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Radiation Chemistry of Bromate Anion In Aqueous Solutions

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Summary: Steady state radiolytic studies were carried out and G($-BrO_3^-$), G(BrO_2^-), G(BrO^-), G(O_2) and G(H_2) were determined. The values obtained are 4.46 ± 0.08, 3.05 ± 0.1, 0.51 ± 0.08, 3.48 ± 0.08 and 0.4 ± 0.08 respectively. A mechanism for the radiolytic decomposition of bromate anions in solution is suggested.

Introduction

Various investigations regarding the transient species produced during the radiolysis and flash photolysis of bromate anions in aqueous solutions have been carried out but not much steady state radiolytic work has been reported in the literature [1-6]. Thus nowhere complete mechanism for the radiolytic decomposition has been reported in the literature. In this paper an attempt is made to establish a mechanism for the decomposition of bromate ion in aqueous solutions.

Experimental

All chemicals used were analar reagent grade.

All solutions were prepared in triply distilled water just before irradiation.

Solutions were saturated with N_2, H_2, or N_2O using usual bubbling procedure described elsewhere [7].

All the analysis for the products BrO_2^-, BrO^-, O, H_2 and reactants BrO_3^- ions were carried out by the methods reported earlier in the literature [5,8].

The experimental arrangement and description about the sources have already been reported [8]. A 10 ml sample was irradiated each time using gamma Co^{60} gamma source with the dose rate of 5.8×10^{18} ev per Sec.

Result and Discussion

N_2 Saturated System

Steady state radiolysis of N_2 saturated 10^{-3} 5×10^{-3}M solution of bromate anion at pH 13 ± 0.1 was carried out. Disappearance yield for the bromate ion and the product yield for BrO_2^-/BrO^-, O_2 and H_2 were measured at various doses. The yield/dose plot were found to be fairly linear except for BrO_2^- ion. At very high doses the yield of BrO_2^- was found to be decreasing. (see table 1).

The G(BrO_2^-), G($-BrO_3^-$), G(BrO^-), G(O_2) and G(H_2) obtained from the slopes of the yield/doses plots are summarized in table 1.

In the pulse radiolysis and flash photolysis studies reported in the lite-

Table-1: The study state radiolysis of nitrogen saturated aqueous solution of bromate ion at pH 13.0 ± 0.1

(a) Variation of radiation chemical yields for BrO_3^- and BrO_2^- with dose rate 5.8×10^{18} ev/sec.

$$(BrO_3^-) = 10^{-3}M \longrightarrow 5 \times 10^{3}M$$

Dose range (ev)	$G(-BrO_3^-)$	$G(BrO_2^-)$
(1) $10^{19} \longrightarrow 5 \times 10^{20}$	4.46 ± 0.08	3.05 ± 0.10
(2) $5 \times 10^{20} \longrightarrow 10^{21}$	4.46 ± 0.08	3.05 ± 0.10
(3) $10^{21} \longrightarrow 8 \times 10^{21}$	4.46 ± 0.08	2.90 ± 0.12
(4) $8\ 10^{21} \longrightarrow 5 \times 10^{22}$	4.40 ± 0.05	2.76 ± 0.10

(b) The measured radiation chemical yields for $G(-BrO_3^-)$, $G(BrO_2^-)$ $G(BrO^-)$, $G(O_2)$ and $G(H_2)$

$G(-BrO_3^-)$ = 4.46 ± 0.08

$G(BrO_2^-)$ = 3.05 ± 0.1

$G(BrO^-)$ = 0.51 ± 0.08

$G(O_2)$ = 3.48 ± 0.08

$G(H_2)$ = 0.4 ± 0.08

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rature [2,5] the transient species BrO_3, BrO_2 and BrO have been identified. It is also reported that the species, BrO_2 and BrO decay by second order process [2,9].

The species BrO_2 and BrO_3 are produced by the following processes.

$$e_{aq}^- + BrO_3^- \longrightarrow BrO_2 + 2\ OH^- \quad (1)$$

$$OH + BrO_3^- \longrightarrow BrO_3 + OH^- \quad (2)$$

and the species OH and e_{aq}^- are produced in the primary act of gamma radiations on water in (3)

$$H_2O \rightsquigarrow e_{aq}^-, OH, H, H_2, H_2O_2 \quad (3)$$

The species BrO_2 was found to decay by second order process. The process may be similar to that reported in case of IO_2 [10]

$$2BrO_2 \rightleftharpoons Br_2O_4 \quad (4)$$

and this may react with OH^-

$$Br_2O_4 + 2OH^- \longrightarrow BrO_3^- + BrO_2^- + H_2O \quad (5)$$

Similar reaction takes place in case of other oxyhalogen radicals [5,8,10, 11].

