compound as illustrated by these results and others reported in the literature. Solidification has been observed to increase the yield in a number of cases[16–18] but to have little or no effect on it in others.[2,3] Since the scavenger studies reported in a preceding section have shown that the stable products of the $Cl^{37}(n,\gamma)Cl^{38}$ reaction in liquid hydrogen-containing organic chlorides are all produced by "high energy processes" it would not have been surprising if the yield had not changed on solidification. The fact that it does must be related either to a higher density of radicals formed by the high energy atom in losing their energy to a solid medium or to a different relative yield of different types of radicals when the medium is solid. These effects might result from either the higher density of the solid or a different average orientation of its molecules as compared to the liquid, or both. They may increase the probability that the tagged atom will become stabilized by combination with an organic radical rather than by reaction with a carbon–hydrogen bond to form hydrogen chloride.

Acknowledgment.—This work has been 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.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Free Radical-Initiated $O^{16}O^{18}$–H_2O^{16} Exchange Reaction in Aqueous Solution

BY EDWIN J. HART, SHEFFIELD GORDON AND DWIGHT A. HUTCHISON

RECEIVED JUNE 24, 1953

A γ-ray-initiated chain exchange reaction of isotopically enriched dissolved oxygen with normal oxygen of the water has been found in alkaline solutions. The yield of this reaction is independent of dosage rate of γ-rays or intensity of ultraviolet light, increases with pH and concentration of enriched dissolved oxygen, and decreases with increasing concentration of hydrogen peroxide. The kinetic study provides evidence for the existence of the equilibrium: $OH = H^+ + O^-$. The propagation steps are concluded to be: $O^- + O^*_2 = O^{*-} + O_2$ and $O^{*-} + OH^- = O^- + O^*H^-$, and the termination steps postulated as: $O^- + H_2O_2 = OH^- + HO_2$ and $O^{*-} + H_2O_2 = O^*H^- + HO_2$.

Hydrogen peroxide is produced by γ-ray irradiation of aqueous solutions containing dissolved oxygen. In the pH range below 9.0 the reaction proceeds with a yield, $G_{H_2O_2}$, of two molecules of hydrogen peroxide per 100 e.v. of absorbed γ-ray energy. Above a pH of 11, $G_{H_2O_2}$ is one.[1] The net reaction is

$$H_2O + {}^1/_2O_2 = H_2O_2 \qquad (1)$$

During the course of an investigation using enriched oxygen to study reaction 1, a γ-ray-initiated chain exchange reaction between dissolved enriched oxygen and water has been found. In the region of high pH where the yield of the chain reaction is high and the yield of the hydrogen peroxide is negligible, the reaction is

$$H_2O + O^*_2 = H_2O^* + O_2 \qquad (2)$$

(O^* is used throughout this paper to designate oxygen of 1.4 atomic per cent. O^{18}).

The effect of dosage rate of γ-rays, intensity of ultraviolet light, and concentration of enriched oxygen, hydrogen ion and hydrogen peroxide on exchange reaction 2 is reported in the present paper. Additional evidence is provided to support the previously postulated ionization of the hydroxyl radical[2,3] in alkaline solution, and a simple mechanism is given for the chain exchange propagation steps.

Experimental

A triply distilled water purified by distillation successively from alkaline potassium permanganate and acid potassium dichromate solution, followed each time by passage through a silica tube heated to 800° was used in these experiments. The enriched oxygen was obtained by electrolysis of Stuart Oxygen Company 1.4 atomic % O^{18} water. The oxygen was purified by recycling through activated platinized asbestos heated to 300° in order to remove traces of hydrogen and finally through an activated charcoal trap cooled by liquid nitrogen. Mass spectrometer analysis showed that no impurities of mass less than 100 are present to an extent more than 0.01%.

The aqueous solution was first degassed by pumping with a Hyvac and mercury diffusion pump backed by carbon dioxide and liquid nitrogen traps. The solution was then saturated with enriched oxygen gas at the desired pressure and forced into a specially designed 100-ml. syringe which served as the irradiation chamber. Suitable precautions were taken to ensure that all air was removed from the syringe by introducing and expelling two 10-ml. portions of the oxygenated solution before the addition of 100 ml. of solution used for the irradiation. Solutions prepared in this manner contained no gas phase and were irradiated by exposure in specially designed chambers[4] to Co^{60} γ-rays. The dosage rates were measured by use of the ferrous sulfate actinometer, and a value of 15.5 Fe^{+++}/100 e.v. was used to convert chemical yield to electron volts/liter.[5] After irradiation, the gas was extracted from the solution in a Van Slyke apparatus, and the isotopic analyses were run on a 60-degree sector-type direction-focusing mass spectrometer recently designed by Hutchison.[6] It was then assumed that the isotopic dilution taking place in the dissolved oxygen during irradiation was due to replacement of enriched dissolved oxygen by normal oxygen of water. The estimated enrichment of the water by exchange of enriched oxygen in all cases amounted to less than 0.002% and in the present experiments was neglected.

