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The photochemical decomposition of gaseous OClO at 436 nm: Dependence of products distribution on total pressure

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Abstract

A systematic experimental study of the photochemical decomposition of 5–80 Torr gaseous OClO at 293 and 303 K has been performed. The photolysis was also investigated in the presence of the added inert gases He, Ar, N_2, O_2, CO_2 and SF_6 at pressures ranging from 10 to 600 Torr. The final products Cl_2O_4, Cl_2O_6, Cl_2 and O_2 are formed. The amount of Cl_2O_4 and Cl_2O_6 was determined by IR and UV spectrophotometry, respectively. Both products reach a limit of about 30% of the total yield. Only very small amounts of $ClClO_2$ have been detected. The quantum yields for Cl_2O_4 and Cl_2O_6 formation satisfy the condition $\Phi(Cl_2O_4) + \Phi(Cl_2O_6) \cong 1$ throughout. In the absence of an inert gas $\Phi(Cl_2O_4)$ decreases from a value close to 1 to about 0.5 as OClO pressure is decreased, indicating the formation of Cl_2O_4 by the reaction $ClO_3 + ClO \rightarrow Cl_2O_4$. For about 5 Torr OClO mean pressure and in the presence of an inert gas, $\Phi(Cl_2O_4)$ increases as total pressure is increased reaching a value close to 1 for 300 Torr of N_2 or 50 Torr of SF_6. At the higher inert gas pressures $\Phi(Cl_2O_4)$ slightly decreases when OClO is increased. This result is attributed to the interplay established between reactive and collisional deactivation process in the excited radical intermediate $Cl_2O_5{}^*$ generated in the process $ClO_3{}^* + OClO \rightarrow Cl_2O_5{}^* \rightarrow ClO_4 + ClO$. The generally accepted reaction for the formation of Cl_2O_6, namely $2ClO_3 \rightarrow Cl_2O_6$, can be ruled out and a complicated mechanism is needed to account for the experimental observations.

Keywords: Chlorine oxides photochemistry; Chlorine dioxide; Chlorine perchlorate; Dichlorine hexoxide

1. Introduction

The photolysis of chlorine dioxide has been studied since 1843 when Millon [1] obtained a red liquid (Cl_2O_6) by exposure of OClO to the sunlight. Later on, in 1923, Bowen [2] obtained the same results using blue-violet light. Booth and Bowen [3] observed that by continued exposure to light, the red liquid was transformed to colorless dichlorine heptoxide (Cl_2O_7), while Bodenstein and Schumacher [4] gave a quantum yield of 0.5 for the Cl_2O_6 formation and proposed a mechanism for the reaction. A lustrum later, Spinks and Porter [5] studied the photolysis of gaseous dry OClO at 366 and 436 nm. They found that a small extent of Cl_2O_6 formation accompanies a large OClO decomposition. More recently, in 1979 we have re-examined the title reaction and it was found that another compound, that is, Cl_2O_4 (chlorine perchlorate, $ClOClO_3$) was also produced in an appreciable yield during this process [6–9]. In the case of preparative purposes high pressures of the reactant OClO were used: 6 Torr with 400 Torr of O_2 added [6]; ~30 Torr of OClO and 700 Torr of N_2 as a buffer gas added at room temperature [7,8]; 100 Torr of OClO at 303 K with no buffer gas added [9]. For kinetic purposes, Zabel [10] uses OClO initial pressure of the order of 0.1 to 0.01 Torr and varying pressures (~1–760 Torr) of buffer gas (O_2 or N_2) at 249 and 300 K.

In 1980 we began the systematical study of the OClO photochemistry by varying widely the initial pressures of OClO and several buffer gases. From the rates of the reactant decomposition and of the reaction products (Cl_2O_4 and Cl_2O_6) formation, a satisfactory mechanism for the reaction may be given, in conjunction with the great development of chlorine oxides chemistry and theoretical studies appeared in last years.

During the preparation of this manuscript a paper by Wayne and co-workers [11] appeared, in which by applying a modern technique practically all previous works on Cl_2O_4 and Cl_2O_6, [9,12,13] are checked. In this last paper it was pointed out

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that Cl_2O_4 and Cl_2O_6 are formed in the photolysis of OClO at 436 nm. However, these authors assert that they 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. With the purpose of clearing this apparent discrepancy enough spectroscopic and chemical evidence will be presented here.

2. Experimental

The reaction was studied by applying the continuous photolysis method. The 436-nm line from a high-pressure mercury arc lamp (HBO 200 W) was isolated by means of a Bausch & Lomb grating monochromator ($\Delta\lambda = 19$ nm). Most of the experiments were performed in a cylindrical quartz cell (5 cm long, 5 cm outer diameter) connected through a capillary tube to a conventional apparatus for static gas-kinetics studies; a U-trap (10 cm total length, 0.4 cm internal diameter) was inserted in this tube. The cell was conveniently adapted in a thermostatic bath as to leave both front windows free to receive the pertinent radiation. Many experiments were performed in a thermostatic portable quartz cell, 3.0 cm long and 4.0 cm outer diameter, which could be joined to the manometer and vacuum line [12]. All the pressure measurements were performed at constant volume and temperature.

A double-beam photometer array, similar to that used in Ref. [14], was employed for OClO photometric determinations. A chopper composed of dark and polished sectors was used to split the light into a sample and a reference beam, which were focused onto an RCA 1P28 phototube by means of mirrors and lenses. The phototube was protected by BG 12 and GG 15 glass filters (Schott & Gen.). The optical signals proportional to the energy transmitted by the sample and to the emitted by the source, were converted into electrical signals and transferred via an amplifier circuit to a recorder. Calibration of the whole system was achieved by recording the relative intensity of both beams, when the reaction cell was evacuated and when it was filled with a known concentration of OClO. The light beam was attenuated by inserting a VG 9 glass filter (Schott & Gen.) at the monochromator outlet with the purpose of minimizing the OClO photolysis during the photometric determination of this substance. The mean absorption cross-section of gaseous OClO was carefully determined at that photolysis selected wavelength 436 ± 9.5 nm. The value obtained at 303 K by varying the OClO pressure (5–20 Torr) was $(1.9 \pm 0.2) \times 10^{-19}$ cm^2 molecule^{-1}. The intensity of the light of photolysis was measured periodically by means of the potassium ferrioxalate actinometer [15]. To this end, a 1 cm optical path length quartz cell was placed before the entrance window of the reaction cell.

