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# THE $Cl_2$ PHOTOSENSITIZED DECOMPOSITION OF $O_3$: THE REACTIONS OF ClO AND OClO WITH $O_3$

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## Summary

$Cl_2$ was photolyzed in the temperature range 254 - 296 K with 366 nm radiation in the presence of $O_3$. $O_3$ was removed with quantum yields of 5.8 ± 0.5, 4.0 ± 0.3, 2.9 ± 0.3 and 1.9 ± 0.2 at 24, 10, 0 and −21 °C respectively, independent of the initial $O_3$ or $Cl_2$ concentration, the extent of conversion or the absorbed intensity $I_a$. The $Cl_2$ removal quantum yields were 0.11 ± 0.2 at 24 °C for $Cl_2$ conversions of about 30%, much higher than expected from mass balance considerations based on the initial quantum yield of 0.089 ± 0.013 for OClO formation at 24 °C. The final chlorine-containing product was $Cl_2O_7$ which was observed. It was produced at least in part through the formation of OClO as an intermediate which was also observed with an initial quantum yield of $\Phi_i\{OClO\} = 2.5 \times 10^3 \exp\{-(3025 \pm 625)/T\}$ independent of $[O_3]$ or $I_a$. The results are consistent with the reaction sequence

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$

$$2ClO \rightarrow ClOO + Cl \quad (2a)$$

$$\rightarrow Cl_2 + O_2 \quad (2b)$$

$$\rightarrow OClO + Cl \quad (2c)$$

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

$$OClO + O_3 \rightarrow \text{sym-}ClO_3 + O_2 \quad (5a)$$

$$2\,\text{sym-}ClO_3 + O_3 \rightarrow Cl_2O_7 + O_2 \quad (6)$$

The relative importance of the channels for reaction (2) at 296 K are the following: $k_{2a}/k_2 = 0.63$; $k_{2b}/k_2 = 0.34$; $k_{2c}/k_2 = 0.032$. Also, $k_{2c}/k_{2b} =$

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$2.5 \times 10^3 \exp\{-(3025 \pm 625)/T\}$. The upper limit for the rate coefficient was found to be less than $1 \times 10^{-18}$ cm$^3$ s$^{-1}$ for channels (4a) and (4b):

$$ClO + O_3 \rightarrow OClO + O_2 \qquad (4a)$$

$$\rightarrow ClOO + O_2 \qquad (4b)$$

The addition of nitrogen had no effect, but oxygen reduced $-\Phi\{O_3\}$ for unknown reasons and several possibilities are discussed. At temperatures below 296 K the equilibrium

$$ClO + OClO + M \rightleftarrows Cl_2O_3 + M \qquad (7, -7)$$

becomes apparent.

The reaction of OClO with $O_3$ was also studied by direct mixing of OClO and $O_3$ in a quartz vessel in the temperature range 253 - 296 K, and in the $Cl_2$–$O_3$ system by monitoring OClO decay in the dark in the temperature range 264 - 296 K:

$$OClO + O_3 \rightarrow \text{products} \qquad (5)$$

The Arrhenius rate coefficient recommended for reaction (5) is

$$k_5 = 2.3 \times 10^{-12} \exp\left(\frac{-4730 \pm 630}{T}\right) \text{cm}^3 \text{ s}^{-1}$$

The low values of $k_4$ and $k_5$ obtained in this study indicate that reactions (4) and (5) are probably not important in atmospheric chemistry.

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## Introduction

An understanding of the $Cl_2$ photosensitized decomposition of $O_3$ is of relevance to the understanding of the atmospheric $ClO_x$ cycle. This system was extensively investigated 30 - 40 years ago [1 - 10], but the details of the mechanism remained obscure. The only recent paper on this subject is by Davidson and Williams [11] who studied the $Cl_2$–$O_3$ system by measuring stable products. The only product observed was $Cl_2O_7$, but the mechanism proposed for its formation is somewhat dubious. We have re-investigated this system in order (1) to clarify the mechanism of the process and (2) to obtain rate coefficients for the reactions of ClO and OClO with $O_3$.

For convenience, we list here the pertinent reactions that must be considered:

$$Cl_2 + h\nu \rightarrow 2Cl \qquad \text{rate} = I_a$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$

$$2ClO \rightarrow ClOO + Cl \qquad (2a)$$

$$\rightarrow Cl_2 + O_2 \qquad (2b)$$

$$\rightarrow OClO + Cl \quad (2c)$$

$$ClOO + M \rightleftarrows Cl + O_2 + M \quad (3, -3)$$

$$ClO + O_3 \rightarrow OClO + O_2 \quad (4a)$$

$$\rightarrow ClOO + O_2 \quad (4b)$$

$$OClO + O_3 \rightarrow \text{sym-}ClO_3 + O_2 \quad (5a)$$

$$\rightarrow ClO + 2O_2 \quad (5b)$$

$$2\,\text{sym-}ClO_3 + O_3 \rightarrow Cl_2O_7 + O_2 \quad (6)$$

$$ClO + OClO + M \rightleftarrows Cl_2O_3 + M \quad (7, -7)$$

Reaction (3) is reversible, but the equilibrium is so far to the right that the back reaction can play no role except possibly in the presence of a great excess of oxygen.

The reactions of ClO with $O_3$, even if relatively slow, are of potential importance in determining the effect of the $ClO_x$ cycle on stratospheric $O_3$. Very little information is available on the reaction of ClO with $O_3$:

$$ClO + O_3 \rightarrow OClO + O_2 \quad (4a)$$

$$ClO + O_3 \rightarrow ClOO + O_2 \quad (4b)$$

Using a discharge flow system with mass spectrometric detection of ClO, Clyne *et al.* [12] obtained a possible value of $5 \times 10^{-15}$ cm$^3$ s$^{-1}$ for reaction (4) if it occurs, this value being a definite upper limit. Lin *et al.* [13], however, found in a steady state photolysis study of the $Cl_2$–$O_3$ system that reaction (4) is unimportant with $k_4 < 1 \times 10^{-18}$ cm$^3$ s$^{-1}$.

The kinetics of the reactions of OClO and $O_3$ had never been studied directly when our work was initiated; however, the very early work did suggest that OClO reacts with $O_3$ to produce $ClO_3$:

$$OClO + O_3 \rightarrow ClO_3 + O_2 \quad (5a)$$

$$\rightarrow ClO + 2O_2 \quad (5b)$$

It is unlikely that this reaction, even if relatively fast and assuming that OClO is present in the atmosphere, would be of much importance in view of the probably rapid photolysis of OClO; nevertheless, it seemed appropriate to obtain some definitive information.

Reaction (5) was studied directly by Birks *et al.* [14] who mixed OClO with $O_3$ and monitored their decay spectrophotometrically. They reported $k_5 = (1.20 \pm 0.15) \times 10^{-19}$ cm$^3$ s$^{-1}$ at 298 K. In the work reported here reaction (5) was studied directly under pseudo first-order conditions by mixing OClO with excess $O_3$ and in the $Cl_2$–$O_3$ photolysis by monitoring the decay of OClO from its steady state value when the radiation was terminated.

## 2. Experimental

$Cl_2$ was photolyzed with 366 nm radiation in the presence of $O_3$ to produce Cl atoms. The 366 nm radiation was obtained from either a Hanovia U-shaped Type SH medium pressure mercury lamp or an Illumination Industries 200 W (Type 202-1003) high pressure mercury arc lamp. The 366 nm line was isolated by passing the radiation through a Corning CS 7-37 filter before it entered the reaction cell.

Conventional high vacuum lines utilizing Teflon stopcocks with Viton O-rings were used. Pressures were measured with a silicone oil manometer, a Wallace and Tiernan gauge or an Alphatron vacuum gauge. The cylindrical reaction vessels for the UV monitoring experiments were either several 200 $cm^3$ quartz cells, 10 cm long and 5 cm in diameter, or a 32 $cm^3$ Pyrex cell, 2 cm in diameter and 10 cm long, with quartz windows. The latter cell was used only for measuring $O_3$ removal. For the IR measurements a cylindrical Pyrex cell, 10 cm long and 5 cm in diameter, with KCl or NaCl windows was used.

$O_3$ removal rates were determined by following the $O_3$ decay as a function of the irradiation time by UV and IR absorption. At high $O_3$ pressures a Cary 14 spectrometer was employed. For low $O_3$ pressures a dual-beam spectrometer with phase-sensitive detection which has been described previously [15] was employed, except that the monitoring tungsten lamp was replaced with a Phillips (93109E) mercury resonance lamp with a $Cl_2$ gas filter and a Corning CS 7-54 filter. A Perkin Elmer 21 or 521 spectrometer was used for the IR measurements.

The reaction mixture absorption was also monitored at about 400 nm (300 W tungsten lamp with a Corning CS 7-59 filter) as a function of irradiation time using the dual-beam spectrometer. Initially the absorption increased linearly, then leveled off and finally reached a steady state (corresponding to several millitorr of OClO). The steady state value slowly increased with continued irradiation until near the end of the reaction, *i.e.* when nearly all the $O_3$ was consumed; the absorption then increased to a sharp maximum and finally declined to zero upon continued irradiation. Condensation of the photolysis mixture at this maximum absorption and distillation at $-130$ °C to remove the $Cl_2$ left a greenish-yellow product which was identified to be OClO by its absorption spectrum.

