlorine oxides, and supports the idea that it has been mistakenly assigned as Cl_2O_6 in the past. The similarity in colour could also have given rise to earlier misassignments. Some Cl_2O_6 could undoubtedly be formed from recombination of ClO_3 radicals (reaction (5)) generated by reaction (9), but the concentration of ClO_3 will be kept low in this system because of the occurrence of reaction (4). Thus, $ClClO_2$ is a more likely reaction product than Cl_2O_6 if reactions (4) and (5) have comparable rate coefficients. In the reaction of O_3 with OClO, which is used to generate Cl_2O_6 (also see later), much higher concentrations of ClO_3 are likely to be generated in reaction (7), so that formation of Cl_2O_6 will be correspondingly favoured.

We turn now to an examination of the results obtained with the photolysis conducted at low temperature. The object of these experiments was to investigate the possible photochemical formation of species that were too unstable at room temperature to build up to observable concentrations. Unfiltered radiation from the Xe-arc lamp propagated collinearly with the spectroscopic probe beam; because of this arrangement, the DAS was 'blinded' during the photolysis periods themselves. In the experiment, ca. 80 Torr of OClO was allowed to flow into the (Pyrex) stopped-flow cell, which was held at $T = 228$ K. Since the OClO was not specially purified, some Cl_2 is inevitably present in the gas sample. The Xe-arc lamp was illuminated, and the pressure monitored. Once the pressure had decreased to ca. 6 Torr, the cell was evacuated to remove the residual gas-phase material and allowed to warm up to just above room temperature. Spectra were recorded every 15 s during this period. Absorptions that matched those of Cl_2O_3 and of $ClClO_2$ were both observed, but that ascribed to Cl_2O_3 decayed fairly rapidly, while that of $ClClO_2$ built up. Our interpretation is that both Cl_2O_3 and $ClClO_2$ are formed in the photolysis, condensed at the reduced temperature, and released again when the temperature is raised. Since Cl_2O_3 is more volatile than $ClClO_2$, it evaporates first, but since it is less stable at room temperature, it is already undergoing decay while $ClClO_2$ is continuing to evaporate. The noise on the spectra, and the high absorbances of OClO, make spectral stripping impractical and quantitative manipulation of the data dubious. However, the experiment shows again that $ClClO_2$ is a product of this photochemical system. It is interesting that no $ClClO_2$ was ever observed in the reduced-temperature discharge-flow system [9] when Cl was generated by a microwave discharge through Cl_2; some $ClClO_2$ *was* observed when the reaction

$$F + HCl \rightarrow Cl + HF \tag{13}$$

was used as the source of atoms, but there is evidence that the production of $ClClO_2$ in this case was a heterogeneous process. It is thus conceivable that the $ClClO_2$ reported in all of the experiments described in this section could have been of heterogeneous origin.

3.4. Products and kinetics of the reaction between O_3 and OClO

Simple scientific curiosity prompted us to examine the effluent gases from the explosions that sometimes accompanied the synthesis of Cl_2O_6 from O_3 and OClO. Immediately after the explosions, these gases contained a species with an absorption spectrum extremely close to that reported in the literature for chloryl chloride, $ClClO_2$ [10,11]. As explained in the preceding section, we have observed this species in photolysis systems where Cl atoms are believed to react with OClO in the termolecular reaction (12). While the possibility of heterogeneous effects forming $ClClO_2$ in either system cannot be ruled out, it seems probable that the species could be formed homogeneously if Cl atoms were chain propagators in the explosions, the elevated pressure favouring their reaction with OClO. Large quantities of Cl_2 were also formed in the explosions, and the $ClClO_2$ was observed along with both Cl_2 and OClO. Fig. 9 shows that, by manipulating a spectrum acquired shortly after an explosion, the presence of chloryl chloride can clearly be seen.

The time taken for the gases to pass from this apparatus to the spectroscopic absorption cell is of the order of 2 s, so the $ClClO_2$ may either be generated along with the Cl_2O_6, or produced as a result of subsequent chemistry. Once this behaviour was recognized, it became a simple matter to remove $ClClO_2$ from condensed Cl_2O_6 just by pumping on the sample. Without adopting this procedure, spectra supposedly of pure Cl_2O_6 were undoubtedly contaminated by absorptions from $ClClO_2$.