After a given photolysis time, the residual OClO and the formed Cl_2O_4 were determined by IR spectrophotometry employing a PerkinElmer 325 Infrared spectrophotometer. The samples were transferred through the U-trap cooled at 233 K to retain Cl_2O_6, to a Pyrex glass cuvette with adapted AgCl windows. Absorbance measurements at 1118 cm^{-1} for OClO, and at 652, 1041 and 1282 cm^{-1} for Cl_2O_4 were performed. The absorption cross-sections for Cl_2O_4 at 652, 1041 and 1282 cm^{-1}, namely 1.3×10^{-18}, 7.9×10^{-19} and 1.8×10^{-18} cm^2 molecule^{-1} were calculated from the spectrum presented in Fig. 1 of Ref. [16]. Calibrated IR spectra for OClO at 1118 cm^{-1} were performed in this laboratory yielding a product an absorption cross-section of 2.8×10^{-19} cm^2 molecule^{-1}.

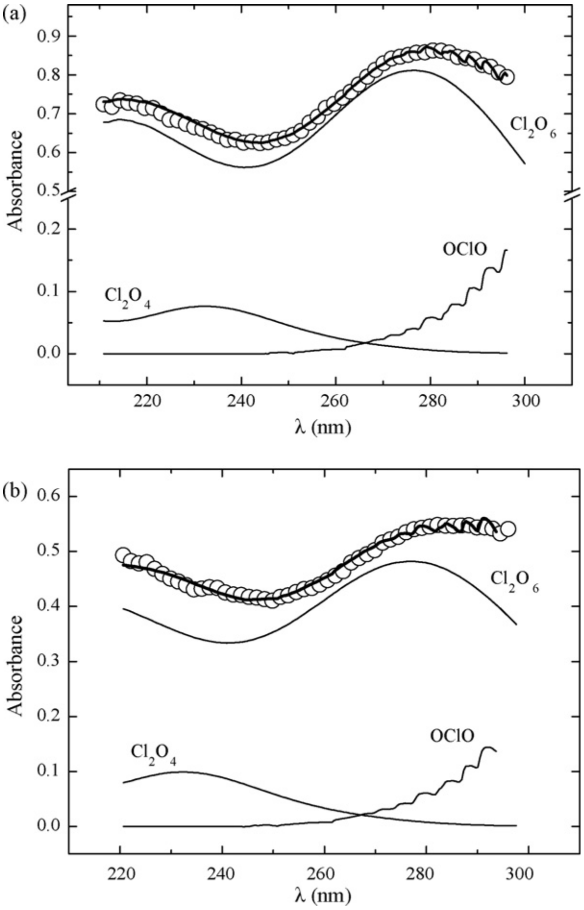

Fig. 1. (a) Total absorption after 27 min photolysis of 21.9 Torr of OClO at 303 K. (◯) Experimental results, (—) calculated absorption, 1.28 Torr Cl_2O_6, 2.0 Torr Cl_2O_4 and 4.0 Torr OClO. (b) Total absorption after the following 15 min without illumination. (◯) Experimental results, (—) calculated absorption, 0.76 Torr Cl_2O_6, 2.6 Torr Cl_2O_4 and 4.0 Torr OClO.

In many other experiments performed employing the thermostatic portable quartz cell ($l = 3.0$ cm), the amount of Cl_2O_6 formed and the residual OClO were determined by UV–Vis spectrophotometry on a Cary 14 Spectrophotometer (mean resolution $\Delta\lambda = 0.1$ nm). The absorbances at 433 and 446 nm, at which Cl_2O_6 and Cl_2O_4 do not absorb, were recorded in order to determine OClO. On the other hand the absorbances at 234 and 280 nm allowed Cl_2O_6 determination. Assuming absorbance additivity of the components of the mixture, the contribution of OClO was subtracted from the total absorbance at 280 nm. The absorbances A_{234} at 234 nm and A_{280} at 280 nm lead to a set of two equations,

$$[Cl_2O_6] = (1.74A_{280} - 0.102A_{234})/RT$$

$$[Cl_2O_4] = (-18.3A_{280} + 26.4A_{234})/RT,$$

where R corresponds to the gas constant and T to the temperature, from which the concentrations of Cl_2O_6 and of Cl_2O_4 were obtained. Absorption cross-section values of 1.05×10^{-17} and 1.49×10^{-17} cm^2 molecule^{-1} determined previously for Cl_2O_6 at 234 and 280 nm were employed [11,13]. Calibrated OClO spectra at 446, 433 and 280 nm lead to the values 5.93×10^{-19}, 1.34×10^{-18} and 3.68×10^{-19} cm^2 molecule^{-1} at 293 K. For Cl_2O_4 absorption cross-section values of 9.5×10^{-19} cm^2 molecule^{-1} at 234 nm and 5.8×10^{-20} cm^2 molecule^{-1} at 280 nm were employed [9].

Due to the fact that analog output type spectrophotometers were employed in the present experiments, total absorbances at just a few selected wavelengths were recorded instead of running the deconvolutions on a properly multiplexed full spectrum. For this reason numerous experiments were performed. However just about three hundreds of the total are presented here.

Chlorine dioxide was prepared, purified and stored as previously described [13].

High quality commercial helium, nitrogen, oxygen and argon were passed through cold traps at 90 K and stored in Pyrex glass bulbs.

Commercial carbon dioxide and sulfur hexafluoride were purified through trap-to-trap low temperature sublimation and stored in a trap at liquid air temperature.

3. Results and discussion

Under the present experimental conditions, the oxides Cl_2O_4 and Cl_2O_6 are the main products of the reaction together with Cl_2 and O_2. The experiments were carried out at 293 and 303 K, constrained by the low vapor pressure of Cl_2O_6 and the instability of both oxides [9,13].

It is important to make clear a controversial matter that rises in the photolysis of OClO. The formation of chloryl chloride ($ClClO_2$) has been observed in advantage to Cl_2O_6 in time resolved experiments [11]. However, in the conditions of the present experiments the conclusion turns out to be the opposite.

Even though the procedure described in the experimental section was employed to determine the amount of OClO, Cl_2O_4 and Cl_2O_6, the measured total absorption was recorded in two exploratory experiments at 303 K. Figs. 1a, 1b, 2a and 2b show the results for different experimental conditions together with the calculated total absorbance assuming additivity of the absorbances of the components of the reaction mixture obtained from the respective absorption cross-sections [11]. For the sake of clarity only a few points have been picked out from the continuous record of the spectrophotometer.

