

THE RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS CONTAINING HYDROGEN AND OXYGEN¹

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Received October 13, 1965

ABSTRACT

The initial yields of H₂O₂ in aerated water, $G(\text{H}_2\text{O}_2)^{\text{O}_2}$, and in water containing H₂ and O₂, $G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2}$, have been measured for alkaline solutions irradiated with ⁶⁰Co γ-rays. $G(\text{H}_2\text{O}_2)^{\text{O}_2}$ decreases with increasing pH from a value of 1.22 in neutral solution to 0.63 in solutions of pH 13.92 and the relationship

$$G(\text{H}_2\text{O}_2)^{\text{O}_2} = G_{\text{H}_2\text{O}_2} - \frac{1}{2}G_{\text{OH}} + \frac{1}{2}G_{\text{red}}$$

is valid over the pH range 7 to 14.

$G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2}$ decreases from 3.30 in neutral solution to a minimum of 2.00 at pH 11.35 and then increases to 2.65 at pH 13.92. The equation

$$G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2} = G_{\text{H}_2\text{O}_2} + \frac{1}{2}G_{\text{OH}} + \frac{1}{2}G_{\text{red}}$$

which is applicable for neutral solutions, is not valid for basic solutions.

A reaction mechanism in accordance with the observed results and the literature values of the rate constants of likely radical reactions has been developed. It is assumed that in the alkaline solutions investigated OH radicals react with OH⁻ ions to form O⁻ radicals which react preferentially with O₂ to form O₃⁻ radicals which then react either with H₂ or H₂O₂. The increase in $G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2}$ at pH > 12 is attributed to a difference in the rate of reaction of O₃⁻ with H₂O₂ and HO₂⁻, $k(\text{O}_3^- + \text{H}_2\text{O}_2)/k(\text{O}_3^- + \text{HO}_2^-) = 2.45$.

INTRODUCTION

Studies of the hydrogen-oxygen-water system have produced valuable information about the yields of the primary products of the radiolysis of neutral water (1-3). Therefore, it was decided to attempt similar studies in the higher pH range where reported primary yields are not in agreement (3).

EXPERIMENTAL

Solutions were prepared with specially purified water (4) and reagent grade KOH and Ba(OH)₂. Solutions of pH 12 or greater were made $5 \times 10^{-3} M$ in Ba(OH)₂ to remove carbonate ions while those of lower pH were prepared with either KOH or Ba(OH)₂. Certified 99.93% H₂ and O₂ gases, after being monitored with flowrators, were passed through activated charcoal, mixed, bubbled through a gas washer containing water at the same pH as the solution to be irradiated, and passed through a trap cooled with a dry ice-acetone mixture. The gas mixture was then bubbled for 30 min through the desired solution which was in a quartz flask equipped with a sidearm vent. After bubbling, the solution was poured through the sidearm to fill clean quartz tubes (4) which had been swept out with the gas mixture. Clamped wet ball-and-socket joints were used throughout the apparatus.

Samples were irradiated with ⁶⁰Co γ-radiation at a dose of 200 rads/min to doses of 2 000 to 8 000 rads. The dosimetry has been described elsewhere (4).

Initial dissolved H₂ and O₂ concentrations were calculated from the partial pressure of each gas at the measured barometric pressure and solution temperature (5).

Hydrogen peroxide was determined by the Ghormley method²(4, 6). To verify the accuracy of the method with solutions of pH > 12, H₂O₂ solutions of known concentration were brought to the desired pH and analyzed. No effect due to high pH could be detected with H₂O₂ solutions which had been neutralized with potassium acid phthalate immediately before analysis.

RESULTS AND DISCUSSION

Typical [H₂O₂] vs. dose plots are given for aerated water in Fig. 1 and for solutions of H₂ and O₂ in Fig. 2. The yield of H₂O₂ increases linearly with dose up to about 6 000 rads. The small intercept on the H₂O₂ axis in some of the plots is probably due to impurities.

¹Issued as DCBRL Report No. 482.

