

## Radiation Chemistry of Bromate Anion In Aqueous Solutions

M.S.SUBHANI

*Department of Chemistry, Faculty of Science,  
University of Caryounis, Benghazi - Libya*

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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  $4.46 \pm 0.08$ ,  $3.05 \pm 0.1$ ,  $0.51 \pm 0.08$ ,  $3.48 \pm 0.08$  and  $0.4 \pm 0.08$  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  $BrO_2^-$ ,  $BrO^-$ ,  $O_2$ ,  $H_2$  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  $5.8 \times 10^{18}$  ev per Sec.

### Result and Discussion

#### *N<sub>2</sub> Saturated System*

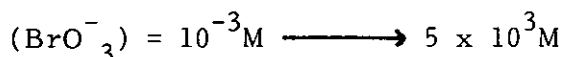
Steady state radiolysis of  $N_2$  saturated  $10^{-3}$   $5 \times 10^{-3}$  M solution of bromate anion at pH  $13 \pm 0.1$  was carried out. Disappearance yield for the bromate ion and the product yield for  $BrO_2^-/BrO^-$ ,  $O_2$  and  $H_2$  were measured at various doses. The yield/dose plot 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 literature

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

(a) Variation of radiation chemical yields for  $\text{BrO}_3^-$  and  $\text{BrO}_2^-$  with dose rate  $5.8 \times 10^{18}$  ev/sec.



Dose range (ev)	$G(-\text{BrO}_3^-)$	$G(\text{BrO}_2^-)$
(1) $10^{19} \longrightarrow 5 \times 10^{20}$	$4.46 \pm 0.08$	$3.05 \pm 0.10$
(2) $5 \times 10^{20} \longrightarrow 10^{21}$	$4.46 \pm 0.08$	$3.05 \pm 0.10$
(3) $10^{21} \longrightarrow 8 \times 10^{21}$	$4.46 \pm 0.08$	$2.90 \pm 0.12$
(4) $8 \times 10^{21} \longrightarrow 5 \times 10^{22}$	$4.40 \pm 0.05$	$2.76 \pm 0.10$

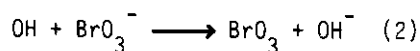
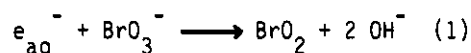
(b) The measured radiation chemical yields for  $G(-\text{BrO}_3^-)$ ,  $G(\text{BrO}_2^-)$

$G(\text{BrO}^-)$ ,  $G(\text{O}_2)$  and  $G(\text{H}_2)$

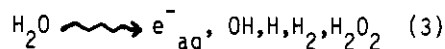
$G(-\text{BrO}_3^-)$	=	$4.46 \pm 0.08$
$G(\text{BrO}_2^-)$	=	$3.05 \pm 0.1$
$G(\text{BrO}^-)$	=	$0.51 \pm 0.08$
$G(\text{O}_2)$	=	$3.48 \pm 0.08$
$G(\text{H}_2)$	=	$0.4 \pm 0.08$

ature [2,5] the transient species  $\text{BrO}_3$ ,  $\text{BrO}_2$  and  $\text{BrO}$  have been identified. It is also reported that the species,  $\text{BrO}_2$  and  $\text{BrO}$  decay by second order process [2,9].

The species  $\text{BrO}_2$  and  $\text{BrO}_3$  are produced by the following processes.



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

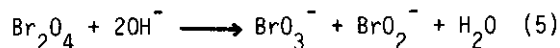


The species  $\text{BrO}_2$  was found to decay by second order process. The process

may be similar to that reported in case of  $\text{IO}_2$  [10]

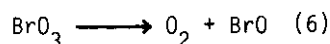


and this may react with  $\text{OH}^-$



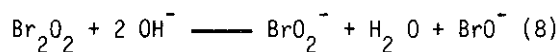
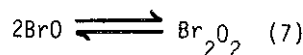
Similar reaction takes place in case of other oxyhalogen radicals [5,8,10,11].

The species  $\text{BrO}$  is most likely to be produced by the reaction

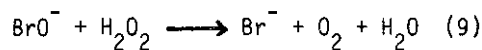


The first order decay  $\text{BrO}_3$  reported in the literature [2] and the measured yield of  $\text{O}_2$  (see table 1) are in favour of reaction (5).

