throughout, and numerically equal to the einsteins per day of light absorbed by the CH_3I. The ratio k_8/k_3 is thus readily calculable, since $k_8/k_3 = R_8[I_2]/R_3[CH_4]$. The activation energy difference, $E_8 - E_3$, was determined from the plot of log k_8/k_3 *vs.* $1/T$ shown in Fig. 4. The best visually determined value for series A was 7 kcal./mole; for series B, 6 kcal./mole; the estimated error is about ±2 kcal./mole. (A great deal of scatter occurred in these early determinations, as is seen in the table. It is hoped that experimental refinements will make possible a more precise figure.)

E_3 has not been directly determined experimentally, though an estimate of 0.5 ± 0.5 kcal./mole has found some support.[6,19] The following line of reasoning leads, we believe, to a more reliable figure. Electronic impact dissociation studies are in general agreement on a value of 101 ± 1 kcal./mole for $D(CH_3-H)$.[31] The activation energy for the reaction

$$\mathrm{Br} + \mathrm{CH_4} \underset{(10)}{\overset{(9)}{\rightleftarrows}} \mathrm{CH_3} + \mathrm{HBr} \qquad (9), (10)$$

has been carefully determined to be 17.8 kcal./mole.[32] The difference between the activation energy for the reverse of 9, which we label 10, and that for 3 is 0.8 ± 0.3 kcal./mole.[19] Combined with the known value of $D(H-Br)$ (86.5 kcal./mole),[33] we have $E_3 = E_9 - D(CH_3\text{-}H) + D(H\text{-}Br) - (E_{10} - E_3) = 2.5 \pm 1$ kcal./mole. Thus $E_8 = 9 \pm 2$ kcal./mole.

The only experimental work with which comparison can be made is that on the reaction $CD_3 + CH_4 \rightarrow CD_3H + CH_3$.[20] The authors estimate an activation energy for this process of about 13 kcal./mole on the basis of a single experiment and an assumed frequency factor. From this, one would predict $E_8 \sim 12$ kcal./mole.[34] Another approach suggests that this estimate is probably too high. Berlie and LeRoy[36] find almost identical energies of activation for the closely related hydrogen abstractions $H + CH_4 \rightarrow H_2 + CH_3$ and $H + C_2H_6 \rightarrow H_2 + C_2H_5$. $E = 10.4$ kcal./mole for the reaction $CD_3 + C_2H_6 \rightarrow CD_3H + C_2H_5$,[37] and one might expect an almost identical result for $CD_3 + CH_4 \rightarrow CD_3H + CH_3$. Whence, correcting for isotope effect as above, E_8 should be about 9 kcal./mole.

Taking the collision diameters for CH_3, CH_4 and I_2 to be 3.5, 3.5 and 8 Å., respectively, it follows that P_8/P_3 is *ca.* 3×10^{-4}. It is clear that reaction 3 must have a frequency factor of the order of unity, if it is accepted that reactions of the type of 8 have factors of the order of 10^{-4}.[37,38]

It is of interest to note that the quantum yield of the "hot" reaction $\underline{CH_3} + CH_4 \rightarrow CH_4 + CH_3$ is about 8×10^{-4},[39] as compared to 2.7×10^{-3} for $\underline{CH_3} + CH_3I \rightarrow CH_4 + CH_2I$ found above.

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission and in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation.

(31) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

(32) G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

(33) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

(34) The 1 kcal./mole lowering for protium methyl is assumed by comparison with the reactions of CH_3 and CD_3 with H_2.[35]

(35) E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953).

(36) M. R. Berlie and D. J. LeRoy, *Disc. Faraday Soc.*, No. 14, 50 (1953).

(37) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

(38) L. M. Dorfman and R. Gomer, *Chem. Revs.*, **46**, 499 (1950).

(39) Obtained by dividing the rate of the hydrogen abstraction reaction at room temperature by the rate of CH_3 radical production (R_3).

MADISON, WISCONSIN

[CONTRIBUTION FROM CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, OAK RIDGE]

Yields of Hydrogen Peroxide in the Decomposition of Water by Cobalt γ-Radiation. I. Effect of Bromide Ion

BY THOMAS J. SWORSKI

RECEIVED DECEMBER 4, 1953

When air-saturated KBr solutions are subjected to cobalt γ-radiation, the initial yield of H_2O_2 is dependent upon the concentration of KBr. It is proposed that the initial yield of H_2O_2 in KBr solutions containing O_2 is equal to "$F + 2E$" when KBr is present in concentrations greater than 10^{-5} molar. The "molecular" yield of H_2O_2 (formed by the combination of OH radicals in regions of high ionization density) is 0.75 molecule per 100 e.v. in sulfuric acid solutions at a *p*H of 2 and 0.78 molecule per 100 e.v. in 0.8 *N* sulfuric acid. A mechanism is presented in which KBr (even at concentrations as low as 10^{-5} molar) decreases the "molecular" yield of H_2O_2 by reaction of bromide ion with OH radical in regions of high ionization density.

