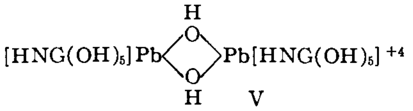

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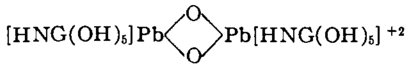

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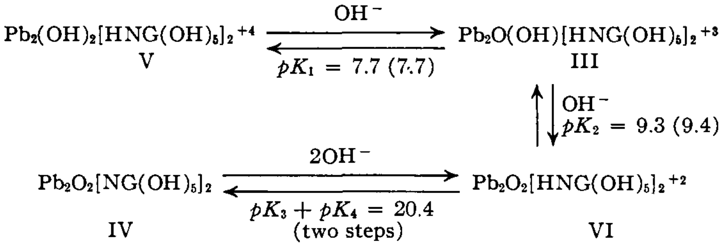

tem.[1b] Above 50 mole % lead the optical rotation again becomes more positive, and a precipitate forms for mixtures in excess of 67 mole % lead. These data can only be explained by the presence of a relatively positive-rotating, soluble 2:1 complex (66.7 mole % Pb). It is interesting to note that above 70 mole % lead the optical activity becomes strongly negative even though an appreciable amount of the mixture has precipitated. A sharp minimum occurs at 75 mole % lead. These results can only be explained by concluding that the precipitate formed is a partially soluble, strongly levorotatory 3:1 solid. Apparently this compound has a large enough solubility to strongly influence the optical activity of the solution.

Preparation and Analysis of the 3:1 Lead N-Methylglucamine Solid.—A mixture of 0.9761 g. (0.005 mole) of N-methylglucamine and 37.50 ml. of 0.4000 *M* (0.015 mole) lead nitrate solution was adjusted to *p*H 12.0 with sodium hydroxide. The mixture was made to volume in a 50-ml. volumetric flask, immersed in a steam-bath for 4 hr. and allowed to stand overnight at room temperature. The white precipitate was filtered under an atmosphere of nitrogen. washed rapidly four times with boiled distilled water and twice with ethanol, and dried *in vacuo* (0.01 μ) for 4.5 hr.

Anal. Calcd. for $Pb_3C_7H_{13}NO_6$: C, 10.15: H, 1.58; N. 1.69: Pb, 75.1. Found: C, 10.21; H, 1.72; N, 2.42; Pb, 73.4 (polarographically).

The high results for nitrogen might be explained by inadequate removal of nitrate nitrogen by this washing technique. No suitable solvent could be found for recrystallization. The analysis is sufficiently consistent with the calculated values to confirm that a 3:1 solid was formed.

Acknowledgment.—The author wishes to acknowledge the assistance of Mr. Kiyoshi Burt Sagawa who carried out several of the preliminary measurements on this system.

URBANA. ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT. BROOKHAVEN NATIONAL LABORATORY]

Radiolysis of Neutral Water by Cyclotron Produced Deuterons and Helium Ions[1]

BY HAROLD A. SCHWARZ, JAMES M. CAFFREY, JR., AND GEORGE SCHOLES

RECEIVED SEPTEMBER 12. 1958

The yields of H_2. H_2O_2. H and OH in neutral aqueous solutions have been determined for 18 Mev. deuterons. 32 Mev. helium ions and 11 Mev. helium ions. H_2 yields were determined in KBr and KNO_2 solutions. H_2O_2 yields in air-saturated KBr solutions and H atom yields in solutions of H_2 and O_2 and in solutions of C_2H_5OH and O_2. The dependence of these yields on solute concentration was studied. The results are interpreted in terms of the radical-diffusion mechanism and are found to be in good agreement with the predictions of Ganguly and Magee. based on a simple model of this mechanism except in the densest tracks, where the yield of water decomposition appears to increase. The mechanism whereby radiation decomposes water into free radicals is discussed in the light of the existing data.

Water is decomposed into four products, H_2, H_2O_2, H and OH, by ionizing radiation.[2] The ratio of the molecular products, H_2 and H_2O_2, to the radical products is greater for radiations with a high rate of energy loss, $-\mathrm{d}E/\mathrm{d}x$, than for radiations of low $-\mathrm{d}E/\mathrm{d}x$.

The H_2 and H_2O_2 are generally postulated to be formed by combination reactions of the two radicals H and OH in the regions of high radical concentration along the track of the radiation.

$$H + H \longrightarrow H_2 \quad (1)$$

$$OH + OH \longrightarrow H_2O_2 \quad (2)$$

$$H + OH \longrightarrow H_2O \quad (3)$$

The last reaction has not been observed, but is inferred from the other two. Radicals that do not combine react with solutes present, giving rise to the "radical yields." In the case of γ-rays and fast electrons, these radicals are produced in isolated spurs of a radius of about 10 Å. containing 5 to 10 radicals[3] (*i.e.*, about 100 e.v. of absorbed energy). For particles of higher $-\mathrm{d}E/\mathrm{d}x$, the spurs may overlap. For a 1 Mev. electron, $-\mathrm{d}E/\mathrm{d}x$ is 0.02 e.v./Å.[4]; for an 18 Mev. deuteron, 0.5 e.v./Å.; for a 32 Mev. helium ion, 2.3 e.v./Å. and for a 3.5 Mev. α-particle, about 10 e.v./Å. Thus at high $-\mathrm{d}E/\mathrm{d}x$, the spur structure is lost and the track consists of a concentrated column of radicals.

This mechanism accounts qualitatively for the variation of the product yields with $-\mathrm{d}E/\mathrm{d}x$ and for the decrease in molecular yields upon the addition of solutes reactive to H and OH.[5,6]

The yields of the molecular and radical products in 0.4 *M* H_2SO_4 for various cyclotron radiations have been determined by Schuler and Allen,[4]

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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

(3) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

(4) R. H. Schuler and A. O. Allen, THIS JOURNAL. **79**, 1565 (1957).

(5) T. J. Sworski, *ibid.*, **76**, 4687 (1954).

(6) H. A. Schwarz. *ibid.*, **77**. 4960 (1955).

Hart, *et al.*,[7] and Barr and Schuler.[8] We have determined these yields in neutral solutions for 18 Mev. deuterons, 32 and 11 Mev. helium ions in order to compare them with the yields in acid solution and have also measured the solute concentration dependence of the molecular yields at these energies. We have interpreted our results in terms of a model proposed by Ganguly and Magee.[9]

The H_2 yield was determined in deaerated KBr[10] and KNO_2 solutions[11] and the H_2O_2 yield in air-saturated KBr solution.[5,12] The radical yields were determined in solutions containing H_2 and O_2[13] and in solutions containing C_2H_5OH and O_2.[14] These systems were chosen because they all have been studied thoroughly with γ- and X-rays.

