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RADIATION RESEARCH 7, 199–216 (1957)

Radiolysis of Aqueous Solutions of Hydrocarbons Benzene, Benzene-d_6, Cyclohexane[1]

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1. INTRODUCTION

The literature contains reports on initial yields of a number of products formed in radiolysis of aqueous solutions of benzene (*1–5*). The study here described provides additional data on the reaction of benzene with irradiated water at various pH's and on the behavior of H atoms in the presence of hydrocarbons in the liquid phase. Experiments on solutions of benzene in D_2O and of benzene-d_6 in H_2O give some information about primary yields in γ-ray-induced decomposition of both heavy and ordinary water.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Water. Ordinary water was purified by triple distillation according to conventional procedures (*6*). High-purity heavy water supplied by Stuart Oxygen Company was distilled only once from alkaline permanganate after a reflux period of about 2 hours.

Benzene. Merck cp thiophene-free benzene was purified by three successive crystallizations, and the residue was then distilled in a 50-theoretical plate column, yielding a middle third with boiling point 80.0°C at 74.9 cm Hg.

Benzene-d_6 was prepared according to the method of Ingold *et al.* (*7*), using eight equilibrations. It had a deuterium content of 99.8 atom %.

Cyclohexane. Spectro-grade Eastman Kodak cyclohexane was employed without further purification.

Sulfuric acid. Baker's AR grade H_2SO_4 was employed without further purification. Solutions of various pH's were made up by weighing and volumetric techniques were occasionally checked analytically.

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[2] Monsanto Fellow, 1955–1956.

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2.2. Techniques

Utmost precautions were exercised to ensure freedom of contamination of samples by accidental admixture of impurities from air, vessel walls, or stopcock grease. For handling of the purified hydrocarbons and of deaerated solutions, high-vacuum procedures were employed throughout.

Aerated or oxygenated samples were 50 ml in volume; deaerated sample volumes were only 20 ml.

Samples were irradiated either in a ca. 200-curie Co^{60} γ-ray source of the Ghormley-Hochanadel type (*8*) or on the 100-curie level of an underground-type source (*9*).

2.3. Analyses

All samples containing air or oxygen were made up in triplicate. Gas analysis of one of these samples established initial composition; the other samples were irradiated and analyzed after irradiation in each case. No blanks were employed for deaerated samples.

Gas was extracted from the irradiated samples by the conventional repeated freezing, evacuation, and melting technique. Volume, pressure, and temperature of the collected gas were measured, and a sample was analyzed on a Nier Consolidated mass spectrometer Model 21–103A. Occasionally, for pure H_2 samples, volume measurements were made after diffusion through a hot palladium thimble.

Phenol was determined by the spectrophotometric method of Sworski (*2*). The extinction coefficients for C_6H_5OD and C_6D_5OH were assumed to be the same as those for C_6H_5OH.

Hydrogen peroxide was measured according to the Ghormley method (*10*) in which hydrogen peroxide is reduced by iodide ion and the resultant triodide is measured spectrophotometrically. For strong acid solution, it was necessary to use the titanium method (*11*), since in this case the iodide ion is rapidly oxidized by dissolved oxygen. Attempts to neutralize the solution prior to employment of the Ghormley technique led to erratic results. The peroxide concentration determined by these methods was not significantly different from that obtained using the ceric ion method at about 2°C (*12*). This fact indicates that the concentration of organic peroxide is negligible.

For diphenyl determination 10 ml of the irradiated solution was extracted twice with 5 ml of research-grade *n*-hexane. This extraction removes all the diphenyl and benzene together with about 10% of the phenol from the aqueous phase. The optical density of the hexane layer was measured at 2800 A. Benzene is completely transparent at this wavelength, but phenol absorbs with a molar extinction coefficient of 562, compared with a value of 1110 for diphenyl. The distribution of phenol between water and hexane was determined experimentally to be 9:1 at room temperature. Since the concentration of phenol in the irradiated solution was known

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from independent determination, the optical density of the hexane extract could be corrected for the contribution of the phenol present and thus the diphenyl concentration could be established. The error was estimated to be 4 or 5%.

Extinction coefficients of $(C_6H_5)_2$ were assumed identical with those of $(C_6D_5)_2$.

2.4. Dosimetry

Dose was calculated by conventional techniques, employing the Fricke dosimeter (*6*, *13*, *14*) and using the value $G(\mathrm{Fe}^{+++}) = 15.6$.

3. RESULTS

3.1. Yields

Yields are reported as 100-ev yields or G values. Initial yields are indicated by the symbol G_0. Following Dewhurst and Burton (*15*), we use G_w to represent the earliest detectable yield of the specified product from the water itself in the particular solution studied.

Table I summarizes all the G_0 values obtained in this investigation. Some of these values were calculated from data summarized in Figs. 1–7; in such case reference is made to the appropriate figure.

Figures 1–7 are included because in each case they present some points of interest regarding the kinetics of the radiolysis. The next sections contain comments on the figures in addition to those included by implication in Table I.

3.2. Comments on Figures

Unbuffered air-free solutions in ordinary water. Figure 1 summarizes the results obtained on exposure of unbuffered air-free benzene solutions as a function of dose. In agreement with Sworski (*2*, *3*), but contrary to Baxendale and Smithies (*4*), no hydrogen peroxide production was observed. Rates of C_6H_5OH and $(C_6H_5)_2$ production are independent of dose for moderate dosage but decrease slightly at higher dose. Rate of H_2 production was independent of dose in the range studied. Yields are indicated in the legend of the figure.

When irradiated over 2 hours, the solution became turbid and gave off a strong odor, characteristic of neither diphenyl nor phenol. When the solution was opened to air, the suspension deposited and the solution assumed a clear straw color.