Equation 3 was used to calculate the molarity, M_e, of the enriched oxygen component in the dissolved gas as obtained

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[1] H. Fricke, *J. Chem. Phys.*, **2**, 556 (1934).

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[6] Description of instrument to be published.

from the mass spectrometric data

$$M_e = \frac{(X_s^{32} - X_n^{32})M_0}{(X_e^{32} - X_n^{32})} \quad (3)$$

where X_s^{32} = mole fraction of $O_2^{16,16}$ in dissolved oxygen of sample
X_n^{32} = mole fraction of $O_2^{16,16}$ in oxygen from the normal reagent water
X_e^{32} = mole fraction of $O_2^{16,16}$ in the enriched reagent oxygen, and
M_0 = initial molarity of dissolved enriched oxygen in aqueous solution

The X's were calculated directly from the isotopic ratios of $O_2^{16,16}/O_2^{16,18}$ obtained on the oxygen gas analyzed in the mass spectrometer. G values, designated $G(O_2)/\text{m}M\ O_2^*$, reported in Table I, were obtained from plots of log $[(O_2^*)/(O_2^*)_0]$ *vs.* energy absorbed and are given in units of molecules of oxygen of normal isotopic content formed per 100 e.v. of γ-ray energy absorbed in the aqueous solution at a concentration of one millimolar enriched oxygen. The quantity k given in column 6 of Table I is the first-order rate constant.

Results and Discussion

The amount of isotopic exchange reaction occurring in reaction 2 is a non-linear function of the dosage regardless of *p*H. In acid and neutral solutions first-order kinetics appear to be followed although insufficient experiments have been carried out to establish this point definitely. Under these conditions the yield of hydrogen peroxide is somewhat higher than the yield of normal oxygen (see Fig. 1). G values are less than 2.6,[7] the free-radical pair yield, indicating a non-chain reaction. In alkaline solutions, however, the normal oxygen formed is much larger than the hydrogen peroxide, the former being produced in high yields indicative of a chain reaction (see Fig. 2). A modified first-order reaction characterized by an initial rapid formation of normal oxygen, followed by a slower first-order reaction is obtained for the data of Fig. 2 (see Fig. 3). This behavior is attributed to the γ-ray-induced formation of hydrogen peroxide in amounts of the order of 10^{-5} to 10^{-6} M. In a later section, hydrogen peroxide is shown to be a powerful inhibitor for the exchange reaction 2.

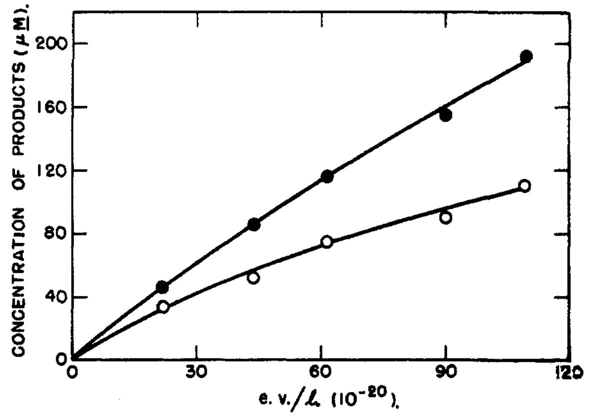

Fig. 1.—γ-Ray-induced isotopic oxygen–water exchange reaction at *p*H 6.0: ○, normal oxygen; ●, hydrogen peroxide.

