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RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF THE HYPOIODITE ION

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Steady state radiolysis of aqueous hypoidoite solution has been carried out both in the presence of N_2 and N_2O. The radiation chemical yield for the disappearance of 10^- and for the products $10^-_3 O_2$ and H_2 has been also determined.

A complete mechanism for the radiolytic decomposition of hypoiodite ion in aqueous system is proposed which is as follows:

$$e^-_{aq} + 10^- \rightarrow I^- + O^-$$
$$\qquad \rightarrow 1 + (O^{2-} \overset{H_2O}{\rightleftharpoons} 2OH^-)$$

$$10^- + I \rightarrow 10 + I^-$$

$$10^- + 0^- \overset{H_2O}{\rightarrow} 10 + 2OH^-$$

$$10^- + OH \rightarrow 10 + OH^-$$

$$2IO \rightleftharpoons I_2O_2$$

$$I_2O_2 + H_2O \rightarrow 10^- + 10^-_2 + 2H^+$$

$$I_2O_2 + IO_2^- \rightarrow 10^-_3 + (I_2O \overset{H_2O}{\rightarrow} 210^- + 2H^+)$$

$$10^- + H_2O_2 \rightarrow 1^- + O_2 + H_2O$$

The calculated radiation chemical yields for G (-10^-), G(IO^-_3) G(O_2) and G(H_2), based on this mechanism are in good agreement with the observed yields.

INTRODUCTION

Several investigations have been made to establish the primary processes taking place in the radiolysis and photolysis of oxyhalogen ions in aqueous solution [1-7]. Studies have also been made to establish a mechanism for the radiolytic and photolytic decomposition of some oxychlorine and oxybromine anions in solution [5-8]. Thus it is of great interest to study the radiation chemistry of some of these systems much in detail in order to establish a complete mechanism for their radiolytic decomposition. (In this paper we intend to establish a complete mechanism for the radiolytic decomposition of hypoiodite ion in aqueous solution.

EXPERIMENTAL

All solutions to be irradiated were prepared from triply distilled water just before irradiation.

These solutions were saturated with nitrogen (white spot) streight from the cylinder using normal bubbling procedure described elsewhere [9]. Nitrous oxide was passed through a column of potassium hydroxide pellets and then through a trap at -80^o to remove any CO_2 and NO.

Sodium hypoiodite solution was prepared in the laboratory by the method reported in the literature [3].

The pH of the solution was measured using pH meter.

Co^{60} (γ -rays) source was used for all steady state experimental work and the set-up for irradiation was similar to that described before [5].

The samples were analysed before and after the irradiation for 10^{-}, IO^{-}_{3}, by methods reported in the literature [1, 5, 10]. using PYE UNICAM spectrophotometer SP1800. Hydrogen and oxygen were measured chromatographically.

RESULTS AND DISCUSSIONS

Steady state radiolysis studies of various nitrogen or nitrous oxide saturated aqueous solutions of hypoiodite ion were carried out at pH 12.9 to 13.1 using different doses by irradiation at different intervals of time. The yield for the disappearance of hypoiodite and that for the products iodate ion, oxygen and hydrogen were measured. 10^{-} was prepared immediately prior to irradiation. However, an allowance for the thermal decomposition of 10^{-} was made by analysing the blank samples for each case of irridiation, which was always found less than 1%.

Yield/dose plots were fairly linear (see Fig. 1), indicating that all radicals are scavenged by the hypoiodite ion. The values for $G(-10^{-})$, $G(10^{3}-)$, $G(H\ )$ and $G(O_2)$ obtained from these yield/dose plots are summarized in Table 1.

The information reported in the literature [3] for the pulse radiolysis of aqueous solutions of hypoiodite ion indicate that a transint species 10 is produced and decays by a second order reaction with a rate constant 5×10^{9} $M^{-1}S^{-1}$. The species BrO and C10 have already been reported in the literature [1, 5], and were also reported to follow second order kinetics.

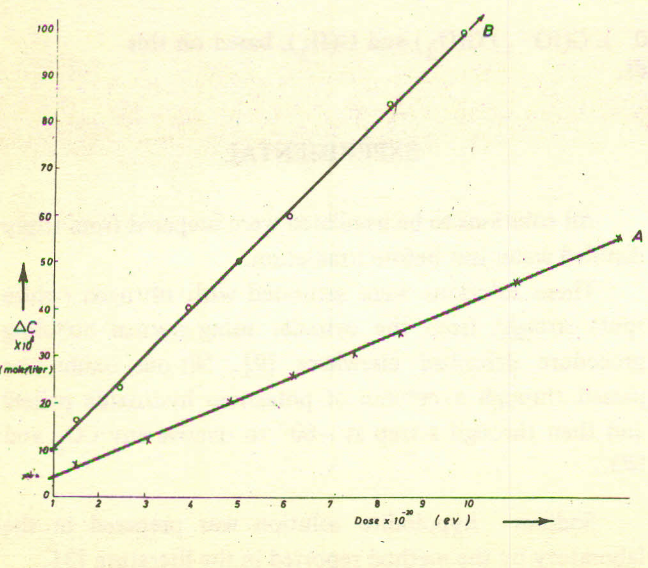

Fig. 1.