The effects of increasing pH on the initial yield of H_2O_2 in irradiated aerated water, $G(\text{H}_2\text{O}_2)^{\text{O}_2}$, and solutions of H_2 and O_2 , $G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2}$, are listed in Table I. These G -values were determined from the slopes of $[\text{H}_2\text{O}_2]$ vs. dose plots. The yield of H_2O_2 in aerated solutions decreases as the pH increases from neutrality to \sim pH 11, remains constant from pH 11 to 13, and then drops sharply at pH $>$ 13. With solutions containing both H_2 and O_2 , the yield of H_2O_2 decreases rapidly as the pH increases from neutrality to \sim pH 11, then increases rapidly at pH $>$ 12. It should be noted that $G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2}$ is dependent on the ratio $[\text{H}_2]/[\text{O}_2]$ only for solutions of pH 10.62 and 11.35.

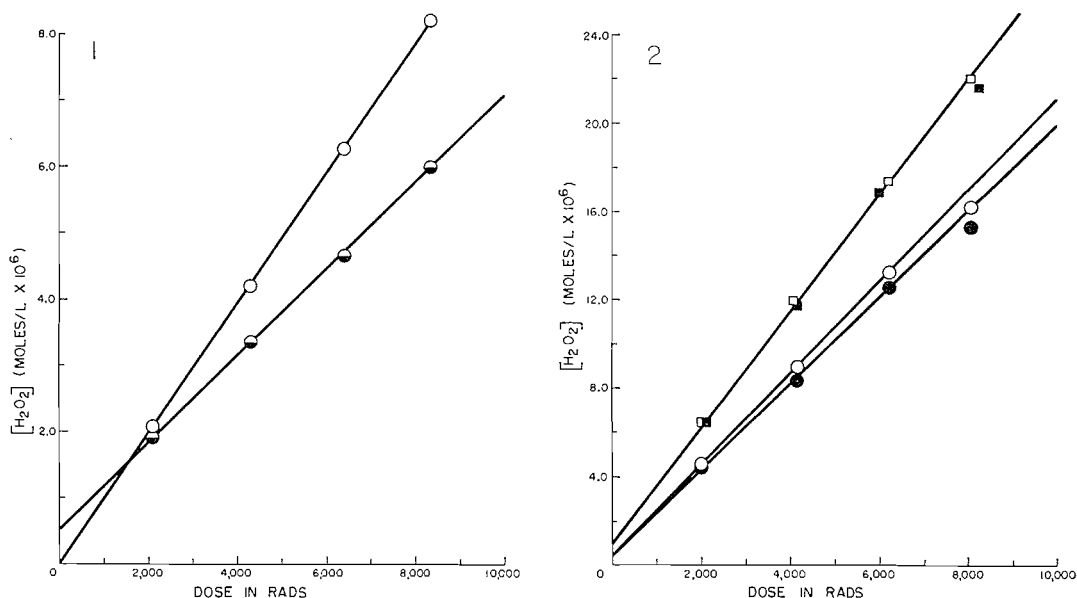


FIG. 1. H_2O_2 yields in aerated water: (O) 5×10^{-4} M KOH, pH 10.62; (●) 0.5 M KOH - 5×10^{-3} M $\text{Ba}(\text{OH})_2$, pH 13.55.

FIG. 2. H_2O_2 yields in water containing H_2 and O_2 : (O) 5×10^{-4} M KOH, pH 10.62; (□) 0.1 M KOH - 5×10^{-3} M $\text{Ba}(\text{OH})_2$, pH 12.85. (Open symbols $[\text{H}_2]/[\text{O}_2] = 1.20$, closed symbols $[\text{H}_2]/[\text{O}_2] = 0.60$.)

Allen (3) has shown that the yield of oxidizing radicals, G_{OH} , may be determined by comparing the initial yields of hydrogen peroxide in neutral water containing both dissolved oxygen and hydrogen and in water containing only oxygen (aerated water).

$$[\text{A}] \quad G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2} = G_{\text{H}_2\text{O}_2} + \frac{1}{2}G_{\text{OH}} + \frac{1}{2}G_{\text{red}}$$

$$[\text{B}] \quad G(\text{H}_2\text{O}_2)^{\text{O}_2} = G_{\text{H}_2\text{O}_2} - \frac{1}{2}G_{\text{OH}} + \frac{1}{2}G_{\text{red}}$$

$$[\text{C}] \quad G_{\text{OH}} = G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2} - G(\text{H}_2\text{O}_2)^{\text{O}_2} \\ = 2.2 \text{ for neutral water.}$$

Where $G_{\text{H}_2\text{O}_2}$ is the "molecular" yield of H_2O_2 , and G_{red} is the sum of the yield of hydrated electrons, $G_{e_{\text{aq}}^-}$, and the yield of H atoms, G_{H} .