The essential features of the kinetics of this reaction may be deduced from the data of Table I. These data are compiled from rate measurements handled in the manner described above on curves of the type shown in Fig. 3. Of particular importance is the quantity $G_{O_2}/\text{m}M\ O_2^*$, which is the yield expressed in terms of the number of molecules

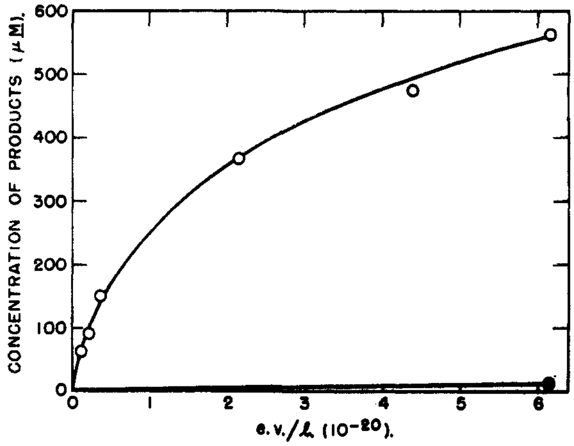

Fig. 2.—γ-Ray-induced isotopic oxygen–water exchange reaction at *p*H 12.0: ○, normal oxygen; ●, hydrogen peroxide.

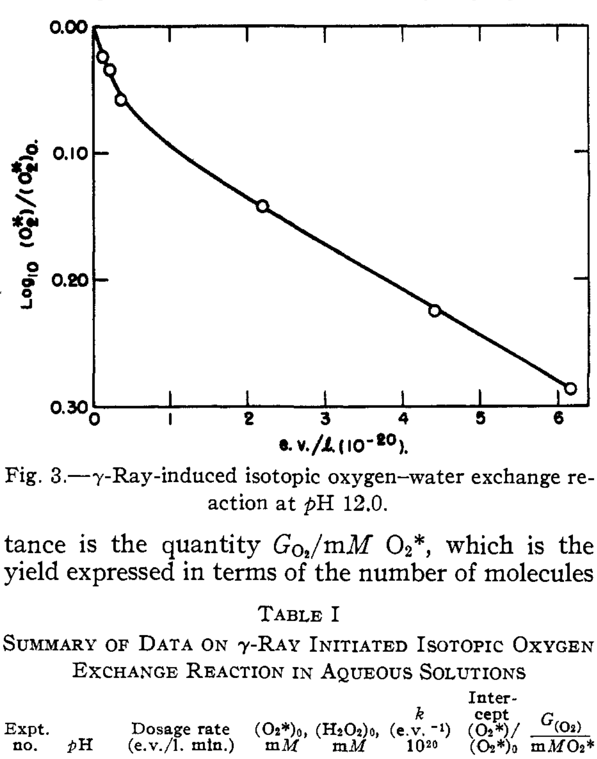

Fig. 3.—γ-Ray-induced isotopic oxygen–water exchange reaction at *p*H 12.0.

TABLE I

SUMMARY OF DATA ON γ-RAY INITIATED ISOTOPIC OXYGEN EXCHANGE REACTION IN AQUEOUS SOLUTIONS

Expt. no.	*p*H	Dosage rate (e.v./l. min.)	$(O_2^*)_0$, mM	$(H_2O_2)_0$, mM	k (e.v.$^{-1}$) 10^{20}	Intercept $(O_2^*)/(O_2^*)_0$	$\frac{G_{(O_2)}}{\text{m}M O_2^*}$
1	11.91	2.19 × 10^{20}	0.99	...	0.073	0.95	44
2	11.89	0.464 × 10^{20}	0.80	...	.082	0.97	49
3	11.62	1.17 × 10^{18}	1.22	...	.183	1.00	110
4	11.89	2.07 × 10^{17}	1.17	...	.087	1.00	52
5	11.86	2.76 × 10^{16}	1.17	...	.17	1.00	102
6	11.99	2.19 × 10^{20}	1.17	...	.076	0.86	46
7	11.70	0.335 × 10^{19}	1.11	...	.207	1.00	125
8	11.70	.11 × 10^{19}	1.11	...	.193	1.006	116
9	11.70	.91 × 10^{17}	1.11	...	.207	1.00	125
10	2.15	2.19 × 10^{20}	1.17	...	.0017	1.00	1.01
11	6.0	2.19 × 10^{20}	1.21	...	.0017	0.97	1.02
12	8.98	2.19 × 10^{20}	1.21	...	.0018	.96	1.08
13	9.65	2.19 × 10^{20}	0.70	...	.0050	.90	3.0
14	11.1	2.19 × 10^{20}	1.18	...	.030	.94	17.9
15	11.65	2.19 × 10^{20}	0.114	...	.103	.94	60
16	12.65	2.19 × 10^{20}	1.08	...	.144	.92	87
17	11.41	0.60 × 10^{19}	1.22	...	.111	1.00	67
18	11.61	.60 × 10^{19}	1.22	...	.23	1.01	139
19	12.0	.60 × 10^{19}	1.22	...	.37	1.00	226
20	12.9	.60 × 10^{19}	1.06	...	.27	1.00	161
21	13.9	.60 × 10^{19}	0.62	...	.97	1.00	585
22	11.65	2.19 × 10^{20}	1.22	0.316	.0145	1.02	8.7
23	11.62	2.19 × 10^{20}	1.18	.160	.0166	1.00	9.4
24	11.90	2.19 × 10^{20}	1.18	.046	.022	0.94	13.2
25	11.95	2.19 × 10^{20}	1.13	.019	.047	1.00	28.0

