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Gamma Radiolysis of Binary Aqueous Systems : Bromate, Periodate, Permanganate & Dichromate Ions

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Gamma radiolysis of neutral aqueous solutions of bromate, periodate, permanganate and dichromate ions both in pure as well as in the presence of various organic solutes, viz. formate, acetate, succinate and ethyl alcohol have been investigated over a wide range of reactant concentrations. It is observed that in each mixed system, the decomposition yield is higher than that in the pure system. Appropriate mechanisms are suggested for the radiolytic reactions on the basis of the observed yields and the participation of primary radiolytic products of water.

THE pulse and steady state radiolysis of pure aqueous solutions of a large number of oxidising and reducing agents have been reported in the past[1,2]. However, the radiation chemical behaviour of these systems under steady irradiations needs further investigation especially in the presence of various scavengers. In continuation of our earlier[3-5] work on radiation-induced redox reactions, we report in this paper results of a comparative study on the steady state radiolysis of BrO_3^-, IO_4^-, MnO_4^- and $Cr_2O_7^{2-}$ alone and in the presence of different organic solutes at neutral *p*H.

Materials and Methods

All the chemicals used were of AR grade and their solutions in conductivity water were irradiated with γ-rays from a ^{60}Co source at a dose rate of 5.2 krad min^{-1}. Br^- was estimated micropotentiometrically, IO_4^- iodometrically in the presence of sodium bicarbonate and permanganate and dichromate ions were determined spectrophotometrically at 545 and 440 nm respectively after centrifuging the irradiated solution.

Results and Discussion

The reduction yields in terms of *G* values for the different systems studied, are given in Tables 1–4.

I. *Bromate*/(*a*) *acetate and* (*b*) *succinate* — The data are recorded in Table 1. The radiolysis of BrO_3^- ions in pure aqueous solutions has been reported by earlier workers[6,7] and also by us[1,8,9] with a saturation value of $G(Br^-) = 0.6$ at 100 m*M* BrO_3^-. The radiolysis of bromate ions, however proceeds by different pathways in the presence of acetate and succinate ions. In the redox mixture acetate and succinate ions react mainly with the OH and the BrO_2 species [Br (IV)][7,8]. The reactivities of these organic ions with the reducing species[4,5] e_{aq}^- and H are much lower compared to BrO_3^- and e_{aq} reaction.

$$k\,(\text{acetate} + e_{aq}^-) = 10^6\ M^{-1}\ sec^{-1}$$

$$k\,(\text{succinate} + e_{aq}^-) = 1.2 \times 10^8\ M^{-1}\ sec^{-1}$$

$$k\,(BrO_3^- + e_{aq}^-) = 2.1 \times 10^9\ M^{-1}\ sec^{-1}$$

Based on the above data mechanisms shown in Schemes 1 and 2 are proposed for the radiolytic decomposition of BrO_3^- ions in the presence of acetate and succinate ions.

The observed yield of 1.3 for $G(Br^-)$ suggests that 40% of BrO_2 species are reduced to Br^- via reaction (8) and the remaining 60% are involved in back reaction[6] : $BrO_2 + BrO_2 \rightarrow$ Products

It has been reported that the formate radical ion $\cdot COO^-$ is formed in the radiolysis of disodium succinate[10]. In this redox system almost 100% of BrO_2

Table 1 — Radiation Chemical Yield G (Br^-) in the Radiolysis of (i) Bromate/Acetate and (ii) Bromate/Succinate Ions

Conc. of BrO_3^- (m*M*)	Conc. of acetate (m*M*)	Conc. of succinate (m*M*)	*G*(Br^-)
10	—	—	0.5
	10	—	1.0
	—	10	1.7
50	50	—	1.3
	—	50	2.0
100	—	—	0.6
	100	—	1.3
	200	—	1.3
	500	—	1.3
	—	100	2.3
	—	200	2.8
	—	500	3.4