Acidified air-free solutions. Figure 2 (see Table I) shows that making an air-free benzene solution acid with 0.8 N H_2SO_4 has little effect on H_2 or phenol formation. The value $G_0(\mathrm{Ph}_2)$ is sharply reduced, however, and there is significant formation of hydrogen peroxide. The value $G_0(H_2O_2) = 0.57$ may be compared with the Sworski value of 0.58 (*2*, *3*) and the Baxendale-Smithies value 0.50 (*4*).

Variation of hydrogen peroxide yield with pH. Figure 3 summarizes the effect of pH on attainable H_2O_2 concentration at a fixed irradiation dose of 5.2×10^{21} ev

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TABLE I
SUMMARY OF 100-EV YIELDS

Solvent	*Solute*	H_2SO_4[a]	*Conditions*	G_0						*Figure*
				H_2O_2 *or* D_2O_2[b]	PhOH *or* PhOD[b]	Ph_2	H_2 *or* D_2[b]	HD	$-O_2$	
H_2O	C_6H_6	0	Air-free	0	0.36 ± 0.02	1.22 ± 0.03	0.42 ± 0.02			1
		0.8 *N*	Air-free	0.57 ± 0.04	0.35 ± 0.02	0.96 ± 0.03	0.39 ± 0.02			2
		0	Aerated	2.88 ± 0.03	2.64 ± 0.04	0	0.42 ± 0.01		5.33	4–7
		0	Oxygenated	3.27 ± 0.03	2.64 ± 0.04	0				4–7
		0.8 *N*	Aerated	2.84 ± 0.03	2.64 ± 0.04	0	0.39 ± 0.01		5.33	4–7
		0.8 *N*	Oxygenated	3.30 ± 0.03	2.64 ± 0.04	0				4–7
	C_6D_6	0	Air-free	0	0.36 ± 0.02	1.22 ± 0.03	0.41 ± 0.02	0.013		
	C_6H_{12}	0	Air-free				1.22 ± 0.03			
		0.8 *N*	Air-free				1.62 ± 0.03			
		0	Aerated				0.43 ± 0.01		2.88 ± 0.08	
D_2O	C_6H_6	0	Aerated	2.60 ± 0.02	2.38 ± 0.02	0	0.32 ± 0.01	0.01	4.40 ± 0.03	
		0.8	Aerated				0.30 ± 0.01			

[a] H_2SO_4 was used for acidification of D_2O as well as H_2O solutions.

[b] In the D_2O samples, yields given are those of the corresponding deuterium compounds.

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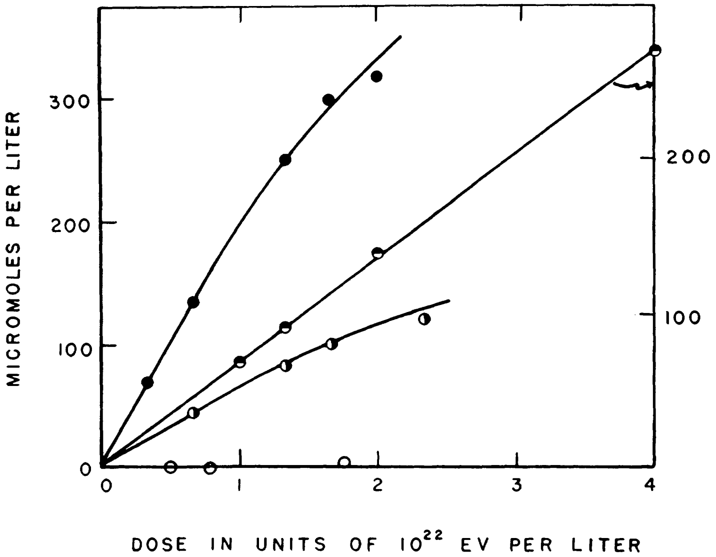

Fig. 1. Radiolysis as a function of dose in air-free neutral solutions of benzene in water. Dose rate: 4.33×10^{19} ev/liter-min. for H_2O_2; 5.48×10^{19} ev/liter-min. for others. Legend: left ordinate scale: ● Ph_2; ◑ PhOH; ○ H_2O_2; right ordinate scale: ◓ H_2. Yields: $G_0(H_2O_2) = 0$; $G_0(H_2) = 0.42$; $G_0(\text{PhOH}) = 0.36$; $G_0(Ph_2) = 1.22$.

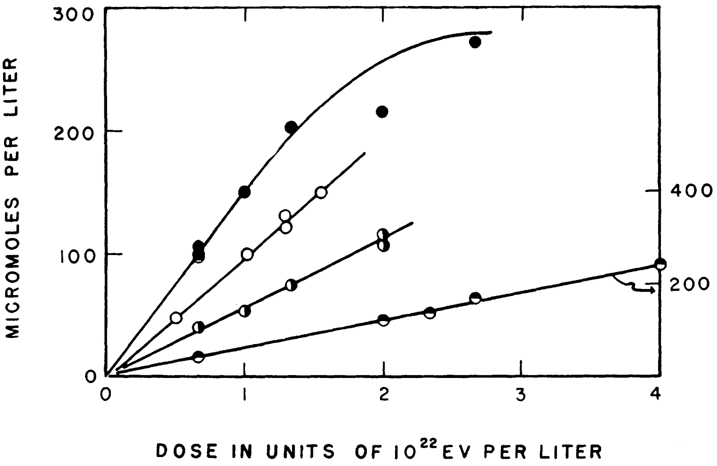

Fig. 2. Radiolysis as a function of dose in air-free aqueous solutions of benzene in 0.8 *N* sulfuric acid. Dose rate: 4.33×10^{19} ev/liter-min for H_2O_2; 5.48×10^{19} ev/liter-min for others. Legend: left ordinate scale: ● Ph_2; ◑ PhOH; ○ H_2O_2; right ordinate scale: ◓ H_2. Yields: $G_0(H_2O_2) = 0.57$; $G_0(\text{PhOH}) = 0.35$; $G_0(Ph_2) = 0.96$; $G_0(H_2) = 0.39$.