The stopped-flow apparatus makes possible the study of kinetics on relatively long timescales (seconds to minutes). We conducted a short investigation of the kinetics of the reaction between OClO and O_3 using this method. This process is of interest to the present study not only as a means of generating Cl_2O_6, but also as a possible source of the species ClO_3 as represented by Eq. (7). Decay traces were obtained of the absorption of either OClO (in excess O_3) or of O_3 (in excess OClO) when mixtures were isolated in the reaction cell in the same manner as that described by Boyd et al. [44] for the study of the reaction between OClO and NO_3. A first-order kinetic analysis was then employed to obtain a *pseudo*-first-order rate coefficient for the decay, and these rate constants then plotted against the concentration of the excess reagent, as shown in Fig. 10, to obtain the second-order rate coefficient. In each case, first-order

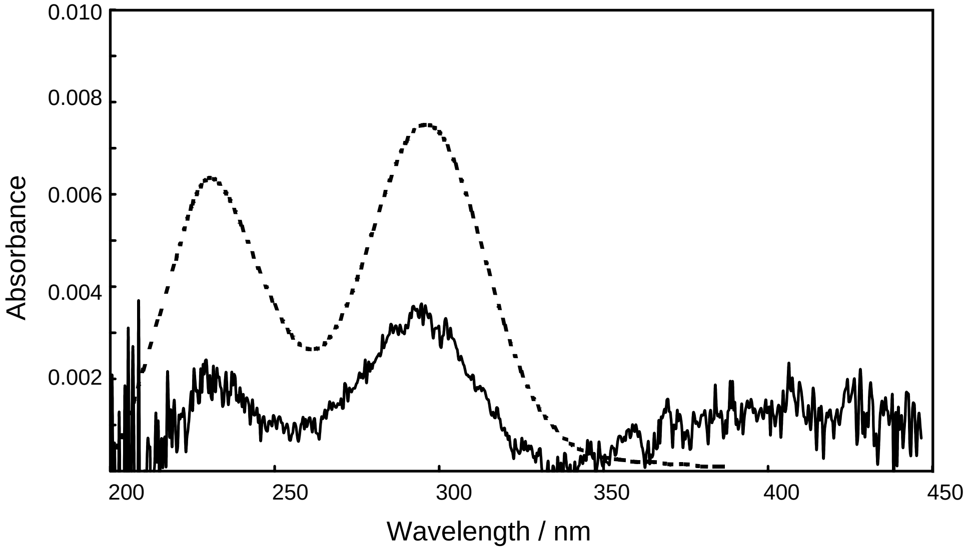

Fig. 9. Absorption spectrum of the products of the explosive reaction between O_3 and OClO (—); compared with the spectrum of $ClClO_2$ (- - -) from Müller and Willner [10,11].

rate constants for photolysis by the probe beam were determined, and applied as corrections to the total measured rate constants plotted in the figure. There does not seem to be any systematic difference between the results of the main series of experiments, conducted in excess O_3, and those where (perhaps incautiously) we used excess OClO. The rate constant obtained for $T = 298\,K$ from the combined points is $(4.6 \pm 0.9) \times 10^{-19}\,cm^3\,molecule^{-1}\,s^{-1}$, where the quoted error is two standard deviations of the slope of the line forced through the origin. This value is rather higher than that of $3.0 \times 10^{-19}\,cm^3\,molecule^{-1}\,s^{-1}$ obtained by Wongdontri-Stuper et al. [45] that still forms the basis for the current NASA/JPL recommendation [41].

We are inclined to prefer our result to that of Wongdontri-Stuper et al. since we apparently had better control of the system, more comprehensive measurements of the reactants, and a more complete understanding of the individual chlorine oxide species. Nevertheless, we accept readily that there could be some unexpected secondary chemistry in our system, especially if some species such as ClO_3 were truly the product of the primary interaction.