Introduction

Water, when subjected to ionizing radiation, has been considered to behave as though two reactions are occurring simultaneously[1]

$$2H_2O \longrightarrow H_2 + H_2O_2 \qquad (F)$$
$$H_2O \longrightarrow H + OH \qquad (R)$$

In reaction (F), H_2 and H_2O_2 result from the combination of many of the H atoms and OH radicals in the regions of high ionization density before these radicals have time to separate by diffusion. Dainton and Sutton[2,3] have recently presented experimental evidence showing that H_2O_2 is formed in excess of H_2 in reaction (F) in dilute ferrous sulfate

(1) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

(2) F. S. Dainton and H. C. Sutton, *Faraday Soc. Disc.*, **12**, 121 (1952).

(3) F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.*, **49**, 1011 (1953).

solutions. If this is so, Allen[4] has suggested that we must add to reactions (F) and (R) a third reaction

$$2H_2O \longrightarrow 2H + H_2O_2 \qquad (E)$$

The notation introduced by Allen[4] will be used in this paper. *F*, *R* and *E* represent the yields (in molecules per 100 e.v.) of the corresponding reactions. The yields (in molecules per 100 e.v.) of the four reaction products (H_2, H_2O_2, H and OH) are denoted by G_{H_2}, $G_{H_2O_2}$, G_H and G_{OH}. In this notation, $F = G_{H_2}$; $E = G_{H_2O_2} - G_{H_2}$; $R = G_{OH}$.

Quantitative determinations of *F* and *R* have been reported for cobalt γ-radiation but it was assumed[5,6] in those studies that H_2 and H_2O_2 are formed in approximately equal amounts. The primary purpose of this paper is twofold: (a) to present values for $G_{H_2O_2}$, the "molecular" yield of H_2O_2 in the terminology of Johnson and Allen,[7] and (b) to present evidence that bromide ion decreases $G_{H_2O_2}$ even at concentrations as low as 10^{-5} molar.

Experimental

Cobalt γ-radiation was provided by an approximately 300 curie cobalt[60] source.[8] The rate of energy absorption in solution was determined by comparison with the rate of ferrous oxidation using a value of 15.6 ferrous ions oxidized per 100 e.v. absorbed in 0.8 *N* sulfuric acid solutions.[9]

The method used for saturating solutions and filling irradiation cells was essentially that previously described by Hochanadel.[5] Solutions containing O_2 were initially air-saturated or oxygen-saturated. Irradiation vessels with no air space were employed; this was found to be unnecessary in oxygenated bromide solutions at a *p*H of 2 or less since the initial rate of H_2O_2 formation was independent of O_2 concentration and bromide ion prevented any effect of the "molecular" H_2. All irradiations were made at a temperature of about 23°.

Water from a Barnstead still was redistilled from an acid permanganate solution and then from an alkaline permanganate solution. Further distillation was made in a silica system and the water then stored in silica vessels. Purification was found to be unnecessary for pure tank helium and O_2. Baker and Adamson reagent grade sulfuric acid and KBr were used without further purification.

H_2O_2 concentrations in pure water and in solutions at a *p*H of 2 were determined by a colorimetric method developed by Ghormley.[5] Iodide ion is oxidized by H_2O_2 and the absorption of the triiodide complex is measured at 350 mμ. In highly acid solutions light-sensitized air-oxidation of the iodide ion is appreciable and, for this reason, H_2O_2 concentrations in 0.8 *N* sulfuric acid were determined by addition of an aliquot of the irradiated solution to an aliquot of a standard ceric sulfate solution in 0.8 *N* sulfuric acid. Determination of ceric ion concentration was made by measurement of its absorption at 320 mμ using a molar extinction coefficient of 5580 at 25°.[9] Analyses for H_2O_2 by reaction with ceric sulfate were carried out as rapidly as possible to minimize error due to the slow reaction of ceric ion with bromide ion.[10] Absorption measurements were made with a Cary recording spectrophotometer.

The acidity of solutions was adjusted with Baker and Adamson reagent grade sulfuric acid. Determinations of *p*H were made using a Beckman *p*H meter, laboratory model G, which was calibrated using Cenco standard buffer mix for a *p*H of 1. The normality of 0.8 *N* sulfuric acid solutions was determined by titration with standard 1 *N* sodium hydroxide solution using phenolphthalein as an indicator.