During the course of the present investigation, Hayon (7) published the results of his studies on the radiolysis of alkaline aqueous solutions of nitrate + formate ions, ferricyanide + formate + O_2 , and ferricyanide + ethanol + O_2 in the pH range 6 to 14. From these data he determined the yields of radicals and molecular products for the radiolysis of water at many pH values. We have used some of these values and expressions

TABLE I

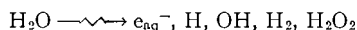
The effect of pH on the initial yields of H₂O₂ in irradiated aerated water and aqueous solutions of H₂ and O₂

pH	G(H ₂ O ₂) ^{O₂}		[H ₂] (moles/l × 10 ⁴)	[O ₂] (moles/l × 10 ⁴)	G(H ₂ O ₂) ^{H₂, O₂}		ΔG(H ₂ O ₂)	
	Meas.	Calcd.*			Meas.	Calcd.†	Meas.	Calcd.
Neutral	1.22	1.01	4.99	4.16	3.30	3.26	2.08	2.25
Neutral			3.72	6.20	3.30			
9.25	1.06		4.99	4.16	2.81		1.75	1.81
9.25			3.72	6.20	2.81		1.75	1.72
10.10	1.00		4.99	4.16	2.29		1.29	1.22
10.10			3.72	6.20	2.29		1.29	1.19
10.62	0.95	0.98	5.02	4.18	2.01	3.25	1.06	1.03
10.62			3.75	6.22	1.89		0.94	0.98
11.35	0.92		5.02	4.18	2.00		1.08	0.98
11.35			3.75	6.22	1.87		0.95	0.94
12.10	0.88	0.90	4.86	4.01	2.10	3.30	1.22	0.99
12.10			3.62	5.98	2.10		1.22	0.96
12.85	0.87		4.86	4.01	2.54	3.52	1.67	1.68
12.85			3.62	5.98	2.54		1.67	1.66
13.25	0.74	0.73	4.63	3.78	2.74		2.00	1.79
13.25			3.45	5.63	2.74		2.00	1.77
13.55	0.63	0.60	4.29	3.39	2.71	3.68	2.08	1.89
13.55			3.20	5.06	2.71		2.08	1.87
13.92	0.63		3.67	2.79	2.65		2.02	2.01
13.92			2.74	4.17	2.65		2.02	2.01

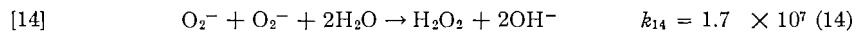
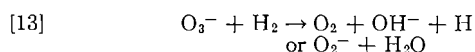
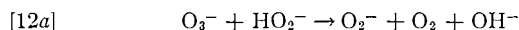
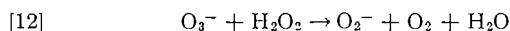
*G(H₂O₂)^{O₂} = G_{H₂O₂} + ½G_{red} - ½G_{OH}, calculated with Hayon's values (7) for G_{H₂O₂}, G_{red}, and G_{OH}.
†G(H₂O₂)^{H₂, O₂} = G_{H₂O₂} + ½G_{red} + ½G_{OH}, calculated with Hayon's values (7) for G_{H₂O₂}, G_{red}, and G_{OH}.

[B] and [A] to determine the calculated values of G(H₂O₂)^{O₂} and G(H₂O₂)^{H₂, O₂} listed in Table I. The measured and calculated values of G(H₂O₂)^{O₂} are in good agreement, whereas those of G(H₂O₂)^{H₂, O₂} are not in agreement. These results infer that each of the oxidizing radicals present in irradiated alkaline aerated water reacts in such a way as to ultimately destroy ½ molecule of H₂O₂, whereas in solutions of H₂ and O₂ the fraction of the oxidizing radicals which reacts with H₂ to ultimately form ½ molecule of H₂O₂ decreases from unity at neutral pH to a minimum at about pH 12 then increases at pH > 12 but does not return to unity. This abrupt change at pH ~ 12 may be related to a difference in the reactivity of the dissociated and undissociated forms of H₂O₂ since the pK value for the dissociation of H₂O₂ is 11.75 (8).

A reaction mechanism in accordance with these observed results may be developed from a consideration of the following reactions and their respective rate constants.