Hart has proposed that another radical product, HO_2, is formed in the radiolysis of water.[15] Donaldson and Miller have found additional evidence for this product.[16] It probably is due to secondary reaction in the track and hence increases sharply

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O$$

with $-dE/dx$. This product amounts to only 16% of the hydrogen yield for Po^{210} α-rays.[16] We have neglected it as it probably occurs to only a small extent in the $-dE/dx$ region we have studied. Our values of G_{OH}, G_{H_2} and G_{-H_2O} are not affected by including this reaction. The values of G_H and $G_{H_2O_2}$ are low and high respectively by the extent of this reaction.

Experimental

The usual purity precautions were observed.[10] The radiation cells were of the type described by Saldick and Allen, with glass enclosed, magnet driven stirrers.[17] The cell volumes were about 25 to 30 cc. The solutions containing H_2 and O_2 were prepared by passing each gas separately through a flow meter, calibrated under operating conditions, then through a fritted glass barrier with water above it, into a small mixing chamber. The mixed gases were bubbled through the water in the radiation cell at a rate of about 30 cc. per minute for 5 to 10 minutes prior to the irradiation. The entrance and exit tubes were fitted with water-lubricated stopcocks, which were closed after saturation, so that the gases did not pass through the solution during irradiation. O_2 saturation was accomplished in a similar manner. Air-free samples for H_2 analysis were prepared as described by Johnson and Allen.[10]

The methods developed by Schuler and Allen for using the Brookhaven 60-inch cyclotron and measuring the beam energy and current were used essentially without change.[18] The rate of oxidation of air-saturated 10^{-3} *M* $FeSO_4$, 10^{-3} *M* in NaCl and 0.4 *M* in H_2SO_4, studied extensively by Schuler and Allen,[4] was determined each day, and our results were normalized to their yields. Actually, our measurements were absolute, but in order to avoid any variation in resistor calibration (used in calibrating the current integrator), we used their determination as standards. Except for one period when for several months our results inexplicably diverged from theirs by 10%. we were always within 3% of their values. The results obtained during that period were used in a relative manner only, as in determining the relative yields of air saturated and O_2-saturated solutions.

The beam energy was determined by reducing the energy with aluminum absorbers and the Pyrex cell window to approximately 4 Mev. and measuring the rate of $FeSO_4$ oxidation in the cell.[4] The energy was found from the curves of Schuler and Allen relating yield per coulomb to energy. The initial energy was then determined from range energy tables.[19] Reduced energy helium ion beams were obtained by removing a known amount of this absorber.

Cell window thicknesses were determined both by the microscope technique described by Schuler and Allen and by determining the residual range in each cell, as above. As was found by Schuler and Allen, these two methods gave excellent agreement but indicate that the stopping power of Pyrex is 10% greater than the stopping power of aluminum. The cell windows used in this work ranged generally from 30 to 60 mg./cm.^{2}. These thicknesses could be measured to ±1 mg./cm.^{2}.

The stirrers in the cells were rotated at a rate of about 800 r.p.m.[4] The beam current entering the cell was kept between 1×10^{-9} and 5×10^{-9} ampere, except when checking intensity dependence.

The Fe(III) and H_2O_2 analyses were performed spectrophotometrically using 2 cm. cells in a Beckman DU ultraviolet spectrophotometer. Fe(III) was measured at 305 mμ. The cells were not thermostated, but the lamp housing on the spectrophotometer was water-cooled and the temperature of the sample was measured after analysis. It was always within 1° of room temperature. The optical densities were corrected to 26.5° assuming a temperature coefficient of +0.6% per degree.[20] The extinction coefficient at 26.5° was taken as 2217.[4]

Hydrogen peroxide was determined by the method of Ghormley.[13] Five cc. of sample was made to 10 cc. with the iodide reagent and the optical density measured at 350 mμ in a 2 cm. cell. The H_2O_2 concentration was found to be 38.8 μ*M* per optical density unit. One batch of iodide reagent was prepared at the beginning of the day. The reagent blank increased slowly. but linearly and reproducibly during the day. Several blanks were run. and the time of analysis was noted in order to find the proper blank. It should be noted that this reagent is light sensitive. and we found best results storing it in dark bottles.

The method of H_2 analysis (combustion in O_2 on a Pt filament) has been described previously.[19]

Results and Discussion

The yields of the four products of the radiation, expressed as molecules per 100 e.v., are denoted by G_{H_2}, $G_{H_2O_2}$, G_H and G_{OH}. The observed yield of water disappearance is denoted by G_{-H_2O} and is equal to $2G_{H_2} + G_H$ or $2G_{H_2O_2} + G_{OH}$. The actual observed yield of H_2O_2, which is a function of the four products, is denoted by $G(H_2O_2)$.

This work was performed at three energies, 18 Mev. deuterons, 32 Mev. helium ions and 11 Mev. helium ions. Since several different radiation cells were used at various times, it was not possible to keep the beam energy constant. In practice, the beam energies were usually within 1 Mev. of these values. The helium ion beam energies in the studies of the H_2 yield varied between 30 and 33 Mev. In order to compare the yields with the results in the other systems, G_{H_2} was corrected by −0.007 per Mev., which appears reasonable from the work of Schuler and Allen.[4] This correction amounted to 3% at most. The reduced energy helium ion H_2O_2 yield in air-saturated KBr solutions was determined at 12.7 Mev. instead of 11 Mev. Again, in order to compare results, we as-

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(7) E. J. Hart, W. J. Ramler and S. R. Rocklin, *Radiation Research*, **4**, 378 (1956).

(8) N. F. Barr and R. H. Schuler, to be submitted for publication.

(9) A. K. Ganguly and J. L. Magee, *J. Chem. Phys.*, **25**. 129 (1956).

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

(11) H. A. Schwarz and A. O. Allen, *ibid.*, **77**. 1324 (1955).

(12) A. O. Allen and R. A. Holroyd, *ibid.*, **77**. 5852 (1955).

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

(14) G. G. Jayson, G. Scholes and J. Weiss, *J. Chem. Soc.*, 1358 (1957).

(15) E. J. Hart, *Radiation Research*, **2**. 33 (1955).

(16) D. M. Donaldson and N. Miller, *Trans. Faraday Soc.*, **52**. 652 (1956).

(17) J. Saldick and A. O. Allen, *J. Chem. Phys.*, **22**. 438 (1954).

(18) R. H. Schuler and A. O. Allen, *Rev. Sci. Instr.*, **26**. 1128 (1955).

(19) W. A. Aron. B. G. Hoffman and F. C. Williams, Document AECU-663, 1951.

(20) R. Bastian. R. Wéberling and F. Palilla, *Anal. Chem.*, **25**, 284 (1953).

sumed the same yield to apply at 11 Mev. In Table I it is seen that this yield is almost independent of energy, so the slight extrapolation should not introduce appreciable error.