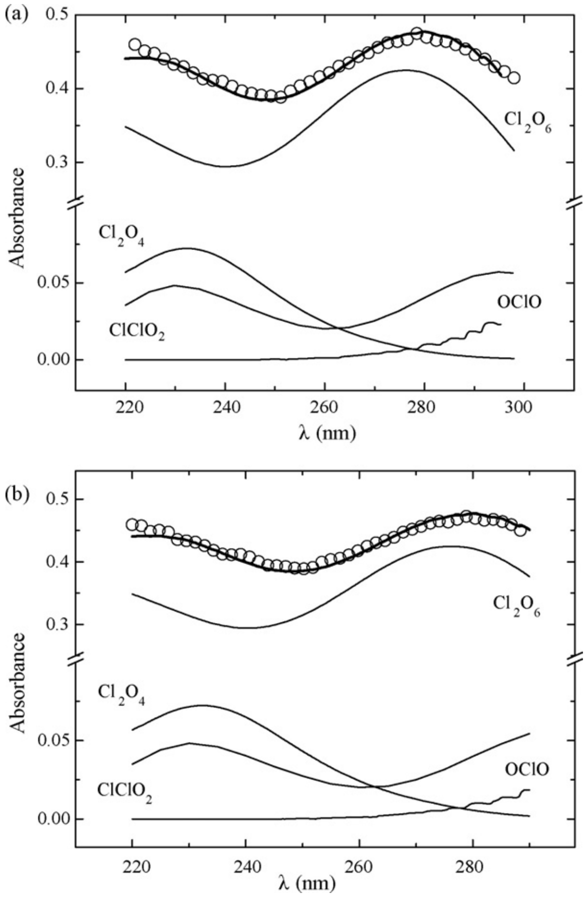

Fig. 2. (a) Total absorption after 27 min photolysis of 17.5 Torr of OClO in the presence of 329 Torr of N_2 at 303 K. (○) Experimental results, (—) calculated absorption, 0.67 Torr Cl_2O_6, 1.9 Torr Cl_2O_4, 0.7 Torr OClO and 0.09 Torr $ClClO_2$. (b) Total absorption after the following 15 min without illumination. (○) Experimental results, (—) calculated absorption, 0.41 Torr Cl_2O_6, 2.2 Torr Cl_2O_4, 0.8 Torr OClO and 0.07 Torr $ClClO_2$.

Fig. 1a shows the resulting total absorption after 27 min photolysis of 21.9 Torr of OClO at 303 K, and Fig. 1b shows the resulting total absorption after the following 15 min without illumination, in which the amount of Cl_2O_6 decreases due to thermal decomposition at 303 K, while Cl_2O_4 increases according to $Cl_2O_6 \rightarrow Cl_2O_4 + O_2$ [13].

Table 1
$\Phi(Cl_2O_4)$ at 293 K calculated from IR and UV spectrophotometric determinations of Cl_2O_4

$P(OClO)_I$ (Torr)	Time (min)	I_0 (Torr min^{-1})	l (cm)	f_{abs}	$P(Cl_2O_4)_{IR}$ (Torr)	$P(Cl_2O_4)_{UV}$ (Torr)	$\Phi(Cl_2O_4)$
4.8	20	0.366	5.0	0.092	0.31	–	0.46
8.2	20	0.366	5.0	0.175	0.61	–	0.48
12.6	20	0.200	5.0	0.294	0.76	–	0.65
19.8	15	0.411	5.0	0.434	1.90	–	0.71
36.0	20	0.200	5.0	0.645	2.09	–	0.81
9.10	10	0.700	3.0	0.119	–	0.65	0.78
18.30	8	1.110	3.0	0.224	–	1.78	0.89
38.7	7	0.650	3.0	0.474	–	1.53	0.71

It is evident that the spectrum presents a maximum at about 280 nm corresponding to the dominant contribution of Cl_2O_6. Chloryl chloride strongly absorbs with two maxima at 230 and 296 nm [17,18]. Both Fig. 1(a) and (b) make clear that $ClClO_2$ does not contribute to the final spectra. The reasons are: (1) the maximum of the continuum spectrum is near 280 nm [13] not at 296 nm as expected for $ClClO_2$ [17]; (2) the rate of thermal decomposition of both species differs absolutely, the time elapsed to decompose Cl_2O_6 from 1.28 to 0.76 Torr is about 15 min, in fair agreement with our determined first-order kinetics ($Cl_2O_6 \rightarrow Cl_2O_4 + O_2$) [13], while for the second-order thermal decomposition for $ClClO_2$ ($2ClClO_2 \rightarrow Cl_2 + 2OClO$ [17]) the time required would be less than 30 s; (3) the amount of Cl_2O_6 decomposed agrees fairly well with the increase of Cl_2O_4 observed [13].

A second exploratory experiment in which 17.5 Torr of OClO were photolysed in the presence of 329 Torr of the inert gas N_2 along 27 min at 303 K was performed. In these conditions, a small amount of $ClClO_2$ is observed besides of Cl_2O_4 and Cl_2O_6 as shown in Fig. 2a. On the other hand, Fig. 2b shows the resulting total absorption after the following 15 min without illumination. In this case, Cl_2O_6 absorption decreases while that of Cl_2O_4 increases, and a decrease in $ClClO_2$ absorption is observed.

As shown in Table 1, the quantum yield for Cl_2O_4 formation, $\Phi(Cl_2O_4)$, calculated, as detailed below, from the amount of Cl_2O_4 determined by UV spectrophotometry at 234 nm in experiments at 293 K, agrees with the results of IR determinations. Therefore, as ratio $\sigma(ClClO_2)/\sigma(Cl_2O_4) \approx 13$ at 234 nm, the presence of even small amounts of $ClClO_2$ would mislead to higher values for $\Phi(Cl_2O_4)$, we conclude that $ClClO_2$ does not contribute significantly to the total absorption of the final products.

However, the determination of $\Phi(Cl_2O_4)$ from spectroscopic data for Cl_2O_4 UV absorption is greatly altered by the presence of Cl_2O_6. In fact, Cl_2O_6 absorption coefficient is eleven times larger than that for of Cl_2O_4 at the maximum ($\lambda = 234$ nm) as shown in Fig. 1a. Therefore IR spectroscopic data for Cl_2O_4 were preferred.

The amount of formed O_2, Cl_2 (both separated by fractional evaporation at 90 and 163 K, respectively), Cl_2O_6 (residue at 233 K), Cl_2O_4 and the OClO consumed (both determined by IR spectrophotometry), are listed in Table 2 for a series of experiments at 303 K. These results are in agreement with the reaction stochiometries: $OClO \rightarrow (1/2)Cl_2 + O_2$, $2OClO \rightarrow Cl_2O_4$ and $3OClO \rightarrow Cl_2O_6 + (1/2)Cl_2$. The extent of conversion may be calculated for the results presented in the tables in each case, and had to be large enough to produce detectable amounts of the products. As mentioned above, the main secondary reaction is the thermal decomposition of Cl_2O_6, which increases Cl_2O_4. However, in view that the amount of Cl_2O_6 and Cl_2O_4 formed are low enough, the contribution of the thermal decomposition of Cl_2O_6 [13] in the final results falls within the quoted experimental error.