TABLE 2 — RADIATION CHEMICAL YIELD $G(-IO_4^-)$ IN THE RADIOLYSIS OF $IO_4^-/HCOO^-$ SYSTEM

[Conc. of IO_4^- = 10.0 m*M*]

Conc. of $HCOO^-$ m*M*	$G(-IO_4^-)$	Conc. of $HCOO^-$ m*M*	$G(-IO_4^-)$
—	7.5	1.0	12.0
0.1	9.0	10.0	221.0

TABLE 3 — RADIATION CHEMICAL YIELD, $G(-MnO_4^-)$ IN THE RADIOLYSIS OF MnO_4^-/CH_3COO^- AND MnO_4^-/Br^- SYSTEMS

Conc. of MnO_4^- m*M*	Conc. of CH_3COO^- m*M*	Conc. of Br^- m*M*	$G(-MnO_4^-)$
0.5	—	—	0.8
	—	1.0	0.4
	—	10.0	0.4
	—	100.0	0.4
	100.0	—	4.2
1.0	—	—	1.1
	1.0	—	1.2
	—	1.0	0.6
	10.0	—	2.8
	—	10.0	0.6
	100.0	—	4.7
	—	100.0	0.6
10.0	100.0	—	6.4

TABLE 4 — RADIATION CHEMICAL YIELD, $G[-Cr(VI)]$ IN THE RADIOLYSIS OF $Cr_2O_7^{2-}/C_2H_5OH$ SYSTEM

Conc. of $Cr_2O_7^{2-}$ m*M*	Conc. of EtOH m*M*	$G[-Cr(VI)]$
1.0	—	0.54
	5.0	1.0
	10.0	1.0
	25.0	1.0
2.5	—	0.52
	5.0	1.32
	10.0	1.32
	25.0	1.32
5.0	—	0.4
	5.0	2.1
	10.0	2.1
	25.0	2.1

$$BrO_3^- + e_{aq}^- \longrightarrow BrO_3^{2-} \quad ..(1)$$

$$BrO_3^- + H \longrightarrow BrO_3^{2-} + H^+ \quad ..(2)$$

$$BrO_3^{2-} \xrightarrow{H_2O} BrO_2[Br(IV)] + 2\,OH^- \quad ..(3)$$

$$CH_3COO^- + OH \longrightarrow CH_3COO^+ + OH^- \quad (4)$$

$$CH_3COO\cdot \longrightarrow \cdot CH_3 + CO_2 \quad ..(5)$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6 \quad ..(6)$$

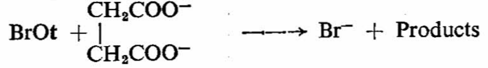
$$CH_3COO^- + \cdot CH_3 \longrightarrow \text{Products} \quad ..(7)$$

$$CH_3COO^- + BrO_2 \longrightarrow Br^- + \text{Products} \quad ..(8)$$

$$CH_3COO\cdot + CH_3COO\cdot \longrightarrow \text{Products} \quad ..(9)$$

Scheme 1

$$BrO_2 + \cdot COO^- \longrightarrow Br^- + CO_2 + O_2 \quad ..(10)$$



$$BrOt + \begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} \longrightarrow Br^- + \text{Products}$$

(11)

Scheme 2

species are reduced to Br^- by the reactions (10) and (11) such that $G(Br^-) = G(e_{aq}^- + H) = 3.4$

In both the redox mixtures $G(Br^-)$ is much higher than the value for the radiolysis of pure bromate solution (Table 1). The low $G(Br^-)$ for the radiolysis of pure bromate solution was explained earlier[8,9].

Periodate/formate system — The data are presented in Table 2. On radiolysis periodate decomposes quantitatively to iodate and oxygen. A plot of the variation of the amount of IO_4^- consumed versus dose at $10^{-2}M$ is found to be linear with $G[-IO_4^-] = 7.5$, which is in agreement with the reported value[12]. The reduction yield increases with increase in formate ions concentration.