Hydrogen Yields in KBr and KNO_2 Solutions.—The hydrogen yield observed in solutions of KBr and KNO_2 is the molecular hydrogen yield, G_{H_2}.[10,11] NO_2^- reacts efficiently with H atoms, and consequently G_{H_2} is a function of the NO_2^- concentration.[6]

The H_2 yields observed in KNO_2 solutions for 18 Mev. deuterons and 32 Mev. helium ions are given in Fig. 1. The data of Schwarz for Co^{60} γ-rays are included.[6] G_{H_2} increases with $-dE/dx$ and decreases with NO_2^- concentration, as is expected on the basis of the radical diffusion mechanism. In deaerated 2×10^{-3} *M* KBr solution, G_{H_2} was found to be 0.71 ± 0.01 for 18 Mev. deuterons, $0.97 + 0.02$ for 32 Mev. helium ions and 1.2 for 11 Mev. helium ions. (Two KNO_2 solutions, 2×10^{-4} *M* also were irradiated with 11 Mev. helium ions. G_{H_2} was 1.2, the same as with the KBr solutions. Yields in this region are less precise, approximately ± 5%, and solute dependence studies were not performed.)

Schuler and Allen found that G_{H_2} was 1.01 in air-saturated $FeSO_4$ solutions, 0.4 *M* in H_2SO_4 for 33 Mev. helium ions.[4] Barr and Schuler, studying the air-saturated $FeSO_4$ to deaerated $FeSO_4$ ratio found G_{H_2} to be 1.05 .[8] These yields are somewhat higher than we have observed for neutral solutions, so we irradiated 2×10^{-3} *M* KBr in 0.4 *N* H_2SO_4 and found $G_{H_2} = 1.05 \pm 0.02$, in agreement with the other authors. Apparently G_{H_2} is 8% higher in acid solution for 33 Mev. helium ions.

Hydrogen Peroxide Yields in Air-saturated KBr Solutions.—Allen has proposed that $G_{H_2O_2}$ can be determined in air saturated water, suggesting the mechanism[2]

$$H_2O \longrightarrow H_2.\ H_2O_2.\ H.\ OH$$

$$H + O_2 \longrightarrow HO_2 \quad (4)$$

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \quad (5)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \quad (6)$$

The O_2 protects the H_2O_2 from attack by H atoms Each H atom produces $^1/_2$ H_2O_2 while each OH radical destroys $^1/_2$ H_2O_2. Hence, the yield is given by $G(H_2O_2) = G_{H_2O_2} + {}^1/_2\ (G_H - G_{OH})$ or (using the material balance relation, $2G_{H_2} + G_H = 2G_{H_2O_2} + G_{OH}$) $G(H_2O_2) = 2G_{H_2O_2} - G_{H_2}$. Sworski has found that the system behaves similarly in the presence of KBr,[5] except that reaction 5 is replaced by

$$OH + Br^- \longrightarrow OH^- + Br \quad (7)$$

followed by

$$Br + H_2O_2 \longrightarrow HBr + HO_2 \quad (8)$$

He found that $G_{H_2O_2}$ decreased with increasing Br^- concentration and also that the mechanism in the absence of Br^- was inadequate, requiring the addition of the step

$$OH + H_2 \longrightarrow H_2O + H \quad (9)$$

which leads to additional H_2O_2 production *via* (4) and (6). Reaction 9 is eliminated in the presence of Br^- due to reaction 7. As H_2O_2 builds up in the solution, another reaction

$$H + H_2O_2 \longrightarrow OH + H_2O \quad (10)$$

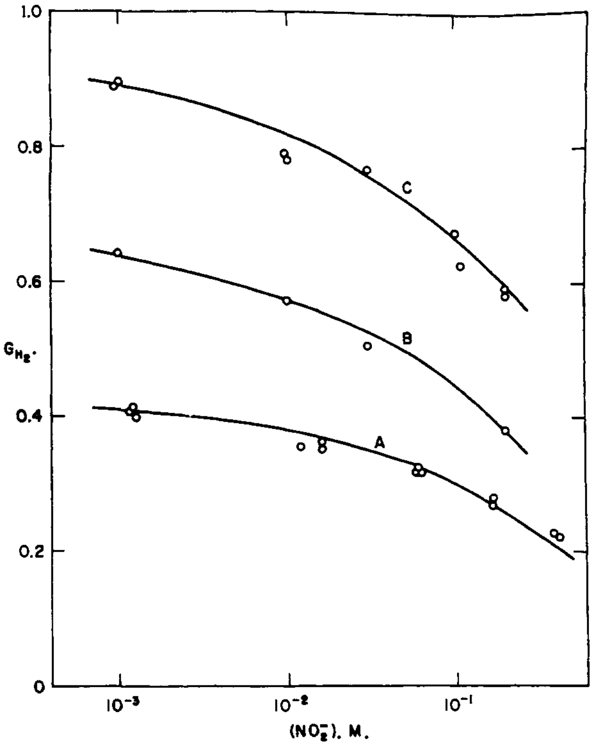

Fig. 1.—The variation of G_{H_2} with NO_2^- concentration: (A) Co^{60} γ-rays (Schwarz[6]); (B) 18 Mev. deuterons: (C) 32 Mev. helium ions. The curves are calculated by Ganguly and Magee.[9]

must be added to this scheme, since H_2O_2 competes effectively with O_2 for H atoms. The ratio of rate constants k_4/k_{10} is 1.85.[21] In air-saturated KBr solution, then, the mechanism consists of reactions 4, 6–8 and 10. The rate expression for this mechanism is

$$G(H_2O_2) = \frac{d(H_2O_2)}{d(\text{dose})} = 2G_{H_2O_2} - G_{H_2} - \frac{2G_H}{1 + \dfrac{k_4(O_2)}{k_{10}(H_2O_2)}}$$

For small values of (H_2O_2) (expanding the logarithmic term in the integral) the solution of the rate equation is

$$(H_2O_2) + \frac{G_H k_{10}(H_2O_2)^2}{G_0(H_2O_2)k_4(O_2)} = G_0(H_2O_2)\ (\text{dose}) \quad (11)$$

where $G_0(H_2O_2)$ is the initial yield of H_2O_2 and is equal to $2G_{H_2O_2} - G_{H_2}$. G_H will be discussed in the next section, and $G_0(H_2O_2)$ can be estimated with sufficient precision from the data for its use in the correction term. The correction term is never larger than 5% of the H_2O_2 concentration.

Two of the three curves shown in Fig. 2 represent data collected in this system, one from air-saturated water and the other from air-saturated 2×10^{-3} *M* KBr solution, both for 18 Mev. deuterons. The curves at the other energies and Br^- concentrations were similar to these. The solid lines represent $G_0(H_2O_2)$ calculated from equation 11 and the dashed lines are the corresponding curves for H_2O_2 production. It can be seen that the deviations of $G(H_2O_2)$ from $G_0(H_2O_2)$ are small.

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[21] A. O. Allen and H. A. Schwarz, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, (1958).