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(7) E. J. Hart, *J. Phys. Chem.*, **56**, 594 (1952).

of normal oxygen produced per 100 e.v. of γ-ray energy absorbed per m*M* enriched oxygen dissolved in the water. An intercept lower than unity as found in experiments 1, 2, 6, 11–16 and 24 indicates that the rate is lowered from its initial value owing to hydrogen peroxide or trace impurity inhibition. Experiments at high *p*H yielding intercepts of 1.00 ± 0.01 were carried out under conditions where peroxide formation was of the order of 10^{-6} *M* or under conditions where peroxide had no effect on the exchange reaction.

$G_{(O_2)}$ has been found to be independent of dosage rate of γ-rays and of intensity of ultraviolet light for alkaline solutions. An 8000-fold range in dosage rate of γ-rays is covered in experiments 1 to 6. Experimentally there is a twofold variation in the results, but since this occurs in a random manner it is concluded that there is no intensity effect. In experiments 7 to 9, an attempt was made to measure the rate of exchange before the formation of 1.0×10^{-6} *M* hydrogen peroxide. Again $G_{(O_2)}$ was found to be strictly independent of dosage rate. Therefore it is concluded that the radicals participating in the chain exchange reactions do not terminate by bimolecular recombination.

The photochemical investigation was carried out with radiation from a zinc spark filtered through 0.001 *N* sodium hydroxide. The transmitted light was then absorbed in a 0.01 *N* sodium hydroxide solution containing dissolved enriched oxygen. The amount of exchange occurring in 0.25 and 1.0 minute at 12 cm. from the source is equal to that occurring in 16 and 64 minutes at 96 cm. from the source (see Table II). Since the intensity decreases as the square of the distance, these data conform to first-order kinetics, and the exchange reaction yield is independent of intensity. In spite of the fact that free radicals are generated in columns by γ-rays and homogeneously by ultraviolet light, the mode of chain termination appears to be identical in both cases. The independence of yield on the dosage rate of γ-rays is expected in reactions having radical–radical termination steps if intercolumnar overlapping does not take place in the intensity range studied. The whole chain reaction could occur with bimolecular termination in a single track. While this possibility is not precluded by the photochemical data, the latter definitely establish the absence of a biradical termination in the kinetics of this reaction for homogeneously generated free radicals.

TABLE II

PHOTOCHEMICAL EXCHANGE REACTION BETWEEN O_2* AND H_2O AT *p*H 12

Δ*t*, min.	Cm. from source	(O_2*), μ*M*	(O_2), μ*M*
0	..	1283	0
0.25	12	1187	96
1.00	12	979	304
16.0	96	1195	88
32.0	96	1126	157
64.0	96	997	286

An extensive study was not made on the effect of concentration of enriched oxygen. The yield of normal oxygen per millimolar dissolved enriched oxygen $[G_{(O_2)}/(O_2^*)]$ is independent of concentration over an 8.7-fold range at an average *p*H of 11.8 (compare experiments 1 and 15).

Hydroxide ion concentration plays a decisive part in the exchange reaction, and its effect is observed by a study of the results of experiments 10 to 22. One notes that the rate of exchange is independent of *p*H between 2.15 and 8.98 and has a $G_{(O_2)}$ of about one. Above *p*H 9 the yield rises rapidly until a $G_{(O_2)}$ of 585 is found at a *p*H of 13.9. (The result obtained in experiment 21 at *p*H 12.9 is unaccountably low but is probably due to incidental impurities.) The chain character of the exchange reaction is firmly established by these results since 2.6 radical pairs are produced per 100 e.v. of γ-ray energy absorbed in the solution.[7] If it is assumed, as is later deduced to be the case, that only the hydroxyl radical produces exchange, then as many as 224 molecules of enriched oxygen exchange per initiating free radical.

