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Radiation-chemical oxidation of bromide ions and formation of tribromide ions in weakly acidic aqueous solutions

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The formation of the Br_3^- ion in the radiation-chemical oxidation of Br^- ions in an aqueous solution was detected by pulse radiolysis, and its optical characteristics and the equilibrium constant were found.

The radiation-chemical oxidation of bromide ions in acidic aqueous solutions is performed by OH radicals to form Br_2^- radical anions. The mechanism of oxidation was studied in detail by a pulse radiolysis technique.[1,2] This mechanism involves the following reactions:

$$OH + Br^- \longleftrightarrow BrOH^- \quad (1)$$
$$H^+ + BrOH^- \longleftrightarrow Br + H_2O \quad (2)$$
$$Br^- + Br \longleftrightarrow Br_2^- \quad (3)$$
$$Br + OH^- \longleftrightarrow BrOH^- \quad (4)$$
$$BrOH^- + Br^- \longrightarrow Br_2^- + OH^- \quad (5)$$

It was found[2] that the Br_2^- species disappeared in the following reactions resulting in the formation of the Br_2 molecule and Br_3^-:

$$Br_2^- + Br_2^- \longrightarrow Br_2 + 2Br^- \quad (6)$$
$$Br_2 + Br^- \longrightarrow Br_3^- \quad (7)$$

The aim of this work was to study the mechanism of the formation of the tribromide ion (Br_3^-) as a product of the radiation-chemical oxidation of bromide ions in aqueous solutions and to determine its optical and kinetic characteristics. For this purpose, we examined weakly acidic ([H^+] = 5×10^{-4} mol dm^{-3}) solutions of sodium bromide saturated with N_2O using a pulse radiolysis technique.

The pulse radiolysis assembly with a Van de Graaf accelerator (electron energy of 3.8 MeV) and the computer software were described previously.[3–5] Experimental conditions and dosimetry were discussed elsewhere.[6]

In aqueous NaBr solutions saturated with N_2O, hydrated electrons e_{aq}^- are converted into OH radicals by the reaction

$$e_{aq}^- + N_2O + H_2O \longrightarrow OH + N_2 + OH^- \quad (8)$$

Thus, the presence of N_2O makes it possible to generate primarily OH radicals under the action of ionising radiation on water. We used reasonably concentrated solutions of NaBr ($\geq$0.1 mol dm^{-3}) in order to shift the equilibrium of reaction (7) to the right and hence to provide the basis for observing the optical signal of the tribromide ion Br_3^-. Figure 1 illustrates changes in the absorbance of a 0.1 M NaBr solution saturated with N_2O (pH 3.3) in time after the action of an electron pulse. The absorption of the Br_2^- radical anion was observed after 1 μs as a band with a maximum at 360 nm ($\varepsilon_{Br_2^-}$ = 9900 dm^3 mol^{-1} cm^{-1}).[1] The disappearance of Br_2^- was accompanied by the appearance of a new absorption band with a maximum at 265 nm which is typical of Br_3^-.[7,8] An isosbestic point was observed at a wavelength of 310 nm. We believe that this process is associated with the formation of the Br_3^- ion as a result of reactions (6) and (7). Figure 2 demonstrates the kinetic curves of (*a*) Br_2^- decay and (*b*) Br_3^- formation.

To correlate the experimental data with the results of computer-assisted calculations, we used the following initial radiation-chemical yields of water radiolysis products typical of weakly acidic solutions in the case of exposure to γ-radiation or accelerated electrons:[9] 2.6 for e_{aq}^-, 0.6 for H, 2.7 for OH, 0.45 for H_2 and 0.7 for H_2O_2. The reactions of water radiolysis products and reaction (8) ($k_8 = 9.1\times10^9$ dm^3 mol^{-1} s^{-1})[9] were taken into account. The rate constants of reactions (1)–(5) were taken from ref. 1 to be (the subscripts 'f' and 'b' refer to the forward and back reactions, respectively) $k_{1f} = 1.06\times10^{10}$ dm^3 mol^{-1} s^{-1} and k_{1b} = 3.3×10^7 s^{-1}; $k_{2f} = 4.4\times10^{10}$ dm^3 mol^{-1} s^{-1} and k_{2b} = 1.4 s^{-1} (ref. 10); $k_{3f} = 1.0\times10^{10}$ dm^3 mol^{-1} s^{-1} and $k_{3b} = 4.6\times10^4$ s^{-1}; k_{4f} = 1.3×10^{10} dm^3 mol^{-1} s^{-1} (ref. 10) and $k_{4b} = 4.2\times10^6$ s^{-1}; k_5 = 1.9×10^8 dm^3 mol^{-1} s^{-1}. In the course of matching, the values of k_6, k_{7f} and k_{7b} were varied. We found that the formation and disappearance of Br_2^- are adequately described with the use of the known values[1] $\varepsilon_{Br_2^-}$ = 9900 dm^3 mol^{-1} cm^{-1} and $k_6 = 3.0\times10^9$ dm^3 mol^{-1} s^{-1} [Figure 2(*a*)]. The obtained value of k_6 is consistent with k_6 = 2.2×10^9 dm^3 mol^{-1} s^{-1} measured in dilute aqueous solutions