The radiolytic reduction of periodate ion has been reported by Bhattacharya and Bardhan[11]. In order to explain the high reduction yield, they suggested that OH acts as a reducing agent. However, Hassan and Heitz[12] rejected this idea. The high decomposition yield obtained in the redox mixture suggcsts that a chain reaction is involved (see Scheme 3).

$$IO_4^- + e_{aq}^- \longrightarrow IO_3^- + O^- \quad ..(12)$$

$$IO_4^- + H \longrightarrow IO_3^- + OH \quad (13)$$

$$IO_4^- + H_2O_2 \longrightarrow IO_3^- + H_2O + O_2 \quad ..(14)$$

$$HCOO^- + OH \longrightarrow \cdot COO^- + H_2O^{14} \quad ..(15)$$

$$\cdot COO^- + IO_4^- \longrightarrow CO_2 + IO_3^- + O^- \quad ..(16)$$

$$O^- + H_2O \longrightarrow OH + OH^- \quad (17)$$

Scheme 3

The regeneration of OH by the step (17) would produce a high concentration of $\cdot COO^-$, thus initiating the chain propogation. The chain is terminated by steps (18) and (19).

$$\cdot COO^- + O_2 \longrightarrow CO_2 + O_2^- \quad ..(18)$$

$$2\,O_2^- + 2\,H_2O \longrightarrow H_2O_2 + 2\,OH^- + O_2 \quad ..(19)$$

H_2O_2 reacts with IO_4^- in a rapid thermal reaction (14)

Permanganate/ (a) acetate and (b) bromide — Our recent study on the radiolysis of pure permanganate solutions[15] shows that the maximum $G[-MnO_4^-]$ is 1.2 at 5 m*M*. In the presence of acetate, a much higher decomposition yield (6.4) is observed (Table 3).

While the primary radiolysis products e_{aq}^-, H, H_2O_2 reduce MnO_4^- ions in steps (20-22) OH is involved in back reactions[15]. In the presence of acetate ion the back reaction is suppressed as OH reacts with acetate ion ($k = 4.6 \times 10^7\ M^{-1}\ sec^{-1}$).

$$MnO_{aq}^- + e_{aq}^- \longrightarrow MnO_4^{2-} \quad ..(20)$$

$$MnO_4^- + H \longrightarrow MnO_4^{2-} + H^+ \quad ..(21)$$

$$MnO_4^- + H_2O_2 \longrightarrow HMnO_3 + O_2 + OH^- \quad ..(22)$$

The products of acetate radiolysis[16], are $\cdot CH_3$, CH_4, C_2H_6 etc. The hydrocarbons (CH_4, C_2H_6) are not oxidised by $KMnO_4$ under normal conditions. Therefore the CH_3 radical alone reacts by step (23).

$$MnO_4^- + \cdot CH_3 \longrightarrow MnO_2 + HCHO + OH^- \quad (23)$$

The formaldehyde formed is readily oxidised by MnO_4^- to formic acid which further reduces permanganate[17]. The manganate ion being unstable in neutral medium, in the presence of CO_2 yields MnO_2 (ref. 15). Thus, the overall mechanism of reduction appears to be complicated.

However, for the radiolysis in the presence of Br^- ions the following explanation is advanced.

It is well known that Br^- ions are efficient scavengers of OH with a high rate constant ($k = 1.1 \times 10^9$ M^{-1} sec^{-1})[4,5]. Thus one should expect G ($-MnO_4^-$) to be higher in the presence of Br^-. However, the low yield (0.6) actually observed suggests that the Br species formed is again attacked by e_{aq}^- to yield Br^-. It is of interest to observe that the value 0.6 observed for G ($-MnO_4^-$) is independent of both MnO_4^- and Br^- ions.