The quantum yields for formation of Cl_2O_4, $\Phi(Cl_2O_4) = P(Cl_2O_4)/(I_{abs}\Delta t)$, and of Cl_2O_6, $\Phi(Cl_2O_6) = P(Cl_2O_6)/(I_{abs}\Delta t)$, relative to the light absorbed by OClO, were taken as a measure

Table 2
Products distribution, OClO consumption, $\Phi(Cl_2O_4)$ and $\Phi(Cl_2O_6)$ at 303 K for OClO pure, in the presence of Ar, and of added O_2

$P(OClO)_I$ (Torr)	$P(O_2)_I$ (Torr)	Time (min)	I_0 (Torr min^{-1})	P_{final} (Torr)	$P(OClO)_f$ (Torr)	$\Delta P(OClO)$ (Torr)	f_{abs}	$P(Cl_2O_4)_{IR}$ (Torr)	$\Phi(Cl_2O_4)$	$\Delta P(O_2)$ (Torr)	$P(Cl_2)$ (Torr)	$P(Cl_2O_6)$ (Torr)	$\Phi(Cl_2O_6)$	$\Delta P(OClO)_{calc}$ (Torr)
11.8	–	15	0.277	11.9	6.9	4.8	0.248	0.43	0.42	–	–	0.5	0.5	–
15.6	–	15	0.402	15.9	7.1	8.5	0.288	1.1	0.63	5.1	3.0	–	–	–
16.2[a]	–	20	0.371	459.3	4.3	11.9	0.263	1.86	0.95	7.9	4.0	<0.2	<0.1	~12.2
16.4[b]	–	20	0.371	462.8	3.8	12.6	0.261	1.89	0.96	7.7	4.1	<0.2	<0.1	~12.1
15.5	431.1	15	0.417	446.0	8.6	6.9	0.303	1.8	0.95	3.9	2.0	<0.2	<0.1	~8.1
31.5	393.4	21	0.417	422.4	14.7	16.8	0.499	4.5	1.02	6.6	3.8	–	–	15.6
60.0	305.1	20	0.424	360.9	–	–	(0.78)[c]	–	–	6.4	3.7	0.8	(0.12)	–
61.9	300.7	20	0.427	358.6	41.9	20.0	0.783	5.2	0.78	–	–	–	–	–
37.5	326.1	35	0.207	361.1	23.2	14.3	0.596	4.3	1.00	–	–	0.5	0.12	–

[a] In the presence of 441.6 Torr of Ar.
[b] In the presence of 445.0 Torr of Ar.
[c] f_{abs} from the experiment in the next row.

of the respective rates of formation. Here P denotes pressure measured at constant volume and temperature, Δt is the photolysis time, I_{abs} denotes the intensity of the light absorbed by OClO, calculated as $I_{\mathrm{abs}} = f_{\mathrm{abs}} I_0$, where I_0 is the measured light intensity at 436 nm, and f_{abs} the fraction of absorbed light by OClO. f_{abs} was calculated from the Lambert–Beer law with the mean value $P(\mathrm{OClO})_{\mathrm{m}} = [P(\mathrm{OClO})_{\mathrm{initial}} + P(\mathrm{OClO})_{\mathrm{final}}]/2$, the optical path length of the respective cell and the absorption coefficient measured at 436 nm. As the amount of reaction products Cl_2O_4, Cl_2O_6 and Cl_2 is small and these substances show a negligible light absorption at 436 nm [9,13,19] no corrections were made on f_{abs}.

Numerous experiments were performed in which 5–70 Torr pure OClO were irradiated at 293 and 303 K until 15–60% of OClO was consumed mostly for up to 30 min. In these conditions, Cl_2O_4 and Cl_2O_6 are the only chlorine oxides observed among the reaction products.

The analysis of the reaction mixture after photolysis was made applying two techniques.

First, the Cl_2O_6 formed was retained in the U-trap cooled at 233 K. Then, in some experiments the gaseous mixture of the reaction vessel was allowed to expand into the IR cell until the pressure was equilibrated. In other experiments, 200 Torr of inert gas (He, Ar or O_2) were introduced in the reaction cell before the expansion. Both techniques led to the same results represented in Fig. 3 at 293 K and at 303 K. The quantum yield for formation of Cl_2O_4 strongly decreases from a value close to one as OClO pressure decreases in the absence of added gas as shown in Fig. 3, and remains practically independent of the temperature taking the value $\Phi(Cl_2O_4) = 0.48 \pm 0.07$ at $P(\mathrm{OClO})_{\mathrm{m}} = 5.0 \pm 0.7$ Torr. At high pressure of OClO, that is for $P(\mathrm{OClO})_{\mathrm{m}} = 38 \pm 9$ Torr, it results $\Phi(Cl_2O_4) = 0.81 \pm 0.05$ at both temperatures. The error limits of the quantum yield correspond to one standard deviation.

Secondly, taking into account that Cl_2O_6 is a problematic substance to manage, the photolysis of a known amount of OClO was made in the portable thermostatic quartz cell ($l = 3$ cm) and the reaction mixture was analyzed by UV–Vis spectroscopy. As the UV-spectra of Cl_2O_4 and Cl_2O_6 are known [9,11,13], the respective pressures were calculated [12] by determining the absorbance at 234 and 280 nm, corrected by the OClO absorption at the last wavelength (1.7×10^{-19} cm^2 molecule^{-1} at 293 K see Fig. 1a). This analysis yields the amount of formed Cl_2O_6 and an estimate of the amount of formed Cl_2O_4 as shown in Table 3.

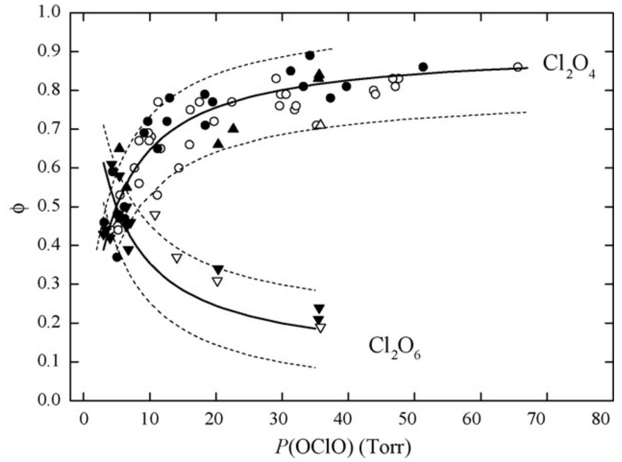

Fig. 3. $\Phi(Cl_2O_4)$ and $\Phi(Cl_2O_6)$ as a function of OClO mean pressure at 293 K: (●) IR determinations of Cl_2O_4; (▲) UV determinations of Cl_2O_4; (▼) Cl_2O_6; and at 303 K: (○) IR determinations of Cl_2O_4; (△) UV determinations of Cl_2O_4; (▽) Cl_2O_6; (—) calculated values employing, respectively Eqs. (I) and (II); (- - -) calculated corresponding error limits.

