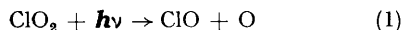


Some New Features in the Flash Photolysis of Chlorine Dioxide

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In their study of the isothermal flash photolysis of ClO_2 , Lipscomb, Norrish, and Thrush¹ showed that, following the primary photolysis

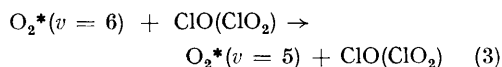


vibrationally excited oxygen was produced in the reaction

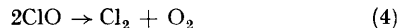


The half-life of $\text{O}_2^*(v = 6)$ (ca. 200—700 $\mu\text{sec.}$) was inversely proportional to the initial ClO_2 pressure and was essentially independent of the overall percentage decomposition of the ClO_2 or the pressure of the moderator (Ar, N_2). It was concluded that ClO_2 and ClO are approximately equally efficient at deactivating O_2^* and that a

value $k_3 = 1 \times 10^8 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ could be assigned to the rate constant for the process



For the decay of ClO , second-order plots were linear at all flash energies, the slope, however, increased to a limiting value as the flash energy increased. Thus the rate constant, k_4 , for the reaction



varied from $1.9 \times 10^7 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ at the lowest energy to $6.2 \times 10^7 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ for energies in excess of 1000 J, the latter value being adopted. The molar extinction coefficient, ϵ , of ClO at 2577 Å was calculated by assuming that the $[\text{ClO}]$ (extrapolated to zero time) could be equated

to the decrease in $[\text{ClO}_2]$. The values obtained also varied with flash energy from $690 \text{ l.mole}^{-1} \text{ cm.}^{-1}$; at the highest energy to a near constant value of *ca.* $1100 \text{ l.mole}^{-1} \text{ cm.}^{-1}$ for energies $< 400 \text{ J}$.

A value of $2.4 \times 10^7 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ for k_4 was obtained from the flash photolysis of Cl_2O ,² while other workers^{3,4} produced ClO in a flow system from atomic chlorine and ClO_2 and found $k_4 = 1.4 \times 10^7 \text{ l.mole}^{-1} \text{ sec.}^{-1}$, $\epsilon = 1270 \text{ l.mole}^{-1} \text{ cm.}^{-1}$. Porter and Wright⁵ found k_4/ϵ from the decay of ClO in the chlorine and oxygen system from which $k_4 = 4.8$ or $2.6 \times 10^7 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ depending on the value of ϵ adopted.

We have reinvestigated the flash photolysis of ClO_2 and Cl_2O and our results reveal several new features of interest which suggest a more complete mechanism for the flash photolysis of ClO_2 and which serve to explain the above differences in the results of previous workers.

Chlorine dioxide was prepared,⁶ distilled under reduced pressure, and stored at the temperature of liquid nitrogen. Argon (99.998%) was passed through a cold trap.

Mixtures of ClO_2 (0.1–0.5 mm.) with argon (75–500 mm.), sometimes containing in addition Cl_2 , Cl_2O , or other gases, were flash photolysed with energies between 150 and 1000 J in a 50 cm. quartz or Pyrex reaction vessel using various light filters. The absorption spectra were recorded on Ilford HP 3 plate using a 3.4 m. grating spectrograph with a plate factor of 5 \AA mm.^{-1} .

We observe the production of vibrationally excited oxygen, O_2^* , in levels up to $v'' = 14$ (?15), *i.e.* up to the limit allowed by the exothermicity of reaction (2), rather than up to $v'' = 8$.

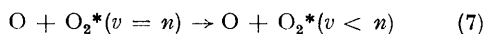
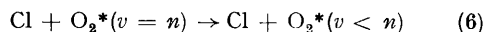
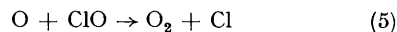
At low flash energies our results are otherwise in agreement with those of Lipscomb *et al.*,¹ with similar values of k_3 and k_4 and ϵ (*ca.* $1100 \text{ l.mole}^{-1} \text{ cm.}^{-1}$). As expected, for $\text{O}_2^*(v'' = 12)$, a somewhat higher value of k_3 was obtained.