- | | | |
|------|---|---|
| [1] | $e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^- + \text{H}_2\text{O}$ | $k_1 = 1.88 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (9) |
| [2] | $e_{\text{aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH} + \text{OH}^-$ | $k_2 = 1.23 \times 10^{10}$ (9) |
| [3] | $\text{H} + \text{O}_2 \rightarrow \text{O}_2^- + \text{H}^+$ | $k_3 = 2.6 \times 10^{10}$ (9) |
| [4] | $\text{H} + \text{OH}^- \rightarrow e_{\text{aq}}^-$ | $k_4 = 1.8 \times 10^7$ (9) |
| [5] | $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$ | $k_5 = 1.7 \times 10^8$ (9) |
| [6] | $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ | $k_6 = 4.5 \times 10^7$ (10) |
| [7] | $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{O}_2^- + \text{H}_2\text{O}$ | $k_7 = 2.25 \times 10^7$ (11) |
| [8] | $\text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O}$ | $k_8 = 6.2 \times 10^8$ (7) |
| [9] | $\text{O}^- + \text{H}_2 \rightarrow \text{OH}^- + \text{H}$ | $k_9 = 8 \times 10^7$ (12) |
| [10] | $\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^-$ | $k_{10} = 2.6 \times 10^9$ (13) |
| [11] | $\text{O}^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^- + \text{H}_2\text{O}$ | |



Many of the above reactions are accepted in the mechanism for the radiolysis of neutral water. However, reactions [4] and [8] to [13] can occur only in basic solutions. Reaction [4] has been demonstrated by Matheson and Rabani (12), and Adams, Boag, and Michael (15) have presented evidence for [8]. The rate constant for reaction [10] has been determined from the optical absorption of the O_3^- (13) species but very little is known about its reactivity. The only demonstrated reaction is the oxidation of ferrocyanide (15).

In aerated solutions for initial yields, reactions [1] and [3] will predominate over [2] and [5] and each reducing radical will result in the formation of $\frac{1}{2}$ molecule of H_2O_2 either via [1] and [14], [3] and [14], or [4], [1], and [14]. Reactions [6], [9], and [13] will be negligible and each oxidizing radical will result in the destruction of $\frac{1}{2}$ molecule of H_2O_2 either directly by [7] or through [8] followed by either [11] or [10] and [12]. Hence

$$G(\text{H}_2\text{O}_2)^{\text{O}_2} = G_{\text{H}_2\text{O}_2} + \frac{1}{2}G_{\text{red}} - \frac{1}{2}G_{\text{OH}}$$

In solutions containing both H_2 and O_2 , each reducing radical will again react to ultimately form $\frac{1}{2}$ molecule of H_2O_2 . For initial yields, reactions [7] and [11] will be negligible and H_2 and OH^- will compete for OH radicals in reactions [6] and [8]. There will also be a competition between H_2 and O_2 for O^- radicals in reactions [9] and [10] and between H_2O_2 and H_2 for O_3^- radicals in [12] and [13]. Assuming this reaction scheme

$$G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2} = G_{\text{H}_2\text{O}_2} + \frac{1}{2}G_{\text{red}} + \frac{1}{2}G_{\text{OH}} \\ - \frac{G_{\text{OH}}}{(1 + (k_6[\text{H}_2]/k_8[\text{OH}^-]))(1 + (k_9[\text{H}_2]/k_{10}[\text{O}_2]))(1 + (k_{13}[\text{H}_2]/k_{12}[\text{H}_2\text{O}_2]))} \\ [D] \quad \Delta G(\text{H}_2\text{O}_2) = G(\text{H}_2\text{O}_2)^{\text{H}_2, \text{O}_2} - G(\text{H}_2\text{O}_2)^{\text{O}_2} = G_{\text{OH}} \left(1 - \frac{G_{\text{OH}}}{(1 + (k_6[\text{H}_2]/k_8[\text{OH}^-]))(1 + (k_9[\text{H}_2]/k_{10}[\text{O}_2]))(1 + (k_{13}[\text{H}_2]/k_{12}[\text{H}_2\text{O}_2]))} \right)$$

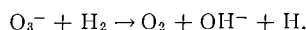
At neutral pH, $k_6[\text{H}_2]/k_8[\text{OH}^-]$ is very large and the expression reduces to $\Delta G(\text{H}_2\text{O}_2) = G_{\text{OH}}$.

