The BrO Radical in Aqueous Solution

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To elucidate some of the obscurities involved in the radiolysis of alkaline aqueous solutions of the hypobromite ion[1,2] we have carried out pulse radiolysis experiments on these solutions. From the acceleration of the decay of the optical absorption of the hydrated electron e^-_{aq}, we have obtained $k_1 = (2 \cdot 3 \pm 0 \cdot 5) \times 10^{10}$ M^{-1} sec.$^{-1}$ in 0·1M-NaOH which leads to a ratio k_1/k_2 in good agreement with the value obtained from studies of the effect of BrO^- on the value of $G(N_2)$ in alkaline solutions of N_2O.[3]

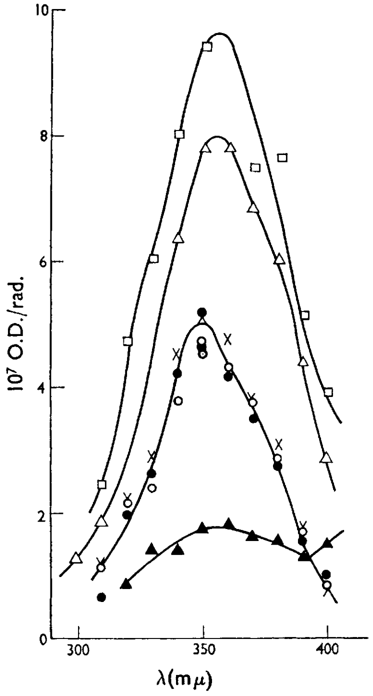
$$e^-_{aq} + BrO^- \rightarrow Br^- + O^- \qquad (1)$$

$$e^-_{aq} + N_2O \rightarrow N_2 + O^- \qquad (2)$$

When a deaerated 1mM-hypobromite solution, from which bromide ions have been removed by precipitation of AgBr, is pulsed with 3 Mev electrons a transient absorption ($\lambda_{max} = 350$ mμ) with a half-life ~ 2μsec. is produced (see Figure). The half-life is inversely proportional to $[BrO^-]$ indicating that the intermediate responsible for this absorption reacts bimolecularly with BrO^- ions and we have obtained $k(BrO + BrO^-) = (3 \cdot 0 \pm 0 \cdot 2) \times 10^8$ M^{-1} sec.$^{-1}$ Saturation of the solution with N_2O, which causes reaction (2) to replace (1), has no effect on this absorption or its decay indicating that the reaction leading to the formation of this new intermediate does not involve e^-_{aq} and is therefore presumed to be (3).

$$OH + BrO^- \rightarrow OH^- + BrO \qquad (3)$$

The amount of the new species, presumed to be the BrO radical, which is formed is the same in 1mM as 0·1M-NaOH solution provided $[Br^-]$ is very small. However, when $[Br^-] = [BrO^-]$ the amount of absorption produced in 1mM-NaOH is larger whilst



FIGURE

Absorption spectra of transient species produced in the pulse radiolysis of alkaline solutions of hypobromite and bromide ions.

0·1M-NaOH: ○ = 1·5mM-BrO^-
▲ = 1·5mM-Br^-
× = 1·5mM-BrO^- + 1·5mM-Br^-

1mM-NaOH: ● = 1·5mM-BrO^-
□ = 1·5mM-Br^- (scale reduced twofold)
△ = 1·5mM-BrO^- + 1·5mM-Br^-

that in 0·1M is almost unchanged. If 1mM-bromide solutions containing no hypobromite ions are pulsed there is a fourfold increase in absorption at 360 mμ for 1mM-NaOH and a threefold decrease for 0·1M-NaOH. The former is attributed to formation of Br_2^- ($\epsilon_{360} = 8,200$ M^{-1} cm.$^{-1}$)[4] *via* reaction (4) whereas the latter is assigned partly to O_3^- formed in reaction (5) because it continues to build up after the pulse.

$$OH + Br^- \rightarrow OH^- + Br\ (+\ Br^- \rightarrow Br_2^-) \tag{4}$$

$$O^- + O_2 \rightarrow O_3^- \tag{5}$$

It is known[5] that $pK_{OH} = 11{\cdot}9$ and thus the primary oxidising radicals will be in the ionised form O^- which will oxidise Br^- much more slowly than OH.[6]

From the dose per pulse and taking $G(e^-_{aq}) + G(OH) \sim 6$ we obtain $\epsilon_{350} \sim 900$ M^{-1} cm.$^{-1}$ which confirms that this absorption is not due to Br_2^-. The assignment to BrO is strengthened by Zeelenberg's observation[7] that this species in the gas phase absorbs in the region 300—350 mμ. The absorption at 460 mμ, obtained by flash photolysis of BrO^- solutions, having a half-life of $10^3\mu$sec. and decaying with second-order kinetics, seems unlikely to be that of BrO to which it was assigned by Bridge and Matheson.[8] The bimolecular reaction between BrO and BrO^- which we have observed may follow either of the two courses (6) or (7).

$$BrO + BrO^- \rightarrow BrO_2^- + Br\ (+Br^- \rightarrow Br_2^-) \tag{6}$$

$$BrO + BrO^- \rightarrow BrO_2 + Br^- \tag{7}$$

Since Br_2^- has a shorter lifetime in the presence of BrO^- we presume that it reacts with this ion according to equation (8). If this is so and

$$Br_2^- + BrO^- \rightarrow 2Br^- + BrO \tag{8}$$

reaction (6) can also occur there should be a chain decomposition of $BrO^- \rightarrow \frac{1}{2}\,Br^- + \frac{1}{2}\,BrO_2^-$ for which there is no evidence in the radiolysis of hypobromite solutions.[1,3] We therefore favour (7) as representing the course of the BrO decay.

The value of k_3 obtained by using the carbonate competition method of Adams *et al.*[9] and taking $k(O^- + CO_3^{2-}) = 4{\cdot}4 \pm 0{\cdot}2) \times 10^7$ M^{-1} sec.$^{-1}$ [10] is $(4{\cdot}80 \pm 0{\cdot}34) \times 10^9$ M^{-1} sec.$^{-1}$ in 0·1M-NaOH.

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