Results

Effect of O_2 Concentration.—The formation of H_2O_2 in air-saturated and oxygen-saturated water is shown in Fig. 1. The rate of formation of H_2O_2 at any particular H_2O_2 concentration is higher in initially oxygen-saturated water than in initially air-saturated water. We conclude, therefore, that the rate of formation of H_2O_2 at any particular H_2O_2 concentration in water containing O_2 is dependent upon the O_2 concentration. This dependence upon the O_2 concentration is interpreted as resulting from a competition for H atoms by O_2 and H_2O_2.

$$H + O_2 \longrightarrow HO_2 \qquad (1)$$

$$H + H_2O_2 \longrightarrow H_2O + OH \qquad (2)$$

The initial yield of H_2O_2 is not dependent upon the O_2 concentration.[11] The importance of reaction 2 in dilute H_2O_2 solutions containing O_2 has been previously considered.[12]

Effect of 10^{-3} Molar KBr.—H_2O_2 formation in oxygen-free bromide solutions has been studied for the determination of the rate of reaction (F) in water irradiated with cobalt γ-radiation[5] since bromide ion apparently acts as a catalyst for the recombination of radicals to water.[1] The reactions involving bromide ion are assumed to be

$$Br^- + OH \longrightarrow Br + OH^- \qquad (3)$$

$$Br + H \longrightarrow Br^- + H^+ \qquad (4)$$

The rate of H_2O_2 formation is approximately the same for bromide solutions containing O_2 or a mixture of H_2 and O_2.[5] This invariance of rate was interpreted as indication that H_2 is not able to compete with bromide ion for the OH radical by reaction 5

$$H_2 + OH \longrightarrow H_2O + H \qquad (5)$$

The effect of reaction 5 is to enhance the rate of H_2O_2 formation in water containing O_2[5,12] but no bromide ion.

Bromide ion has no effect upon the quantum yield in the photochemical decomposition of H_2O_2.[13] The absence of any effect has been explained by the reactions

$$Br^- + OH \longrightarrow Br + OH^- \qquad (3)$$

$$Br + H_2O_2 \longrightarrow Br^- + H^+ + HO_2 \qquad (6)$$

A mechanism for the photochemical decomposition, consistent with experimental observations at high light intensity, is

$$H_2O_2 + h\nu \longrightarrow 2OH$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (7)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (8)$$

The sequence of reactions 3 and 6 is equivalent to reaction 7.

The effect of 10^{-3} molar KBr upon the rate of formation of H_2O_2 in air-saturated and oxygen-saturated water and sulfuric acid solutions is shown in Fig. 2. The presence of bromide ion does not remove the effect of O_2 concentration. Figures 1 and 2 show that the presence of bromide ion does result in a lower concentration of H_2O_2 at any particular dose in all solutions. A similar effect of iodide ion

---

(4) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

(5) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

(6) E. J. Hart, *ibid.*, **56**, 594 (1952).

(7) E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

(8) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instr.*, **22**, 473 (1953).

(9) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1951).

(10) E. L. King and M. L. Pandow, THIS JOURNAL, **75**, 3063 (1953).

(11) H. Fricke, *J. Chem. Phys.*, **2**, 556 (1934).

(12) W. J. Toulis, Univ. of California Radiation Lab. Report, 583 (1950).

(13) J. P. Hunt and H. Taube, THIS JOURNAL, **74**, 5999 (1952).

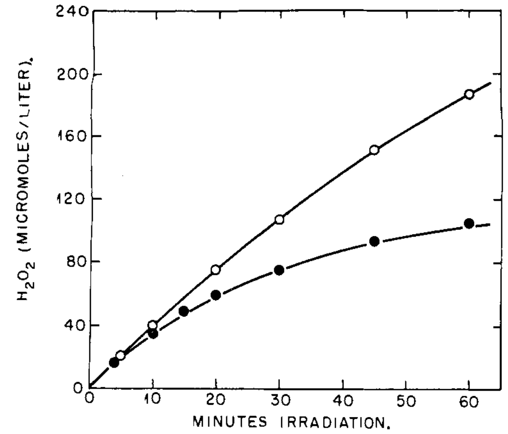

Fig. 1.—Hydrogen peroxide formation by cobalt γ-radiation: pure water, ○ oxygen-saturated, ● air-saturated; dose rate, 1.81 × 10^{20} e.v./liter, min.

has been reported by Lefort.[14] The decreased rate in the presence of bromide ion indicates that some of the H_2O_2 formed in the absence of bromide ion results from either (a) the influence of H_2 formed in reaction (F) through reaction 5 or (b) the combination of OH radicals.