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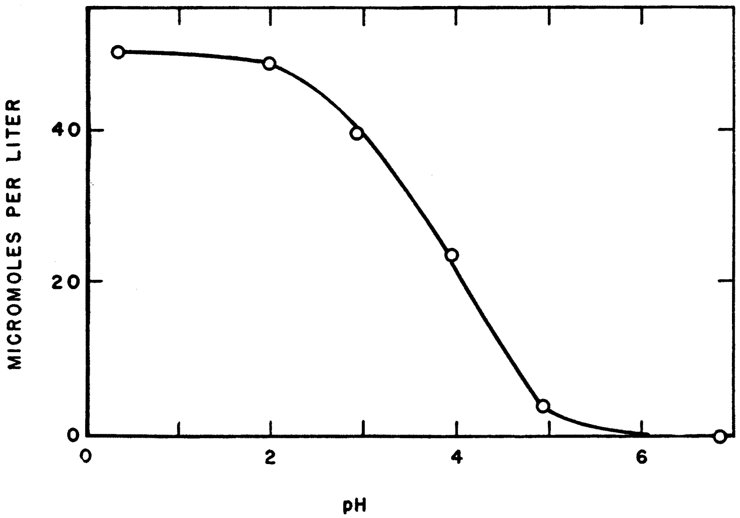

Fig. 3. Production of H_2O_2 as a function of pH in radiolysis of air-free solutions of benzene in water: H_2O_2 concentrations after 120-minute irradiation. Dose rate: 4.33×10^{19} ev/liter-min.

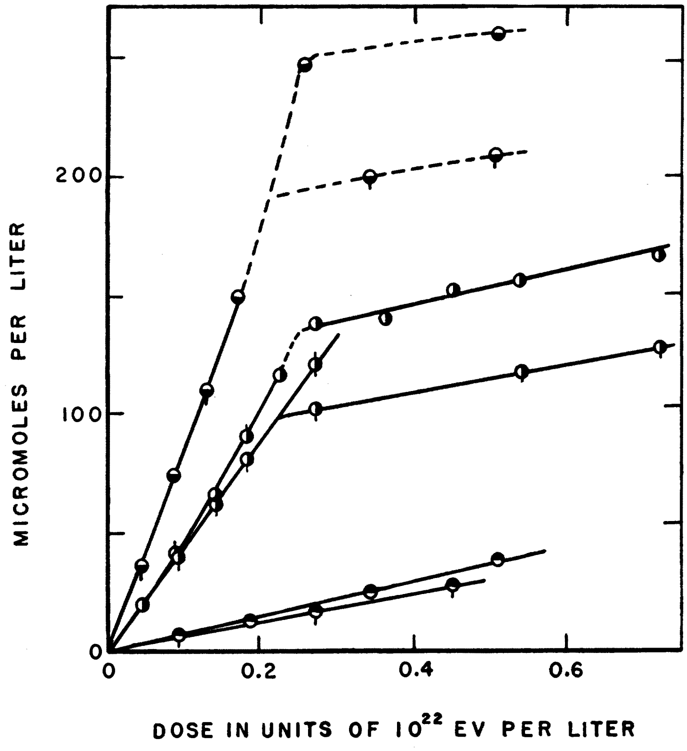

Fig. 4. Effect of oxygen on radiolysis in solutions of benzene in water. Dose rate: 2.89×10^{19} ev/liter-min for H_2, $-O_2$; 3.03×10^{19} ev/liter-min for PhOH. Legend: ◓ H_2 in unbuffered solution; ◓ H_2 in 0.8 *N* H_2SO_4; ◑ PhOH in unbuffered, aerated solution; ◑ PhOH in unbuffered, oxygenated solution; ◑ PhOH in 0.8 *N* H_2SO_4, aerated solution; ◑ PhOH in 0.8 *N* H_2SO_4, oxygenated solution; ◒ $-O_2$ in unbuffered, aerated solution; ◒ $-O_2$ in 0.8 *N* H_2SO_4, aerated solution. Yields: $G_0(H_2) = 0.42$ unbuffered; 0.39, 0.8 *N* H_2SO_4; $G_0(\mathrm{PhOH}) = 2.64$ for all conditions specified; $G_0(-O_2) = 5.33$ for all conditions specified.

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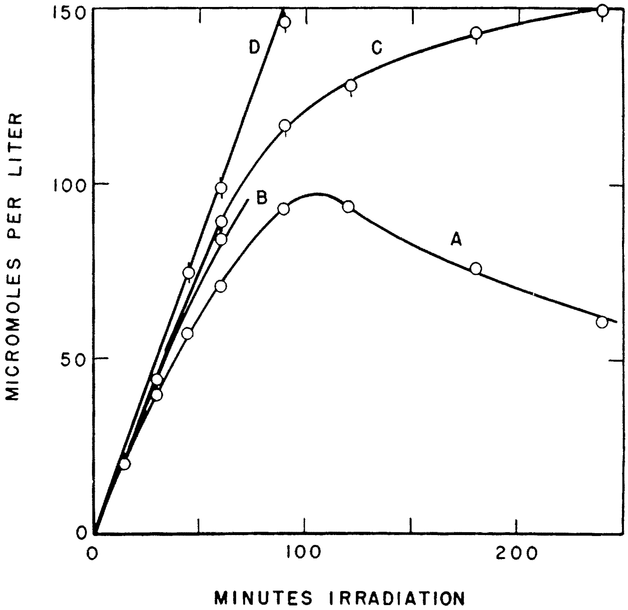

FIG. 5. Effect of oxygen on production of H_2O_2 in radiolysis of solutions of benzene and water. Dose rate: 3.03 × 10^{19} ev/liter-min. Legend: ○ H_2O_2 in unbuffered, aerated solution: ȯ H_2O_2 in unbuffered, oxygenated solution; ϙ H_2O_2 in 0.8 N H_2SO_4, aerated solution; ϕ H_2O_2 in 0.8 N H_2SO_4, oxygenated solution. Yields: $G_0(H_2O_2) = 2.88$ unbuffered, aerated; $G_0(H_2O_2) = 3.27$ unbuffered, oxygenated; $G_0(H_2O_2) = 2.84$, 0.8 N H_2SO_4, aerated; $G_0(H_2O_2) =$ 3.30, 0.8 N H_2SO_4, oxygenated.

liter^{-1}. The yield drops sharply beginning at pH ~ 2.5 and is hardly measurable at pH 6.