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



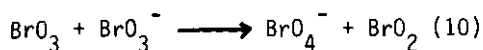
In addition to reaction (6) leading to the product oxygen,  $\text{O}_2$  can also be produced by the reaction of primary product  $\text{H}_2\text{O}_2$  and  $\text{BrO}^-$  produced in reaction (8).



The measured yield for  $\text{O}_2$  is in agreement with reactions (6) and (9) and also the radiation chemical yield for  $\text{BrO}^-$  is in agreement with reaction (8) and (9).

Unlike  $\text{IO}_3$  the decay of transient species  $\text{BrO}_3$  does not depend on

$\text{BrO}_3^-$  concentration thus reaction (10)



does not occur. The expected values of  $G(-\text{BrO}_3^-)$ ,  $G(\text{BrO}_2^-)$ ,  $G(\text{BrO}^-)$ ,  $G(\text{O}_2)$  and  $G(\text{H}_2)$  in terms of primary radiation chemical yield  $G_{\text{OH}}$ ,  $G_{\text{e}_{\text{aq}}^-}$ ,  $G_{\text{H}}$ ,  $G_{\text{H}_2\text{O}_2}$  can be obtained from the following equations based on the possible reactions (1), (2), (3), (4), (5), (6), (7), (8), and (9) mentioned above

$$G(-\text{BrO}_3^-) = G_{\text{OH}} + 0.5 (G_{\text{H}} + G_{\text{e}_{\text{aq}}^-}) \quad (11)$$

$$G(\text{BrO}_2^-) = 0.5 (G_{\text{OH}} + G_{\text{e}_{\text{aq}}^-} + G_{\text{H}}) \quad (12)$$

All H atoms are converted to  $\text{e}_{\text{aq}}^-$  at this alkaline pH.

$$G(\text{BrO}^-) = 0.5 G_{\text{OH}} - G_{\text{H}_2\text{O}_2} \quad (13)$$

$$G(\text{O}_2) = G_{\text{H}_2\text{O}_2} + G_{\text{OH}} \quad (14)$$

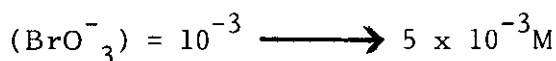
$$G(\text{H}_2) = G_{\text{H}_2}$$

On substitution of the values of  $G_{\text{e}_{\text{aq}}^-}$ ,  $G_{\text{OH}}$ ,  $G_{\text{H}}$ ,  $G_{\text{H}_2}$  and  $G_{\text{H}_2\text{O}_2}$  reported in the literature [12], in the equations (11), (12), (13), (14) and (15) the values of  $G(\text{BrO}_3^-)$ ,  $G(\text{BrO}_2^-)$ ,  $G(\text{BrO}^-)$ ,  $G(\text{O}_2)$  and  $G(\text{H}_2)$  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<sub>2</sub>O Saturated Systems*

Steady state radiolysis was also carried out using  $\text{N}_2\text{O}$  saturated aqueous solution of  $10^{-3}\text{M}$  to  $5 \times 10^{-3}\text{M}$   $\text{BrO}_3^-$ .

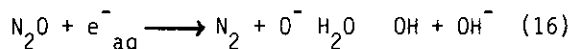
Table-2: The steady state radiolysis of nitrous oxide saturated aqueous solution of bromate ion at pH 13  $\pm$  0.1. The measured radiation chemical yield  $G(-BrO_3^-)$ ,  $G(BrO_2^-)$ ,  $G(O_2)$  are  $G(H_2)$  as follows:-



$G(BrO_3^-)$	=	$6.2 \pm 0.5$
$G(BrO_2^-)$	=	$3.12 \pm 0.05$
$G(BrO^-)$	=	$2.25 \pm 0.06$
$G(O_2)$	=	$7.17 \pm 0.08$
$G(H_2)$	=	$0.39 \pm 0.08$

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]



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  $G(O_2)$  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.