A large increase for $\Phi(Cl_2O_6)$ as the OClO pressure decreases, e.g. $\Phi(Cl_2O_6) = 0.48 \pm 0.06$ at $P(\mathrm{OClO}) = 4.7 \pm 1.0$ Torr and 0.21 ± 0.02 at 39.6 ± 0.2 Torr may be observed from Fig. 3. Besides, $\Phi(Cl_2O_4) + \Phi(Cl_2O_6) \cong 1$ over the OClO pressure range investigated in the present experiments.

Table 3
$\Phi(Cl_2O_4)$ and $\Phi(Cl_2O_6)$ as a function of OClO initial pressure at 293 and 303 K

T (K)	$P(\mathrm{OClO})_{\mathrm{i}}$ (Torr)	Time (min)	I_0 (Torr min^{-1})	f_{abs}	$P(Cl_2O_4)_{\mathrm{UV}}$ (Torr)	$P(Cl_2O_6)_{\mathrm{UV}}$ (Torr)	$\Phi(Cl_2O_4)$	$\Phi(Cl_2O_6)$
293	4.04	15	0.31	0.054	–	0.12	–	0.48
	4.70	10	0.800	0.062	–	0.22	–	0.44
	5.10	10	0.800	0.072	–	0.24	–	0.42
	5.19	15	0.34	0.076	–	0.24	–	0.61
	7.20	10	0.800	0.093	–	0.36	–	0.48
	7.50	10	0.700	0.096	0.44	0.39	0.65	0.58
	7.60	15	0.195	0.114	–	0.15	–	0.45
	8.10	5	0.66	0.124	–	0.19	–	0.46
	8.90	10	0.800	0.113	0.50	0.45	0.55	0.50
	9.10	10	0.700	0.119	0.65	0.32	0.78	0.39
	9.20	10	0.800	0.119	0.77	0.44	0.81	0.46
	26.1	7	0.72	0.343	1.21	0.69	0.70	0.40
	26.3	15	0.72	0.315	2.25	1.16	0.66	0.34
	39.7	15	0.36	0.484	–	0.54	–	0.21
	40.1	15	0.36	0.485	–	0.63	–	0.24
303	15.3	8	1.429	0.176	–	0.96	–	0.48
	18.3	8	1.110	0.224	1.78	0.73	0.89	0.37
	21.9	4	0.512	0.304	–	0.19	–	0.31
	38.7	7	0.65	0.474	1.53	0.41	0.71	0.19

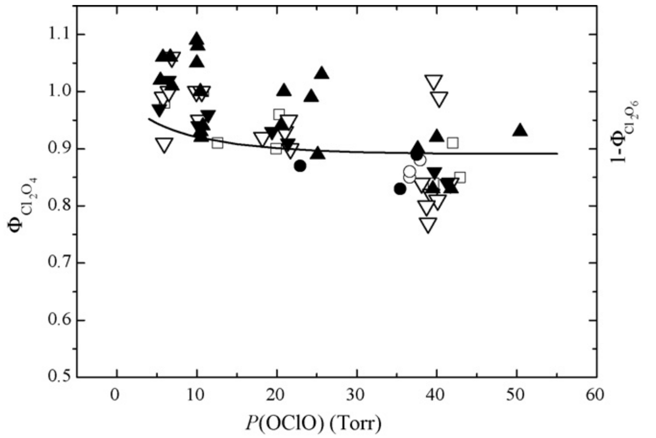

Fig. 4. $\Phi(Cl_2O_4)$ for 300 Torr N_2 (▽); 600 Torr N_2 (▼); 300 Torr O_2 (▲); 300 Torr CO_2 (□); $1-\Phi(Cl_2O_6)$ for 300 Torr Ar (○); 300 Torr O_2 (●) as a function of OClO mean pressure at 293 K. (—) calculated with Eq. (I) for 300 Torr O_2.

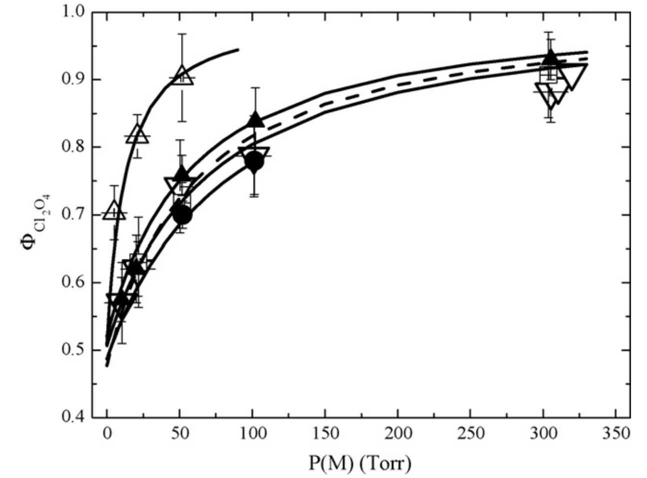

Fig. 5. $\Phi(Cl_2O_4)$ as a function of the amount of added gas at 303 K and $(OClO)_m \approx 5$ Torr; for N_2 (▽); CO_2 (□); SF_6 (△); He (●); O_2 (▲). (—) and (- - - -) calculated with Eq. (I).

Series of experiments were made at 293 and 303 K in which the pressure of OClO was varied between 5 and 45 Torr in the presence of an inert gas N_2 (300–600 Torr), or O_2, Ar or CO_2 (300 Torr).

Independent of temperature, $\Phi(Cl_2O_4)$ exhibits the same trend with OClO for the different added gases, as shown in Fig. 4. That is, $\Phi(Cl_2O_4)$ decreases as OClO is increased for the higher added gas pressures. Some results are presented in Table 4 at 293 K and 5 at 303 K, where a few without added gas are included for the sake of facilitating the comparison. At the lowest OClO pressure measured (≈5 Torr) a value near the unity was obtained and a value 0.86 with $P(OClO)_m \approx 40$ Torr results. The behavior of $\Phi(Cl_2O_6)$ is also shown in Fig. 4, where $1-\Phi(Cl_2O_6)$ is represented in clear agreement with the $\Phi(Cl_2O_4)$ trend.

More illustrative appear to be experiments made with a fixed amount of OClO, in which an increasing amount of inert gas, 10–600 Torr for N_2, 20–300 for CO_2 and O_2, 50–300 for He, 5–50 for SF_6 is added. Fig. 5 shows that $\Phi(Cl_2O_4)$ increases as the inert gas pressure rises. This trend is also shown in Table 5, when comparing the quantum yields at constant initial OClO as a function of the amount of added gas at 303 K. The value of $\Phi(Cl_2O_4)$ for $P(OClO)_m \approx 5$ Torr extrapolated to zero pressure added gas, tends to an average value of 0.5 in agreement with the observations presented in Fig. 3.