Aerated and oxygenated solutions. Figure 4 shows that instead of remaining constant, or falling, while O_2 is still present, the rate of phenol production in unacidified solution actually increases slightly with time at fixed dose rate; in 0.8 N H_2SO_4, however, the rate of formation remains constant. In both cases, the rate falls sharply as oxygen becomes nearly entirely consumed.

Figure 5 shows that increase in O_2 concentration of the solution favors formation of H_2O_2; sulfuric acid has a similar but more pronounced effect. Curve D of Fig. 5 shows a combined effect, with $G_0(H_2O_2) = 3.30$.

Figure 4 shows that rate of H_2 production is independent of the presence of oxygen, the rate remaining constant even after the oxygen is fully depleted.

The rate of oxygen consumption, $G_0(-O_2) = 5.33$ in both acid and unacidified solution, is fairly constant so long as the concentration of oxygen is relatively high[3] (cf. Fig. 5).

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[3] It may be noted that in a similar solution exposed to 2537-A light the quantum yield of oxygen consumption is <0.01 (*16*).

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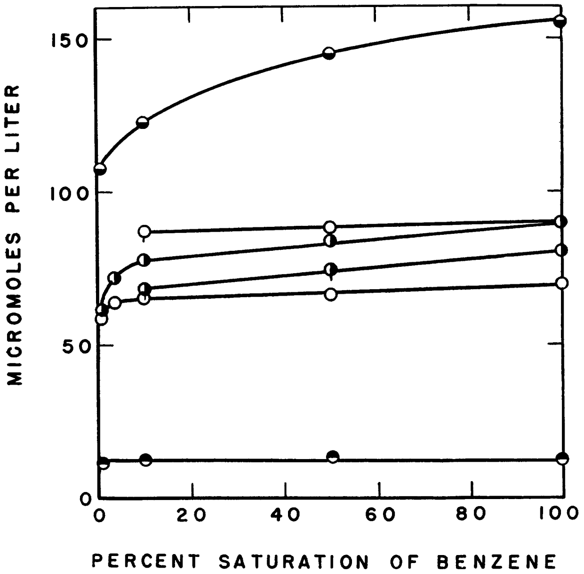

FIG. 6. Effect of benzene concentration on products obtainable on 60 minutes of irradiation of various benzene-water-oxygen solutions. Concentrations of products after 60-minute irradiation. Dose rate: 2.89 × 10^{19} ev/liter-min for H_2, $-O_2$; 3.03 × 10^{19} ev/liter-min for others. Legend: ◓ H_2; ○ H_2O_2 in unbuffered solution; ϙ H_2O_2 in 0.8 *N* H_2SO_4; ◑ PhOH in unbuffered solution; ♁ PbOH in 0.8 *N* H_2SO_4; ◒ $-O_2$ in unbuffered solution.

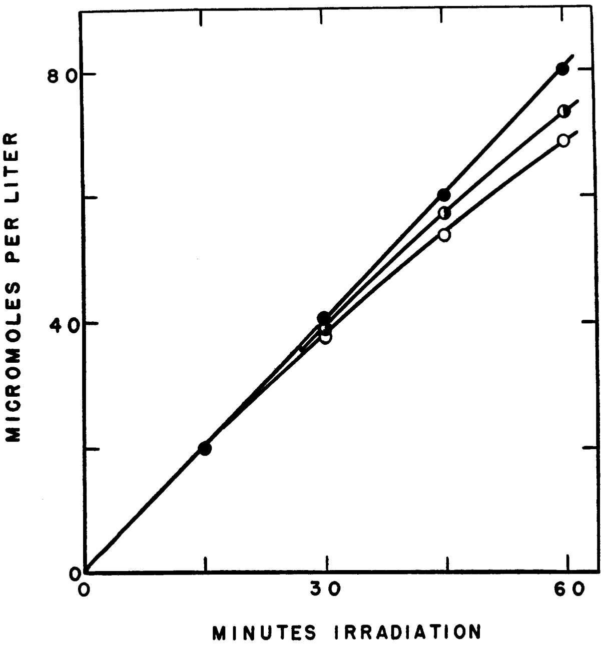

FIG. 7. Effect of benzene concentration on rate of production of phenol in radiolysis of aerated aqueous solutions of benzene in 0.8 *N* sulfuric acid. PhOH concentrations at different doses. Dose rate: 3.03 × 10^{19} ev/liter-min. Legend: ● saturated benzene solution; ◑ 50% saturated benzene solution; ○ 10% saturated benzene solution. Yields: G_0(PhOH) = 2.64 for all benzene concentrations employed.

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Effect of benzene concentration. Figure 6 shows that for a dose of ca. 1.8×10^{21} ev liter^{-1}, $G(H_2)$ is unaffected by change in initial benzene concentration but that rate of oxygen consumption decreases markedly at low benzene concentration. Figure 7 shows that the effect of benzene depletion during irradiation on rate of phenol production is easily detectable when the initial benzene concentration corresponds to 50 % saturation and is quite marked when the initial concentration is only 10 % that corresponding to saturation. The G_0(PhOH) values, however, are not significantly affected by initial benzene concentration in that range and are conveniently determinable.