The species BrO is most likely to be produced by the reaction

$$BrO_3 \longrightarrow O_2 + BrO \quad (6)$$

The first order decay BrO_3 reported in the literature [2] and the measured yield of O_2 (see table 1) are in favour of reaction (5).

The species BrO is also reported to decay by a second order process [2,8] and the reactions and the products reported are [8]

$$2BrO \rightleftharpoons Br_2O_2 \quad (7)$$

$$Br_2O_2 + 2\ OH^- — BrO_2^- + H_2O + BrO^- \quad (8)$$

In addition to reaction (6) leading to the product oxygen, O_2 can also be produced by the reaction of primary product H_2O_2 and BrO^- produced in reaction (8).

$$BrO^- + H_2O_2 \longrightarrow Br^- + O_2 + H_2O \quad (9)$$

The measured yield for O_2 is in agreement with reactions (6) and (9) and also the radiation chemical yield for BrO^- is in agreement with reaction (8) and (9).

Unlike IO_3 the decay of transient species BrO_3 does not depend on BrO_3^- concentration thus reaction (10)

$$BrO_3 + BrO_3^- \longrightarrow BrO_4^- + BrO_2 \quad (10)$$

does not occur. The expected values of G ($-BrO_3^-$) $G(BrO_2^-)$, $G(BrO^-)$, $G(O_2)$ and $G(H_2)$ in terms of primary radiation chemical yield G_{OH}, G_{eaq} G_H, G_H and $G_{H_2O_2}$ can be obtained from the following equations based on the possible reactions (1), (2), (3), (4),(5), (6), (7), (8), and (9) mention above

$$G(-BrO_3^-) = G_{OH} + 0.5\ (G_H + G_{e_{aq}^-}) \quad (11)$$

$$G(BrO_2^-) = 0.5\ (G_{OH} + G_{e_{aq}^-} + G_H) \quad (12)$$

All H atoms are converted to e_{aq}^- at this alkaline pH.

$$G(BrO^-) = 0.5\ G_{OH} - G_{H_2O_2} \quad (13)$$

$$G(O_2) = G_{H_2O_2} + G_{OH} \quad (14)$$

$$G(H_2) = G_{H_2}$$

On substitution of the values of $G_{e_{aq}^-}$, G_{OH}, G_H, G_{H_2} and $G_{H_2O_2}$, reported in the literature [12], in the equations (11), (12), (13), (14) and (15) the values of $G(BrO_3^-)$ $G(BrO_2^-)$, $G(BrO^-)$, $G(O_2)$ and $G(H_2)$ are 4.63, 3.2, 0.62, 3.65 and 0.45 respectively. These values are in very good agreement with the observed values (see table 1).

N_2O Saturated Systems

Steady state radiolysis was also carried out using N_2O saturated aqueous solution of 10^{-3}M to 5 x 10^{-3}M BrO_3^-.

Table-2: The steady state radiolysis of nitrous oxide saturated aqueous solution of bromate ion at pH 13 $\pm$ 0.1. The measured radiation chemical yield $G(-BrO^-_3)$, $G(BrO^-)$, $G(O_2)$ are $G(H_2)$ as follows:-

$(BrO^-_3) = 10^{-3} \longrightarrow 5 \times 10^{-3}M$

$G(BrO^-_3)$ = 6.2 ± 0.5

$G(BrO^-_2)$ = 3.12 ± 0.05

$G(BrO^-)$ = 2.25 ± 0.06

$G(O_2)$ = 7.17 ± 0.08

$G(H_2)$ = 0.39 ± 0.08

The yield $G(BrO_3^-)$, $G(BrO_2^-)$ $G(BrO^-)$, $G(O_2)$ and $G(H_2)$ observed from the slope of yield/dose plots are summarized in table 2.

Under these conditions all the e^-_{aq} will react with N_2O, [5,12]

$$N_2O + e^-_{aq} \longrightarrow N_2 + O^- \ H_2O \quad OH + OH^- \quad (16)$$

and reactions (1), (4) and (5) should not be taking place. Reaction (2), (6), (7), (8) and (9) are expected to take place.