At this point it is interesting to note the sum of the quantum yields of formation of Cl_2O_4 and Cl_2O_6 in the range of OClO pressure (5–40 Torr), is close to 1 (see Fig. 3). In the case of the photolysis pure OClO $\Phi(Cl_2O_6)$ ranges between 0.5 and 0.2, while at the same OClO mean pressures $\Phi(Cl_2O_4)$ takes the complementary values to one, within the experimental errors. Besides, $\Phi(Cl_2O_4)$ increases as the inert pressure increases, with a value tending to one (see Fig. 5 and Table 5).

4. Reaction mechanism

The reaction begins with the photodissociation

$$OClO + h\nu(436\,\text{nm}) \rightarrow ClO + O(^3P) \qquad (1)$$

Table 4
$\Phi(Cl_2O_4)$ as a function the pressure of added gases at 293 K

$P(OClO)_I$ (Torr)	$P(M)$ (Torr)	Time (min)	I_0	f_{abs}	$P(Cl_2O_4)_{IR}$ (Torr)	$\Phi(Cl_2O_4)$
7.05[a]	–	30	0.0171	0.157	0.38	0.47
12.6[a]	–	20	0.20	0.294	0.76	0.65
36.0	–	20	0.20	0.643	2.09	0.81
56.8	–	30	0.186	0.795	3.80	0.86
12.6	285.9(O_2)	30	0.219	0.269	1.91	1.08
28.4	296.4(O_2)	30	0.216	0.529	3.38	0.99
43.7	280.7(O_2)	30	0.267	0.688	4.96	0.90
55.5	303.5(O_2)	30	0.183	0.790	4.02	0.93
11.9[a]	300.3(N_2)	30	0.191	0.265	1.52	1.00
21.2	298.8(N_2)	30	0.210	0.430	2.50	0.92
42.5	310.3(N_2)	30	0.210	0.692	3.67	0.84
7.5[a]	301.6(CO_2)	30	0.159	0.169	0.95	0.98
14.1[a]	300.0(CO_2)	25	0.159	0.322	1.36	1.06
23.6	301.1(CO_2)	30	0.182	0.460	2.27	0.90
45.5	302.3(CO_2)	40	0.204	0.706	4.81	0.84

[a] Spectrophotometric data.

Table 5
$\Phi(Cl_2O_4)$ as a function the pressure of added gases at 303 K

$P(OClO)_I$ (Torr)	$P(M)$ (Torr)	Time (min)	I_0 (Torr min^{-1})	f_{abs}	$P(Cl_2O_4)_{IR}$ (Torr)	$\Phi(Cl_2O_4)$
7.6[a]	–	30	0.200	0.141	0.41	0.48
23.2	–	15	0.341	0.446	1.64	0.72
33.7	–	15	0.326	0.586	2.27	0.79
51.3	–	15	0.324	0.736	3.0	0.83
71.1	–	20	0.281	0.859	4.14	0.86
12.0	26.1(Ar)	13	0.55	0.213	1.02	0.67
12.1	52.1(Ar)	13	0.55	0.201	1.11	0.77
12.1	101.5(Ar)	13	0.55	0.201	1.16	0.81
13.2	206.0(Ar)	13	0.55	0.215	1.41	0.92
8.28[a]	52.4(O_2)	30	0.200	0.158	0.72	0.76
7.72[a]	109.4(O_2)	30	0.200	0.142	0.73	0.85
7.71[a]	304.8(O_2)	30	0.200	0.154	0.85	0.92
8.0[a]	10.8 (N_2)	20	0.250	0.160	0.51	0.64
7.33[a]	20.6 (N_2)	30	0.160	0.160	0.45	0.65
7.77[a]	49.9(N_2)	20	0.250	0.145	0.56	0.77
8.02[a]	100.7(N_2)	30	0.200	0.130	0.71	0.87
7.92[a]	305.6(N_2)	30	0.200	0.139	0.75	0.90
7.87[a]	623.6(N_2)	30	0.170	0.144	0.66	0.90
12.48[a]	298.0(N_2)	20	0.178	0.236	0.89	1.0
22.5	301.4(N_2)	20	0.188	0.437	1.56	0.95
43.6	302.2(N_2)	30	0.178	0.680	3.13	0.86
7.14[a]	21.9(CO_2)	30	0.240	0.120	0.53	0.61
7.83[a]	101.2(CO_2)	30	0.226	0.129	0.70	0.80
7.17[a]	289.3(CO_2)	30	0.210	0.128	0.74	0.92
12.74[a]	307.5(CO_2)	20	0.224	0.250	1.15	1.03
23.6	310.1(CO_2)	20	0.220	0.454	1.93	0.97
47.2	300.6(CO_2)	10	0.220	0.741	1.37	0.84
7.54[a]	5.0(SF_6)	30	0.170	0.127	0.45	0.69
7.32[a]	20.6(SF_6)	30	0.216	0.126	0.67	0.82
7.84[a]	51.2(SF_6)	30	0.170	0.141	0.66	0.92

[a] Spectrophotometric data.

This is the dominant channel [20,21], while a second channel to form Cl and O_2 contributes less than 3% within our experimental error, such that it will not be considered here.

The primary process is followed by fast reactions involving the reaction products of reaction (1) ClO and $O(^3P)$ (O in the following) with the excess of OClO.

The kinetics of the reactions between the ground-state oxygen atom with OClO was studied at 298 K [22], and explained in terms of an association reaction

$$O + OClO \leftrightarrow ClO_3^* \tag{2}$$

The vibrationally excited molecule ClO_3^* can be stabilized by molecular collisions with the present gases M,

$$ClO_3^* + M \rightarrow ClO_3 + M \tag{3}$$

and

$$ClO_3^* \rightarrow ClO + O_2 \tag{4}$$

The UV–Vis spectrum of ClO_3 isolated in Ne matrix has been recently detected [23]. Another channel $O + OClO \rightarrow ClO + O_2$ should not contribute appreciably in the present experimental conditions of OClO and total pressure conditions [19].

Reaction (2) is exothermic with an enthalpy of reaction $\Delta H_{298} = -163.6$ kJ mol^{-1}. This value was derived from O and OClO enthalpies of formation of 249.4 and 94.5 kJ mol^{-1} [24] besides of the calculated for ClO_3 of 180.3 kJ mol^{-1} [25].

The other product of the photolysis, ClO, reacts with excess OClO to form dichlorine trioxide

$$ClO + OClO \leftrightarrow Cl_2O_3 \tag{5}$$

Reaction (5) is shifted to the right [26], such that Cl_2O_3 may be considered as a reservoir of ClO. In this way, the stable final product Cl_2O_4 may be formed by reaction of ClO with ClO_3 [8]:

$$ClO_3 + ClO \rightarrow Cl_2O_4 \tag{6}$$

or

$$ClO_3 + Cl_2O_3 \rightarrow Cl_2O_4 + OClO \tag{7}$$

Now, when a quantum is absorbed by OClO, one ClO_3 is obtained according to reactions (1), (2) and (3). From each ClO_3 one Cl_2O_4 is formed via reaction (6) or (7). The set of reactions (1)–(7) allows interpreting the experimental quantum yield close to 1 for Cl_2O_4 formation at low OClO and high added gas total pressures.