4. DISCUSSION

4.1. Primary Reactions

The over-all chemical change produced in water by absorption of high-energy radiation is represented here by

$$H_2O \rightsquigarrow H, OH, H_2, H_2O \tag{0}$$

where the assumption is made that these are actually the earliest detectable products produced. Stoichiometry requires that

$$2G_w(H_2) + G_w(H) = 2G_w(H_2O_2) + G_w(OH)$$

4.2. Mechanism in Air-Free Solution

The value of $G_0(H_2)$ is equal to a generally accepted value (*15*, *22*) for $G_w(H_2)$. The inference is that the reaction

$$H + PhH \rightarrow H_2 + Ph \tag{1}$$

occurs to a limited, if any, extent under the conditions here employed. The fate of the H atoms can be explained by the reaction

$$H + PhH \rightarrow PhH_2 \rightarrow \text{Polymer} \tag{2}$$

which has been suggested to explain other results obtained in this laboratory (*17*, *18*) as well as some experiments of Forbes and Cline (*19*). In Baxendale and Magee's study on the oxidation of benzene by Fenton's reagent (*20*), the oxidation balance obtained indicates that all OH radicals either oxidize Fe^{++} ions or react with benzene to give phenyl radicals. It is thus reasonable to assume that all the OH radicals produced in radiolysis react with benzene according to

$$OH + PhH \rightarrow Ph + H_2O \tag{3}$$

One might imagine an ensuant reaction:

$$Ph + H_2O_2 \rightarrow PhOH + OH \tag{4}$$

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The chain set up by reactions 3 and 4 could account for the absence of hydrogen peroxide. Baxendale and Magee, however, have shown that reaction 4 does not occur in the oxidation of benzene by Fenton's reagent (*20*).

Figure 3 shows that concentration of H_2O_2 attained at fixed dose depends on pH, i.e., that decomposition of H_2O_2 product occurs rapidly in the less acidic solutions. On the other hand, Fig. 5 shows that in the presence of dissolved air or oxygen the rate of peroxide formation falls off less rapidly in acid than in neutral solution. A similar effect of pH has been observed by Ebert and Boag (*21*) in the radiation-induced formation of hydrogen peroxide in aerated water and by Sworski (*22*) in oxygenated bromide solution. According to Ebert and Boag, this pH effect results from the ionization of HO_2, with the peroxide decomposition at high pH being attributable to the influence of O_2^- ions. Sworski did not accept this interpretation because there is no pH effect in the photodecomposition of hydrogen peroxide although the presence of HO_2 is commonly postulated (*23*, *24*). Whether this view is correct is difficult to establish; the matter of irradiation intensity is involved (*25*), and it is questionable whether the conditions cited correspond to those employed in the radiation-chemistry studies. The explanation, however, certainly does not apply in this case because HO_2 radicals are most probably not present. The reaction

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (5)$$

cannot compete efficiently with reaction 3. The only other species that can decompose hydrogen peroxide is the H atom:

$$H + H_2O_2 \rightarrow H_2O + OH \qquad (6)$$

To explain the pH dependence of this reaction we merely speculate that in acid solution the $H_2{}^+{}_{aq}$ ion (*26*) is less reactive toward hydrogen peroxide,

$$H_2{}^+{}_{aq} + H_2O_2 \rightarrow H_2O + OH + H^+{}_{aq} \qquad (6')$$

than is the H atom and that $H_2{}^+{}_{aq}$ can react with benzene just as H atoms do:

$$H_2{}^+{}_{aq} + PhH \rightarrow PhH_2 + H^+{}_{aq} \qquad (2')$$

Experimental data are insufficient to support such a postulate. Reaction 6′, however, apparently yields three bodies in the primary process; thus, it may be expected to be less probable than reaction 6 on the basis of the microscopic reversibility principle. Furthermore, reaction 6′ requires a special orientation of the solvating water molecules, so that $-\Delta S_{6'}‡ > -\Delta S_6‡$ ($\Delta S‡$ being entropy of activation) and reaction 6 is correspondingly favored.

Since reactions 2 and 6 predominate over the reaction

$$H + Ph \rightarrow PhH \qquad (7)$$

most of the phenyl radicals react to give phenol:

$$Ph + OH \rightarrow PhOH \qquad (8)$$

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or diphenyl:

$$Ph + Ph \rightarrow Ph_2 \tag{9}$$

The fact that H_2O_2 concentration in degassed acid solution is a linear function of dose apparently indicates that reaction 5 does not compete favorably with reaction 8 if H_2O_2 is not added initially.

Thus the reaction scheme in air-free solution is 0, 2, 3, 6, 8, 9. Steady-state treatment gives the expression

$$\frac{d(PhOH)}{dt} = \frac{1}{2(\alpha + 1)}\left[r_{O,OH} + r_{O,H}\frac{\kappa_6(H_2O_2)}{\kappa_6(H_2O_2) + k_2(PhH)}\right] \tag*{1}$$

where κ_6 is the rate "constant" of the pH-dependent reaction 6, r_0 is the rate of that portion of reaction 0 resulting in the formation of the species indicated by the second subscript, and α is the ratio $\frac{d(Ph_2)}{dt}\bigg/\frac{d(PhOH)}{dt} = \frac{G(Ph_2)}{G(PhOH)}$. This ratio is constant at low doses because both $d(Ph_2)/dt$ and $d(PhOH)/dt$ are found to be constant under this condition.