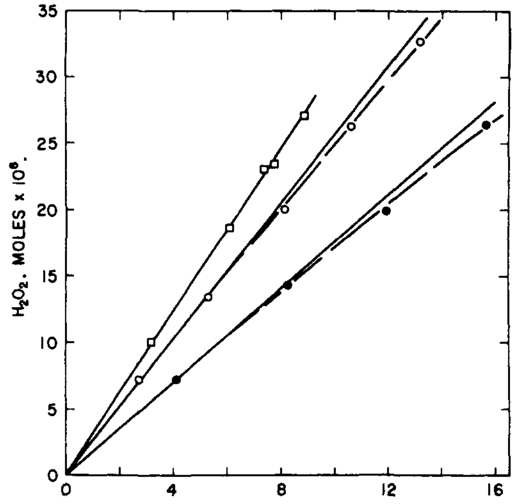

Fig. 2.—Typical hydrogen peroxide production curves. ●, air-saturated 2×10^{-3} *M* KBr irradiated with 18 Mev. deuterons; ○, air-saturated water irradiated with 18 Mev. deuterons; □, O_2-saturated 10^{-2} *M* C_2H_5OH solutions irradiated with 32 Mev. helium ions.

The initial yields in this system are given in Table I. $G_0(H_2O_2)$ is seen to be a function of Br^- concentration. In the γ-irradiation of air-saturated KBr solutions, $G_0(H_2O_2)$ varies linearly with the cube root of Br^- concentration.[5,12] This relation does not hold accurately for the cyclotron results. $G_0(H_2O_2)$ for cyclotron beams does extrapolate smoothly to the yield observed in the absence of KBr, in contrast to the results with γ-rays of Sworski and of Allen and Holroyd, who noted a sharp increase in $G_0(H_2O_2)$ below 10^{-6} *M* KBr due to the onset of reaction 9. Apparently reaction 9 does not occur with cyclotron radiation. The only obvious explanation is a dose rate effect. The energy input per unit volume at the currents we employ is orders of magnitude greater than obtained in cobalt sources. The most logical source of this effect is the reaction

TABLE I

THE INITIAL YIELDS OF H_2O_2 IN AIR-SATURATED KBr SOLUTIONS

(Br^-), *M*	$G_0(H_2O_2)$ 18 Mev. D^+	 32 Mev. H^{++}	 11 Mev. He^{++}
0	1.31	1.21	1.24
2×10^{-5}	1.21	1.10	1.18
2×10^{-4}	1.10	0.98	1.06
2×10^{-3}	0.90	0.81	0.85
2×10^{-2}	0.48	0.47	0.43

$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad (12)$$

which would occur instead of (5) and (9) at high dose rate. The over-all rate expression would still be the same except that the complication of reaction 9 is avoided. Additional evidence for this dose rate effect is reported in the next section.

In order to evaluate $G_{H_2O_2}$ we need to know G_{H_2}. We have not measured G_{H_2} in O_2 solution, but in previous work, it was noted that a given oxygen concentration has the same effect on G_{H_2} for Co^{60} γ-rays as twice that concentration of NO_2^-.[6,22] Hence G_{H_2} in air-saturated water would be the same as in 5×10^{-4} *M* KNO_2, and in O_2-saturated water would be the same as in 2.5×10^{-3} *M* KNO_2. These yields can be found in Fig. 1, *i.e.*, G_{H_2}(air) = 0.66 for 18 Mev. deuterium ions and 0.90 for 32 Mev. helium ions. From the data of the previous section on G_{H_2}, it is seen that G_{H_2}(air) is probably about 1.1 for 11 Mev. helium ions. $G_{H_2O_2}$ is given in Fig. 3. The data of Allen and Holroyd for Co^{60} γ-rays are included.[12] $G_{H_2O_2}$ increases regularly with $-dE/dx$, as expected, and Br^- depresses $G_{H_2O_2}$ in all cases, also as expected.

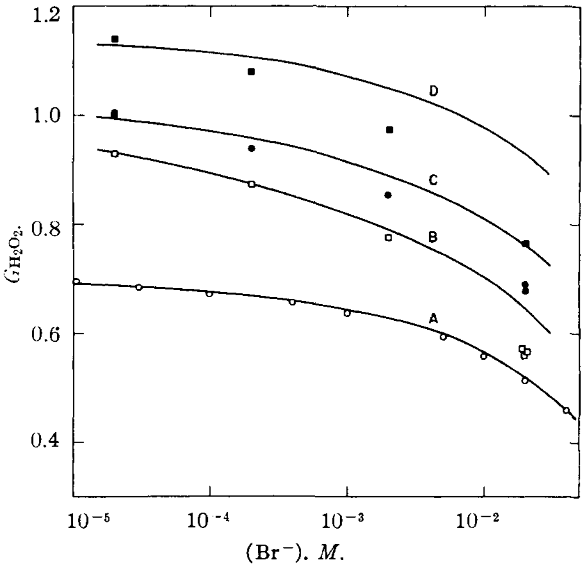

Fig. 3.—The variation of $G_{H_2O_2}$ with Br^- concentration: (A) ○. Co^{60} γ-rays (Allen and Holroyd)[12]; (B) □. 18 Mev. deuterons; (C) ●. 32 Mev. helium ions; (D) ■. 11 Mev. helium ions. The curves are calculated by Ganguly and Magee.[9]

$G_0(H_2O_2)$ is given in Table II as a function of acid and oxygen concentration. In 10^{-2} *M* H_2SO_4, both $G_0(H_2O_2)$ and $G_{H_2O_2}$ are greater than in neutral solution. Barr and Schuler find $G_{H_2O_2}$ = 1.25 for 32 Mev. helium ions in 0.4 *M* H_2SO_4 indicating a further increase in $G_{H_2O_2}$.[8] Allen and Holroyd found the same effect with γ-rays. Increasing the O_2 concentration also increases $G_0(H_2O_2)$. A small part of the increase in O_2 solution is due to a decrease of about 3% in G_{H_2}, but in neutral solution, $G_{H_2O_2}$ is definitely higher at the higher O_2 concentration. O_2 concentration in this region does not affect $G_{H_2O_2}$ in 10^{-2} *M* H_2SO_4, however. An explanation of these effects is apparent in the studies of Sworski[5] and of Hochanadel[23] on this system at high H_2O_2 concentration. The effect of reaction 10 is less noticeable in acid solution. Acid protects H_2O_2 from attack by H atoms, probably *via* formation of H_2^+. Reaction 10 is very efficient,[22] occurring on most encounters,[6] so that it is probably important as a track reaction, *i.e.*, a H atom and an H_2O_2 from the same spur or track react before diffusing intertrack distances. This reaction would lower $G_{H_2O_2}$ and would be repressed by acid and O_2 which remove the H atoms. Since H_2O_2 is not

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[22] J. A. Ghormley and C. J. Hochanadel, *Radiation Research*, **3**, 227 (1955).

[23] C. J. Hochanadel, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **7**, 521 (1956).

present when the spur is formed, the majority of the reaction would occur while the reactants are in a looser distribution than the initial one. Hence solutes would have a greater effect per unit concentration on this reaction than on reactions 1–3.