Intermediate dimers, Cl_2O_2 and Br_2O , having an equilibrium with the transient species C10 and BrO respectively have been reported (1, 5). Most probably a similar equilibrium hight for the transient 10 according to the reaction:

$$210 \rightleftharpoons I_2O_2 \qquad (1)$$

The species 10 is most likely to be formed by the following reaction:

$$10^{-} + e^{-}_{aq} \rightarrow I^{-} + O^{-} \qquad (2)$$

$$\rightarrow I + (O^{2-} \overset{H_2O}{\rightleftharpoons} OH^{-} + OH^{-}) \qquad (3)$$

$$10^{-} + I \rightarrow 10 + I^{-} \qquad (4)$$

$$10^{-} + O^{-} \rightarrow 10 + (O^{2-} \overset{H_2O}{\rightarrow} 2OH^{-}) \qquad (5)$$

$$10^{-} + OH \rightarrow 10 + OH^{-} \qquad (6)$$

The radicals e^{-}_{aq}, OH are produced by gamma rays the primary reaction:

$$H_2O \rightarrow e^{-}_{aq}, OH, H, H_2, H_2O_2 \qquad (7)$$

Thus a transient species is produced by oxidizing radicals. The species I_2O_2 in equilibrium with 10 (eq. 1) may react with H_2O to produce 10^{-} which further reacts with I_2O_2 [2] to produce $10^{\cdot}_{+}$ ions just the same way as in hypobromite and hypochlorite systems [1, 5]:

$$I_2O_2 + H_2O \rightarrow IO_2^{-} + 10^{-}\ 2H^{+} \qquad (8)$$

$$10_2^{-} + I_2O_2 \rightarrow 10^{-}_{3} + I_2O \qquad (9)$$

$$\downarrow H_2O$$

$$210^{-} + 2H^{+}$$

The product 10^{-}_{3} was identified but IO_2^{-} being a very unstable species was not identified as end products [2]. The observed oxygen is most likely to come from the well known reaction (10) similar to that which occurs in $C10^{-}$ and BrO^{-} systems [1, 5]. Thus the reactions occurring in the radiolysis of aqueous solution of the hypoiodite ion would be expected to follow the reactions:

$$H_2O \rightarrow e^{-}_{aq}\ OH, H, H_2\ H_2O_2 \qquad (7)$$

$$10^- + e^-_{aq} \to I^- + O^- \quad (2)$$

$$\to I + (O^{2-} \overset{H_2O}{\rightleftharpoons} \to 2OH^-) \quad (3)$$

$$10^- + I \to 10 + I^- \quad (4)$$

$$10^- + O^- \to 10 + (O^{2-} \overset{H_2O}{\to} 2OH^-) \quad (5)$$

$$10^- + OH \to 10 + OH^- \quad (6)$$

$$210 \rightleftharpoons I_2O_2 \quad (1)$$

$$I_2O_2 + H_2O \to 10^- + 10^-_2 + 2H^+ \quad (8)$$

$$I_2O_2 + 10^-_2 \to 10^-_3 + I_2O \overset{H_2O}{\downarrow} \to 210^- + 2H^+ \quad (9)$$

$$10^- + H_2O_2 \to I^- + O_2 + H_2O \quad (10)$$

Evidence for the transient species 10 is reported in the literature [3] and the second order kinetics supports the formation of dimer I_2O_2 in equilibrium with 10 (reaction 1).

$$G(-10^-) = G_{e^-_{aq}} + G_H + \tfrac{1}{4}(G_{e^-_{aq}} + G_H + G_{OH}) + GH_2O_2 \quad (11)$$

$$G(10^-_3) = \tfrac{1}{4}(G_{e^-_{aq}} + G_H + G_{OH}) \quad (12)$$

$$G(O_2) = G_{H_2O_2} \quad (13)$$

$$G(H_2) = G_{H_2} \quad (14)$$

On substitution of values of $G_{e^-_{aq}}, G_H, G_{OH}, G_{H_2O_2}$, reported in the literature [11], in eq 11 to 14 the calculated values for $G(-10^-)$, $G(10^-_3)$, $G(O_2)$ and $G(H_2)$, obtained are 5.9, 1.6, 0.80 and 0.42 respectively which are in very good agreement with the experimentally observed values (see Table 1).

This supports the above mentioned mechansim for the radiolytic decomposition of hypoiodite.

The radiation chemical yield for the disappearance of hypoiodite ion in the presence of nitrous oxide decrease from a value of

$$G(-10^-) = 6.0 \pm 0.06 \text{ to the value of}$$

Table 1

(a) Yield for the N_2 saturated aqueous solution of $10^{-3} - 5 \times 10^{-4}$ M hypoiodite ion.		
pH	=	13 ± 0.1
$G(-10^-)$	=	6.0 ± 0.06
$G(10^{3-})$	=	1.6 ± 0.06
$G(O_2)$	=	0.81± 0.05
$G(H_2)$	=	0.41b 0.05
(b) Yields for the N_2O saturated aqueous solution of $10^{-3} - 5 \times 10^{-4}$ M hypoiodite ion.		
pH	=	13 ± 0.1
$G(-10^-)$	=	2.5 ± 0.05
$G(10^-_3)$	=	1.6 ± 0.05
$G(O_2)$	=	0.80 b 0.05
$G(H_2)$	=	0.41 ± 0.05

$$G(-10^-) = 2.5 \pm 0.05$$

This decrease in disappearance yield is due to the face that all the hydrated electrons are scavenged by N_2O in the reaction:

$$N_2O + e^-_{aq}, \overset{H_2O}{\to} N_2 + OH + OH^- \quad (15)$$

instead of reactions 2 and 3 involving 10^- ion under the experimental conditions employed [12, 13, 14].

The $G(-10^-)$ in N_2O saturated system can be expressed as

$$G(-10^-) = \tfrac{1}{4}(G_{e^-_{aq}} + G_H + G_{OH}) + GH_2O_2 \quad (16)$$

All the other yields $G(10^-)$, $G(O_2)$ and $G(H_2)$ are expted to be the same in both systems if the above mentioned mechanism for the radiolytic decomposition is correct. The results mentioned in Table 1 are in very good agreement, thus giving full support to this mechansim.

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