$$OH + OH \longrightarrow H_2O_2 \qquad (9)$$

Effect of Sulfuric Acid.—Steady-state concentrations of H_2O_2 of the order of 140 μM/liter are observed in the irradiation of air-saturated pure water.[15,16] In air-saturated acid solutions, high non-equilibrium concentrations of H_2O_2 have been reported for solutions at a pH of 2 to 3 irradiated with 1 Mev. electrons (1,030 μM/liter)[15] and for 0.8 N sulfuric acid irradiated with cobalt γ-radiation (2,840 μM/liter).[16] This marked effect of pH has been interpreted by Ebert and Boag[15] as resulting from the ionization of the HO_2 radical. They concluded that the important back reaction causing the low steady state in pure water is

$$O_2^- + H_2O_2 \longrightarrow OH^- + OH + O_2 \qquad (10)$$

The effect of pH was then explained by concluding that the corresponding reaction in acidic solutions does not occur

$$HO_2 + H_2O_2 \longrightarrow H_2O + OH + O_2 \qquad (11)$$

In the photochemical decomposition of H_2O_2 solutions, the HO_2 radical is a postulated intermediate. There is no effect of variation of sulfuric acid concentration in the range of pH of 1 to 7 upon the quantum yield for H_2O_2 disappearance.[13,17] From this pH independence, it was concluded that the ionic species HO_2^- and O_2^- are not involved.[17] It thus seems unlikely that the pH effect in the radiation-induced formation of H_2O_2 is to be associated with the ionization of the HO_2 radical.

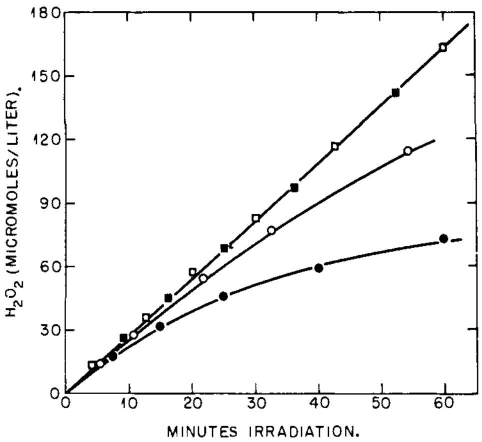

Fig. 2.—Effect of 10^{-3} M KBr upon hydrogen peroxide formation by cobalt γ-radiation: pure water, ○ oxygen-saturated, ● air-saturated; sulfuric acid solutions at a pH of 2, □ oxygen-saturated, ■ air-saturated; dose rate, 1.81 × 10^{20} e.v./liter, min.

Figure 2 shows that the rate of H_2O_2 formation is approximately the same in initially air-saturated or oxygen-saturated sulfuric acid solutions containing bromide ion at a pH of 2. The effect of acidity is to decrease the dependence of the rate of H_2O_2 formation upon the O_2 concentration (compare Figs. 1 and 2). It thus appears that reaction 2 does not compete as effectively with reaction 1 in acid solutions as in pure water. No mechanism is suggested for this effect but it may be the result of processes involving the hydrated H_2^+ ion.[18]

Effect of KBr Concentration.—The initial yield of H_2O_2 in oxygen-free acidic KBr solutions is independent of bromide ion concentration[5] over a wide range. KBr concentrations as low as 10^{-5} molar were sufficient to prevent the "molecular" H_2 from reaction with the OH radical according to reaction 5. Figures 3 and 4 show that in KBr solutions containing O_2 the rate of formation of H_2O_2 is dependent upon the KBr concentration both in 0.8 N sulfuric acid and in sulfuric acid solutions at a pH of 2. The initial yields of H_2O_2 as a function of KBr concentration are listed in Table I.

TABLE I

INITIAL YIELDS OF H_2O_2 AS A FUNCTION OF KBr CONCENTRATION

KBr concn., moles/l.	Initial H_2O_2 yields[a] 0.8 N Sulfuric acid	pH 2
Air-saturated		
10^{-2}		0.69
5 × 10^{-3}	0.87	
10^{-3}	0.96	0.90
10^{-4}	1.06	0.98
10^{-5}	1.13	1.04
10^{-6}		1.16
No KBr present	1.17	1.30
Helium-purged		
10^{-4}	0.39	0.42

[a] Molecules of H_2O_2 formed per 100 e.v. absorbed in solution.

H_2O_2 yields were measured in air-saturated solutions containing from 10^{-6} to 10^{-2} molar KBr. In helium-purged solutions (oxygen removed by bubbling helium through the solution), only 10^{-4} molar KBr solutions were irradiated. All the observed rates of formation of H_2O_2 were, to a first approximation, linear. The yields in Table I are believed to

---

(14) M. Lefort, *J. chim. phys.*, **47**, 776 (1950).