3.5. Thrmal decomposition of Cl_2O_6

As an adjunct to our studies of the absorption of Cl_2O_6, we wished to determine the rate at which this molecule decomposed in our system in order to be certain that losses in the transfer and spectroscopic analysis would not make a significant contribution to the error of the cross-section determinations. To this end, we employed the stopped-flow technique to follow the thermal decay of Cl_2O_6.

The vapour released from the red–brown liquid reservoir of Cl_2O_6 was allowed to flow into the reaction cell, being entrained in a flow of helium as carrier gas. Once a steady flow had been established, actuation of the solenoid valves stopped the flow through the cell. The DAS was

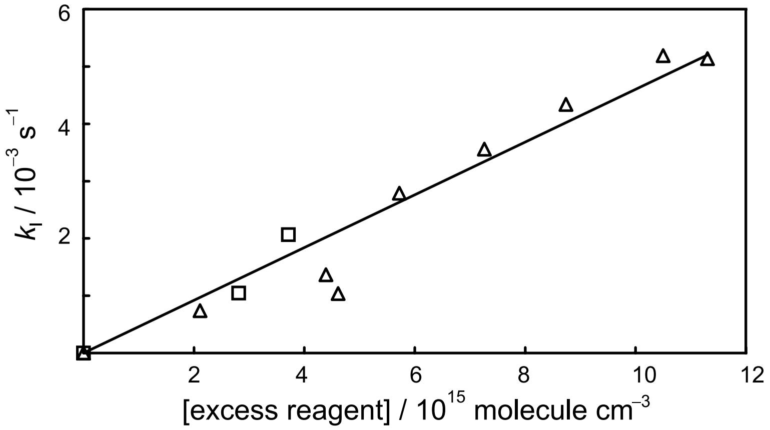

Fig. 10. Second-order plot for the reaction of OClO with O_3: (□) OClO in excess; (△) O_3 in excess.

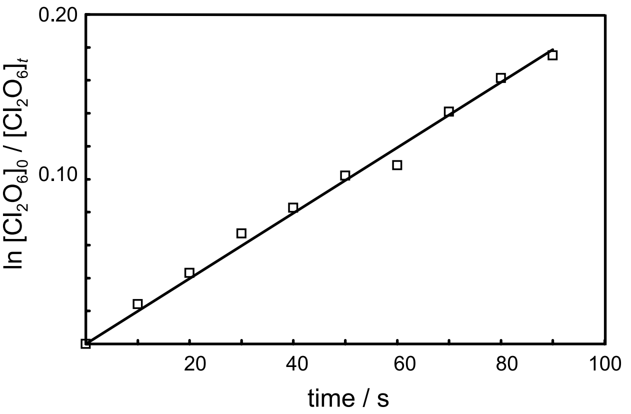

Fig. 11. First-order decay of Cl_2O_6 measured using the stopped-flow technique in a quartz cell: $[Cl_2O_6] = 5.0 \times 10^{15}$ molecule cm^{-3}; $[OClO] = 4.3 \times 10^{15}$ molecule cm^{-3}. The slope of this figure yields $k_I = 1.92 \times 10^{-3}$ s^{-1} for these particular concentrations.

set up to record several spectra over the wavelength range 200–500 nm during a fixed time interval. With the exception of experiments carried out with unusually low initial concentrations of Cl_2O_6, the decomposition of Cl_2O_6, monitored at $\lambda = 276$ nm, was found to follow first-order kinetics for the greater part of the decay (at long times, interfering absorption by OClO caused deviation from first-order behaviour). A typical first-order plot is shown in Fig. 11; from such plots, an effective first-order rate coefficient k_I for loss of Cl_2O_6 could be extracted. For those experiments in which first-order kinetics were followed well (the large majority), there was no evidence for any systematic dependence of k_I on $[Cl_2O_6]_i$. On the other hand, there was a clear dependence on $[OClO]_i$ at low concentrations. Fig. 12 shows all the values of k_I obtained using a quartz reaction cell displayed as a function of $[OClO]_i$, the initial concentration of the reactant. Within a fairly large scatter, k_I appears to be approaching a constant value (ca. 0.002 s^{-1}) as $[OClO]_i$ approaches 1.5×10^{16} molecule cm^{-3}, although there appears to be a real increase for low values of $[OClO]_i$.