TABLE II

THE DEPENDENCE OF THE INITIAL YIELDS OF H_2O_2 AND THE MOLECULAR H_2O_2 YIELDS ON OXYGEN AND ACID CONCENTRATION

	$G_0(H_2O_2)$		$G_{H_2O_2}$	
	2×10^{-5} *M* KBr	2×10^{-4} *M* KBr	2×10^{-5} *M* KBr	2×10^{-4} *M* KBr
32 Mev. He^{++}. air-sat.	1.10	0.98	1.00	0.94
O_2 sat.	1.23	1.17	1.05	1.02
0.01 *M* H_2SO_4, air-sat.	1.27		1.09	
32 Mev. He^{++}. 0.01 *M* H_2SO_4, O_2 sat.	1.31		1.09	
18 Mev. D^+, air-sat.		1.10		0.88
O_2 sat.		1.32		0.96

When O_2 concentration is increased, there is another track reaction that would tend to increase $G_{H_2O_2}$, *i.e.*, $H + HO_2 \rightarrow H_2O_2$. The increase in $G_{H_2O_2}$ from this reaction should parallel the decrease in G_{H_2}, since the HO_2 formed would maintain a similar distribution to its H atom precursor and would have a similar probability of reacting with another H atom.

Ghormley and Hochanadel find that $G_0(H_2O_2)$ is 1.10 for solutions bubbled with O_2 while being irradiated with Co^{60} γ-rays.[24] Since the H_2 is being removed by bubbling, this should represent the value of $2G_{H_2O_2} - G_H$ in the absence of KBr. It is 10% higher than is found by extrapolating to infinite dilution of KBr the results obtained in air-saturated solution by Allen and Holroyd.[12] In view of the otherwise excellent agreement between the two laboratories, this difference is probably real and is of the same origin as our oxygen concentration effects.

In an attempt to study $G_{H_2O_2}$ at higher (Br^-) in 10^{-2} *M* acid solution with 32 Mev. helium ions, we found that the apparent $G(H_2O_2)$ increased rapidly when (Br^-) was greater than 10^{-3} *M* and leveled off at about 2.5 to 3 around 2×10^{-2} *M* (Br^-), but was irreproducible. This product was not all H_2O_2 but contained some bromine, as shown by following its rate of reaction with the iodide reagent in the absence of the molybdate catalyst.

No Br_2 at *p*H 2 was noted with Co^{60} γ-rays at (Br^-) below 0.1 *M*. This difference from the cyclotron work must be due to the increased dose rate with the helium ion beam. Br_2 catalyzes the decomposition of H_2O_2 after the irradiation,[25] accounting for the lack of reproducibility.

Hydrogen Peroxide Yield in Solutions of Hydrogen and Oxygen.—Hochanadel measured the H atom yield for Co^{60} γ-rays by studying solutions containing H_2 and O_2.[13] He gave the mechanism as reactions 4, 9 and 6. This system has been studied further by Barr and Allen.[26] They find that for small amounts of H_2O_2, reactions 5 and 10 can be neglected.

The rate expression from this mechanism is simply $G(H_2O_2) = G_{H_2O_2} + \frac{1}{2}(G_H + G_{OH})$, or, using material balance, $G(H_2O_2) = G_{H_2} + G_H$. $G(H_2O_2)$ is given in Fig. 4 for this system irradiated with 18 Mev. deuterons, and it is seen that it does not obey these kinetics. There is a marked dependence on the beam current, even down to the lowest currents easily accessible. The same effect, more accentuated, was observed with 32 Mev. helium ions. The results support the conclusion of the last section on aerated water, that reaction 12 is important in these systems. The competition between (12) and (9) would produce the dose rate effect. Presumably, this effect would disappear at higher H_2 concentration, but we cannot work above atmospheric pressure with the required thin windows. All that can be said is that for 18 Mev. deuterons, $G(H_2O_2)$ extrapolates to about 2.2 at low currents.

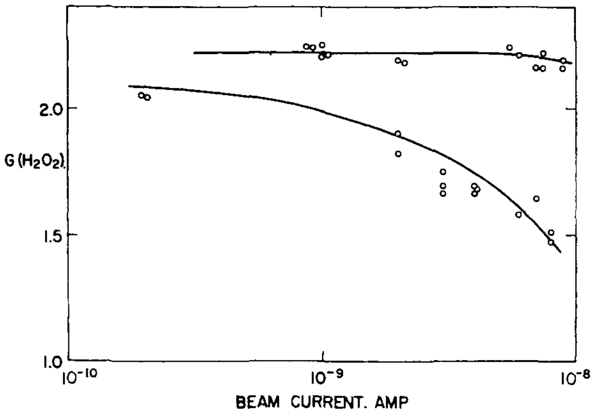

Fig. 4.—The variation of $G(H_2O_2)$ with beam current for 18 Mev. deuterons: lower curve. solutions containing 500 μM H_2 and 420 μM O_2: upper curve. O_2 saturated solutions of 10^{-2} *M* C_2H_5OH.

Hydrogen Peroxide Yields in Solutions of Ethyl Alcohol and Oxygen.—Jayson, Scholes and Weiss have made an extensive study of solutions of C_2H_5OH and O_2, concluding that this system can be used to measure G_H.[14] Their results can be expressed by the mechanism

$$H_2O \longrightarrow H_2.\ H_2O_2.\ H.\ OH$$

$$H + O_2 \longrightarrow HO_2 \tag{4}$$

$$OH + C_2H_5OH \longrightarrow C_2H_4OH + H_2O \tag{13}$$

$$C_2H_4OH + O_2 \longrightarrow CH_3CHO + HO_2 \tag{14}$$

$$2HO_2 \longrightarrow H_2O_2 \tag{6}$$

Reaction 14 is not necessarily mechanistic, but agrees with the observed product distribution. It is possible that some organic peroxides are formed instead of H_2O_2, but Jayson, *et al.*, could not find any. They did establish that the most probable ones would react with the iodide reagent as if they were H_2O_2. The rate expression for this mechanism is simply $G(H_2O_2) = G_{H_2} + G_H$, the same as in solutions of H_2 and O_2. If the reaction $H + C_2H_5OH \rightarrow C_2H_4OH + H_2$ is added to the scheme. the rate expression for $G(H_2O_2)$ remains unchanged as C_2H_4OH will also produce $\frac{1}{2}$ H_2O_2.

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[24] J. A. Ghormley and C. J. Hochanadel, THIS JOURNAL, **76**, 3351 (1954).

[25] W. C. Bray and R. S. Livingston, *ibid.*, **50**, 1654 (1928).

[26] N. F. Barr and A. O. Allen, presented at A.C.S. meeting, San Francisco. April, 1958.

A sample H_2O_2-dose curve is given in Fig. 2 for O_2-saturated, 10^{-2} M C_2H_5OH irradiated with 32 Mev. helium ions. In Fig. 4, there is a comparison of the beam current effect in the H_2, O_2 system and in 10^{-2} M C_2H_5OH,O_2 saturated solutions for 18 Mev. deuterons. There is possibly a slight current effect at 10^{-8} ampere but certainly none in our usual working range.