For ample conditions, the formation of Cl_2O_4 is accompanied by Cl_2O_6. In such case, Cl_2O_6 formation through the generally proposed reaction $2ClO_3 + M \rightarrow Cl_2O_6 + M$, would require two quanta to yield one molecule. This would lead to

$\Phi(Cl_2O_4) + \Phi(Cl_2O_6) = 0.75$ for instance at the limit condition of 5 Torr OClO, in clear contradiction with the results shown in Fig. 3, where $\Phi(Cl_2O_4) + \Phi(Cl_2O_6) = 1$ within the experimental errors. This last relation holds for all the experimental conditions presented here.

Therefore it is necessary to find out another way in which only one ClO_3 be consumed to yield one Cl_2O_6 per absorbed quantum. It is known [11,27] that Cl_2O_6 can be formed by the reaction

$$ClO_4 + OClO + M \leftrightarrow Cl_2O_6 + M \qquad (8)$$

This equilibrium is also strongly shifted to the right. For the formation of ClO_4 [23] the reaction $ClO_3 + OClO \rightarrow ClO_4 + ClO$, with an endothermicity of 11.7 kJ mol^{-1} has been suggested [28]. Taking into account the more reliable new calculated values for the heats of formation of ClO_3 and ClO_4 [25] we obtain for the enthalpy of reaction $\Delta H_{298} = 56.1$ kJ mol^{-1}, such that this channel has been ruled out.

The reaction $O + OClO \rightarrow$ products, was investigated by the laser photolysis-long pass transient absorption technique at 260 K and 100–400 Torr of He, N_2 and Ar [29]. As a first stage an adduct (O·OClO) is formed, that further reacts with OClO to yield a product stable on the time scale of 100 ms, which is assumed to be Cl_2O_5 identified by UV absorption.

The formation of the relatively stable isomer $O_2ClOClO_2$ for Cl_2O_5 has been predicted from a bond energy additivity scheme [27]. More recently an enthalpy of formation for perchloryl chloroperoxide, $O_3ClOOCl$, of 222.6 kcal mol^{-1} has been obtained at 298 K from theoretical calculations [25]. Applying the same procedure, the values 202.6 and 259.8 kJ mol^{-1} have been obtained by C.J. Cobos (private communication) for the enthalpy of formation of $O_2ClOClO_2$ and $O_3ClOClO$. These results together with the standard enthalpy of formation of 101.7 and 229.3 kJ mol^{-1} for the species ClO and ClO_4 [25], and the value calculated for $ClO_3{}^*$ from the enthalpy of reaction (2), allow us to construct the standard enthalpy diagram for the three more stable isomers of Cl_2O_5 shown in Fig. 6. Calculations performed at the high B3LYP/6-311 + G(3df) level of the density functional theory show that no electronic energy barriers (localized transition states) are present in the considered association reactions.

For the equilibrium

$$ClO_3 + OClO \leftrightarrow O_2ClOClO_2 \qquad (9)$$

The $\Delta H_{298} = -72.4$ kJ mol^{-1} and $\Delta S^\circ = -127$ J K^{-1} mol^{-1} values obtained by Cobos (private communication) lead to $Kp = 1.1 \times 10^6$ atm^{-1} at 298 K. Then, for $P(OClO) = 7$ Torr the ratio $[O_2ClOClO_2]/[ClO_3] = 10^4$ results, that is, the equilibrium is shifted to the right for the present experimental conditions. However, the occurrence of this process does not allow to explain our experimental observations. Therefore, the participation of vibrationally excited $ClO_3{}^*$ radicals generated in reaction (2) is proposed here. This assumption implies that their reaction with OClO is significantly faster than collisional process degrading its internal energy. Even though no measurements for the $ClO_3{}^*$ deactivation by collisions are available, this process could be enough slow to allow this species to react with OClO. In addition, the rate of this last process could be significantly enhanced by the vibrational energy. In this context, even for efficient bath colliders, slow phenomenological rate coefficients for the degradation of vibrational energy in fluorosulphate radicals, FSO_3, have been measured by laser flash photolysis in our laboratory [30].

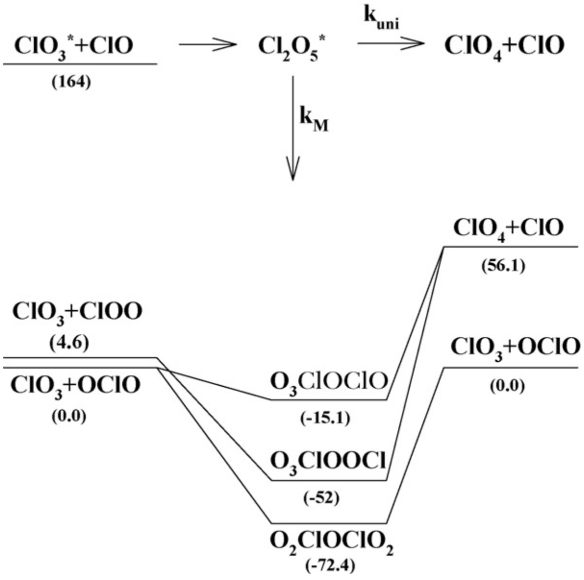

Fig. 6. Schematic enthalpy diagram for the ClO_3 + OClO reaction (in kJ mol^{-1}).

In this way, in a first path an excited $Cl_2O_5{}^*$ radical is formed by the following reaction

$$ClO_3{}^* + OClO \rightarrow Cl_2O_5{}^* \qquad (10)$$

As in other complex-forming bimolecular reactions, this process is likely to proceed thorough a configuration corresponding to an intermediate vibrationally excited complex, which allows energy randomization. Assuming that $O_3ClOClO^*$ is formed, as Fig. 6 shows, this radical can either decay back to the reagents or, due to their high vibrational energy, form products ClO_4 and ClO through the reaction

$$Cl_2O_5{}^* \rightarrow ClO_4 + ClO \qquad (11)$$

with an energy-dependent specific (microcanonical) rate coefficient k_{uni}, or be collisionally stabilized as

$$Cl_2O_5{}^* + M \rightarrow Cl_2O_5 + M \qquad (12)$$

with an almost energy-independent rate coefficient k_M.

The large energy contents over the threshold dissociation energy of thermalized ClO_4 + ClO products of about 107 kJ mol^{-1} suggest, as for other calculated systems [31–34], an average k_{uni} value over 10^{10} s^{-1}. This value is markedly larger than those estimated for k_M of 10^7 to 10^9 s^{-1} over the present total pressure range. As a consequence, the dissociation of $O_3ClOClO^*$ to products according to reaction (11) is probably the dominant fate for this excited species.