The initial rates of OClO formation and its steady state concentration were determined from the initial increase in absorption and the initial steady state value respectively. The effective absorption cross section for the lamp–filter combination was determined using known amounts of OClO in order to obtain absolute OClO concentrations.

The rate of the reaction of OClO with $O_3$ was determined in two ways. In the first method $Cl_2$–$O_3$ mixtures were photolyzed until some OClO (usually the steady state value) was produced; the light was then turned off and the OClO decay monitored as a function of time. This method could be used only at room temperature because at lower temperatures $Cl_2O_3$ complicated the kinetics.

In the second method OClO and excess $O_3$ were mixed directly in the quartz cell and the OClO decay was monitored as a function of reaction time. In this direct technique experiments were possible at low temperatures because $Cl_2O_3$ formation could not occur. However, at lower temperatures it was necessary to warm the cell to room temperature and pump the cell for some time after every run and clean it periodically with $HNO_3$ solution in order to obtain the "minimum" rate of reaction. If this procedure was not followed, the rate of the reaction was always significantly higher for subsequent runs.

$Cl_2$ removal rates (Table 5) were determined in the photolysis experiments by measuring the chlorine concentration at 366 nm with the dual-beam spectrometer. In order to observe a significant change in the $Cl_2$ pressure (about 30%; signal/noise about 10%) irradiations of approximately 1 h duration were required. Because of instrument base line drift over the long irradiation times, the change in $Cl_2$ concentration was determined by observing the change in the signal level during the short pump-out time of the cell. To ensure that OClO did not interfere in the measurements, excess $O_3$ was added at the end of some experiments and the mixture was allowed to stand for some time to allow for the reaction of OClO with $O_3$.

The $O_2$ production rates were measured by photolyzing $O_3$ and $Cl_2$ in a 200 $cm^3$ quartz cell. The $O_2$ produced was measured by condensing the reaction mixtures in a trap at −196 °C and measuring the pressure of the non-condensable $O_2$ with an oil manometer. The $O_2$ was then removed by pumping on the reaction mixture at −196 °C. The reaction mixture was warmed to −189 °C and the residual $O_3$ was collected at −196 °C. The pressure of the unconverted $O_3$ was then measured with an oil manometer. Calibration for expansion was done with comparable known pressures of $O_2$.

$ClO_3$ also absorbs at 366 nm; however, it was calculated using the known cross section that the maximum expected $ClO_3$ concentration would not contribute significantly to the absorption at 366 nm. $Cl_2O_7$ also does not interfere, because it does not absorb at 366 nm.

The formation of the compound $Cl_2O_7$ was determined by photolyzing a mixture of $Cl_2$ (16.2 Torr) and $O_3$ (8.3 Torr) in a Pyrex bulb of volume 1 l for 5 h. The reaction mixture was transferred to a cell with KCl windows and the IR spectrum over the range 650 - 2000 $cm^{-1}$ was obtained with a Perkin–Elmer 21 or 521 spectrometer. The only new band observed was at 1310 $cm^{-1}$. In this frequency range gaseous $Cl_2O_7$ has only three bands centered at 1310 $cm^{-1}$ (strong), 1025 $cm^{-1}$ (weak) and 690 $cm^{-1}$ (weak) [16]. The band at 1310 $cm^{-1}$ was assumed to be due to $Cl_2O_7$, since no other known chlorine oxide has a band at this frequency. Presumably the weaker bands were not observed because of the low $Cl_2O_7$ pressure. The $Cl_2O_7$ could be kept in the IR cell overnight without any detectable decomposition. $Cl_2O_7$ formation was never observed when the photolysis was done directly in the IR cell, but bands due to $ClO_4^-$ at 1100 $cm^{-1}$ and 650 $cm^{-1}$ were always observed.

Actinometry was done by photolysis of an optically equivalent amount of azomethane. The $N_2$ produced was measured by gas chromatography using a 5 Å molecular sieve column. The absorption cross sections for $Cl_2$ and azomethane were determined to be $4.2 \times 10^{-20}$ and $5.7 \times 10^{-20}$ $cm^2$ respectively, independent of temperature. The quantum yield $\Phi\{N_2\}$ of $N_2$ for this system is known to be 1.0 [17].

Low temperatures were produced by passing cold nitrogen gas through a Styrofoam box in which the reaction vessel was enclosed. The temperature was measured with an iron–constantan thermocouple.

OClO was prepared by slowly passing $Cl_2$ over a column packed with glass beads and dry $AgClO_3$ at 80 ± 10 °C. OClO was separated from the excess $Cl_2$ by distillation from —130 °C to —160 °C and then further distillation from —60 °C to —196 °C. $O_3$ was prepared by a Tesla coil discharge of $O_2$. It was purified by distillation from —189 °C (liquid argon) to —196 °C.

The oxygen and nitrogen were C.P. grade (Matheson & Co.) and were used without further purification. The chlorine (Matheson high purity research grade) was first degassed at —196 °C and then purified by distillation from —130 °C to —160 °C.

## 3. Results

### 3.1. $Cl_2$ photosensitized decomposition of $O_3$

#### 3.1.1. $O_3$ removal quantum yields

The photolysis of $O_3$–$Cl_2$ mixtures at 366 nm and 25 °C leads to the removal of $O_3$ and $Cl_2$ and to the production of $O_2$ and $Cl_2O_7$ as final products, with OClO produced as an intermediate. When the photolysis is performed in an IR cell with either NaCl or KCl windows, $Cl_2O_7$ was not observed but $ClO_4^-$ was deposited on the windows.

The $O_3$ removal quantum yields $-\Phi\{O_3\}$ were monitored during the reaction until the $O_3$ was consumed (more than 90% removal) and were found to be zero order in $O_3$ pressure. Many experiments were done covering a wide range of initial $O_3$ pressures (0.007 - 14 Torr) and absorbed intensities $I_a$ ($7.6 \times 10^{-15}$ - $2.3 \times 10^{-12}$ $cm^{-3}$ $s^{-1}$). Values of $-\Phi\{O_3\}$ measured by UV absorption are given in Table 1. The results are invariant to changes in either $[O_3]_0$ or $I_a$, and as mentioned previously are zero order in $[O_3]$ during any experiment. The values of $-\Phi\{O_3\}$ are 5.9 ± 0.6 in the 200 $cm^3$ cells and 5.7 ± 0.33 in the 32 $cm^3$ cell at 24 °C, and 4.0 ± 0.3 at 10 °C, 2.9 ± 0.3 at 0 °C and 1.9 ± 0.2 at —21 °C in the 200 $cm^3$ cells. (The uncertainties are the mean deviations.) For the one run in the 32 $cm^3$ cell in which the cell was coated with NaCl, $-\Phi\{O_3\}$ is also 5.7. The addition of up to 680 Torr $N_2$ had no effect in the 200 $cm^3$ cell (low $O_3$ pressures), but reduced $-\Phi\{O_3\}$ to 4.7 in the 32 $cm^3$ cell (high $O_3$ pressures). This reduction may not be statistically significant. The addition of $O_2$ does make a difference and reduced $-\Phi\{O_3\}$. At 2 - 5 Torr $O_3$ in the 32 $cm^3$ cell, this reduction is to 3.7.

TABLE 1

Quantum yields of $O_3$ removal as measured by UV absorption in the $Cl_2$-photosensitized decomposition of $O_3$ at 366.0 nm

| $[O_3]_0$ (Torr) | $[Cl_2]$ (Torr) | $[O_2]$ (Torr) | $[N_2]$ (Torr) | $10^{-13} I_a$ ($cm^{-3} s^{-1}$) | $-\Phi\{O_3\}$ |
|---|---|---|---|---|---|
| Experiments in a 200 $cm^3$ cell at 24 ± 3 °C | | | | | |
| 0.007 | 11.6 | 640 | — | 0.050 | 1.7 |
| 0.007 | 11.6 | — | — | 0.050 | 4.7 |
| 0.009 | 11.6 | — | — | 0.050 | 4.7 |
| 0.010 | 11.0 | — | — | 0.048 | 5.0 |
| 0.010 | 11.6 | — | — | 0.016 | 4.8 |
| 0.018 | 11.6 | — | — | 0.050 | 6.1 |
| 0.032 | 11.6 | 640 | — | 0.050 | 2.6 |
| 0.041 | 11.0 | — | — | 0.048 | 5.8 |
| 0.048 | 8.6 | — | — | 3.2 | 5.5 |
| 0.065 | 3.1 | — | — | 0.014 | 5.8 |
| 0.073 | 11.6 | — | — | 0.016 | 5.4 |
| 0.076 | 11.3 | 640 | — | 0.050 | 2.9 |
| 0.077 | 28.8 | — | — | 0.104 | 6.1 |
| 0.112 | 3.31 | — | — | 1.23 | 5.6 |
| 0.117 | 11.6 | — | — | 0.050 | 6.4 |
| 0.126 | 3.6 | — | — | 0.016 | 5.6 |
| 0.141 | 11.6 | 640 | — | 0.050 | 3.8 |
| 0.145 | 10.7 | — | — | 0.046 | 6.1 |
| 0.150 | 11.8 | — | — | 0.052 | 6.5 |
| 0.152 | 11.6 | — | — | 0.016 | 4.8 |
| 0.153 | 11.6 | 85 | — | 0.050 | 4.6 |
| 0.155 | 11.6 | — | 100 | 0.050 | 5.9 |
| 0.165 | 11.6 | — | 680 | 0.050 | 5.6 |
| 0.171 | 11.6 | — | — | 0.050 | 5.7 |
| 0.175 | 28.8 | — | — | 0.104 | 7.1 |
| 0.176 | 11.6 | — | — | 0.050 | 5.8 |
| 0.179 | 11.2 | — | — | 0.049 | 7.0 |
| 0.194 | 11.8 | — | — | 0.052 | 6.7 |
| 0.314 | 11.6 | 540 | — | 0.050 | 4.4 |
| 0.345 | 11.6 | 640 | — | 0.050 | 4.7 |
| 0.385 | 11.2 | — | — | 0.049 | 7.0 |
| 0.403 | 11.6 | — | — | 0.050 | 6.7 |
| 0.480 | 11.6 | — | — | 0.050 | 6.3 |
| 0.482 | 11.1 | — | — | 4.1 | 6.2 |
| 0.534 | 10.3 | — | — | 3.8 | 6.2 |
| Experiments in a 200 $cm^3$ cell at 11.1 ± 0.5 °C | | | | | |
| 0.098 | 11.5 | — | — | 4.9 | 3.7 |
| 0.099 | 11.1 | — | — | 4.7 | 3.4 |
| 0.106 | 11.6 | — | — | 4.9 | 3.8 |
| 0.114 | 11.1 | — | — | 4.7 | 3.8 |
| 0.146 | 4.90 | — | — | 2.1 | 4.2 |
| 0.147 | 11.1 | — | — | 4.7 | 4.1 |