(15) M. Ebert and J. W. Boag, *Faraday Soc. Disc.*, **12**, 189 (1952).

(16) T. J. Sworski, *J. Chem. Phys.*, **21**, 375 (1953).

(17) D. E. Lea, *Trans. Faraday Soc.*, **45**, 81 (1949).

(18) J. Weiss, *Nature*, **165**, 728 (1950).

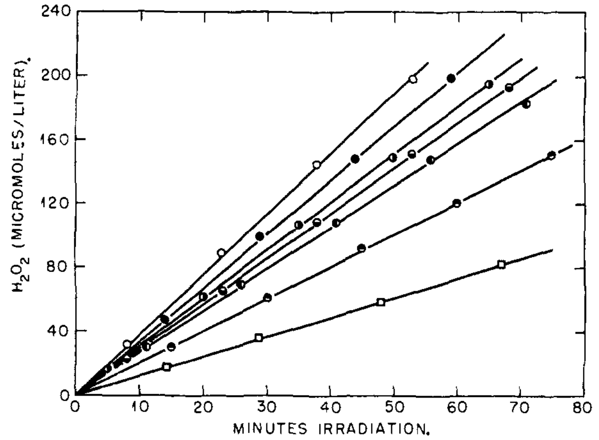

Fig. 3.—Effect of bromide ion concentration upon the yield of H_2O_2 by cobalt γ-irradiation of sulfuric acid solutions at a *p*H of 2; air-saturated solutions with KBr concentrations of: ◓, 10^{-2} *M;* ◐, 10^{-3} *M;* ◒, 10^{-4} *M;* ◑, 10^{-5} *M;* ●, 10^{-6} *M;* ○, no KBr present. □, helium-purged solution with 10^{-4} *M* KBr; dose rate, 1.76 × 10^{20} e.v./liter, min.

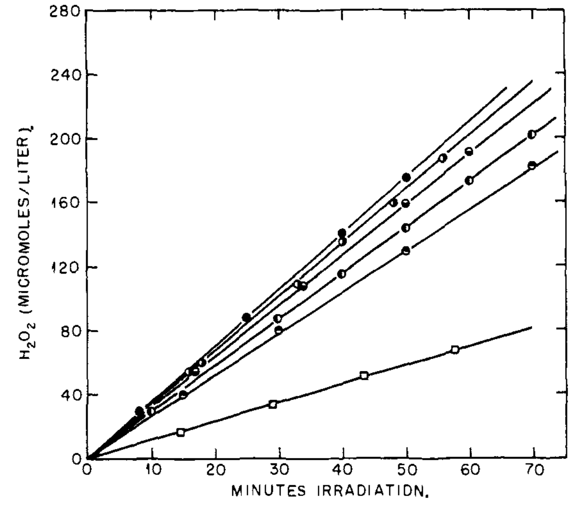

Fig. 4.—Effect of bromide ion concentration upon the yield of H_2O_2 by cobalt γ-irradiation of 0.8 *N* sulfuric acid solutions; air-saturated solutions with KBr concentrations of: ◓, 5 × 10^{-3} *M;* ◐, 10^{-3} *M;* ◒, 10^{-4} *M;* ◑, 10^{-5} *M;* ●, no KBr present; □, helium-purged solution with 10^{-4} *M* KBr; dose rate, 1.80 × 10^{20} e.v./liter, min.

be good to ±2% relative to each other. Bromine was observed as an additional product in air-saturated 10^{-1} molar KBr solutions at a *p*H of 2. Similar results were reported by Johnson[19]; no iodine was observed in 10^{-3} molar KI solutions, but iodine formation was observed in more concentrated solutions.

The yield of 1.17 molecules per 100 e.v. for H_2O_2 formation in air-saturated 0.8 *N* sulfuric acid is lower than the previously reported[16] value of 1.26. The value of 1.26 was based upon H_2O_2 determinations by the iodometric method developed by Ghormley[5] in which light-sensitized air-oxidation becomes more of a problem with increasing acidity and reduces the accuracy of the method. In helium-purged 10^{-4} molar KBr solution at a *p*H of 2, the yield of 0.42 molecule per 100 e.v. for H_2O_2 formation is in fair agreement with the reported yields for reaction (F) of 0.35 by Hart,[6] 0.46 by Hochanadel[5] and 0.60 by Johnson and Allen.[7]

Discussion

Allen[4] has suggested recently, on the basis of a critical examination of available experimental data, an interesting hypothesis for the formation of H_2O_2 in water containing O_2. He has suggested that the effect of every H atom, formed in reaction (R), is neutralized by the effect of the OH radical with no resultant formation of H_2O_2. The following sequence of reactions illustrates this hypothesis

$$H_2O \longrightarrow H + OH \tag{R}$$
$$H + O_2 \longrightarrow HO_2 \tag{1}$$
$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \tag{7}$$
$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{8}$$