Hydrogen peroxide added initially to the solution causes a marked decrease in the isotopic exchange reaction at *p*H's in the range 11.62 to 11.95 (see experiments 23 to 26). These yields are appreciably lower than the yields obtained in experiments 1 to 6 containing no hydrogen peroxide. Since the chain reaction is independent of dosage rate and strongly dependent on hydrogen peroxide concentration, at least one termination process involves a reaction of free radicals with hydrogen peroxide molecules.

No evidence is found for a thermal exchange reaction between dissolved enriched oxygen and normal oxygen of water at *p*H 11.88 during 119 hours standing at room temperature. This result is in contrast to a moderately rapid thermal exchange reaction at 25.5 ± 0.5° between 0.179 m*M* hydrogen peroxide of normal oxygen content and 1.19 m*M* dissolved enriched oxygen at *p*H 11.75. Mass spectrometer analyses were run on the dissolved oxygen and on oxygen liberated from the hydrogen peroxide by reaction with ceric sulfate in acid solution. Under these conditions the oxygen liberated has the same isotopic composition as the hydrogen peroxide.[8] The data are given in Table III and are in accord with a second-order reaction within the limits of experimental error. The time for 50% reaction is about 150 minutes at this *p*H and concentration. While 10% of the hydrogen peroxide decomposed in 390 minutes, 83% of the normal hydrogen peroxide was converted to enriched hydrogen peroxide in this period of time. The net reaction is

$$H_2O_2 + O^*_2 = H_2O^*_2 + O_2 \qquad (4)$$

TABLE III

THERMAL EXCHANGE REACTION BETWEEN H_2O_2 AND O_2* AT 25.5° AND *p*H 11.75

Δ*t*, min.	Total (H_2O_2)	(O_2*),[a] μ*M*	(H_2O_2*),[a] μ*M*	(H_2O_2), μ*M*
5	179.2	1190	5.1	174.1
30	179.3	1171	17.9	161.4
90	172.5	1153	64.6	107.9
270	170.0	1081	115.3	54.6
390	160.0	1058	149.4	10.6

[a] Asterisk indicates that the molecule as designated contains O^{18}.

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[8] A. E. Cahill and H. Taube, THIS JOURNAL, 74, 2312 (1952).

No evidence of an exchange between hydrogen peroxide and enriched oxygen is found in neutral or acid solutions. This result agrees with the work of Winter and Briscoe,[9] and Halperin and Taube,[10] who report that the exchange between hydrogen peroxide and water is very slow.

Mechanism

Since up to 224 oxygen molecules of normal isotopic composition are produced per radical pair through reaction 2, it is clear that efficient propagation steps must exist. A second observation of major importance is that hydrogen peroxide acts as a chain terminator for the free radical-induced reaction whereas it induces a slow thermal exchange reaction. Furthermore, the chain exchange reaction sets in at a *p*H of 9.0. This is in fact the *p*H at which the yield of hydrogen peroxide and hydrogen deuteride from the water–oxygen[3] and water–deuterium[2] reactions, respectively, diminish. A study of the latter reaction has led us to suggest the equilibrium

$$\mathrm{OH = O^- + H^+}$$

Since reaction 2 begins at *p*H 9 and continues to develop at *p*H 13.9 we postulate participation of O^-, O^*_2 and OH^- as indicated in the mechanism

Eq. number	Reaction	Rate or equilibrium constant
5	$H_2O = H + OH$	I_d
6	$H_2O = {}^1/_2H_2 + {}^1/_2H_2O_2$	I_r
7	$OH = O^- + H^+$	K_{OH}
8	$H + O^*_2 = HO^*_2$	I_d
9	$HO^*_2 = H^+ + O^{*-}_2$	K_{HO_2}
10	$O^- + O^*_2 = O^{*-} + O_2$	k_{10}
11	$O^{*-} + OH^- = O^- + O^*H^-$	k_{11}
12	$O^- + H_2O_2 = H_2O + O^-_2$	k_{12}
12′	$O^{*-} + H_2O_2 = H_2O^* + O^-_2$	k_{12}
13	$O^-_2 + O^-_2 = O^{=}_2 + O_2$	k_{13}

In view of the clear evidence that bimolecular termination processes are not involved in the chain exchange reaction, a derivation of the kinetics with peroxide termination only will be made. For reasons to be developed later, only the (O^-) free radical participates in the exchange reaction, and in the *p*H region of long chains, 11.5 to 14, complete and rapid ionization in reaction 8 will be assumed so that reactions of the OH radical may be neglected.