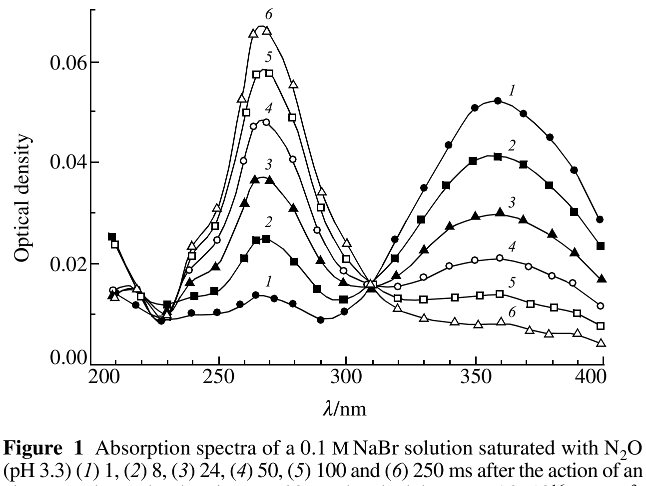

Figure 1 Absorption spectra of a 0.1 M NaBr solution saturated with N_2O (pH 3.3) (*1*) 1, (*2*) 8, (*3*) 24, (*4*) 50, (*5*) 100 and (*6*) 250 ms after the action of an electron pulse. Pulse duration was 20 ns; absorbed dose was 5.2×10^{16} eV cm^{-3}.

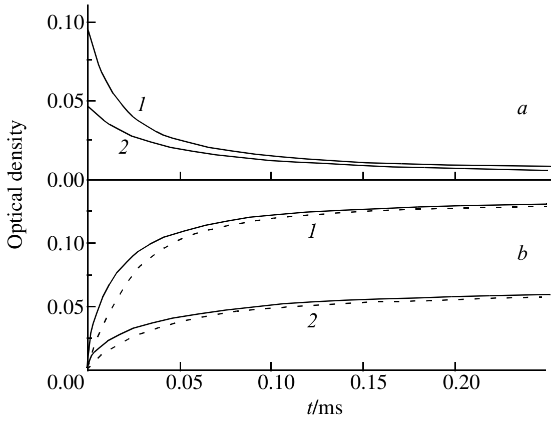

Figure 2 Kinetic curves for changes in the absorption at (*a*) 360 and (*b*) 265 nm: (*1*) 20 ns pulse, dose of 5.1×10^{16} eV cm^{-3}; (*2*) 40 ns pulse, dose of 1.1×10^{17} eV cm^{-3}. Points indicate the experimental data, and curves illustrate the computed results. Solid lines: calculations at $k_6 = 3.0\times10^9$ dm^3 mol^{-1} s^{-1}, $k_{7f} = 9.6\times10^8$ dm^3 mol^{-1} s^{-1}, $k_{7b} = 5.5\times10^7$ s^{-1} and $\varepsilon_{Br_3^-} = 4.4\times10^4$ dm^3 mol^{-1} cm^{-1}. Dashed lines: calculations at $k_6 = 3.0\times10^9$ dm^3 mol^{-1} s^{-1}, k_{7f} = 1.0×10^8 dm^3 mol^{-1} s^{-1}, $k_{7b} = 5.7\times10^6$ s^{-1} and $\varepsilon_{Br_3^-} = 4.4\times10^4$ dm^3 mol^{-1} cm^{-1}.

containing bromide ions.[11] The goodness of fit in the kinetics of the appearance of Br_3^- [Figure 2(*b*)] was attained at k_{7f} = $= 9.6\times10^8$ dm^3 mol^{-1} s^{-1}, $k_{7b} = 5.5\times10^7$ s^{-1} and $\varepsilon_{Br_3^-} = 4.4\times10^4$ dm^3 mol^{-1} cm^{-1}. The calculated curve fell off from the experimental function [Figure 2(*b*)] at lower values of k_{7f} and k_{7b}; this discrepancy was particularly pronounced at the initial stage. The equilibrium constant of reaction (7) $K_7 = k_{7f}/k_{7b}$ was calculated to be equal to 17.4 dm^3 mol^{-1} with the use of k_{7f} and k_{7b} values obtained by optimisation. That is, the values of $\varepsilon_{Br_3^-}$ and K_7 are consistent with the values equal to 4.1×10^4 dm^3 mol^{-1} s^{-1} and 16.1 dm^3 mol^{-1}, respectively, which were measured previously[8] in a study of equilibrium (7) in weakly acidic solutions of Br_2 and Br^-.

References

1 D. Zehavi and J. Rabani, *J. Chem. Soc., Faraday Trans*., 1973, **69**, 1579.

2 M. D'Angelantonio, M. Venturi and Q. Mulazzani, *Radiat. Phys. Chem*., 1988, **32**, 319.

3 E. Janata, *Radiat. Phys. Chem*., 1992, **40**, 437.

4 E. Janata, *Radiat. Phys. Chem*., 1994, **44**, 449.

5 E. Janata and W. Gutsch, *Radiat. Phys. Chem*., 1998, **51**, 65.

6 B. G. Ershov, M. Kelm and E. Janata, *Radiat. Phys. Chem*., 2000, **59**, 309.

7 L. Raphael, in *Bromine Compounds Chemistry and Applications*, eds. D. Price, B. Iddon and B. J. Wakefield, Elsevier, New York, 1988, pp. 369–384.

8 T. X. Wang, M. D. Kelley, J. N. Cooper, R. C. Beckwith and D. W. Margerum, *Inorg. Chem*., 1994, **33**, 5872.

9 G. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.

10 U. K. Klaning and T. Wolf, *Ber. Bunsenges. Phys. Chem*., 1985, **89**, 243.

11 P. Neta, R. E. Huie and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027.

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