Over the timescale during which the kinetic data were gathered, the spectra show the accumulation of Cl_2O_4 as the main new absorbing product, although it is heavily masked by the absorption of Cl_2O_6 itself. Careful stripping of the absorption due to Cl_2O_6 reveals the build up to Cl_2O_4 with time. The rate of formation of this oxide is consistent with the rate of loss of Cl_2O_6, although the large errors introduced by the spectral stripping procedure preclude a quantitative kinetic analysis. In a typical experiment with $[Cl_2O_6]_i = 7.2 \times 10^{15}$ molecule cm^{-3}, the spectrum at the end of the kinetic run (a few hundred seconds) suggested the formation of 5.6×10^{15} molecule cm^{-3} of Cl_2O_4. In some experiments, there was evidence for the formation of a smaller amount of OClO. After 12 h or more, the only observable chlorine-containing species was Cl_2, but it is impossible to detect formation of Cl_2 during the earlier period because its absorption is masked by the oxides.

We should now like to offer a simple explanation of these observations, based on reactions proposed by López and co-workers [38,46]. The reaction scheme

$$Cl_2O_6 \rightarrow ClO_4 + OClO \quad (14)$$

$$ClO_4 + OClO \rightarrow Cl_2O_6 \quad (6)$$

$$ClO_4 + OClO \rightarrow Cl_2O_4 + O_2 \quad (15)$$

$$ClO_4 \rightarrow OClO + O_2 \quad (16)$$

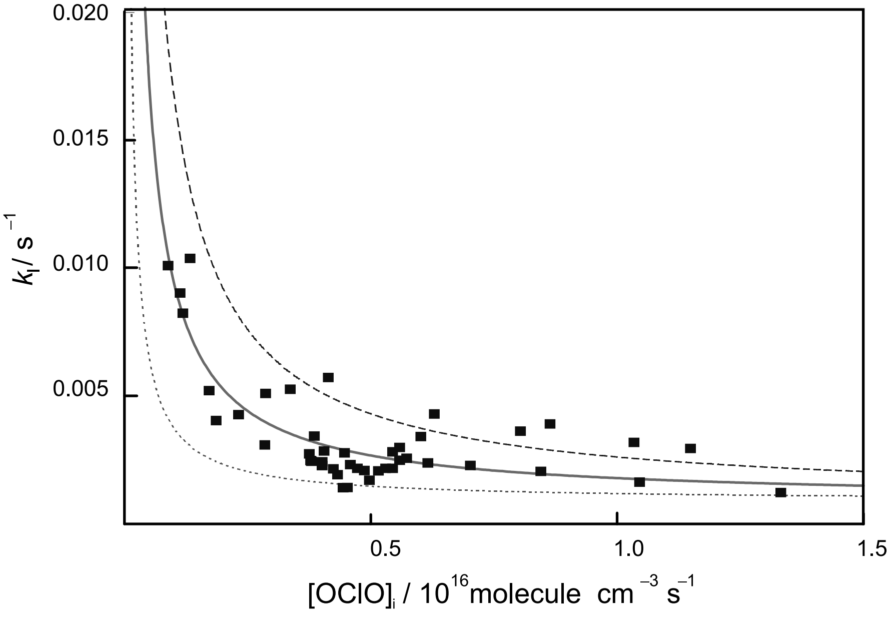

Fig. 12. *Pseudo*-first-order constant for decay of Cl_2O_6 in a quartz cell, displayed as a function of [OClO] in the system: (■) experimental data; curves are predicted behaviour with (···) $k_{16} = 1$ s^{-1}; (—) $k_{16} = 3$ s^{-1}; (- - -) $k_{16} = 5$ s^{-1}.

is put forward to explain the kinetic behaviour. Reaction (16) may be heterogeneous (as, indeed, might reaction (14)). A process such as this is needed to provide an [OClO]-independent loss of ClO_4; as written, it is also a source of OClO, which would otherwise remain constant in the system.