C_2H_5OH,O_2 solutions are convenient to use as the C_2H_5OH concentration can be varied over a wide range. $G(H_2O_2)$ in air-saturated solution is shown as a function of C_2H_5OH concentration in Fig. 5 for 32 Mev. helium ions. $G(H_2O_2)$ is constant ± 0.7% independent of C_2H_5OH concentration between 10^{-3} and 10^{-1} M. This was the experience of Jayson, Scholes and Weiss in their X-ray studies. 10^{-3} M C_2H_5OH solutions do not exhibit the intensity dependence observed in 500 μM H_2 solutions. Apparently OH radicals react with C_2H_5OH more readily than with H_2. Since this system is independent of intensity and C_2H_5OH concentration, it should serve as a good measure of G_H.

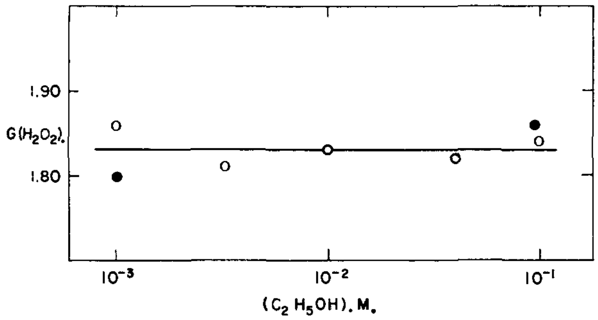

Fig. 5.—The dependence of $G(H_2O_2)$ on C_2H_5OH concentration in air-saturated solutions irradiated with 32 Mev. helium ions: ○. beam current of 2×10^{-9} amp.: ●. beam current of 8×10^{-9} amp.

The effect of C_2H_5OH concentration and O_2 concentration on $G(H_2O_2)$ for other radiations is given in Table III. C_2H_5OH concentration has little or no effect, but $G(H_2O_2)$ increases slightly with O_2 concentration. This is to be expected since more H atoms react with O_2 producing H_2O_2 at the higher concentration rather than combine with other radicals in the track. C_2H_5OH does not react efficiently with H atoms, so it should not have much effect on the yield.

TABLE III

H_2O_2 YIELDS IN SOLUTIONS CONTAINING ETHYL ALCOHOL AND OXYGEN

	$G(H_2O_2)$		
Solution	18 Mev. D^+	32 Mev. He^{++}	11 Mev. He^{++}
10^{-2} M EtOH, air-sat.	2.21	1.83	1.38
10^{-2} M EtOH. O_2-sat.	2.27	1.91	..
10^{-1} M EtOH, air-sat.	2.27	1.84	1.32

$G(H_2O_2)$ for air-saturated 10^{-2} M C_2H_5OH with 18 Mev. deuterons is 2.21, which agrees with the extrapolated yield in the H_2,O_2 system (2.2). This is the only check possible between the two systems, but it is quite satisfactory.

Garrison and co-workers[27] have studied O_2-saturated 0.05 M formic acid solutions at pH 3 and 12 in which $G(H_2O_2)$ is also believed to equal G_{H_2} + G_H. For 10 Mev. protons, which should be similar to 20 Mev. deuterons, they find $G(H_2O_2)$ = 3.02, and for 30 Mev. helium ions they find $G(H_2O_2)$ = 2.14. These yields can be compared with ours for C_2H_5OH,O_2 solutions, 2.27 and 1.91 for 18 Mev. deuterons and 32 Mev. helium ions, respectively. The difference may arise from pH effects or from the fact that the H_2O_2 yield in formic acid, O_2 solutions increases with increasing HCOOH concentrations.[28]

The Radical Yields.—In the above C_2H_5OH,O_2 system, $G(H_2O_2)$ = G_{H_2} + G_H. Both radical yields can be found from this since G_{H_2} and $G_{H_2O_2}$ are known and from material balance, $2G_{H_2} + G_H = 2G_{H_2O_2} + G_{OH}$. All of these yields are functions of the solute concentration, however, and many different solutes have been used in these studies. In order to avoid difficulties due to differing solute effects, we will attempt to construct the radical and molecular yields for an imaginary solute that reacts with equal efficiency with H and OH radicals. This will facilitate comparison with the one-radical model of Ganguly and Magee.

As noted earlier, 0.26×10^{-3} M and 1.3×10^{-3} M O_2 decrease G_{H_2} to the same extent as 0.5×10^{-3} M and 2.5×10^{-3} M (NO_2^-), respectively. G_{H_2} for the latter concentrations were extrapolated and interpolated from Fig. 1. These yields are given in Table IV for values of the parameter q, which is the concentration parameter employed by Ganguly and Magee in the diffusion theory and is essentially equal to the molar O_2 concentration. For the NO_2^- solutions, $q = 0.5(NO_2^-)$. Data for Co^{60} γ-rays[13,26] and 3.4 Mev. α-particles are included for comparison. The α-particle G_{H_2} is from Senvar and Hart and is the H_2 yield in pure deaerated H_2O.[29] There is probably a small amount of back reaction with OH radicals tending to lower the H_2 yield, but this effect should be small, of the order of 10%.[21]

From the values of $G(H_2O_2)$ in Table III, we can calculate G_H for the two oxygen concentrations for each radiation quality. The effect of C_2H_5OH on G_{H_2} and G_H may be safely neglected in comparison to the effect of O_2, as the ratio of rate constants for H reacting with O_2 and C_2H_5OH is about 500 as may be determined from acetaldehyde production in these solutions.[14] Since the combined effect of two solutes on G_{H_2} is that produced by an effective concentration which is a linear combination of the product of the solute concentrations by their relative rate constants for reaction with H, 10^{-2} M C_2H_5OH would act as only a 10% increase in O_2 concentration in air-saturated solution, which is negligible. G_H is given in Table IV.

$G_{H_2O_2}$ (and consequently G_{OH}) can be obtained from the yields in Br^- solution when a relation between q and bromide concentration has been established. Schwarz finds that for Co^{60} γ-rays Br^- at a given concentration has the same percentage effect on $G_{H_2O_2}$ as NO_2^- at three times this

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(27) W. M. Garrison, UCRI-3653.

(28) E. J. Hart, THIS JOURNAL, **76**, 4312 (1954).

(29) C. B. Senvar and E. J. Hart, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, (1958).

TABLE IV

THE MOLECULAR AND RADICAL YIELDS FOR VARIOUS ENERGIES AND SOLUTE CONCENTRATIONS (q)

Radiation	q	G_{H_2}	$G_{H_2O_2}$	G_H	G_{OH}	$G_{H_2}^{acid}$[4]	G_H^{acid}[4]
Co^{60} γ-rays	2.5×10^{-4}	0.42	0.67[12]	2.78[13]	2.28	0.39	3.68
	1.3×10^{-3}	.40[22]					
18 Mev. D^+	2.5×10^{-4}	.66	0.87	1.55	1.13	0.75	2.52
	1.3×10^{-3}	.62	0.91	1.65	1.07		
32 Mev. He^{++}	2.5×10^{-4}	.90	0.94	0.93	0.85	1.01	1.56
	1.3×10^{-3}	.87	1.00	1.04	.78		
11 Mev. He^{++}	2.5×10^{-4}	1.19	1.08	0.19	.41		
3.4 Mev. α	$\sim 10^{-4}$	1.5[29]	(1.4)[a]	(0.2)[a]	(.4)[a]	1.66	

[a] Estimated from results of Barr and Schuler assuming the product distribution to be the same in neutral solution.

concentration has on G_{H_2}.[6] This suggests that q = 1.5 (Br^-). $G_{H_2O_2}$ yields for Br^- concentrations corresponding to our two values of q are given in Table IV. Note that $G_{H_2O_2}$ is higher at $q = 1.3 \times 10^{-3}$ than at 2.5×10^{-4}. This is a reflection of the 9% increase in $G_{H_2O_2}$ upon O_2 saturation given in Table II. Actually, the O_2-saturated data of Table II cannot be extrapolated to the proper Br^- concentrations by themselves, so it was assumed that the 9% increase observed for both deuterons and helium ions at 2×10^{-4} M Br^- applied at other Br^- concentrations. This assumption cannot introduce more than a few per cent. error.