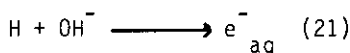
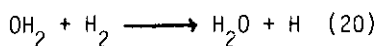
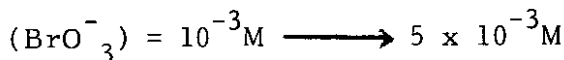
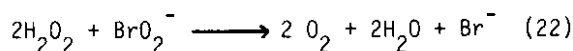
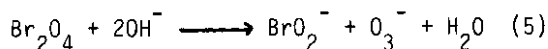
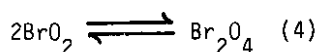
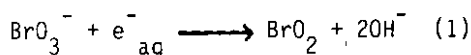


Table-3: The steady radiolysis of hydrogen saturated aqueous solution of bromate ion at  $\text{pH} = 13 + 0.1$ . The measured radiation chemical yields  $G(-\text{BrO}_3^-)$ ,  $G(\text{BrO}_2^-)$  and  $G(\text{O}_2)$  are as follows:-



$G(-\text{BrO}_3^-)$	=	$3.08 \pm 0.1$
$G(\text{BrO}_2^-)$	=	$2.62 \pm 0.05$
$G(\text{O}_2)$	=	$0.72 \pm 0.08$



The relationships, based on reactions (1), (4), (5), (20), (21) and (22) for  $G(-\text{BrO}_3^-)$ ,  $G(\text{BrO}_2^-)$  and  $G(\text{O}_2)$  in terms of primary radiation chemical yields can be written as

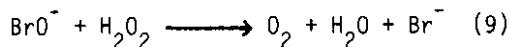
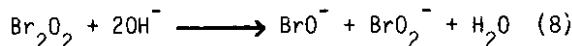
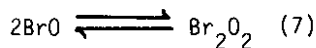
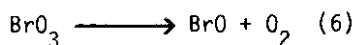
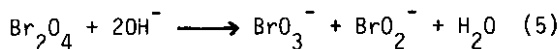
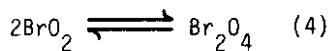
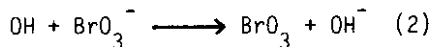
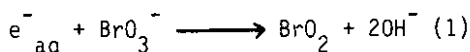
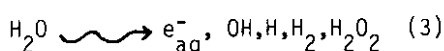
$$G(-\text{BrO}_3^-) = 0.5 (G_{e^-} + G_{\text{H}} + G_{\text{OH}}) \quad (23)$$

$$G(\text{BrO}_2^-) = 0.5 (G_{e^-} + G_{\text{H}} + G_{\text{OH}} - G_{\text{H}_2\text{O}}) \quad (24)$$

$$G(\text{O}_2) = G_{\text{H}_2\text{O}} \quad (25)$$

The calculated values of  $G(-\text{BrO}_3^-)$ ,  $G(\text{BrO}_2^-)$  and  $G(\text{O}_2)$  based on equations (23), (24) and (25) and the values of  $G_{e^-}$ ,  $G_{\text{H}}$ ,  $G_{\text{OH}}$  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 the conclusion that the following is the most probable mechanism for the radiolytic decomposition of bromate anion in aqueous solution.



## References

1. M.K.Bridge and M.S.Matheson, *J.Phys.Chem.*, **64**, 2280 (1960)
2. O.Amichai, C.Czapski and A. Treinin, *Israel J.Chem.*, **7**, 351 (1969)
3. M.S.Matheson and L.M.Dorfman, *J.Chem.Phys.*, **32**, 1870 (1960)
4. O.Amichai and A.Treinin, *Chem.Phys.Let.*, **3**, 611 (1969)
5. G.V.Buxton and F.S.Dainton, *Proc.Roy.Soc.(London)*, **A304**, 427 (1968)
6. O.Amichai and A.Treinin, *J.Phys.Chem.*, **74**, 830 (1970)

7. M.S. Subhani and T. Kauser,  
*Rev. Roumaine Chim.*, **23**, 1619  
(1978)
8. M.S. Subhani,  
*Rev. Roumaine Chim.*, **25**, 986 (1980)
9. A. Treinin,  
*Israel J. Chem.*, **8**, 305 (1970)
10. M.S. Subhani,  
*Rev. Roumaine Chim.*, **28**, 281 (1983)
11. G.V. Buxton and M.S. Subhani,  
*J. Chem. Soc. Faraday Trans.*, **1**, **68**,  
947 (1972)
12. G.V. Buxton,  
*Radiation Res.*, **1**, 209 (1968)