A steady-state analysis for [ClO_4] shows that this scheme predicts

$$k_{\mathrm{I}} = \frac{k_{14}(k_{15}[\mathrm{OClO}] + k_{16})}{(k_6 + k_{15})[\mathrm{OClO}] + k_{16}} \tag{I}$$

if [OClO] stays substantially constant throughout the experiment. Since the OClO produced is always dominated by OClO present in the initial sample of Cl_2O_6, this approximation will hold at the level of the present discussion. Eq. (I) evidently simplifies to

$$k_{\mathrm{I}} = \frac{k_{14}k_{15}}{k_6 + k_{15}} \tag{II}$$

if $k_{15}[\mathrm{OClO}] \gg k_{16}$. That is, at sufficiently high [OClO], k_{I} will be independent of [OClO] and [Cl_2O_6]. Fig. 12 suggests that in our experiments the inequality would be reached for $[\mathrm{OClO}]_{\mathrm{i}} \gtrsim 1.5 \times 10^{16}$ molecule cm^{-3}.

With these approximate values in mind, we attempted a four-parameter fit to the data shown in Fig. 12. There is certainly no way in which the data that we obtained could be used to extract the four parameters reliably, but the results returned from the procedure are displayed in Table 4 for comparison with those derived by López et al. [46]. The equilibrium constant $K = k_{14}/k_6$ is better defined than the individual rate coefficients. Nevertheless, the agreement in all cases between our values and those of López et al. is surprisingly good. What is clear, however, is that the additional process proposed by us of first-order (possible wall) loss of ClO_4 is essential to obtain a good fit to the data. The lines in Fig. 12 are the curves calculated for $k_{16} = 1$, 3 and 5 s^{-1}. The experimental points certainly demand that $k_{16} \gtrsim 1$ s^{-1}, and that it probably lies in the range 3–5 s^{-1}.

We remarked earlier that either or both of reactions (14) and (16) might be heterogeneous. There is some supporting, but not conclusive, evidence for this assertion. In a preliminary set of measurements of the rate of decomposition of Cl_2O_6, in which a Pyrex cell with quartz windows was used before the all-quartz cell was constructed, rates of decomposition were observed of up to 10 times those determined in the quartz cell.

The objective of the present series of experiments was fulfilled, since they demonstrated that a static approach to the determination of the absorption cross-section of Cl_2O_6 would fail because it decomposed too rapidly. In this respect, the earlier results of López and Sicre [38] would have been misleading. On the other hand, we were not able to work at such high Cl_2O_6 concentrations as López and Sicre and we did observe a non-linear effect of initial Cl_2O_6 concentration on the measured decomposition rate. López and Sicre reported unusual behaviour in the initial few minutes of the thermal decomposition. We were unable to follow the decomposition after the first few minutes as the Cl_2O_6 had all decomposed. Our decompositions all seemed to exhibit excellent first-order kinetics for each individual run. The additional information revealed by the studies of López et al. [46] certainly advances our understanding of this system, but it appears that there may yet be a place for a dedicated further study of the decomposition of Cl_2O_6, perhaps deploying a DAS or similar instrumentation to study as many species as possible simultaneously. Any such study should particularly focus on the effects of surfaces, and on the details of the influence of OClO. Of course, ideally it would be desirable to demonstrate explicitly the participation of the intermediate ClO_4 in the mechanism, and to measure independently the kinetics of the elementary reaction steps in which the species is suggested to participate.