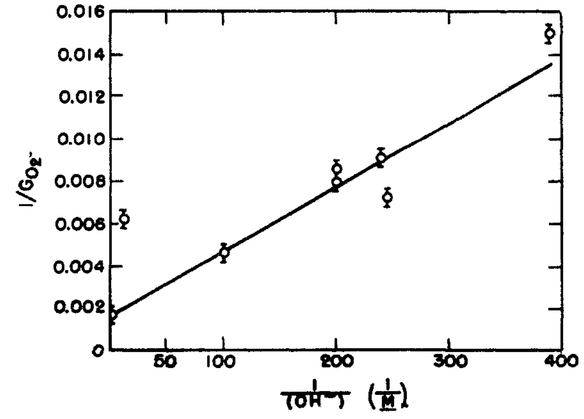

Fig. 4.—Effect of hydroxyl ion concentration on the γ-ray-induced isotopic oxygen–water exchange reaction.

The rate of (O_2) formation is given by eq. 14 for long chains.

$$d(O_2)/dt = k_{10}(O^-)(O^*_2) = k_{11}(O^{*-})(OH^-) \quad (14)$$

Steady state equations are

$$d(O^-)/dt = I_d - k_{10}(O^-)(O^*_2) + k_{11}(O^{*-})(OH^-) - k_{12}(O^-)(H_2O_2) = 0$$

$$d(O^{*-})/dt = k_{10}(O^-)(O^*) - k_{11}(O^{*-})(OH^-) - k_{12}(O^{*-})(H_2O_2) = 0$$

leading to eq. 15

$$I_d = k_{12}(H_2O_2)[(O^-) + (O^{*-})] \quad (15)$$

Solving 14 for (O^{*-}) and substituting this quantity in 15 gives an expression for (O^-) which yields eq. 16 after substitution in 14

$$\frac{d(O_2)}{dt} = \frac{I_d}{k_{12}(H_2O_2)\left[\frac{1}{k_{10}(O^*_2)} + \frac{1}{k_{11}(OH^-)}\right]} \quad (16)$$

Dividing both sides by $I_d(O^*_2)$ gives eq. 17

$$\frac{G_{(O_2)}}{(O^*_2)} = \frac{1}{k_{12}(H_2O_2)\left[\frac{1}{k_{10}} + \frac{(O^*_2)}{k_{11}(OH^-)}\right]} \quad (17)$$

Equation 17 expresses the yield in terms of hydrogen peroxide, enriched oxygen and hydroxyl ion concentrations and has the correct general form for these variables if k_{10} is small compared to k_{11} (see Fig. 4; $G_{(O_2)}/(O^*_2)$ appears in column 8 of Table I). Experiments having an intercept, $(O^*_2)/(O^*_2)_0$, of 1.00 ± 0.01 (see Table I) were used in the preparation of Fig. 4. In these experiments hydrogen peroxide formation during irradiation was of the order of 10^{-6} *M*. (Owing to very small reactions and high experimental error, experiments 4 and 5 were not used in the preparation of Fig. 4.) Experiments 22–25 inclusive demonstrate a qualitative inverse dependence of the exchange reaction on initial hydrogen peroxide concentration as expected from eq. 17. This equation also predicts that the yield is independent of dosage rate.

The yield of hydrogen peroxide in alkaline solution is nearly four times that furnished by reaction 6. Therefore some additional reaction leading to hydrogen peroxide formation must occur. Since the kinetic treatment eliminates homogeneous recombination of (O^-) radical ions, it is necessary to assume that this recombination process

$$O^- + O^- = O^{=}_2$$

occurs in individual recoil electron tracks. Otherwise hydrogen peroxide formed in reactions 6 and 13 would be destroyed by (O^-) radical ions produced by reactions 5 and 7 in view of the preponderance of reaction 5 over 6 for Co^{60} γ-rays.[7] Further work on the mechanisms of hydrogen peroxide formation is in progress in this Laboratory.

The above assumption is equivalent to the one advanced by Allen[11] that a primary reaction of the type

$$2H_2O = 2H + H_2O_2$$

occurs in addition to reactions 5 and 6.