At $\text{pH} > 12$, $k_6[\text{H}_2]/k_8[\text{OH}^-]$ is negligibly small and as the $\text{p}K$ value for the dissociation of H_2O_2 is 11.75 (8), reaction [12a] replaces [12]. Substitution in [D] of the appropriate values from Table I for solutions of pH 12.85 along with the literature values for the rate constants k_9 and k_{10} and Hayon's value (7) of $G_{\text{OH}} = 2.72$ at pH 12.90 gives $k_{13}[\text{H}_2]/k_{12a}[\text{H}_2\text{O}_2] = 1.52$. A similar calculation with literature values for k_6 , k_8 , k_9 , and k_{10} , experimental results at pH 10.60, and Hayon's $G_{\text{OH}} = 2.27$ at this pH gives $k_{13}[\text{H}_2]/k_{12}[\text{H}_2\text{O}_2] = 0.62$. Thus $k_{12}/k_{12a} = 2.45$.

During an investigation of transient species in irradiated alkaline oxygenated solutions, Dorfman (14) observed a dependence on pH of the half-life of the transient absorption at $430 \text{ m}\mu$ due to O_3^- . The half-life increased from 0.4 ms at pH 11 to 2 ms at pH 13. On the assumption that the O_3^- disappeared by reaction with hydrogen peroxide, this observation supports our contention that the rate of reaction of O_3^- with H_2O_2 is greater than that with HO_2^- ($k_{12} > k_{12a}$).

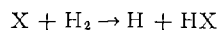
In the final column of Table I, the values of $\Delta G(\text{H}_2\text{O}_2)$ calculated with expression [D] using the G_{OH} figures of Hayon and $k_{13}[\text{H}_2]/k_{12}[\text{H}_2\text{O}_2] = 0.62$ for solutions of $\text{pH} < 12$ and $k_{13}[\text{H}_2]/k_{12a}[\text{H}_2\text{O}_2] = 1.52$ for solutions of $\text{pH} > 12$ are compared with the measured values. Differences between the two throughout the entire alkaline pH range are never greater than 10% except at $\text{pH} 12.10$ where the experimental value lies between the two calculated values of 0.99, assuming $k_{13}[\text{H}_2]/k_{12}[\text{H}_2\text{O}_2] = 0.62$, and 1.50, assuming $k_{13}[\text{H}_2]/k_{12a}[\text{H}_2\text{O}_2] = 1.52$. Since the experimental error in measuring $G(\text{H}_2\text{O}_2)^{\text{H}_2\text{O}_2}$ or $G(\text{H}_2\text{O}_2)^{\text{O}_2}$ at a given pH is about $\pm 5\%$, the proposed mechanism fits the data reasonably well.

One reaction that might be questioned is



If this does not occur, only O^- can react with H_2 at $\text{pH} > 12$ and the high yield of $G(\text{H}_2\text{O}_2)^{\text{H}_2\text{O}_2}$ will require k_9/k_{10} to be approximately 2 instead of the value 0.0308 derived from rate constants appearing in the literature. Also $G(\text{H}_2\text{O}_2)^{\text{H}_2\text{O}_2}$ will be more dependent on $[\text{H}_2]/[\text{O}_2]$ than is indicated by the experimental results. In most alkaline systems the formation of O_3^- can be suppressed by employing a solute concentration much greater than the oxygen concentration. The low solubility of hydrogen prevented this in the present investigation.

The observed effects of increasing pH on $G(\text{H}_2\text{O}_2)^{\text{H}_2\text{O}_2}$ may also be explained by postulating the presence in irradiated H_2O of an additional oxidizing species, X, different from OH . This proposed radical, first suggested by Allen (3), would have to react much less readily with H_2 than with H_2O_2 . If such a species were present, reaction [13] could be replaced by



and all O_3^- radicals could be assumed to react with H_2O_2 or its precursors. The increase in $G(\text{H}_2\text{O}_2)^{\text{H}_2\text{O}_2}$ at $\text{pH} > 12$ might then be explained by assuming $k_{\text{X}+\text{H}_2\text{O}_2} > k_{\text{X}+\text{H}_2}$.

Since there is no direct evidence for the presence of radical X in irradiated water, we prefer to base the mechanism on reactions of known species.

ACKNOWLEDGMENT

The author wishes to thank Mr. W. G. Humphreys for valuable technical assistance and Drs. P. J. Dyne and A. W. Boyd for helpful discussions.

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