*(continued)*

TABLE 1 *(continued)*

| $[O_3]_0$ (Torr) | $[Cl_2]$ (Torr) | $[O_2]$ (Torr) | $[N_2]$ (Torr) | $10^{-13} I_a$ ($cm^{-3} s^{-1}$) | $-\Phi\{O_3\}$ |
|---|---|---|---|---|---|
| 0.162 | 17.9 | — | — | 8.3 | 3.6 |
| 0.174 | 10.5 | — | — | 4.5 | 3.9 |
| 0.185 | 10.8 | — | — | 4.6 | 3.9 |
| 0.244 | 11.8 | — | — | 5.0 | 4.2 |
| 0.306 | 11.3 | — | — | 4.8 | 4.2 |
| 0.340 | 6.07 | — | — | 2.6 | 4.5 |
| 0.369 | 21.2 | — | — | 9.0 | 3.8 |
| 0.449 | 11.1 | — | — | 4.7 | 4.7 |
| Experiments in a 200 $cm^3$ cell at 0.2 ± 0.3 °C | | | | | |
| 0.113 | 11.1 | — | — | 5.7 | 2.4 |
| 0.124 | 3.93 | — | — | 2.0 | 2.7 |
| 0.149 | 20.0 | — | — | 11.3 | 2.6 |
| 0.154 | 18.2 | — | — | 9.3 | 2.6 |
| 0.180 | 11.1 | — | — | 5.7 | 2.7 |
| 0.193 | 5.14 | — | — | 2.6 | 3.3 |
| 0.220 | 11.1 | — | — | 5.7 | 2.9 |
| 0.363 | 8.64 | — | — | 4.4 | 2.7 |
| 0.429 | 20.9 | — | — | 10.7 | 3.2 |
| 0.449 | 6.00 | — | — | 3.1 | 3.0 |
| 0.494 | 10.7 | — | — | 5.5 | 3.4 |
| 0.537 | 11.1 | — | — | 5.7 | 3.2 |
| 0.547 | 11.1 | — | — | 5.7 | 2.9 |
| Experiments in a 200 $cm^3$ cell at −21.4 ± 0.3 °C | | | | | |
| 0.131 | 10.6 | — | — | 9.2 | 1.9 |
| 0.155 | 10.7 | — | — | 9.3 | 1.7 |
| 0.188 | 11.4 | — | — | 9.9 | 1.9 |
| 0.395 | 10.7 | — | — | 9.3 | 1.9 |
| 0.413 | 3.97 | — | — | 3.4 | 1.1 |
| 0.473 | 10.7 | — | — | 9.3 | 1.8 |
| 0.465 | 14.4 | — | — | 15.1 | 2.2 |
| Experiments in the 32 $cm^3$ cell at 24 ± 3 °C | | | | | |
| 1.32 | 5.91 | — | — | 0.98 | 5.64 |
| 2.20 | 5.30 | — | — | 1.26 | 5.47 |
| 2.33 | 6.88 | — | — | 0.18 | 5.10 |
| 2.33 | 5.95 | — | — | 0.16 | 6.30 |
| 2.41 | 6.22 | — | — | 0.43 | 5.60 |
| 2.41 | 6.69 | — | — | 0.46 | 5.40 |
| 2.57[a] | 6.46 | — | — | 3.0 | 5.71 |
| 2.64 | 5.91 | 600 | — | 0.98 | 3.80 |
| 2.80 | 6.53 | — | — | 0.58 | 5.02 |
| 2.96 | 6.26 | — | — | 0.16 | 6.30 |
| 3.03 | 5.76 | — | — | 1.95 | 6.05 |

*(continued)*

TABLE 1 *(continued)*

| $[O_3]_0$ (Torr) | $[Cl_2]$ (Torr) | $[O_2]$ (Torr) | $[N_2]$ (Torr) | $10^{-13} I_a$ ($cm^{-3}\ s^{-1}$) | $-\Phi\{O_3\}$ |
|---|---|---|---|---|---|
| 3.11 | [a]6.77 | — | 600 | 1.00 | 4.72 |
| 3.27 | 6.78 | — | — | 1.13 | 5.54 |
| 3.27 | 5.29 | — | — | 3.3 | 6.27 |
| 3.66 | 6.07 | — | 600 | 1.00 | 4.72 |
| 3.73 | 6.22 | — | — | 3.9 | 5.78 |
| 5.45 | 6.10 | 600 | — | 1.00 | 3.71 |
| 5.76 | 6.15 | 600 | — | 2.1 | 3.65 |

[a]Walls coated with NaCl.

TABLE 2

Quantum yields of $O_3$ removal as measured by IR spectroscopy in the $Cl_2$-photosensitized decomposition of $O_3$ at 366.0 nm and 24 °C

| $[O_3]_0$ (Torr) | $[Cl_2]$ (Torr) | $[O_2]$ (Torr) | $[N_2]$ (Torr) | $10^{-13} I$ ($cm^{-3}\ s^{-1}$) | $-\Phi\{O_3\}$ |
|---|---|---|---|---|---|
| 4.5 | 5.85 | — | — | 1.35 | 8.8 |
| 10.1 | 5.83 | — | — | 1.33 | 10.1 |
| 14.4 | 5.80 | — | — | 1.39 | 8.8 |
| 14.5 | 5.64 | 600 | — | 1.37 | 9.6 |
| 14.6 | 5.53 | — | 600 | 1.33 | 10.0 |
| 14.8 | 5.85 | — | 600 | 1.42 | 11.1 |
| 14.8 | 6.06 | — | — | 0.35 | 9.2 |
| 14.8 | 5.22 | — | — | 0.31 | 9.6 |
| 14.8 | 5.85 | — | 600 | 1.38 | 12.4 |
| 14.8 | 5.64 | — | — | 1.33 | 10.1 |
| 14.8 | 27.0 | — | — | 4.7 | 7.6 |
| 14.8 | 27.0 | 600 | — | 4.7 | 8.1 |
| 14.8 | 27.0 | 600 | — | 4.7 | 6.8 |
| 14.8 | 27.0 | 600 | — | 4.7 | 6.7 |
| 14.8 | 5.53 | — | — | 1.34 | 10.5 |
| 14.9 | 5.32 | 600 | — | 1.29 | 8.9 |
| 14.9 | 27.2 | — | 600 | 4.7 | 8.3 |
| 14.9 | 5.32 | 600 | — | 1.26 | 9.2 |

At the low $O_3$ pressures in the 200 $cm^3$ cells, $-\Phi\{O_3\}$ is reduced to 4.7 at 400 mTorr $O_3$ and falls to 1.7 as $[O_3]$ is reduced to 7 mTorr.

Our results agree qualitatively with those of Norrish and Neville [10] and Lin *et al.* [13] who found that $-\Phi\{O_3\} \approx 6$ in the absence of oxygen but that large amounts of oxygen (or chlorine) depressed the value.