This explanation for the low observed G ($-MnO_4^-$) is not satisfactory. The competition of Br with electrons seems unlikely as MnO_4^- has a high rate constant with e_{aq}^- (10^{10} M^{-1} sec^{-1})[18]. The fate of Br species may be decided from the consideration of the reactions (24-30).

$$Br + Br \longrightarrow Br_2 \qquad ..(24)$$
$$Br_2 + e_{aq}^- \longrightarrow Br_2^- \qquad ..(25)$$
$$Br_2 + Br^- \longrightarrow Br_3^- \qquad ..(26)$$
$$Br_2^- + Br_2^- \longrightarrow Br_3^- + Br^- \qquad ..(27)$$
$$Br_2^- + H_2O_2 \longrightarrow 2\,Br^- + HO_2 + H^+ \qquad ..(28)$$
$$Br + H_2O_2 \longrightarrow HBr + HO_2 \qquad ..(29)$$
$$Br + HO_2 \longrightarrow HBr + O_2 \qquad ..(30)$$

It may be mentioned that the irradiated mixtures do not contain a trace of Br_2. The formation of HBr under present conditions is unlikely, because the yield is low, otherwise a high $G(-MnO_4^-)$ could be obtained since HBr readily reduces MnO_4^- ions. Therefore, this explanation is also not valid. As the redox yield in mixtures is comparatively lower (0.6) than that of pure solutiont (1.2), itappears that permanganate reduction is inhibited by the presence of Br^-. So it is plausible to assume that the initial reduced product is possibly smoothly oxidised again leading to the reformation of MnO_4^-. Br species only can satisfy this condition, because this is a powerful electron acceptor. This is explained if one considers the reactions (20) and (31).

$$MnO_4^- + e_{aq}^- \longrightarrow MnO_4^{2-} \qquad ..(20)$$
$$MnO_4^{2-} + Br \longrightarrow MnO_4^- + Br^- \qquad ..(31)$$

Thus the radiation decomposition of permanganate is exclusively due to H and H_2O_2.

The reduction yield corresponds to

$$G[-MnO_4^-] = \tfrac{1}{3}\,[G_{e_{aq}^-} - G_{OH} + G_H + G_{H_2O_2}] = 0.5$$

which is close to the experimental value observed.

Dichromate/ethyl alcohol — Table 4 contains all the data for this system. In the radiolysis of neutral aqueous solution of pure $Cr_2O_7^{2-}$ ions e_{aq}^- and H have a reducing action while OH is involved in a back reaction[19,20]. In the presence of alcohol, OH is scavanged. The reaction pathways may be as shown in Scheme 4.

$$Cr(VI) + e_{aq}^- \longrightarrow Cr(V) \qquad ..(32)$$
$$Cr(VI) + H \longrightarrow Cr(V) + H^+ \qquad ..(33)$$
$$CH_3CH_2OH + OH \longrightarrow CH_3CHOH + H_2O \qquad ..(34)$$
$$Cr(V) + H_2O_2 \longrightarrow Cr(III) + 2H^+ + O_2 \qquad ..(35)$$
$$Cr(V) + CH_3CHOH \longrightarrow Cr(IV) + \text{Products} \qquad ..(36)$$
$$Cr(VI) + CH_3CHOH \longrightarrow Cr(III) + \text{Products} \qquad ..(37)$$

Scheme 4

Since Cr(VI) reduction involves three-electron transfer, Eqs (32-37) lead to the following G[—Cr(VI)][19,20]:

$$G[-Cr(VI)] \approx \tfrac{1}{3}\,[G_{e_{aq}^-} + G_H + 2G_{H_2O_2} + \tfrac{1}{2}G_{OH}] \approx 2.1$$

which is in excellent agreement with the experimental value.

It is known that solutions of many oxidising agents are reduced under gamma radiation with a yield of about 2.3 atom-equivalents per 100 eV. In terms of molecules the yield may amount to one half or one third of this number, depending upon the number of equivalents involved in the reduction process.

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