In neutral solution, all the peroxide is decomposed. Hence

$$r_{O,H_2O_2} = -\kappa_6(H)(H_2O_2) \tag*{2}$$

After substitution for (H_2O_2), equation *1* becomes

$$\frac{d(PhOH)}{dt} = \frac{1}{2(\alpha + 1)}[r_{O,OH} + r_{O,H_2O_2}] \tag*{3}$$

Consequently,

$$2(\alpha + 1)G(PhOH) = 2[G(PhOH) + G(Ph_2)] = G_w(OH) + G_w(H_2O_2) \tag*{4}$$

Since the observed values are $G(PhOH) = 0.36$ and $G(Ph_2) = 1.22$, we have for neutral solution

$$G_w(OH) + G_w(H_2O_2) = 3.16$$

Data shown in Fig. 4 indicate that reaction 6 is not significant when the pH is less than about 2. Therefore, at high acidity equation *1* becomes

$$\frac{d(PhOH)}{dt} = \frac{1}{2(\alpha + 1)} r_{O,OH} \tag*{5}$$

and

$$2[G(PhOH) + G(Ph_2)] = G_w(OH) = 2.62 \text{ (observed)}$$

4.3. Effect of Oxygen

In the presence of oxygen, the reactions

$$H + O_2 \rightarrow HO_2 \tag{10}$$

$$Ph + O_2 \rightarrow PhO_2 \tag{11}$$

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must be considered. The HO_2 radicals most probably give hydrogen peroxide:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (12)$$

while PhO_2 radicals give phenol by hydrolysis:

$$PhO_2 + H_2O \rightarrow PhOH + HO_2 \qquad (13)$$

Reaction 6, with its pH dependence in air-free solution (see Section 4.2), is employed here to explain (1) that the rate of hydrogen peroxide formation decreases less and less rapidly as the acidity increases, and (2) that the rate of phenol formation is constant in 0.8 N sulfuric acid, although in neutral solution it increases with dose. This increase is attributable to the OH radicals produced in reaction 6 and consequently to the increased extent of reaction 3.

One might expect that $G(-O_2)$ resultant from reactions 10, 11, and 12 should be equal to $\frac{1}{2}[G_w(OH) + G_w(H)]$, i.e., about 2.9; however, the observed value for $G(-O_2)$ is 5.33. On the other hand, the absorption spectrum of the irradiated solution shows that, besides phenol, some other product is also formed from the benzene. A possible explanation examined in this work is that benzene might be excited by low-energy electrons and thereafter react with oxygen:

$$PhH \rightsquigarrow PhH^* \qquad (14)$$

$$PhH^* + O_2 \rightarrow \text{Product} \qquad (15)$$

We have found, however, in a separate study (*16*) of the photolysis of aerated aqueous benzene solution with 2537-A light that the quantum yield for oxygen disappearance is less than 0.01. Thus, the probability of oxygen being consumed in reaction 15 is too small to account for the high value of $G(-O_2)$.

Daniels *et al.* (*27*) obtained some evidence that mucondialdehyde is formed in irradiation of aqueous solution of benzene in the presence of oxygen, with $G = 0.2$, i.e., much too small to account for the excess oxygen consumption found in our work. Until more extensive data are available, we assume the over-all reaction

$$PhO_2 + PhH \rightarrow \text{Oxygenated product} + OH \qquad (16)$$

where OH in turn may react with benzene via reaction 3 to yield another free phenyl radical.

Not much information has been obtained about the products in this reaction. The mass spectrum of the gaseous mixture extracted over ethyl bromide mush showed no peaks except those due to benzene, water, and the components of dissolved air. The absorption spectrum of an irradiated sample has a broad maximum in the region 3300 to 3600 A.

Thus, the scheme adopted for aerated solution is 0, 2, 3, 6, 10, 11, 12, 13, 16.

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Assuming steady-state concentration of intermediates, we obtain the following rate expressions:

$$\frac{d(PhOH)}{dt} = r_{O,OH} + r_{O,H} \frac{\kappa_6(H_2O_2)}{\kappa_6(H_2O_2) + k_{10}(O_2) + k_2(PhH)} \qquad 6$$

$$\frac{d(H_2O_2)}{dt} = r_{O,H_2O_2} + \frac{1}{2} r_{O,OH} + \frac{1}{2} r_{O,H} \frac{k_{10}(O_2) - \kappa_6(H_2O_2)}{\kappa_6(H_2O_2) + k_{10}(O_2) + k_2(PhH)} \qquad 7$$

$$\frac{d(-O_2)}{dt} = \left(\frac{1}{2} + f\right) r_{O,OH} + \frac{1}{2} r_{O,H} \frac{(1 + 2f)\kappa_6(H_2O_2) + k_{10}(O_2)}{\kappa_6(H_2O_2) + k_{10}(O_2) + k_2(PhH)} \qquad 8$$

where f is the ratio $k_{16}(PhH)/k_{13}(H_2O)$.

Equation *6* shows that if κ_6 is zero (high acidity) the rate of phenol formation is constant and equal to $r_{O,OH}$; if κ_6 is not zero, this rate *increases* with dose. In either case the initial rate is equal to $r_{O,OH}$; in other words $G_0(PhOH) = G_w(OH) = 2.64$.