The over-all effect, by algebraic addition of the above reactions, is the combination of H atoms and OH radicals to form water. The formation of H_2O_2 in water containing O_2 then results only from the following reactions

$$2H_2O \longrightarrow H_2 + H_2O_2 \tag{F}$$
$$2H_2O \longrightarrow 2H + H_2O_2 \tag{E}$$
$$H + O_2 \longrightarrow HO_2 \tag{1}$$
$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{8}$$

The total H_2O_2 yield in this mechanism is $F + 2E$.

Allen has concluded that all OH radicals, in water containing O_2, initially react either with H_2O_2 according to reaction 7 or with HO_2 according to reaction 12

$$OH + HO_2 \longrightarrow H_2O + O_2 \tag{12}$$

but that none react with H_2 according to reaction 5. This conclusion, based upon a study of H_2 formation in water containing O_2,[7] is not in agreement with the reported value[5] of 0.94 for k_5/k_7, the ratio of rate constants of reaction 5 and reaction 7. KBr, in concentrations as low as 10^{-5} molar, prevents reaction 5 from occurring initially.[5] The effect of having KBr present in water containing O_2 should be to assure the same result as that expected from reaction 7, through the sequence of reactions 3 and 6, as so nicely shown[13] in the photochemical decomposition of H_2O_2. Thus, the H_2O_2 yield in water containing O_2 and also containing more than 10^{-5} molar KBr should be equal to $F + 2E$.

Since H_2 and H_2O_2 are formed initially in equal amounts in acidic oxygen-free bromide solutions,[20] the products of reaction (E) must recombine to form water and the H_2O_2 yield is then the same as the H_2 yield and is equal to F. $G_{H_2O_2}$, equal to $F + E$, can be calculated if we accept the conclusion that the H_2O_2 yield in oxygen-free bromide solutions is equal to F and the H_2O_2 yield in air-saturated bromide solutions is equal to $F + 2E$. The results of such a calculation are shown in Table II.

Table II shows that $G_{H_2O_2}$ is dependent upon the KBr concentration. This dependence upon KBr concentration is interpreted as resulting from the reaction of bromide ion with the OH radical according to reaction 3 in regions of high ionization density. Reaction 3, in competition with reaction 9,

---

[19] E. R. Johnson, *J. Chem. Phys.*, **21**, 1417 (1953).

[20] H. Fricke and E. J. Hart, *ibid.*, **3**, 596 (1935).

TABLE II

$G_{H_2O_2}$ AS A FUNCTION OF KBr CONCENTRATION

	$G_{H_2O_2}$	
KBr concn., moles/l.	0.8 *N* Sulfuric acid	*p*H 2
10^{-2}		0.555
5×10^{-3}	0.63	
10^{-3}	.675	.66
10^{-4}	.725	.70
10^{-5}	.76	.73
No KBr present	.78	(.75)[a]

[a] Extrapolated value (see Fig. 5).

results in lower yields of H_2O_2 in regions of high ionization density. Figure 5 shows that, as a first approximation, a linear relationship exists between $G_{H_2O_2}$ and $(KBr)^{1/3}$; this relationship suggests that the rate of reaction of bromide ion with the OH radical in regions of high ionization density is to be related with the average *distance* separating the bromide ion from the regions of high ionization density.

This mechanism for the effect of bromide ion upon $G_{H_2O_2}$ would require that, when $G_{H_2O_2}$ is less than G_{H_2}, bromine would be formed as an initial product of irradiation. This indeed is observed in air-saturated 10^{-1} molar KBr solutions of sulfuric acid at a *p*H of 2. Ultimately, as the concentration of KBr is increased, no H_2O_2 would be formed and the initial products would be H_2 and Br_2 in equal amounts. This is exactly what has been reported[19] for KI solutions. A more extensive study of KI solutions irradiated with both X-rays and α-rays was reported by Lefort.[14] Since H_2O_2 reacts thermally with iodide ion, Lefort suggested as a mechanism (to explain results somewhat similar to that reported in this paper) that iodide ion reacts more rapidly with H_2O_2 formed in regions of high ionization and excitation density. In Table III are listed the oxidation-reduction potentials of half-reactions, relative to the hydrogen gas-hydrogen ion couple, pertinent to this discussion. From these potentials it is evident that, while it is energetically possible for the OH radical to react with both bromide ion and iodide ion, the free energy is unfavorable for the reaction of H_2O_2 with bromide ion. It thus seems reasonable to conclude that the effect of bromide and iodide ions is to be attributed to their reaction with OH radicals in preference to their reaction with H_2O_2.

