Some New Features in the Flash Photolysis of Chlorine Dioxide

By N. BASCO* and S. K. DOGRA

(*Chemistry Department, University of British Columbia, Vancouver* 8, *Canada*)

IN their study of the isothermal flash photolysis of ClO_2, Lipscomb, Norrish, and Thrush[1] showed that, following the primary photolysis

$$ClO_2 + h\nu \rightarrow ClO + O \qquad (1)$$

vibrationally excited oxygen was produced in the reaction

$$O + ClO_2 \rightarrow O_2^*(v \leqslant 8) + ClO \qquad (2)$$

The half-life of $O_2^*(v = 6)$ (*ca.* 200—700 μsec.) 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 $k_3 = 1 \times 10^8$ l.mole^{-1} sec.$^{-1}$ could be assigned to the rate constant for the process

$$O_2^*(v = 6) + ClO(ClO_2) \rightarrow O_2^*(v = 5) + ClO(ClO_2) \qquad (3)$$

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

$$2ClO \rightarrow Cl_2 + O_2 \qquad (4)$$

varied from $1{\cdot}9 \times 10^7$ l.mole^{-1} sec.$^{-1}$ at the lowest energy to $6{\cdot}2 \times 10^7$ l.mole^{-1} 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 [ClO] (extrapolated to zero time) could be equated to the decrease in $[ClO_2]$. The values obtained also varied with flash energy from 690 l.mole^{-1} cm.$^{-1}$; at the highest energy to a near constant value of *ca.* 1100 l.mole^{-1} cm.$^{-1}$ for energies < 400 J.

A value of $2{\cdot}4 \times 10^7$ l.mole^{-1} 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 $k_4 = 1{\cdot}4 \times 10^7$ l.mole^{-1} sec.$^{-1}$, $\epsilon = 1270$ l.mole^{-1} cm.$^{-1}$. Porter and Wright[5] found k_4/ϵ from the decay of ClO in the chlorine and oxygen system from which $k_4 = 4{\cdot}8$ or $2{\cdot}6 \times 10^7$ l.mole^{-1} 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 Å 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 l.mole^{-1} cm.$^{-1}$). As expected, for $O_2^*(v'' = 12)$, 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 $[ClO]^{-1}$ *vs.* time at delay times below *ca.* 50 μsec., 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 μsec., were very much lower (*ca.* 700 l.mole^{-1} cm.$^{-1}$). The values of ϵ obtained by extrapolation of the experimental results below 50 μsec. 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 μsec. at low flash energies to *ca.* 15 μsec. 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:

$$O + ClO \rightarrow O_2 + Cl \qquad (5)$$

$$Cl + O_2^*(v = n) \rightarrow Cl + O_2^*(v < n) \qquad (6)$$

$$O + O_2^*(v = n) \rightarrow O + O_2^*(v < n) \qquad (7)$$

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 [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 μsec. 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 [ClO] gives, approximately, the [O] produced in excess of that required for 100% overall decomposition of the ClO_2.

On this basis, a value of k_5 *ca.* 6×10^9 l.mole^{-1} 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 $(k_6[Cl] + k_7[O])/([Cl] + [O]) = 10^{10}$ l.mole^{-1} sec.$^{-1}$. The consequence that at least one of the constants k_6, k_7, has the exceptionally high value of *ca.* 10^{10} l.mole^{-1} 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:

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$

$$O + Cl_2O \rightarrow 2ClO$$

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

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