For the runs in one of the 200 $cm^3$ cells it was noted that, when azomethane was kept in the cell for a long time before removal preceding the photolysis of $Cl_2$–$O_3$ mixtures, $-\Phi\{O_3\}$ decreased significantly to about 2.2. Under these conditions the presence of oxygen had no effect, but the

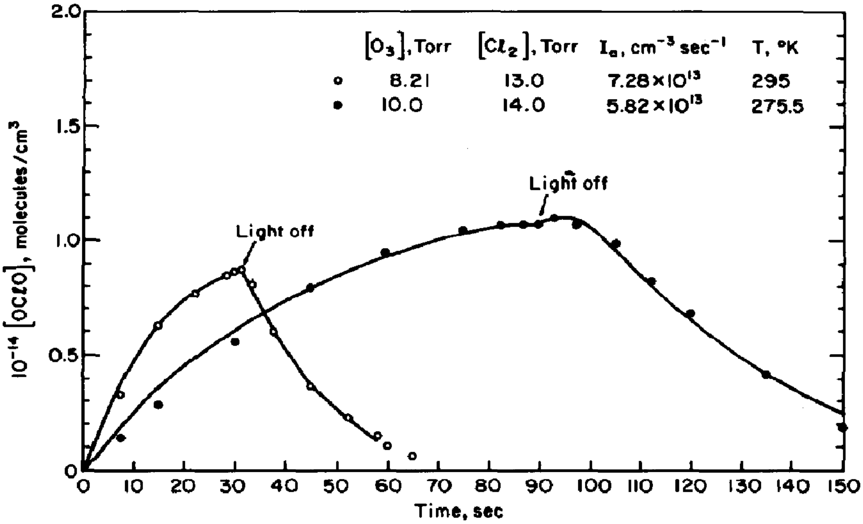


**Fig. 1. OClO profiles in the photolysis of $Cl_2$–$O_3$ mixtures: the points are experimental values and the solid curves are computer simulations with the following rate coefficients.**

| $T$ (K) | 275.5 | 295 |
|---|---|---|
| $k_1$ ($cm^3\ s^{-1}$) | $1.06 \times 10^{-11}$ | $1.13 \times 10^{-11}$ |
| $k_{2b}$ ($cm^3\ s^{-1}$) | $2.09 \times 10^{-14}$ | $1.42 \times 10^{-14}$ |
| $k_{2c}$ ($cm^3\ s^{-1}$) | $1.19 \times 10^{-15}$ | $1.40 \times 10^{-15}$ |
| $k_2$ ($cm^3\ s^{-1}$) | $4.4 \times 10^{-14}$ | $4.4 \times 10^{-14}$ |
| $k_5$ ($cm^3\ s^{-1}$) | $8.0 \times 10^{-20}$ | $2.65 \times 10^{-19}$ |
| $k_7$[M] ($cm^3\ s^{-1}$) | $1.00 \times 10^{-15}$ | — |
| $k_{-7}$[M] ($s^{-1}$) | 0.25 | — |

presence of nitrogen increased $-\Phi\{O_3\}$ to about 3.3. Subsequent to these runs the cell was washed with $HNO_3$ solution. A deposit was removed as indicated by a yellow color imparted to the $HNO_3$ solution. Also the transmittance at 2537 Å increased after washing the cell. Experiments with the freshly washed cell at first gave erratic values of $-\Phi\{O_3\}$ of about 3 - 4 and the rate of reaction varied throughout the course of the reaction. After some conditioning of the cell $-\Phi\{O_3\}$ became more reproducible at values of 4 - 5. These experiments show that at low values of $[O_3]$ the walls can inhibit the $Cl_2$-photosensitized decomposition of $O_3$. No such effects were observed at high pressures of $O_3$ (above 2 Torr).

Further evidence that surfaces can influence the reaction comes from the work in the IR cells with KCl windows in which $ClO_4^-$ was observed. The $O_3$ removal quantum yields for these runs are presented in Table 2, and they are larger than in the quartz or Pyrex cells. The average values and the mean deviations for $-\Phi\{O_3\}$ are 9.34 ± 0.74 in the absence of oxygen or nitrogen, 10.45 ± 1.30 in the presence of nitrogen and 8.22 ± 1.02 in the presence of oxygen. Some runs were done at relatively high $Cl_2$ pressures (27 Torr) in this group, and the inhibiting effect of $Cl_2$ reported by earlier workers [10, 13] is discernible. For one run at 27 Torr $Cl_2$ in the absence of oxygen or nitrogen $-\Phi\{O_3\} = 7.6$. In the presence of nitrogen the runs at low and high $[Cl_2]$ are 12.4 and 8.3 respectively; in the presence of oxygen $-\Phi\{O_3\} = 9.2 \pm 0.2$ at low $[Cl_2]$ and $7.2 \pm 0.6$ at high $[Cl_2]$. The effect of oxygen is not so apparent.

*3.1.2. OClO formation quantum yields and OClO decay in the dark*

A typical OClO growth profile during irradiation and decay profile when the light is turned off is shown in Fig. 1. The OClO grows linearly initially and then levels off to a steady state value. When the light is turned off the OClO decays ($O_3$ is still present in excess) exponentially at 295 K. At lower temperatures there is a clear induction period for OClO decay in the dark (Fig. 1).

The OClO formation quantum yields were obtained from the initial OClO growth rate determined from the initial slopes of the absorption profiles. The results are presented in Table 3 (column 5). From Table 3 it is apparent that $\Phi_i\{OClO\}$ is independent of the $O_3$ pressure in the range of 4 - 13 Torr, though there may be a small reduction in the presence of excess nitrogen or oxygen. $\Phi_i\{OClO\}$ clearly decreases with decreasing temperature. An Arrhenius plot of $\Phi_i\{OClO\}$ obtained from initial rates is presented in Fig. 2. The plot is reasonably linear and leads to the Arrhenius expression

$$\Phi_i\{OClO\} = 2.5 \times 10^3 \exp -\left(\frac{3025 \pm 625}{T}\right)$$

The addition of up to 600 Torr of nitrogen or oxygen reduced $\Phi_i\{OClO\}$ slightly at 298 K and 275 K.

Figure 1 shows that OClO decays when the radiation is terminated. Presumably the decay is due to reaction with $O_3$:

$$OClO + O_3 \rightarrow \text{products} \qquad (5)$$

Typical first order plots of OClO decay after the radiation is terminated are shown in Fig. 3. It is apparent that the plot is linear only at 296 K. Below this temperature there is a significantly increasing deviation from linearity with decreasing temperature. The data at 296 K are summarized in Table 3 in the form of the first order coefficient $k_5$. The average value is $(3.02 \pm 0.49) \times 10^{-19}$ cm$^3$ s$^{-1}$. The data at the lower temperatures cannot be summarized in this form and are not given in Table 3. However, in Section 4 these data are employed in the computer analysis of the proposed mechanism.

The OClO profile at 298 K shown in Fig. 1 can be analyzed quantitatively for self-consistency over the entire region (light and dark) by integrating the differential equations for OClO formation and decay. The differential equation during irradiation is

$$\frac{d}{dt}[OClO] = \Phi_i\{OClO\}I_a - k_5[O_3][OClO] \qquad (I)$$

TABLE 3

Photolysis of $Cl_2$–$O_3$ mixture at 366 nm

| $[O_3]$ (Torr) | $[Cl_2]$ (Torr) | Temp. (°C) | $10^{-13} I_a$ ($cm^{-3}$ $s^{-1}$) | $\Phi_i\{OClO\}^a$ | $\Phi_i\{OClO\}^b$ | $[OClO]_{ss}$ (mTorr) | $10^{19} k_5{}^c$ ($cm^3$ $s^{-1}$) | $10^{19} k_5{}^d$ ($cm^3$ $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $T = 24 \pm 3$ °C | | | | | | | | |
| 3.42 | 7.78 | 24.0 | 4.34 | 0.076 | 0.061 | 3.38 | 2.61 | 2.68 |
| 3.40 | 6.87 | 25.0 | 3.84 | 0.14 | 0.12 | 4.45 | 2.24 | 3.34 |
| 3.81 | 12.9 | 23.7 | 7.19 | 0.079 | 0.085 | 5.55 | 2.81 | 2.52 |
| 4.08 | 12.8 | 22.0 | 7.12 | 0.083 | 0.087 | 5.69 | 2.22 | 2.39 |
| 4.66[e] | 16.8 | 23.0 | 9.38 | 0.067 | 0.057 | 4.48 | 3.04 | 2.83 |
| 5.48[f] | 13.7 | 27.1 | 7.67 | 0.070 | 0.075 | 2.43 | 3.35 | 3.78 |
| 5.91 | 13.4 | 27.0 | 7.47 | 0.13 | 0.12 | 3.61 | 2.28 | 4.17 |
| 5.95[f] | 14.1 | 27.0 | 7.08 | 0.090 | 0.086 | 4.43 | 3.80 | 2.59 |
| 5.95 | 13.4 | 23.1 | 7.47 | 0.11 | 0.13 | 3.30 | 2.82 | 3.93 |
| 5.97[f] | 14.0 | 27.0 | 7.81 | 0.074 | 0.083 | 3.90 | 3.72 | 2.40 |
| 6.38 | 13.1 | 23.0 | 7.30 | 0.085 | 0.095 | 3.67 | 2.93 | 2.49 |
| 6.87[e] | 13.8 | 27.2 | 7.71 | 0.070 | 0.13 | 2.23 | 3.35 | 3.40 |
| 7.08[f] | 13.9 | 27.0 | 7.76 | 0.074 | 0.072 | 3.33 | 2.93 | 2.35 |
| 7.90 | 13.0 | 23.4 | 7.28 | 0.12 | 0.14 | 2.71 | 3.14 | 3.84 |
| 7.93[f] | 13.0 | 26.7 | 7.45 | 0.068 | 0.11 | 2.39 | 3.66 | 2.54 |
| 7.94 | 14.3 | 22.4 | 7.99 | 0.087 | 0.095 | 2.78 | 2.62 | 2.96 |
| 8.01 | 13.6 | 26.9 | 7.58 | 0.10 | 0.13 | 2.80 | 3.49 | 3.17 |
| 8.21 | 13.0 | 22.0 | 7.28 | 0.083 | 0.090 | 2.66 | 2.60 | 2.60 |
| 8.91 | 13.2 | 22.0 | 7.39 | 0.079 | 0.085 | 2.35 | 2.62 | 2.62 |
| 9.41[f] | 13.2 | 27.1 | 7.39 | 0.063 | 0.16 | 1.76 | 3.48 | 2.64 |
| 9.57 | 13.4 | 27.0 | 7.47 | 0.10 | 0.14 | 2.54 | 3.76 | 2.89 |
| 9.61[f] | 14.9 | 27.0 | 8.32 | 0.075 | 0.079 | 2.61 | 3.03 | 2.40 |
| 10.3 | 14.0 | 21.7 | 7.84 | 0.092 | 0.13 | 2.73 | 3.44 | 2.43 |
| 10.5[e] | 15.2 | 27.2 | 8.49 | 0.072 | 0.069 | 2.37 | 3.37 | 2.36 |
| 10.7[f] | 16.1 | 27.0 | 9.01 | 0.067 | 0.069 | 2.32 | 3.77 | 2.35 |
| 11.3 | 14.2 | 21.2 | 7.91 | 0.080 | 0.081 | 1.78 | 2.44 | 2.96 |
| 11.4 | 13.0 | 23.5 | 7.28 | 0.075 | 0.098 | 2.10 | 2.80 | 2.14 |
| 12.5[e] | 13.5 | 23.8 | 7.55 | 0.092 | 0.080 | 1.29 | 3.53 | 4.06 |