TABLE III

OXIDATION-REDUCTION COUPLES IN ACID SOLUTIONS[a]

Couple	E^0
$2I^- = I_2 + 2e^-$	−0.5355
$OH + H_2O = H_2O_2 + H^+ + e^-$	−0.72
$2Br^- = Br_2 + 2e^-$	−1.087
$H_2O = OH + H^+ + e^-$	−2.08

[a] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1952.

The mechanism suggested here for the effect of bromide ion upon $G_{H_2O_2}$ appears to be inconsistent with the following observation: NaBr (2×10^{-3} molar) has no effect upon the quantum yield in the photochemical decomposition of H_2O_2 at 0° even though the primary efficiency is only 0.38.[13] There is a distinct difference to be expected, however, between scavenger effects in the photochemistry and radiation chemistry of H_2O_2 solutions. To increase the quantum yield in the photochemical decomposition of H_2O_2, the bromide ion has to prevent the recombination of OH radicals trapped in a solvent cage. To decrease $G_{H_2O_2}$, the bromide ion has only to prevent the combination of OH radicals which are not trapped in a solvent cage but which are randomly diffusing.

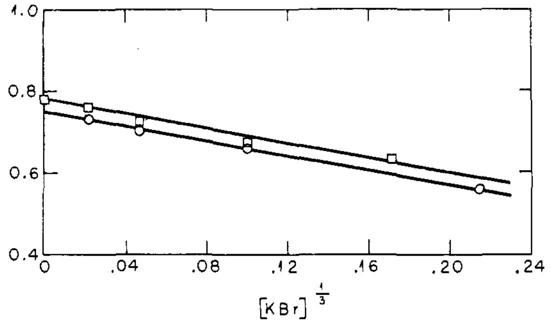

Fig. 5.—G_{H_2O} as a function of bromide ion concentration: ○, *p*H 2.0; □, 0.8 *N* sulfuric acid.

The decomposition of water into the "molecular" products H_2 and H_2O_2 is, therefore, not independent of the type or concentration of solute present. Such a conclusion has been reached by Rigg[21] based upon some preliminary measurements of H_2 yields from a variety of solutions; many of the solutes, however, have not been clearly shown to prevent the reaction of H_2 with the OH radical. Dainton and Sutton[3] reported that, in degassed 0.8 *N* sulfuric acid solutions of ferrous sulfate, $G_{H_2O_2}$ decreases with increasing ferrous ion concentration; their study was carried out, however, in the range of ferrous ion concentrations where secondary reactions between the four products (H_2, H_2O_2, H and OH) of the decomposition of water may occur since the rate of ferrous ion oxidation was dependent upon ferrous ion concentration. Johnson and Allen,[7] however, have concluded that (a) G_{H_2} is independent of the type and concentration of a variety of solutes and (b) the "molecular" H_2 is formed by a direct decomposition of water without the intermediate formation of randomly diffusing H atoms; the term "molecular" was introduced although the intermediate formation of H atoms and OH radicals was not entirely excluded.

In addition to the formation of H_2 and H_2O_2 from the combination of H atoms and OH radicals in regions of high ionization density, many radicals combine to form water according to reaction 13

$$H + OH \longrightarrow H_2O \qquad (13)$$

Johnson[19] has shown that iodide ion does not alter G_{H_2} (except for mass absorption effects) even at KI concentrations which result in no formation of H_2O_2 as an initial product of decomposition. G_{H_2} is also independent of KBr concentration over a wide range.[5,20] The reaction of bromide or iodide ion with OH radicals in regions of high ionization density decreases the importance of reaction 13 but does not "free" more H atoms for combination to form H_2 since reaction 4 then replaces reaction 13. Thus, with increasing concentration of bromide or iodide

---

(21) T. Rigg, *Faraday Soc. Disc.*, **12**, 119 (1952).

ion, reaction 13 becomes replaced by the sequence of reactions 3 and 4 with no net effect upon G_{H_2}.