Equation *7* is consistent with experimental data shown in Fig. 6. At any pH, the initial rate of hydrogen peroxide formation is

$$\left[\frac{d(H_2O_2)}{dt}\right]_0 = r_{O,H_2O_2} + \frac{1}{2} r_{O,OH} + \frac{1}{2} r_{O,H} \frac{k_{10}(O_2)_0}{k_{10}(O_2)_0 + k_2(PhH)_0} \qquad 9$$

At infinite oxygen concentration equation *9* becomes

$$\left[\frac{d(H_2O_2)}{dt}\right]_0 = r_{O,H_2O_2} + \frac{1}{2} r_{O,OH} + \frac{1}{2} r_{O,H} \qquad 10$$

Although the initial rate of H_2O_2 formation has not been extensively studied as a function of oxygen concentration, a plot of $[d(H_2O_2)/dt]_0$ versus $1/(O_2)_0$ was attempted in order to estimate a value of $r_{O,H_2O_2} + \frac{1}{2} r_{O,OH} + \frac{1}{2} r_{O,H}$. To obtain the initial rates of peroxide formation, the four curves in Fig. 5 were fitted, using a four-constant function of the form $(H_2O_2) = At + Bt^2 + Ct^3 + Dt^4$, and the time derivatives of these functions at zero time were computed. Extrapolation gave a value of $1.72 \mu M$ liter^{-1} min^{-1} for $[d(H_2O_2)/dt]_0$ or 3.4 for $G_0(H_2O_2)$ at infinite oxygen concentration. This is only an *approximate* value for $G_w(H_2O_2) + \frac{1}{2} G_w(OH) + \frac{1}{2} G_w(H)$, because data for both acid and neutral solution were used in the same plot and only four points were available.

Values for $G_w(H)$ and k_2/k_{10} can be computed from equation *9* which can be converted to the form

$$G_0(H_2O_2) = G_w(H_2O_2) + \frac{1}{2} G_w(OH) + \frac{1}{2} G_w(H) \frac{1}{1 + \frac{k_2(PhH)_0}{k_{10}(O_2)_0}} \qquad 9'$$

The various data summarized in the figures lead, when appropriate substitutions are made, to values of $G_w(H)$ and k_2/k_{10} shown in Tables II and III, respectively.

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TABLE II

PRIMARY YIELDS IN RADIOLYSIS OF WATER

(Derived from this work and from the work of others)

Yield	*Ordinary water*			
	Unbuffered		0.8 *N* H_2SO_4	
	This work	*Others*	*This work*	*Others*
$G_w(H_2)$	0.41 ± 0.01	0.45 (*29*) 0.41 (*30*)	0.39 ± 0.01	0.39 (*22*)
$G_w(H_2O_2)$	0.61[a]	0.70 (*29*) 0.76 (*30*)	0.57 ± 0.04	0.78 (*22*)
$G_w(OH)$	2.64 ± 0.04	2.16 (*29*) 2.1 (*30*)	2.64 ± 0.04	2.92 (*22*)
$G_w(H)$	3.04 ± 0.03		3.16 ± 0.04	3.70 (*22*)

Yield	*Heavy water*[b]	
	Unbuffered	0.8 *N* H_2SO_4
$G_w(D_2)$	0.32 ± 0.01	0.30 ± 0.01
$G_w(D_2O_2)$	0.51[a]	
$G_w(OD)$	2.38 ± 0.02	
$G_w(D)$	2.76 ± 0.04	

[a] Derived from stoichiometry of water decomposition

[b] Hart (*31*) found a value of 0.30 for $G(D_2)$ and 3.4 for $G(OD)$ in the decomposition of formic acid-oxygen solutions.

TABLE III

RATIOS OF RATE CONSTANTS

Ratio	*Unbuffered*	0.8 *N* H_2SO_4
k_2/k_{10}	6.3×10^{-3}	5.9×10^{-3}
κ_6/k_{10}	1.5–2.5	0
k_{16}/k_{13}	—	3.4×10^3
k_5/k_3	—	18–25

A number of the primary yields given in Table II are somewhat lower than corresponding best (or most recently accepted) values obtained with inorganic solutes. The G_w's can be combined, in terms of the known chemistry of the intermediates, to calculate an anticipated value for $G(Fe^{++} \rightarrow Fe^{+++})$ in the Fricke dosimeter; this calculated value from our data is 13.4, which may be compared with the experimental value 15.6. Whether the discrepancies represent a fundamental unsuitability of the organic system for the purpose of determination of G_w values, or a result of our lack of completely detailed knowledge of the products, or the result

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of some fundamental effect by benzene on mechanism of water radiolysis is not evident. It is interesting to note that Baxendale and Smithies (*28*), working with solutions of benzene and ferric ion containing 0.1 N H_2SO_4, obtained a value of 5.5 for $G_w(H) + G_w(OH)$, not much different from our values of 5.7 for unbuffered solution and 5.8 for 0.8 N sulfuric acid.

Equation *7* also can be used to calculate a value for κ_6/k_{10}. In terms of G values, we have

$$G(H_2O_2) = G_w(H_2O_2) + \frac{1}{2}G_w(OH) + \frac{1}{2}G_w(H)\ \frac{1 - \dfrac{\kappa_6(H_2O_2)}{k_{10}(O_2)}}{1 + \dfrac{\kappa_6(H_2O_2)}{k_{10}(O_2)} + \dfrac{k_2(PhH)}{k_{10}(O_2)}} \tag{7'}$$

where $G(H_2O_2)$ is the instantaneous yield of hydrogen peroxide. For a given dose $G(H_2O_2)$ can be determined by differentiating the fitted function with respect to t and substituting a numerical value for t. A small dose (i.e., a small value of t) should be chosen, since at high doses the reaction scheme adopted might not be adequate. Values of (H_2O_2) and (O_2) can be derived from experimental curves. The exact value for (PhH) is not known, since, besides phenol, other products are formed from benzene in reactions 2 and 16 and $G(-PhH)$ for these processes is unknown. Thus, employment of $(PhH)_0$, which is 2.3×10^4 $\mu M/liter^{-1}$, results in an error. This error will not be very large, however, if the dose considered is small. Values for κ_6/k_{10} are independent of oxygen concentration; they are shown in Table III.