TABLE 3 *(continued)*

| | | | | | | |
|---|---|---|---|---|---|---|
| $T = 10 \pm 0.5$ °C | | | | | | |
| 3.91 | 10.1 | 10.2 | 4.56 | 0.053 | 4.23 | 1.25 |
| 6.54 | 13.5 | 10.2 | 6.09 | 0.059 | 5.59 | 0.84 |
| 9.14 | 13.0 | 10.3 | 5.86 | 0.077 | 3.98 | 0.98 |
| 9.45 | 12.8 | 10.0 | 5.77 | 0.071 | 3.71 | 1.00 |
| 11.3 | 13.5 | 10.5 | 6.09 | 0.057 | 2.56 | 1.03 |
| $T = 1.5 \pm 1.1$ °C | | | | | | |
| 3.62 | 13.5 | 3.3 | 5.50 | 0.042 | 6.63 | 0.78 |
| 4.08 | 13.0 | 2.1 | 5.29 | 0.042 | 4.98 | 0.87 |
| 4.90[f] | 13.7 | 1.0 | 5.57 | 0.036 | 4.88 | 0.67 |
| 5.41 | 15.3 | 2.0 | 6.24 | 0.043 | 5.92 | 0.67 |
| 5.84 | 14.4 | 1.4 | 5.86 | 0.048 | 4.69 | 0.84 |
| 5.94 | 13.7 | 2.2 | 5.58 | 0.049 | 5.45 | 0.69 |
| 7.55 | 12.8 | 2.2 | 5.21 | 0.045 | 3.98 | 0.64 |
| 7.62[e] | 12.9 | 0.0 | 5.25 | 0.040 | 3.34 | 0.66 |
| 8.56[f] | 14.7 | 0.7 | 5.98 | 0.030 | 3.70 | 0.45 |
| 8.89 | 13.5 | 2.5 | 5.50 | 0.041 | 3.64 | 0.57 |
| 9.26 | 12.8 | 2.5 | 5.21 | 0.036 | 3.18 | 0.52 |
| 10.0 | 14.3 | 2.3 | 5.82 | 0.044 | 2.90 | 0.72 |
| 11.2 | 13.4 | 2.3 | 5.46 | 0.033 | 2.32 | 0.57 |
| 11.4 | 15.1 | 0.0 | 6.14 | 0.033 | 2.97 | 0.48 |
| 11.6[e] | 15.7 | 0.0 | 6.40 | 0.024 | 2.09 | 0.51 |
| 11.7[f] | 14.2 | 0.0 | 5.76 | 0.034 | 2.32 | 0.58 |
| 11.9[e] | 11.6 | 0.0 | 4.74 | 0.037 | 2.82 | 0.42 |
| $T = -9.4 \pm 0.3$ °C | | | | | | |
| 3.93 | 13.5 | −9.2 | 5.82 | 0.022 | 7.29 | 0.33 |
| 4.01 | 13.1 | −9.2 | 5.65 | 0.027 | 8.70 | 0.33 |
| 7.20 | 12.6 | −9.1 | 5.44 | 0.027 | 4.93 | 0.31 |
| 9.96 | 13.0 | −9.7 | 5.61 | 0.022 | 2.81 | 0.34 |
| 11.1 | 12.8 | −9.7 | 5.52 | 0.027 | 2.98 | 0.34 |

[a]From initial rate of formation. [b]From eqn. (II). [c]From decay curve. [d]From the steady state value of OClO. [e]With 450 - 640 Torr nitrogen also present. [f]With 600 - 660 Torr oxygen also present.

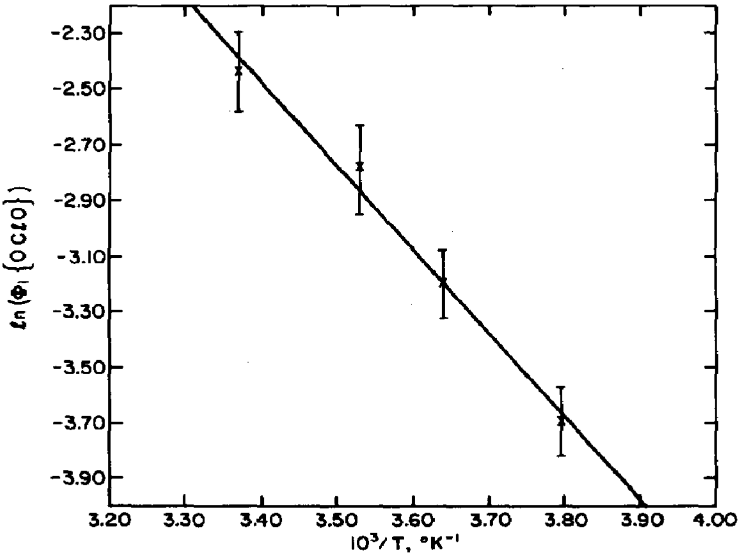


Fig. 2. Arrhenius plot of $\Phi_i$ {OClO} in the photolysis of $Cl_2$–$O_3$ mixtures.

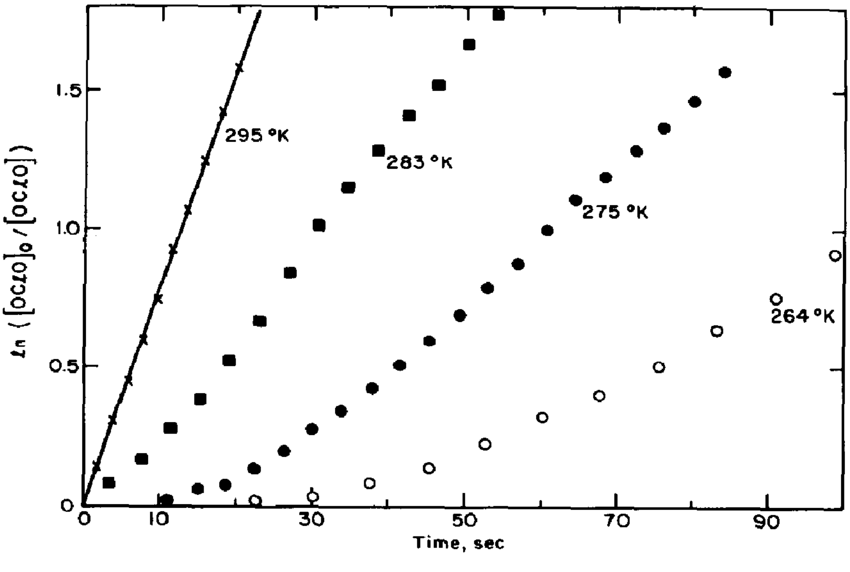


Fig. 3. First order plots of OClO decay in the dark after the photolysis of $Cl_2$–$O_3$ mixtures. The reaction conditions are as follows.

| Temperature (K) | $[O_3]$ (Torr) | $[Cl_2]$ (Torr) |
|---|---|---|
| 296.1 | 8.91 | 13.2 |
| 283.1 | 9.45 | 12.8 |
| 275.5 | 9.26 | 12.8 |
| 264.0 | 7.20 | 12.6 |

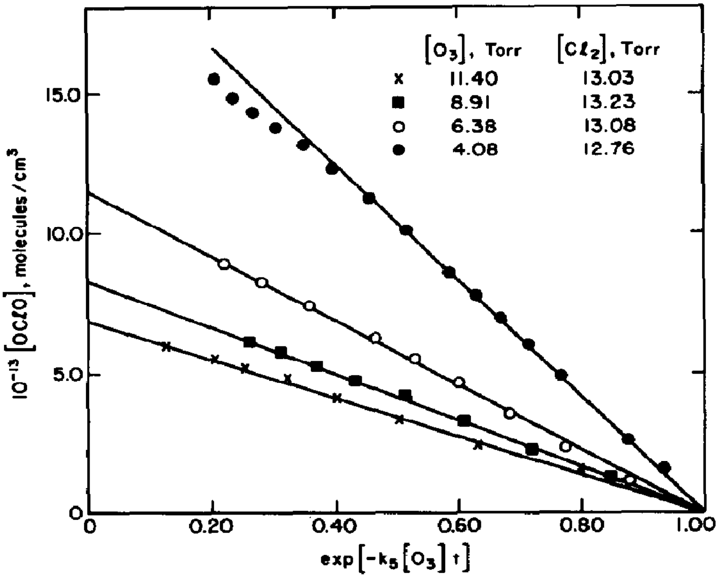


Fig. 4. Plots of [OClO] *vs.* exp ($k_5[O_3]t$) for selected data at 24 ± 3 °C.

and integration gives

$$[OClO]_t = \frac{\Phi_i\{OClO\}I_a}{k_5[O_3]}\,(1 - \exp\{-k_5[O_3]t\}) \qquad \text{(II)}$$

A plot of [OClO] *versus* $\exp\{-k_5[O_3]t\}$ should be linear with a slope and intercept of $\Phi_i\{OClO\}I_a/k_5[O_3]$. Figure 4 shows that the plots at 24 ± 3 °C are reasonably linear as required. Values of $\Phi_i\{OClO\}$ obtained from the slopes of these plots are presented in Tables 3 and 4. They are in good agreement with the values obtained from the initial growth rates. At lower temperatures plots of eqn. (II) are not linear because of $Cl_2O_3$ formation (see Section 4).