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[9] E. R. S. Winter and H. V. A. Briscoe, *ibid.*, **73**, 496 (1951).

[10] J. Halperin and H. Taube, *ibid.*, **74**, 380 (1952).

[11] A. O. Allen, Radiation Research Society Meeting, Iowa City, Iowa, June 22–24, 1953.

The oxygen radical ion, (O^-_2), is assumed to play no role in the chain exchange reaction. The evidence for this assumption is based on the complete absence of chain reactions below a *p*H of 9.0 although $K_{HO_2} = 10^{-2}$.[12] Further support is provided by the fact that hydrogen peroxide is an inhibitor for the exchange reaction. Since (O^-_2) is a product of inhibition reactions 12 and 12′, the chain should continue propagation if O^-_2 is a chain carrier. If (O^-_2) reacted with H_2O_2 as

$$O^-_2 + H_2O_2 = H_2O + O_2 + O^-$$

then the chain again should continue. Therefore it is concluded that (O^-_2) does not participate in the chain although the non-chain reaction

$$O^-_2 + O^*_2 = O^{*-}_2 + O_2$$

is possible.

An estimate of the ionization constant of the hydroxyl radical in aqueous solution has been made using the cycle

Eq. no.	Reaction	ΔH, kcal./mole	ΔS, cal./mole deg.
18	$OH(g) = O(g) + H(g)$	101.2	21.97
19	$O(g) + e = O^-(g)$	−72.28	0
20	$H(g) = H^+(g) + e$	315.0	0
21	$H^+(g) + O^-(g) = H^+(aq) + O^-(aq)$	−345.4	−73.80
22	$OH(aq) = OH(g)$	10.51	28.39
7	$OH(aq) = H^+(aq) + O^-(aq)$	9.03	−23.4

ΔH for reactions 18, 19 and 20 was calculated from standard heats of formation.[13] ΔS for reaction 18 was also calculated from standard entropies.[13] ΔS for reactions 19 and 20 was assumed to be zero at 25°. ΔH and ΔS for reaction 21 were assumed to be equal to the sum of the heats of hydration and entropies of hydration of H^+ and OH^-, respectively. It is probable that ΔH of hydration for O^- is greater than ΔH of hydration of OH^- by about 6 kcal./mole[14] so that the ionization constant we have calculated would be a lower limit. The sum of the heats of hydration of H^+ and OH^- was calculated using the cycle

Reaction	ΔH
$H_2O(aq) = H^+(aq) + OH^-(aq)$	$-\Delta H_{(neut.)}$
$H_2O(g) = H_2O(aq)$	$-\Delta H_{(v.)}$
$H^+(g) + OH^-(g) = H_2O(g)$	$\Delta H_{(f)_{H_2O(g)}} - \Delta H_{(f)_{H^+(g)}} - \Delta H_{(f)_{OH^-(g)}}$

From the above three equations one deduces that

$$H^+(g) + OH^-(g) = H^+(aq) + OH^-(aq)$$

and

$$\Delta H = \Delta H_{(f)_{H_2O(g)}} - \Delta H_{(f)_{H^+(g)}} - \Delta H_{(f)_{OH^-(g)}} - \Delta H_{(neut.)} - \Delta H_{(v)}$$

Using the values of ΔH and ΔS obtained from reference 13 one calculates for reaction 7 that ΔH = 9,030 cal./mole, and $\Delta S = -23.4$ cal./mole deg.

Therefore at 25° $\Delta F = 9{,}030 + 298 \times 23.4 = 16{,}050$ cal., and $\log K = -16{,}050/1380 = -11.63$, and $K = 2.3 \times 10^{-12}$.

If one assumes Magat's[14] estimate of ΔH (hydration of O^-) − ΔH (hydration of OH^-), then ΔH for reaction 7 is 3.03 kcal./mole and $\log K = -13{,}050/1380 = -7.28$, and $K = 4.8 \times 10^{-8}$.

Since the experimental results interpreted on the basis of the proposed mechanism indicate an increase in the O^- concentration at a *p*H of about 9, the higher value would seem to be the more reasonable one.

Acknowledgment.—The authors wish to express their thanks to Miss P. D. Walsh for chemical analyses, to L. G. Pobo and L. F. Daum for mass spectrometer analyses, and to M. S. Matheson and J. L. Weeks for the ultraviolet irradiations.

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