It should be noted that if the more stable oxide $O_2ClOClO_2$ is eventually formed in reaction (10), it may isomerize to

Table 6
The ratios k_3/k_{10} and k_{12}/k_{11} for OClO and for the various added gases

M	OClO	He	N_2	O_2	Ar	CO_2	SF_6
k_3/k_{10}	<0.01	0.016	0.02	0.03	0.03	0.02	0.1
(k_{12}/k_{11}) (Torr^{-1})	0.24	0.024	0.03	0.036	0.034	0.034	0.17

$O_3ClOClO$ or to the other oxide able to generate $ClO_4 + ClO$ products, $O_3ClOOCl$, provided that the isomerization high barriers for these processes are below the maximum available energy (see Fig. 6).

We assume that the formation of Cl_2O_4 is independent of the isomer involved because both lead, respectively to one ClO_3.

However, as $\Phi(Cl_2O_4)$ decreases as OClO increases at the higher M pressures, as shown in Fig. 4, a direct reaction

$$ClO_3^* + OClO \rightarrow ClO_4 + ClO \quad (13)$$

occurs.

The ClO_4 radical reacts with OClO via reaction (8) to form Cl_2O_6, and the rates of formation of Cl_2O_4 and Cl_2O_6 are simply given by the reactions (6) and (8), respectively.

With the set of reactions (1), (2), (3), (5) and (6) and (8), (9), (10)–(13), the application of Bodenstein steady state approximation allows to obtain for the respective quantum yields

$$\Phi(Cl_2O_4) = \left\{ \frac{1}{[1 + (k_3(M)/k_{10}(OClO)) + (k_4/(k_{10}(OClO))) + (k_{13}/k_{10})]} \right\} \left\{ \left[\frac{k_3(M)}{(k_{10}(OClO))} \right] + \left[\frac{1}{(1 + [k_{11}/(k_{12}(OClO))] + [k_{11}/(k_{12}(M))]} \right] \right\} \quad (I)$$

and

$$\Phi(Cl_2O_6) = \left\{ \frac{1}{[1 + (k_3(M)/k_{10}(OClO)) + (k_4/k_{10}(OClO))) + (k_{13}/k_{10})]} \right\} \left\{ \left[\frac{k_{13}}{k_{10}} \right] + \left[\frac{1}{(1 + [k_{12}(OClO)/k_{11}] + [k_{12}(M)/k_{11})])} \right] \right\} \quad (II)$$

Fitting the data depicted in Figs. 3–5 with Eqs. (I) and (II) for OClO and the various inert gases here employed, leads to $k_{13}/k_{10} = 0.1$, such that $k_{10}(OClO) \gg k_4$, and to the values k_3/k_{10} and k_{12}/k_{11} shown in Table 6. The rate coefficient ratios k_3/k_{10} and k_{12}/k_{11} reflect the relative collisional deactivation efficiencies for the ClO_3^* and $Cl_2O_5^*$ energized radicals by the various bath gases. The observed trends are in satisfactory agreement with those derived from direct energy transfer measurements of highly vibrationally excited molecules [35].

According to the mechanism presented so far, for each light quantum absorbed, the formation of Cl_2O_6 is accompanied by the consumption of 4OClO and the formation of 2ClO radicals. The bimolecular channels

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (14)$$

$$ClO + ClO \rightarrow Cl + ClOO \quad (15)$$

$$ClO + ClO \rightarrow Cl + OClO \quad (16)$$

have been extensively studied [19] and the ratio k_{14}:k_{15}:k_{16} = 0.29:0.50:0.21 at 298 K, using N_2 as bath gas has been measured [36]. In the case that O_2 was used as bath gas, the ratio k_{14}:k_{15}:k_{16} = 0.39:0.41:0.20 at 298 K was determined [37] such that O_2 seems more actively involved and the three elementary pathways would represent a more complex mechanism involving the unimolecular decomposition of various short-lived $(ClO)_2$ intermediates [37].

The formation of the rest of the products of the reaction, namely, O_2, Cl_2 and $ClClO_2$, may be interpreted as follows. ClOO is an unstable molecule that decomposes readily to form Cl atoms [19]:

$$ClOO + M \rightarrow Cl + O_2 + M \quad (18)$$

It is well known [19] that atomic chlorine reacts readily with OClO as

$$Cl + OClO \rightarrow ClO + ClO \quad (19)$$

The formation of chloryl chloride

$$Cl + OClO + M \rightarrow ClClO_2 + M \quad (20)$$

has been proposed [11] and has been studied [17,18]. In our experimental conditions the presence of $ClClO_2$ can be neglected, remaining less than 0.1 Torr in experiments with added inert gas. Reactions (15)–(17), together with (18) and (19) would lead to a chain reaction rendering the system unstable [38]. Therefore, a stabilizing effect of OClO due to Cl_2O_3 formation is expected in this case, similar to that observed in the thermal decomposition [38].

On the other hand ClOOCl may be formed through the reaction: $ClO + ClO + M \leftrightarrow ClOOCl + M$ [24,39], but in the presence of large excess of OClO that peroxide acts only as a reservoir of ClO radicals.

5. Conclusions

- Relatively high yields of Cl_2O_4 and Cl_2O_6 are produced in the 436 nm photolysis of gaseous OClO at 293 and 303 K under the pressure conditions of the present experiments. Both products reach a limit of about 30% of the total besides of Cl_2 and O_2. Only very small amounts of $ClClO_2$ have been detected.
- The quantum yield for Cl_2O_4 and for Cl_2O_6 formation satisfy the condition $\Phi(Cl_2O_4) + \Phi(Cl_2O_6) \cong 1$ throughout.
- In the absence of an inert gas $\Phi(Cl_2O_4)$ decreases from a value close to 1 at the higher OClO (∼40 Torr) to 0.5 at the

lower (∼5 Torr). In this limit the observed $\Phi(Cl_2O_6)$ correspondingly takes a value close to 0.5.

- In the presence of an inert gas and a fixed OClO mean pressure (∼5 Torr), the quantum yields for Cl_2O_4 formation increase as total pressure is increased reaching a value close to 1 for 300 Torr of N_2 or 50 Torr of SF_6. These results are interpreted through the behaviour of $Cl_2O_5{}^*$ radical as a function of total pressure (reaction (11) and (12)).
- However, at the higher inert gas pressures the quantum yields for Cl_2O_4 formation slightly decrease when OClO is increased. This fact is attributed to the reaction $ClO_3{}^* + OClO \rightarrow Cl_2O_5{}^* \rightarrow ClO + ClO_4$.

From the above detailed results, as one 436 nm quantum is required to form one ClO_3 radical, the generally accepted reaction for the formation of Cl_2O_6, namely $2ClO_3 \rightarrow Cl_2O_6$, can be ruled out and a complicated mechanism is needed to account for the experimental observations.

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