The rate expression for oxygen consumption as shown in equation *8* seems to contradict experimental results, since it depends on many variables, whereas in Fig. 4 the amount of oxygen consumed appears to be a linear function of dose. Actually expression *8* contains a decreasing term involving $k_{10}(O_2)$ combined with an increasing term involving $(1 + 2f)\kappa_6(H_2O_2)$ in the numerator, so that their variations would tend partially to cancel. The factor f itself, which is $k_{16}(PhH)/k_{13}(H_2O)$, slowly decreases with increase in dose. A value of 1.14 can be computed for the factor f by substituting experimental values for $G_0(-O_2)$, $G_w(OH)$, and $G_w(H)$ in equation 8.

As the initial concentration of benzene is reduced, the yields of various products more or less decrease. These results cannot be explained by the rate expressions *6*, *7*, and *8* because, in the reaction scheme, we implicitly assumed that the benzene was so concentrated that it captured every OH radical in reaction 3. This assumption may be justified in saturated solution, but in more dilute solutions some OH radicals can react with substances other than benzene, for example, with hydrogen peroxide:

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \tag{5}$$

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Including this reaction in the scheme we obtain

$$\frac{d(\mathrm{PhOH})}{dt} = \frac{k_3(\mathrm{PhH})}{k_3(\mathrm{PhH}) + (f+1)k_5(\mathrm{H_2O_2})}[r_{\mathrm{O,OH}} + \kappa_6(\mathrm{H_2O_2})F] \qquad 11$$

$$\frac{d(\mathrm{H_2O_2})}{dt} = r_{\mathrm{O,H_2O_2}} + \left[\frac{1}{2}k_{10}(\mathrm{O_2}) - \kappa_6(\mathrm{H_2O_2})\right]F + \frac{1}{2}\frac{k_3(\mathrm{PhH}) - (f+1)k_5(\mathrm{H_2O_2})}{k_3(\mathrm{PhH}) + (f+1)k_5(\mathrm{H_2O_2})}[r_{\mathrm{O,OH}} + \kappa_6(\mathrm{H_2O_2})F] \qquad 12$$

$$\frac{d(-\mathrm{O_2})}{dt} = \frac{1}{2}k_{10}(\mathrm{O_2})F + \frac{1}{2}\frac{(2f+1)k_3(\mathrm{PhH}) - (f+1)k_5(\mathrm{H_2O_2})}{k_3(\mathrm{PhH}) + (f+1)k_5(\mathrm{H_2O_2})}[r_{\mathrm{O,OH}} + \kappa_6(\mathrm{H_2O_2})F] \qquad 13$$

where

$$F = \frac{r_{\mathrm{O,H}}}{\kappa_6(\mathrm{H_2O_2}) + k_{10}(\mathrm{O_2}) + k_2(\mathrm{PhH})}$$

When we apply equation *11* to the case of 0.8 N H_2SO_4 solution, in which κ_6 is zero, the last term in the bracket vanishes. As the dose increases, (H_2O_2) also increases and the rate of phenol formation drops, as indicated by the curves in Fig. 7. With $f = 1.14$ in saturated solution, the curves of Fig. 7 can be used to calculate the approximate values of k_5/k_3 shown in Table III. Likewise, from the value of f, the value of k_{16}/k_{13} shown in Table III is calculated on the basis that the saturated solution is 2.3×10^{-2} M in benzene.

4.4. Yields in Heavy Water

It is reasonable to assume that the D, OD, and D_2O_2 species react with the solute in the same manner as the corresponding light species. Then

$$G_0(\mathrm{PhOD}) = G_w(\mathrm{OD}) = 2.38$$

$$G_0(\mathrm{D_2}) = G_w(\mathrm{D_2}) = 0.32 \text{ in neutral solution}$$

$$= 0.30 \text{ in } 0.8\ N \text{ sulfuric acid}$$

The value of G_w(D) can be obtained from an equation similar to *9* by noting that the last factor is equal to 0.65 in air-saturated solution. The experimental value for $G_0(D_2O_2)$ is 2.60, and $G_w(D_2O_2)$ can be expressed as in Section 4.1. Then an equation like *9* leads to a value of 2.76 for G_w(D).

The observed initial yield for oxygen consumption is 4.40. This value should be given by an equation like *8* if we substitute proper values for $r_{\mathrm{O,OD}}$ and $r_{\mathrm{O,D}}$. Converting rates to G values, the equation becomes

$$G_0(-\mathrm{O_2}) = \left(\frac{1}{2} + f\right)G_w(\mathrm{OD}) + \frac{1}{2}G_w(\mathrm{D})\frac{k_{10}(\mathrm{O_2})_0}{k_{10}(\mathrm{O_2})_0 + k_2(\mathrm{PhH})_0}$$

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Substituting 2.38 for G_w(OD), 2.76 for G_w(D), 1.14 for f,[4] and 0.65 for the last fraction,[4] and assuming that $(O_2)_0$ is still 255 μM/liter^{-1} as in the case of ordinary water, we obtain $G_0(-O_2) = 4.8$, in reasonably good agreement with the experimental value in view of the necessary assumptions involved in the calculation.

5. SUMMARY

Studies of Co^{60} γ-ray-induced radiolysis of benzene in oxygenated, aerated, and deaerated aqueous solution at various pH's yield information regarding G_w values in the radiolysis of water (see Table II) as well as G values for oxygen consumption and for formation of products from benzene. Rate of oxygen consumption indicates a short-chain reaction. Rate laws consistent with the experimental data are derived on the basis of a proposed mechanism.

Use of benzene-d_6 makes it clear that the hydrogen abstraction reaction by H atom occurs with very low probability in aqueous solution compared to the addition process. The abstraction reaction does occur readily, however, with cyclohexane.

Results are consistent with the notion that the reaction $H + H_2O_2 \rightarrow H_2O + OH$ is pH-dependent.

Studies of radiolysis of benzene in D_2O yield G_w values for the latter (see Table II).

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[4] This substitution involves the assumption of equality of ratios of corresponding rate constants. The assumption is not strongly based.

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