G_{OH}, found by material balance, is also given in Table IV. $G_{H_2O_2}$, G_H and G_{OH} for 3.5 Mev. α-particles have been estimated by assuming that their ratio to G_{H_2} is the same as has been observed in studies of the $B^{10}(n,\alpha)Li^7$ reaction in 0.8 N H_2SO_4,[8] and using the yield of Senvar and Hart for G_{H_2}. This calculation tends to overestimate G_H and G_{OH}, but since they are small, it will not cause appreciable trouble. Lefort finds values of G_{H_2} approximately 10% higher than Senvar and Hart.[30] No attempt will be made to compare the yields for 3.5 Mev. α-particles to calculated ones, but they are of interest in connection with the amount of water decomposed.

By the above procedure we have developed yields for solute concentrations reduced to a standard solute. Before the yields in Table IV can be used to represent those arising in a solution of a single solute reacting with equal efficiency with H and OH, certain questions concerning the effect of solutes reacting with one radical only on the yield of the other radical should be considered. These questions do not arise in the case of G_{H_2}, as NO_2^- does react with approximately equal efficiency with both radicals.[6] The values of $G_{H_2O_2}$ are given for solutions containing Br^- and O_2 at equivalent reduced concentrations, and there is no real problem in considering this combination as equivalent to one solute reacting with both radicals. G_H, however, was determined in the presence of C_2H_5OH and O_2 only. O_2 does not react with OH while C_2H_5OH does at an unknown rate. Varying the C_2H_5OH concentration between 10^{-3} and 10^{-1} M does not affect $G_{H_2} + G_H$, so that to a first approximation, G_H is independent of the concentration of solutes capable of reacting with OH.

G_{-H_2O}, the observable rate of water decomposition, equal to $2G_{H_2} + G_H$ or $2G_{H_2O_2} + G_{OH}$, is given in Table V. The total yield of water decomposition should be constant, but this includes the amount of water reformed in the track reactions, especially reaction 3. The yield of (3), which we will call G_{HOH}, would increase with $-dE/dx$ so that the observable yield, G_{-H_2O} should decrease. It does between Co^{60} γ-rays and 11 Mev. helium ions as is seen from Table V. However, G_{-H_2O} increases again at still higher $-dE/dx$. That G_H for 3.4 Mev. α-particles probably represents an upper limit does not affect this conclusion, since if G_H were zero, G_{-H_2O} would still be 3.0. Radical-product reactions occurring in the spur, such as (5), (9) and (10), all have H_2O as a product, tending to lower G_{-H_2O}. accentuating the problem. Except at high $-dE/dx$, the behavior of G_{-H_2O} with $-dE/dx$ is qualitatively as expected. The exception will be discussed more fully later.

The total amount of water decomposing, which should be independent of $-dE/dx$, is G_{-H_2O} + G_{HOH}. We cannot measure G_{HOH}, but reaction 3 should proceed as easily as reactions 1 and 2. On a purely statistical model, G_{HOH} would equal $2G_{H_2}$ or $2G_{H_2O_2}$, but G_{H_2} and $G_{H_2O_2}$ are not equal. In lieu of any other information, we have assumed that $G_{HOH} = G_{H_2} + G_{H_2O_2}$. $G_{-H_2O} + G_{H_2} + G_{H_2O_2}$ is given in Table V and is seen to be constant at 4.62 ± 0.14 between Co^{60} γ-rays and 11 Mev. helium ions, with a possible slight increase for 11 Mev. helium ions. (Again, it is much larger for 3.4 Mev. α-particles.) This constancy is excellent support of the mechanism and suggests that water is re-formed by reaction 3 in amounts to be expected by comparison with reactions 1 and 2.

TABLE V

WATER DECOMPOSITION YIELDS AND THE FRACTION OF RADICALS COMBINING TO FORM MOLECULAR PRODUCTS (FROM TABLE IV)

Radiation	q	G_{-H_2O} (= $2G_{H_2}$ + G_H)	G_{-H_2O} + G_{H_2} + $G_{H_2O_2}$	$\frac{2(G_{H_2} + G_{H_2O_2})}{G_{-H_2O} + G_{H_2} + G_{H_2O_2}}$	$1 - S$[9]
Co^{60} γ-rays	2.5×10^{-4}	3.62	4.71	0.46	0.48
18 Mev. D^+	1.3×10^{-3}	2.89	4.42	.69	.67
	2.5×10^{-4}	2.87	4.40	.69	.71
32 Mev. He^{++}	1.3×10^{-3}	2.78	4.65	.80	.82
	2.5×10^{-4}	2.73	4.58	.80	.85
11 Mev. He^{++}	2.5×10^{-4}	2.57	4.84	.94	.91
3.4 Mev. α	$\sim 10^{-4}$	(3.2)	(6.1)		

Comparison with the Model of Ganguly and Magee.—Ganguly and Magee have developed a model which predicts the magnitude of the de-

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(30) M. Lefort, *J. chim. phys.*, **51**, 351 (1954).

pendence of the radical and molecular yields on $-\mathrm{d}E/\mathrm{d}x$ and solute concentration.[9] In this model, one type of radical, R, is formed with a yield of 6 per 100 e.v. Initially, each spur contains 6 of these radicals in a gaussian distribution. The spurs are spaced randomly along a linear track, the average spacing being inversely proportional to $-\mathrm{d}E/\mathrm{d}x$. In order to make the model amenable to mathematical analysis, they invoke the method of "prescribed diffusion," *i.e.*, as the radicals diffuse, each spur maintains the gaussian distribution. (If there were no bimolecular reactions occurring, this would be exact.) The only reactions considered during the expansion of the track are

$$\mathrm{R} + \mathrm{R} \longrightarrow \mathrm{R}_2 \qquad k$$

$$\mathrm{R} + \mathrm{S} \longrightarrow \mathrm{RS} \qquad k_\mathrm{S}$$

where S is any scavenger present. The parameters involved in their theory are D, the diffusion coefficient of the R radical; t_0, expressing the size of the spur (equal to the time it would require for the spur to expand from a point to its initial distribution); k, the rate constant of the combination reaction; $-\mathrm{d}E/\mathrm{d}x$ and q, which is proportional to the solute concentration, as noted earlier. q is equal to $k_\mathrm{S}t_0(C_\mathrm{S})$ where k_S is the rate constant for the reaction with solute and C_S is the solute concentration. They calculate S, the fraction of the radicals that react with the solute. $(1 - S)$ of the radicals react to form R_2.