The steady state expression for OClO during irradiation is

$$[OClO]_{ss} = \frac{\Phi_i\{OClO\}I_a}{k_5[O_3]} \qquad \text{(III)}$$

Values of $k_5$ computed from eqn. (III) using the observed values of $[OClO]_{ss}$ are also presented in Table 3. At 24 °C these values are in good agreement with those obtained from the decay plots.

### *3.1.3. $Cl_2$ removal and $O_2$ formation quantum yields*

The $Cl_2$ removal quantum yields $-\Phi\{Cl_2\}$ were measured at 296 K for several experiments with $[O_3]_0$ = 15.4 ± 1.6 Torr, $[Cl_2]_0$ = 1.16 ± 0.16 Torr and $I_a$ = (2.82 ± 0.44) × $10^{13}$ photons $cm^{-3}$ $s^{-1}$. To make the measurements, about 30% of the $Cl_2$ was consumed. For these conditions $-\Phi\{Cl_2\}$ = 0.11 ± 0.02 independent of the absence or presence of 650 Torr of nitrogen or oxygen.

TABLE 4

Reaction of OClO with $O_3$

| $[O_3]$ (Torr) | $[OClO]_0$ (mTorr) | Temperature (K) | $10^{19} k_5$ ($cm^3 s^{-1}$) |
|---|---|---|---|
| $T$ = 296.3 ± 1.7 K | | | |
| 4.82 | 54.9 | 297.7 | 2.67 |
| 4.90 | 37.3 | 297.7 | 2.69 |
| 5.45 | 59.7 | 297.6 | 3.02 |
| 5.91 | 43.5 | 297.4 | 2.98 |
| 5.99 | 38.2 | 297.6 | 2.82 |
| 7.39[a] | 40.2 | 295.0 | 3.36 |
| 7.43[a] | 42.2 | 293.4 | 3.12 |
| 8.36 | 42.8 | 293.2 | 3.44 |
| 8.40 | 35.0 | 295.0 | 3.39 |
| 8.71 | 44.1 | 296.5 | 3.48 |
| 11.1 | 65.9 | 297.7 | 3.06 |
| 17.5 | 53.1 | 297.4 | 3.24 |
| 19.2 | 31.1 | 295.1 | 2.79 |
| $T$ = 273.4 ± 1.0 K | | | |
| 2.84 | 161 | 273.5 | 0.73 |
| 4.47 | 88.4 | 275.5 | 0.89 |
| 4.75 | 201.0 | 273.0 | 0.92 |
| 5.41 | 75.1 | 274.5 | 0.73 |
| 5.52 | 40.9 | 273.0 | 0.62 |
| 6.02 | 34.9 | 273.0 | 0.73 |
| 8.48 | 50.3 | 274.0 | 0.92 |
| 8.79 | 43.5 | 273.5 | 0.74 |
| 8.87 | 48.3 | 273.0 | 0.93 |
| 9.49 | 43.5 | 273.3 | 0.94 |
| 9.49 | 43.5 | 273.1 | 0.87 |
| 11.2 | 41.5 | 273.0 | 0.92 |
| 23.8 | 44.2 | 272.8 | 0.94 |
| 29.0 | 41.5 | 273.0 | 0.88 |
| $T$ = 262.0 ± 1.0 K | | | |
| 2.53 | 131.3 | 262.0 | 0.48 |
| 4.40 | 49.05 | 263.0 | 0.48 |
| 4.59 | 153.7 | 262.0 | 0.41 |
| 6.42 | 58.75 | 261.4 | 0.46 |
| 7.70 | 131.3 | 261.7 | 0.45 |

[a]With 100 Torr nitrogen also present.

The ratio of $O_2$ produced to $O_3$ lost was also measured at 20 ± 1 °C for $O_3$ conversions ranging from 78 to 100%. The initial $O_3$ pressures ranged from 5.76 to 12.7 Torr and the initial $Cl_2$ pressures ranged from 6.85 to 25.9 Torr. In all experiments $I_a = 2.25 \times 10^{12}$ photons $cm^{-3}$ $s^{-1}$ per torr of

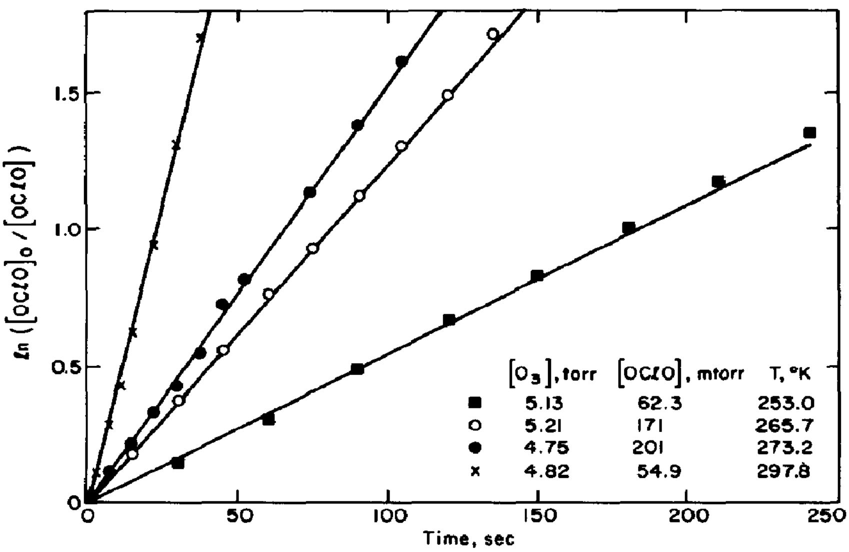


Fig. 5. First order plots of OClO decay in the presence of excess $O_3$ (direct reaction of OClO with $O_3$).

$Cl_2$. The ratio of $O_2$ formed to $O_3$ consumed was about 1.5 in all experiments (1.39 - 1.55) as expected for a catalyzed decomposition of $O_3$. The average value of $\Phi\{O_2\}$ at 20 °C is 8.6 ± 0.3 in the absence of added oxygen or nitrogen. The uncertainties due to pressure measurements by the expansion method are less than 2%.

### *3.2. Kinetics of the OClO + $O_3$ reaction*

The kinetics of the OClO + $O_3$ reaction were studied by direct mixing of OClO with excess $O_3$ (pseudo first order conditions). The OClO decay was observed to be first order in OClO in the presence of excess $O_3$. Typical first order plots at four temperatures are shown in Fig. 5. The rate coefficients $k_5$ obtained from the plots are presented in Table 4. The value of $k_5$ is independent of the $O_3$ pressure; thus the reaction is first order in $O_3$. An Arrhenius plot of $k_5$ is shown in Fig. 6. The best straight line through the three data points gives an Arrhenius expression of $k_5 = 6.1 \times 10^{-13} \exp\{-4308/T\}$ $cm^3\ s^{-1}$. Also shown in Fig. 6 are the data points obtained from the steady state of OClO in the photolysis of $Cl_2$–$O_3$ mixtures. The Arrhenius expression which best fits these data is $1.9 \times 10^{-11} \exp\{-5360/T\}$ $cm^3\ s^{-1}$. The average of the two Arrhenius expressions is $2.3 \times 10^{-12} \exp\{-(4730 \pm 630)/T\}$ $cm^3\ s^{-1}$, and this is the value we recommend.