3.6. *Photolysis of Cl_2O_6*

The possibility of photolysis of Cl_2O_6 by the probe beam from the deuterium lamp was evaluated by use of a shutter to cut off the probe beam while Cl_2O_6 continued to decompose thermally. No change in the rate of decomposition could be seen, so it is evident that the rate of photolysis by the probe beam is negligible in comparison with the thermal process. In order to examine further the photolysis of Cl_2O_6, we therefore illuminated the (quartz) cross-piece of the absorption cell used for the cross-section measurements with the radiation from a low-pressure Hg-lamp. The lamp output is primarily at $\lambda = 254$ nm, a wavelength at which

Table 4
Rate and equilibrium parameters obtained in the thermal decomposition of Cl_2O_6

Reaction	Rate coefficient ($T = 298$ K)	
	This work	López et al. [46]
$Cl_2O_6 \rightarrow ClO_4 + OClO$ (14)	0.195 ± 0.005 s^{-1}	0.135 s^{-1}
$ClO_4 + OClO \rightarrow Cl_2O_6$ (6)	$(6.7 \pm 0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}	1.2×10^{-14} cm^3 molecule^{-1} s^{-1}
$ClO_4 + OClO \rightarrow Cl_2O_4 + O_2$ (15)	$(3.1 \pm 0.2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}	2.7×10^{-16} cm^3 molecule^{-1} s^{-1}
$ClO_4 \rightarrow OClO + O_2$ (16)	3.1 ± 0.2 s^{-1}	Not considered
$K = k_{14}/k_6$	2.9×10^{12} molecule cm^{-3}	1.8×10^{12} molecule cm^{-3}

The errors ascribed to our own work are 1σ returned by the integration and fitting routine. They are presented to indicate that the routine can find satisfactorily a global minimum in the least-square deviations between calculated and observed concentrations, but we do not suggest that this procedure can realistically provide unique values for the four rate parameters, and certainly not with the relatively small errors given here.

Cl_2O_6 absorbs significantly (Fig. 5). A significant decrease in absorbance due to Cl_2O_6 was observed on exposure of the cell to the ultraviolet radiation, showing that Cl_2O_6 is indeed photolysed. However, no additional spectra could be found, even after elaborate spectral stripping was applied. This result can be translated into a limit for the absorption cross-section of the products of photolysis. Changes in absorbance of Cl_2O_6 at $\lambda = 276$ nm of up to 0.3 were obtained as a result of photolysis. If just one absorbing fragment or product molecule is formed for each Cl_2O_6 lost, then assuming a limit of detection of twice the noise on the spectrum ($\pm 5 \times 10^{-4}$ absorbance units) suggests a cross-section for the product of $\lesssim 2.5 \times 10^{-19}\,\mathrm{cm}^2\,\mathrm{molecule}^{-1}$. The obvious species that matches this specification is Cl_2 itself, suggesting either that the photolysis of Cl_2O_6 produces Cl_2 directly, or that the initial photofragments are converted rapidly to Cl_2.

4. Conclusions

The absorption cross-sections of Cl_2O_6 and Cl_2O_4 have been measured directly using a DAS for the first time. The use of a DAS gives better confidence in the spectral shape of the absorption features. The absolute values of the absorption cross-sections are within the error limits reported by previous workers and are reported with greater precision than those of earlier studies. The relative intensities of the primary and secondary peaks of Cl_2O_6 reported here differ somewhat from the only other published work [38]. We believe our data to be more reliable for the reasons outlined earlier.

Reported differences in Cl_2O_6 spectra can be explained by invoking $ClClO_2$ as an impurity. Indeed this species has a potential impact on numerous past studies of chlorine oxides. Since the present work did not set out to study $ClClO_2$, we have been unable to adequately quantify its reactivity. Nonetheless, in view of the potential importance of this oxide, it may warrant further study.

We have made further studies on the thermal decomposition of Cl_2O_6, and it seems that our data can be reconciled with those of other workers on the basis of quite reasonable assumptions. Unfortunately, the data obtained in this study are not adequately constrained to distinguish between homogeneous and heterogeneous processes, and some of the reactions suggested here and by others remain hypothetical.

ClO_3 has not been positively identified, in spite of a considerable effort made to detect the species. Thus the reaction pathways to Cl_2O_4 and Cl_2O_6 remain unproven. A transient species in the reaction of $O+OClO$ has been observed which has also been reported by other workers [34]. This transient may be ClO_3; if not, it is an as yet unidentified chlorine oxide. More specific analytical tools are required, in conjunction with UV spectroscopy, to prove the existence of ClO_3 in the gas-phase.

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