At high flash energies, two important new features were observed. Firstly, a pronounced departure from linearity occurs in the second-order plot of $[\text{ClO}]^{-1}$ *vs.* time at delay times below *ca.* $50 \mu\text{sec.}$, the initial decay of ClO being very much more rapid. The values of the extinction coefficient for ClO, obtained from linear extrapolations of the second-order plots, *i.e.* ignoring experimental points below $50 \mu\text{sec.}$, were very much lower (*ca.* $700 \text{ l.mole}^{-1} \text{ cm.}^{-1}$). The values of ϵ obtained by extrapolation of the experimental results below $50 \mu\text{sec.}$ were, however, in approximate agreement with the low flash-energy values.

The second feature was the dramatic decrease in the half-life of O_2^* from *ca.* $550 \mu\text{sec.}$ at low flash energies to *ca.* $15 \mu\text{sec.}$ at high flash energies.

At high energies, the half-life of O_2^* was increased by the presence of Cl_2O in the ClO_2 -Ar mixture, only the ClO_2 being photolysed. At low flash energies, the rate of decay of O_2^* was slightly increased when Cl_2 was present, but with a filter to prevent appreciable photolysis of the chlorine. A much greater increase in the decay rate was observed when, in the absence of this filter, a larger degree of photolysis of the Cl_2 occurred.

The difference between the experimental results at low and high flash energies can be explained by the reactions:



The relative importance of reactions (2) and (5) depends, of course, on the ratio k_2/k_5 , which is given as *ca.* 4 by Clyne and Coxon.³ It also depends on the flash energy, since this will determine the relative concentrations of ClO_2 and ClO with which the oxygen atom produced in the primary photolysis will react. At flash energies sufficiently high to photolyse $>50\%$ of the ClO_2 directly, there will be an excess of oxygen atoms over that required to decompose the ClO_2 remaining and reaction (5) will occur even if $k_2/k_5 > 1$.

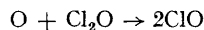
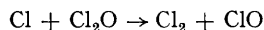
At low flash energies (corresponding to $<40\%$ primary photolysis) reactions (5)–(7) may be neglected to a first approximation. The second-order plot for ClO is then linear and a reasonably accurate value of ϵ is obtained by equating $[\text{ClO}]$ at zero time with the amount of ClO_2 decomposed overall. Likewise, under these conditions, the decay of O_2^* is determined largely by ClO and ClO_2 , and values of k_3 may be determined.

At high flash energies ($>60\%$ primary photolysis), an appreciable amount of ClO is removed rapidly by reaction (5) and the second-order plot becomes linear only after the oxygen atoms are consumed. A linear extrapolation of this plot yields the concentration of ClO after reactions (2) and (5) are completed. An extrapolation of the experimental points below $\sim 50 \mu\text{sec.}$ yields an approximate value for the concentration of ClO which would have been produced in the absence of reaction (5). The difference between the two values of $[\text{ClO}]$ gives, approximately, the $[\text{O}]$ produced in excess of that required for 100% overall decomposition of the ClO_2 .

On this basis, a value of k_5 *ca.* $6 \times 10^9 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ was obtained from the initial rapid decay of ClO. The same value has been given as a lower limit for k_5 .³

The increased rate of decay O_2^* is due to the extremely high efficiency of chlorine and/or oxygen atoms and we calculate an approximate value $(k_6[Cl] + k_7[O])/([Cl] + [O]) = 10^{10} \text{ l.mole}^{-1} \text{ sec.}^{-1}$. The consequence that at least one of the constants k_6, k_7 , has the exceptionally high value of *ca.* $10^{10} \text{ l.mole}^{-1} \text{ sec.}^{-1}$ is acceptable in view of the strong interactions expected to exist between the atoms and oxygen. The experimental results with added Cl_2 support this interpretation as far as the Cl atom is concerned. The effect of Cl_2O is consistent

with the rapid removal of Cl (and probably O) atoms in the fast reactions:



Further work to test this mechanism and to obtain more accurate values of the rate constants is in progress.

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¹ F. J. Lipscomb, R. G. W. Norrish, and B. A. Thrush, *Proc. Roy. Soc.*, 1956, *A*, **233**, 455.

² F. H. C. Edgecombe, R. G. W. Norrish, and B. A. Thrush, *Proc. Roy. Soc.*, 1957, *A*, **243**, 24.

³ M. A. A. Clyne and J. A. Coxon, *Trans. Faraday Soc.*, 1966, **62**, 1175.

⁴ M. A. A. Clyne and J. A. Coxon, *Proc. Roy. Soc.*, 1968, *A*, **303**, 207.

⁵ G. Porter and F. J. Wright, *Discuss. Faraday Soc.*, 1953, **14**, 23.

⁶ *Inorg. Synth.*, 1953, **4**, 152.