Consideration of the dependence of $G_{H_2O_2}$ upon the KBr concentration (see Fig. 5) leads the author to conclude that the H_2O_2 yield in air-saturated 0.8 N sulfuric acid is equal to $F + 2E$ in experimental agreement with the hypothesis of Allen. In sulfuric acid solutions at a *p*H of 2, the extrapolated value of $G_{H_2O_2}$ is 0.75 (see Fig. 5) which would correspond to a value of 1.08 for $F + 2E$; the observed yield for H_2O_2 formation (see Table I) is 1.30. The increase in yield of H_2O_2 from 1.08 to 1.30 is interpreted as indication that the initial H_2 yield must have decreased[22] by a corresponding amount from 0.42 to 0.20 by secondary reaction of H_2 with OH according to reaction 5 and in competition with reaction 7. By this mechanism, an increase in yield from 1.08 to 1.32 would be expected from the following: (a) a value of 0.94 for the ratio k_5/k_7, (b) a value of 2.12 for G_{OH}, and (c) a value of 0.42 for G_{H_2}. This interpretation is in disagreement with the H_2 yield in oxygen-saturated water measured by Johnson and Allen[7] but is substantiated by measurements of H_2 production from aqueous systems in this Laboratory.[23] It is concluded that H_2O_2 formation in air-saturated sulfuric acid solutions at a *p*H of 2 (or in air-saturated pure water) is not a measure of $F + 2E$ in disagreement with the hypothesis of Allen.

The determination of G_{H_2} and $G_{H_2O_2}$ enables us to calculate G_H and G_{OH} if we assume, as pointed out by Allen,[4] that (a) the yield of ferrous oxidation in 0.8 N sulfuric acid is equal to $2F + 8E + 4R$ and (b) the H_2O_2 yield in water containing a mixture of H_2 and O_2 is equal to $F + 2E + R$. The results of such a calculation are shown in Table IV.

TABLE IV

YIELDS IN THE DECOMPOSITION OF WATER BY COBALT γ-RADIATION

	0.8 N Sulfuric acid[a]	*p*H 2[b]
F	0.39	0.42
E	0.39	0.33
R	2.92	2.12
G_{H_2}	0.39	0.42
$G_{H_2O_2}$	0.78	0.75
G_H	3.70	2.78
G_{OH}	2.92	2.12

[a] Based upon a yield[9] of 15.6 ferrous ions oxidized per 100 e.v. [b] Based upon a yield[5] of 3.2 molecules of H_2O_2 formed per 100 e.v. in solutions of a mixture of H_2 and O_2.

From Table IV, the ratio of $G_{H_2O_2}$ to ferrous ion oxidation in air-saturated 0.8 N sulfuric acid is 0.78/15.6 (= 0.050). This ratio is higher than the value of 0.80/20 (= 0.040) which Dainton and Sutton reported, based upon measurements in degassed ferrous sulfate solutions in 0.8 N sulfuric acid. Their value may be lower due to (a) an effect of ferrous ion similar to that of bromide ion or (b) reactions of H_2O_2 with H atoms or OH radicals since their study was carried out in the range of ferrous ion concentrations where the rate of ferrous ion oxidation was not independent of ferrous ion concentration. From Table IV it can be calculated that the fraction of ferrous ions oxidized by radical reaction with HO_2 and OH in air-saturated solution would be 0.424 if ferrous ion does not lower $G_{H_2O_2}$. This is just the fraction reported by Dainton and Sutton[3] (0.425) as their limiting value for ferrous ion concentrations greater than 10^{-4} molar. It thus appears that ferrous ion concentrations of 10^{-4} molar or less have little effect upon $G_{H_2O_2}$.

In this paper it is assumed that G_{H_2} is the same in helium-purged and in air-saturated water. This assumption is in agreement with (a) the report of Fricke and Hart[20] that the initial H_2 yield in bromide solutions is the same whether H_2O_2 or O_2 is the other product of decomposition of water and (b) the absence of an O_2 effect in the reduction of ceric sulfate in 0.8 N sulfuric acid solutions.[24] If the O_2 in air-saturated KBr solutions decreases G_{H_2} through reaction 1 in regions of high ionization density, the values for $G_{H_2O_2}$ in Table II would have to be decreased by an amount equal to the decrease of G_{H_2} by O_2. A criticism of the method used in this paper for calculation of $G_{H_2O_2}$, therefore, is that the H_2 yield was not measured in air-saturated KBr solutions for determinations of F.

Acknowledgments.—The author is indebted to Dr. J. A. Ghormley, Dr. C. J. Hochanadel and Dr. A. C. Stewart for many stimulating discussions. He is also indebted to Dr. H. A. Dewhurst and Prof. M. Burton for their helpful criticism. He is especially indebted to Dr. H. A. Schwarz and Dr. A. O. Allen for their helpful criticism which revealed some inconsistencies in the preliminary treatment of this subject.

OAK RIDGE, TENNESSEE

---

[22] It was pointed out to the author by H. A. Schwarz and A. O. Allen (private communication) that, if we accept the value of 0.94 for k_5/k_7, the initial H_2 yield in water containing O_2 is not equal to F but must be less than F.

[23] J. A. Ghormley and C. J. Hochanadel, forthcoming publication.

[24] T. J. Hardwick, *Can. J. Chem.*, **30**, 23 (1952).