At room temperature both determinations give essentially the same value for $k_5$ (($3.08 \pm 0.25) \times 10^{-19}$ $cm^3\ s^{-1}$ from direct mixing and ($2.88 \pm 0.59) \times 10^{-19}$ $cm^3\ s^{-1}$ from the steady state value of OClO in the $Cl_2$–$O_3$ photolysis). Furthermore the value obtained in the dark decay of OClO after the photolysis of $Cl_2$–$O_3$ mixtures is ($3.02 \pm 0.49) \times 10^{-19}$ $cm^3\ s^{-1}$ in excellent agreement with the other two values. De More [18] has made

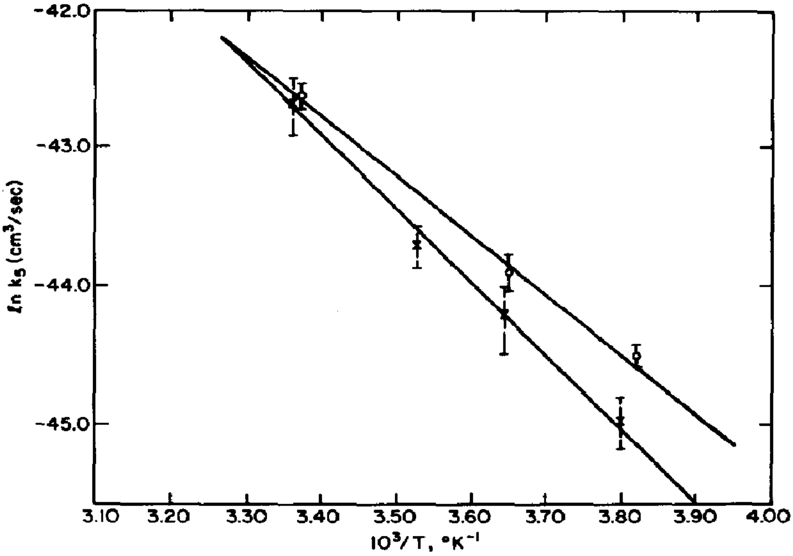


**Fig. 6. Arrhenius plots of $k_5$: ○, from the direct OClO–$O_3$ reaction; ×, from the steady state OClO values during photolysis.**

two independent determinations of $k_5$ at room temperature, both of which give $3.0 \times 10^{-19}$ cm$^3$ s$^{-1}$ in excellent agreement with our three determinations. The value for $k_5$ of $(1.20 \pm 0.15) \times 10^{-19}$ cm$^3$ s$^{-1}$ obtained by Birks *et al.* [14] at 298 K appears to be too low.

## 4. Discussion

The low values of $\Phi_i\{OClO\}$ and $-\Phi\{Cl_2\}$ as well as the ratio of $O_2$ produced to $O_3$ consumed indicate that the photolysis is primarily a photosensitized decomposition of $O_3$. The mechanism of the photolysis can be discussed in terms of a set of reactions which have been shown to be important. There is no doubt that the initial photolysis act is

$$Cl_2 + h\nu\ (366\ \text{nm}) \rightarrow 2Cl \qquad (\text{rate} = I_a)$$

followed by the well-known reaction

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$

where $k_1 = 2.5 \times 10^{-11} \exp(-250/T)$ cm$^3$ s$^{-1}$ [19 - 24].

Now for the sake of argument we can consider two extreme cases: (a) the ClO radicals produced in reaction (1) do not react with $O_3$ under any conditions; (b) the ClO radicals always react with $O_3$. Thus for case (a)

$$2ClO \rightarrow Cl + ClOO \qquad (2a)$$

$$\rightarrow Cl_2 + O_2 \qquad (2b)$$

$$\rightarrow OClO + Cl \qquad (2c)$$

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

and for case (b)

$$ClO + O_3 \rightarrow OClO + O_2 \qquad (4a)$$

$$\rightarrow Cl + 2O_2 \qquad (4b)$$

and in either case (a) or case (b) the subsequent reactions of OClO will be

$$OClO + O_3 \rightarrow \text{sym-}ClO_3 + O_2 \qquad (5a)$$

$$2ClO_3 + O_3 \rightarrow Cl_2O_7 + O_2 \qquad (6)$$

since $Cl_2O_7$ is a product and OClO is an intermediate. Reaction (5) might also give ClO + $2O_2$ as products, but the data of Birks *et al.* [14] are inconsistent with the occurrence of this channel. We ignore this channel since it does not significantly alter the kinetic analysis.

The ClOO radical is unstable and decomposes rapidly at room temperature [12] via reaction (3), but the reaction with $O_3$ cannot be ruled out *a priori* (see later). Reaction (5) is known. Presumably the reaction leads to symmetrical $ClO_3$ initially, but an asymmetrical form cannot be ruled out.

The subsequent fate of $ClO_3$ is not entirely clear. Early workers observed both $Cl_2O_6$ and $Cl_2O_7$ as products of $Cl_2$-photosensitized decomposition of $O_3$ [25]. The relative amounts of the oxides appeared to depend on the experimental conditions. At higher temperatures (about 30 °C) $Cl_2O_7$ is favored, whereas with photosensitization at lower temperatures $Cl_2O_6$ could be observed [25]. It seems likely that under conditions such that $ClO_3$ formation is rapid and the temperature low, $Cl_2O_6$ condensation would be favored which suggests that the reaction of $ClO_3$ with $O_3$ is slow and has an activation energy. Recently, however, Davidson and Williams [11] could detect only $ClO_4^-$ after hydrolysis of the reaction products which indicates that $Cl_2O_7$ was the only product even though they worked under conditions similar to those of the early workers which led to $Cl_2O_6$ formation. In the present work $ClO_3$ formation was not observed by spectroscopic methods ($[ClO_3] < 20$ mTorr), but the formation of $Cl_2O_7$ and the reaction of OClO with $O_3$ requires that $ClO_3$ must have been present as an intermediate.

Mechanisms (a) and (b) are mutually exclusive, because the data show that $-\Phi\{O_3\}$ is independent of $[O_3]$ and $I_a$. If both mechanisms were operating simultaneously $-\Phi\{O_3\}$ would depend on $[O_3]$, because reaction (4) involves $O_3$ but reaction (2) does not, and on $I_a$, because reaction (2) is bimolecular in radicals and reaction (4) is not. Therefore our task is to decide whether mechanism (a) or mechanism (b) is operative.

First let us consider that mechanism (b) is operating. This mechanism predicts that $-\Phi\{O_3\} = \Phi\{O_2\} = 7$, $\Phi\{OClO\} = 2$ and $-\Phi\{Cl_2\} = 1$. The measured $-\Phi\{O_3\}$ is nearly 7, but $\Phi\{O_2\}$ is 50% greater than $-\Phi\{O_3\}$, $\Phi_i\{OClO\} = 0.089 \pm 0.013$ and $-\Phi\{Cl_2\} = 0.11 \pm 0.02$ at 297 K; clearly mechanism (b) is not important and need not be considered any further.

Mechanism (a) leads to the following rate laws:

$$\Phi_i\{OClO\} = \frac{2}{1 + 2k_{2b}/k_{2c}} \quad (IV)$$

$$-\Phi\{O_3\} = \frac{4 + 3k_{2c}/k_2}{2k_{2b}/k_2 + k_{2c}/k_2} \quad (V)$$

$$-\Phi\{Cl_2\} = \Phi_i\{OClO\}/2 \quad (VI)$$

With measured values of $-\Phi\{O_3\} = 5.8$ and $\Phi_i\{OClO\} = 0.089$ at 297 K, the values computed from eqns. (IV) and (V) are $k_{2a}/k_2 = 0.63$, $k_{2b}/k_2 = 0.34$ and $k_{2c}/k_2 = 0.032$. Since $-\Phi\{O_3\}$ is nearly pressure independent these ratios are also pressure independent over the range of pressures employed in this study. The fact that $-\Phi\{Cl_2\} \neq \Phi_i\{OClO\}/2$ is discussed later. $\Phi_i\{OClO\}$ was determined as a function of temperature (Table 4 and Fig. 2); therefore since $\Phi_i\{OClO\}$ is very nearly $k_{2c}/k_{2b}$, the Arrhenius expression for $k_{2c}/k_{2b}$ is the same as for $\Phi_i\{OClO\}$ or $k_{2c}/k_{2b} = 2.5 \times 10^3 \exp\{-(3025 \pm 625)/T\}$.

The ratio of $k_2/k_{2b}$ is obtained from the study of the temperature dependence of $-\Phi\{O_3\}$. At low temperatures $k_2/k_{2b} \approx 0.5(-\Phi\{O_3\})$. The values of $k_2/k_{2b}$ are 1.99 at 11 °C, 1.45 at 0 °C and 1.0 at −21 °C. This implies that reaction (2) proceeds predominantly through channel (2b) at low temperatures.

The large value of the pre-exponential factor $A_{2c}/A_{2b}$ suggests that reaction channels (2b) and (2c) proceed through very different transition states. It is reasonable to assume that reaction (2b) involves a four-center transition state whereas reaction (2c) is an atom abstraction reaction with a linear transition state.

The reactions of ClO with itself have been studied recently in some detail, but there is still controversy about the relative importance of the three channels at higher pressures. Basco and Dogra [26, 27] have interpreted their flash photolysis data at high pressures (above 75 Torr argon) in terms of reaction (2b) exclusively. Johnston *et al.* [28], working at low light intensities, found a pressure effect on ClO disproportionation and proposed the reaction

$$2ClO + M \rightarrow Cl_2 + O_2 + M$$

In a more recent paper Wu and Johnston [29] confirmed the effect of total pressure on their results but now feel that the pressure effect may actually be associated with other reactions in their system or that at low light intensity the mechanism of ClO disproportionation differs from that at high light intensity.

At low pressures, however, Clyne and coworkers [12, 30, 31] have conclusively shown that reaction (2a) is dominant and in their most recent paper [12] have shown that the distribution at low pressures is as follows: reaction (2a), 95%; reaction (2c), 5%. They have also done computer modelling of the results of Basco and Dogra and find that their results can be re-interpreted in terms of reaction (2a) as the dominant channel contrary to the interpretation of Basco and Dogra.

Recently Clyne and Watson [32] have re-evaluated all the data in terms of reactions (2a) and (2c) only and recommend the expressions

$$k_{2a} = 1.2 \times 10^{-12} \exp\left(\frac{-9.8 \text{ kJ mol}^{-1}}{RT}\right) \text{cm}^3 \text{ s}^{-1}$$

$$k_{2c} = 2.1 \times 10^{-12} \exp\left(\frac{-18.3 \text{ kJ mol}^{-1}}{RT}\right) \text{cm}^3 \text{ s}^{-1}$$

although the data do not exclude reaction (2b) occurring to some extent and $k_{2a}$ may really represent $k_{2a} + k_{2b}$.