The G value for BrO^-_3, BrO_2^-, BrO^-, O_2 and H_2 can be related with the primary radiation chemical yield as follows

$$G(-BrO_3^-) = G_{OH} + G_H + G_{e^-_{aq}} \quad (16)$$

$$G(BrO_2^-) = 0.5\ (G_{OH} + G_H + G_{e^-_{aq}}) \quad (17)$$

$$G(BrO^-) = 0.5\ (G_{OH} + G_H + G_{e^-_{aq}}) - G_{H_2O_2} \quad (18)$$

$$G(O_2) = G_{H_2O_2} + G_{OH} + G_{e^-_{aq}} + G_H \quad (19)$$

$$G(H_2) = G_{H_2} \quad (15)$$

The calculated values for $G(-BrO_3^-)$, $G(BrO_2^-)$, $G(BrO^-)$, $G(H_2)$ and (GO_2) using relationships (15), (16), (17), (18) and (19) are 6.4, 3.25, 2.45, 0.45 and 7.3 respectively. These values are also in good agreement with the experimentally observed values (see table 2). Thus giving a further support for the above mentioned series of reactions for the radiolytic decomposition of bromate anion.

H_2 Saturated System

Steady state radiolysis of H_2 saturated aqueous solution of 10^{-3}-$5 \times 10^{-3}M$ bromate anions at pH 13. $\pm$ 0.1 was carried out.

The measured yield for $G(-BrO^-_3)$ and $G(BrO_2^-)$ and $G(O_2)$ was obtained from the yield/dose plots and are summarized in table 3.

In this case most probably the following reactions are taking place.

$$OH_2 + H_2 \longrightarrow H_2O + H \quad (20)$$

$$H + OH^- \longrightarrow e^-_{aq} \quad (21)$$

Table-3: The steady radiolysis of hydrogen saturated aqueous solution of bromate ion at pH = 13 ± 0.1. The measured radiation chemical yields $G(-BrO^-_3)$, $G(BrO^-_2)$ and $G(O_2)$ are as follows:-

$$(BrO^-_3) = 10^{-3}M \longrightarrow 5 \times 10^{-3}M$$

$G(-BrO^-_3)$	=	3.08 ± 0.1
$G(BrO^-_2)$	=	2.62 ± 0.05
$G(O_2)$	=	0.72 ± 0.08

$$BrO_3^- + e^-_{aq} \longrightarrow BrO_2 + 2OH^- \quad (1)$$

$$2BrO_2 \rightleftharpoons Br_2O_4 \quad (4)$$

$$Br_2O_4 + 2OH^- \longrightarrow BrO_2^- + O_3^- + H_2O \quad (5)$$

$$2H_2O_2 + BrO_2^- \longrightarrow 2\ O_2 + 2H_2O + Br^- \quad (22)$$

The relationships, based on reactions (1), (4), (5), (20), (21) and (22) for $G(-BrO_3^-)$, $G(BrO_2^-)$ and $G(O_2)$ in terms of primary radiation chemical yields can be written as

$$G(-BrO_3^-) = 0.5\ (G_{e^-} + G_H + G_{OH}) \quad (23)$$

$$G(BrO_2^-) = 0.5\ (G_{e^-} + G_H + G_{OH} - G_{H\ O}) \quad (24)$$

$$G(O_2) = G_{H\ O} \quad (25)$$

The calculated values of $G(-BrO^-_3)$ $G(BrO^-_2)$ and $G(O_2)$ based on equations (23), (24) and (25) and the values of $G_{e^-_{aq}}$, G_H, G_{OH} reported in the literature[12], are 3.2, 2.8 and 0.8 respectively and a best agreement is found between the observed and calculated values (see table 3).

All the above mentioned data and related observations lead to he conclusion that the following is the most probable mechanism for the radiolytic decomposition of bromate anion in aqueous solution.

$$H_2O \rightsquigarrow e^-_{aq}, OH, H, H_2, H_2O_2 \quad (3)$$

$$e^-_{aq} + BrO_3^- \longrightarrow BrO_2 + 2OH^- \quad (1)$$

$$OH + BrO_3^- \longrightarrow BrO_3 + OH^- \quad (2)$$

$$2BrO_2 \rightleftharpoons Br_2O_4 \quad (4)$$

$$Br_2O_4 + 2OH^- \longrightarrow BrO_3^- + BrO_2^- + H_2O \quad (5)$$

$$BrO_3 \longrightarrow BrO + O_2 \quad (6)$$

$$2BrO \rightleftharpoons Br_2O_2 \quad (7)$$

$$Br_2O_2 + 2OH^- \longrightarrow BrO^- + BrO_2^- + H_2O \quad (8)$$

$$BrO^- + H_2O_2 \longrightarrow O_2 + H_2O + Br^- \quad (9)$$

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