The Flash Photolysis of Aqueous Solutions of Halate Ions

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Summary XO_2 radicals are formed in the flash photolysis of XO_3^- ions.

THREE species, having absorption spectra situated between 300 and 600 nm (see Figure), have been observed after the flash photolysis of neutral, aerated solutions of the halate ions ClO_3^-, BrO_3^-, and IO_3^- in the wavelength range 190—260 nm. The absorption spectra of these ions have been studied by Farkas and Klein.[1] The energy of the photolytic flash was 1300 J and its width of half-intensity was 4 μsec.

The photolysis of $KClO_3$ (2×10^{-3} M) gave a spectrum with a maximum between 350 and 360 nm and belonging to a stable species identified as chlorine dioxide, ClO_2.[2]

In the case of $NaBrO_3$ (10^{-3}M), the observed spectrum had a maximum at 480 nm and decayed with a half life of about 400 μsec. Following the work of Buxton and Dainton[3] this spectrum has been attributed to the transient species BrO_2.

The spectrum observed after the photolysis of KIO_3 (10^{-3}M) also had a maximum at 480 nm and decayed with a half life of about 50 μsec. In view of the results obtained with ClO_3^- and BrO_3^-, this spectrum is probably due to the species IO_2.

That these spectra are observed immediately after the photolytic flash indicates that one of the primary decomposition process of the halate ion is

$$XO_3^-{\cdot}H_2O \xrightarrow{h\nu} (XO_3^-{\cdot}H_2O)^* \longrightarrow XO_2 + OH + OH^- \quad (1)$$

This result is in agreement with the recent observations of Amichai and Treinin[4] who have identified, by its reaction with the carbonate ion, the radical O^- (or OH), as a product of the flash photolysis of BrO_3^- in de-aerated solution.

Another primary process of halate ion photolysis suggested by Farkas and Klein[1] and by Bridge and Matheson[5] is that of electron transfer to the hydration layer

$$XO_3^-{\cdot}H_2O \xrightarrow{h\nu} (XO_3{\cdot}H_2O)^- \longrightarrow XO_3 + e^-_{aq} \quad (2)$$

The reactions of the solvated electron with IO_3^- and BrO_3^- are too rapid[6] to permit detection of this transient species under the experimental conditions employed here, but its reaction with the ClO_3^- ion is relatively slow, $k_{e^- + ClO_3^-} = 4 \times 10^6$ M^{-1} sec^{-1}.[7] Nevertheless, in the flash photolysis of deaerated solutions of potassium chlorate ($KClO_3 = 2 \times 10^{-3}$M), no sign of the solvated electron spectrum was seen 5 μsec. after the photolytic flash, even though its half life under these conditions is about 100 μsec., which leads us to conclude that the dissociation reaction (2) does not occur in this particular case.

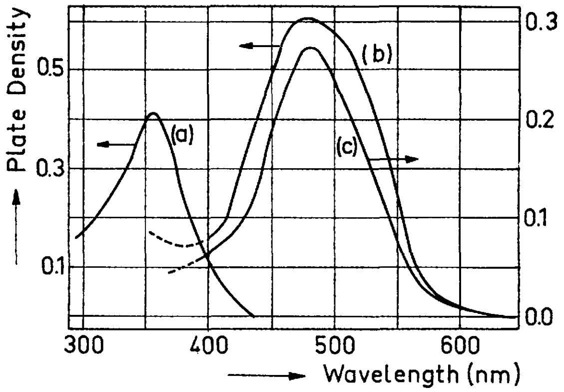

FIGURE. *Spectra of radicals* XO_2 *observed in the flash photolysis of the halate ions* XO_3^-:
(a) ClO_2 *produced from* 2×10^{-3}M-$KClO_3$; *left scale.*
(b) BrO_2 *produced from* 10^{-3}M-$NaBrO_3$; *left scale.*
(c) IO_2 *produced from* 10^{-3}M-KIO_3; *right scale.*

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