It is not clear how all these results can be brought into harmony. However, it seems likely to us that reactions (2a) and (2b) are important under all pressure conditions. The data of Clyne *et al.* [12] are not inconsistent with a contribution from both reactions (2a) and (2b), and in fact in our system reaction (2b) must be the major termination step. It is possible that Cl atom formation may have been overlooked in the work of Basco and Dogra [26, 27].

The upper limit for $k_4$ may be computed by requiring that reaction (4) be negligible compared with reaction (2) which has a room temperature rate coefficient of $2.3 \times 10^{-14}$ cm$^3$ s$^{-1}$ according to Clyne and Watson [32] and of $4.4 \times 10^{-14}$ cm$^3$ s$^{-1}$ according to Watson [33]. Even at our highest value of $[O_3]/I_a^{1/2} = 1.6 \times 10^{11}$ (s cm$^{-3}$)$^{1/2}$ there is no variation of $\Phi_i\{OClO\}$. For this to be true, $k_4 < (k_2/k_{2b}^{1/2})(I_a^{1/2}/[O_3])$ or $k_4$ must be less than $1 \times 10^{-18}$ cm$^3$ s$^{-1}$, a conclusion reached by Lin *et al.* [13]. The low value of $k_4$ is also consistent with the upper limit of about $5 \times 10^{-15}$ cm$^3$ s$^{-1}$ obtained by Clyne *et al.* [12] and $5 \times 10^{-14}$ cm$^3$ s$^{-1}$ obtained by Birks *et al.* [14]. However, Clyne *et al.*, using a discharge flow technique, found that in the presence of $O_3$ more OClO was produced than could be explained by reaction (2c) alone and considered it probable that their upper limit was the actual rate coefficient.

At temperatures below 297 K the OClO decay profiles in the dark show an induction period (Fig. 1) and the integrated growth curves (eqn. (II)) are not linear which indicates that the mechanism thus far outlined is not complete at lower temperatures. These observations can be interpreted in terms of the equilibrium

$$ClO + OClO + M \rightleftarrows Cl_2O_3 + M \qquad (7, -7)$$

The $Cl_2O_3$ acts as a reservoir of OClO leading to the slow initial rate of OClO depletion upon the termination of light.

As a test of this hypothesis, profiles for OClO were calculated for all temperatures by numerically integrating the rate equations for ClO and $Cl_2O_3$. The only assumption made in this computation was that Cl has its steady state value. An adaptive pattern search routine [34] was used to integrate the rate equations. This algorithm varies the rate constants $k_7$, $k_{-7}$, $k_{2c}$ and $k_5$ such that the mean square error between the calculated and the experimental values of OClO is minimized. The OClO growth is controlled initially by the parameter $k_{2c}/k_{2b}$ and the decay is controlled by $k_5$. However, absolute values for $k_{2c}$ and $k_{2b}$ are needed for the computation. These were obtained from the values of $\Phi_i\{OClO\}$ and $-\Phi\{O_3\}$ and the literature value for $k_2$ ($4.4 \times 10^{-14}$ cm$^3$ s$^{-1}$) [33].

In order to test the validity of this integration method room temperature profiles for OClO were also fitted, and in this case the values $k_7$ and $k_{-7}$ used were zero (which is equivalent to having the equilibrium shifted completely to dissociation).

At 275 K and 264 K, $k_7$ was varied from $1.00 \times 10^{-11}$ to $1.00 \times 10^{-16}$ cm$^3$ s$^{-1}$ and $k_{-7}$ from 10.00 to 0.01 s$^{-1}$. $k_{2c}$ was allowed to vary within ±20% of the calculated value from $\Phi_i\{OClO\}$, $-\Phi\{O_3\}$ and $k_2$. $k_5$ was varied within the range of values obtained from the steady state of OClO and from the direct mixing experiments. Typical computer profiles together with the experimental profiles are shown in Fig. 1. The overall errors of the computed profiles were within ± 20% of the experimental profiles. The average value for $k_7$ [M] is $(1.2 \pm 0.4) \times 10^{-15}$ cm$^3$ s$^{-1}$ at 275.5 K and $(5.5 \pm 1.5) \times 10^{-16}$ cm$^{-3}$ s$^{-1}$ at 264 K. The average value for $k_{-7}$ [M] is $(0.19 \pm 0.08)$ s$^{-1}$ at 275.5 K and $(0.08 \pm 0.03)$ s$^{-1}$ at 264 K. The results are the average of six runs at 275.5 K and four runs at 264 K. At both temperatures the average pressures for the runs used to determine $k_7$[M] and $k_{-7}$[M] were 20.2 ± 3.2 Torr. When converted to third order and second order rate coefficients we obtain $k_7 = 1.70 \times 10^{-33}$ and $1.15 \times 10^{-33}$ cm$^6$ s$^{-1}$ at 275.5 and 264 K respectively, and $k_{-7} = 2.68 \times 10^{-19}$ and $1.08 \times 10^{-19}$ cm$^3$ s$^{-1}$ at 275.5 and 264 K respectively.

We estimate that these values are accurate to within a factor of 2. Of course, at 296 K $Cl_2O_3$ formation is not important because of the rapid reverse reaction, and below 264 K the reactions are too slow to obtain meaningful results.

The values of $k_7$ show a slight positive activation energy, although this may just reflect the error in the measurements. The rate coefficients for $k_{-7}$ are consistent with a bond dissociation enthalpy of about 12 kcal mol$^{-1}$ for $Cl_2O_3$.

So far we have neglected a discussion of $-\Phi\{Cl_2\}$ in interpreting the data. Mass balance considerations require that in the initial part of the experiment $-\Phi\{Cl_2\} = \Phi_i\{OClO\}/2$. In our experiments $-\Phi\{Cl_2\}$ was measured, by necessity, for large conversions and it was found to be much greater than $\Phi_i\{OClO\}/2$. Possibly secondary reactions may be involved in which the higher oxides of chlorine ($ClO_3$, $ClO_4$ and possibly $Cl_2O_5$ or $Cl_2O_6$) react either with $Cl_2$ or ClO to produce $Cl_2O_7$. This may be a surface reaction. The details of such a reaction cannot be determined from our data.

If the reaction removing additional $Cl_2$ does not involve OClO as an intermediate, then the OClO concentration is not affected by it. However, if additional OClO is produced, as seems likely, then the steady state concentration of OClO should show an accelerated rise as the reaction proceeds toward completion. We attempted to monitor [OClO] for long conversions, but the uncertainty in the measurements due to instrument drift made it difficult to determine if [OClO] increased more than would be expected owing to the depletion of $O_3$. ($[OClO]_{ss}$ is inversely proportional to $[O_3]$ even if OClO is not an intermediate in the secondary reaction.)

Finally the effect of $O_2$ on $-\Phi\{O_3\}$ must be considered. Our results indicate that at room temperature $-\Phi\{O_3\}$ drops from 5.8 to 3.7 at 2 - 5 Torr $O_3$ and high intensity, to 4.7 at 400 mTorr $O_3$ at low intensity and 1.7 as $[O_3]$ is reduced to 7 mTorr. These results are qualitatively in agreement with the early work of Norrish and Neville [10], and the fall-off from 5.8 to 4.7 has been observed by Lin *et al.* [13]. Thus there remains little doubt that the effect is real.

However, the interpretation of this result poses some difficulties and no definitive answer can be given. One possibility is the sequence

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

$$ClOO + O_3 \rightarrow \text{asym-}ClO_3 + O_2 \qquad (8)$$

Such a scheme requires that $-\Phi\{Cl_2\}$ be enhanced in the presence of $O_2$, which is not observed. Perhaps asym-$ClO_3$ reverts to $Cl_2$. Another possibility is

$$ClO + O_2 + M \rightarrow \text{asym-}ClO_3 + M \qquad (9)$$

or

$$ClO^* + O_2 + M \rightarrow \text{asym-}ClO_3 + M \qquad (10)$$

where the asterisk refers to vibrational excitation. This scheme also requires that $-\Phi\{Cl_2\}$ increases in the presence of $O_2$, unless asym-$ClO_3$ reverts to $Cl_2$. Both of the above schemes would lead to a lower value of $\Phi_i\{OClO\}$ in the presence of $O_2$, which may in fact be the case (see Table 4). Numerous mundane possibilities exist (wall effects), a discussion of which would be purely speculative and serve no useful purpose. Our results also show that at low $[O_3]$ (less than 100 mTorr) $-\Phi\{O_3\}$ approaches 2 in the presence of $O_2$. It is possible that the $O_2$ contains a minute quantity of impurity which at low $[O_3]$ competes for the Cl atoms, but no evidence for this possibility is available and any further speculation is not warranted.

## 5. Atmospheric implications

The values of the rate coefficients for the reaction of ClO and OClO with $O_3$ of not more than $1 \times 10^{-18}$ and $3 \times 10^{-19}$ $cm^3$ $s^{-1}$ (at 296 K and less at lower temperatures) respectively are too low to make these reactions of any significance in the earth's atmosphere.

The inhibiting effect of $O_2$ on the $Cl_2$-photosensitized decomposition of $O_3$ has not been explained. The possibility that ClO might react with $O_2$

or ClOO with $O_3$ could be of potential atmospheric significance and a further understanding of this effect is desirable.

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