Some of the assumptions made in their treatment are rather drastic, but their effect can be minimized by evaluating the parameters such that they agree with experiment at one point. Apparently they did this for Co^{60} γ-rays, assuming R to represent all the radicals produced, both H and OH.

We have made one change in their calculations concerning the method by which $-\mathrm{d}E/\mathrm{d}x$ is introduced. They find that S is a function of the integral $\int_0^\mathrm{R} (1/z_1{}^2)\ \mathrm{d}\rho$ where R is the range of the particle, $R - \rho$ is the residual range and Z_1 is the average spacing of spurs at ρ. Ganguly and Magee evaluate this integral explicitly by noting that $(\mathrm{d}n/\mathrm{d}\rho) = (1/Z_1)$ where n is the number of spurs in the track, and using the empirical range–energy relationship, $(R - \rho)/R = (E\rho/E_0)^\eta$ where η is a not-too-sensitive function of the energy. With this approximation (η treated as constant) they evaluate the above integral as $\eta^2/[(2 - n)\eta R]$. This expression is not exact and leads to large errors at low energies.

We have evaluated this integral directly from curves of $-\mathrm{d}E/\mathrm{d}x$ *vs.* E.[31] Noting the $\frac{1}{Z_1} = \frac{1}{\epsilon}\left(-\frac{\mathrm{d}E}{\mathrm{d}x}\right)$ where ϵ is the energy released per spur (100 e.v.), we have ($\mathrm{d}\rho = \mathrm{d}x$)

$$\int_0^R \frac{1}{Z_1{}^2}\,\mathrm{d}\rho = \frac{1}{\epsilon^2}\int_0^\mathrm{E}\left(-\frac{\mathrm{d}E}{\mathrm{d}x}\right)\mathrm{d}E$$

which is a convenient form for evaluation.

We will first check the solute dependence of the molecular yields. Ganguly and Magee calculate $1 - S$, the fraction recombining, as a function of solute concentration. This includes reaction 3, $\mathrm{H} + \mathrm{OH} \rightarrow \mathrm{H_2O}$. However, G_{H_2} and $G_{\mathrm{H_2O_2}}$ should be proportional to $1 - S$. For γ-rays, the proportionality factors and relationship between q and solute concentration were taken to give the best fit with the data, giving $G_{\mathrm{H}_2} = 0.865(1 - S)$, $q = 0.5(\mathrm{NO_2}^-)$, $G_{\mathrm{H_2O_2}} = 1.39(1 - S)$ and $q = 1.5(\mathrm{Br}^-)$. For the other radiations, the expressions for q were kept constant, and the normalizing factors for $1 - S$ were evaluated at 10^{-3} M for $\mathrm{H_2}$ yields from $(\mathrm{NO_2}^-)$ and at 2×10^{-5} M for $\mathrm{H_2O_2}$ yields from Br^- solutions, giving $G_{\mathrm{H}_2} = 0.923(1 - S)$ and $1.06(1 - S)$ for 18 Mev. deuterons and 32 Mev. helium ions, respectively, and $G_{\mathrm{H_2O_2}} = 1.24(1-S)$, $1.13(1 - S)$, and $1.22(1 - S)$ for 18 Mev. deuterons, 32 Mev. and 11 Mev. helium ions, respectively. Thus, for each product. n curves are specified by $n + 1$ parameters, which is reasonable.

The agreement with the data is excellent for G_{H_2} and poor for $G_{\mathrm{H_2O_2}}$. Several things might account for the poor agreement of the $\mathrm{H_2O_2}$ curves. First, in a two radical system, the parameters D, t_0 and k should be different for each radical, so that values which fit G_{H_2} well should not be the best choice for $G_{\mathrm{H_2O_2}}$. It is difficult to predict whether a reasonable change in parameters would make an appreciable difference. Secondly, radical-product reactions, in particular $\mathrm{H} + \mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \mathrm{OH}$, occurring in the track would tend to cause a divergence between experiment and theory. Another possible cause of the discrepancy is solute depletion. The model assumes that the solute concentration is unaffected by the occurrence of the reaction $\mathrm{R} + \mathrm{S} \rightarrow \mathrm{RS}$. Actually, this reaction will depress the solute concentration in the neighborhood of the spur, forming a sort of "negative" of the radical concentration. As the spurs become more closely spaced at high $-\mathrm{d}E/\mathrm{d}x$, this depression becomes more severe. In the helium ion tracks, the initial radical concentration averages about 1 M, so that it is obvious that solute depletion should be a serious effect.

The last check between our experiments and the model of Ganguly and Magee is the comparison of the calculated $1 - S$ with the observed fraction of radicals recombining. Since $1 - \mathrm{S}$ includes reaction 3, we evaluate it as

$$(1 - S)_\mathrm{exptl} = \frac{G_{\mathrm{H}_2} + G_{\mathrm{H_2O_2}} + G_\mathrm{HOH}}{G_{-\mathrm{H_2O}} + G_\mathrm{HOH}}$$

$$= \frac{2(G_{\mathrm{H}_2} + G_{\mathrm{H_2O_2}})}{G_{-\mathrm{H_2O}} + G_{\mathrm{H}_2} + G_{\mathrm{H_2O_2}}}$$

using the same expression for G_HOH as before. These ratios are given in Table V along with $1 - S$ calculated by Ganguly and Magee. The agreement is remarkably good. Note that Ganguly and Magee predict a larger value of $1 - S$ at lower solute concentration (more combination of radicals) which is not apparent in the experiments. This discrepancy is more apparent than real and is due to assuming $G_\mathrm{HOH} = G_{\mathrm{H}_2} + G_{\mathrm{H_2O_2}}$. The explanation for the increase in $G_{\mathrm{H_2O_2}}$ with $\mathrm{O_2}$ concentration (a decrease in the reaction $\mathrm{H} + \mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \mathrm{OH}$ and an increase in $\mathrm{H} + \mathrm{HO_2} \rightarrow \mathrm{H_2O_2}$) would not predict an increase in G_HOH. If G_HOH were evaluated as being proportional to G_{H_2} the discrepancy would disappear.

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(31) R. H. Schuler and A. O. Allen, unpublished calculations, and H. A. Bethe, *Revs. Modern Phys.*, **22**, 213 (1950).

In general, the agreement between the calculations of Ganguly and Magee and our data is excellent, considering that theirs is a one radical model with several approximations. The various reactions proposed to account for the deficiency in calculating $G_{H_2O_2}$ would require the introduction of several new parameters into the model which might require much more effort than it is worth. Certainly, the over-all mechanism is well substantiated.

Radical Distribution in the Track.—In their calculations, Ganguly and Magee assume that all of the radicals are formed in spurs of about 10 Å. radius. In order to support this, Samuel and Magee proposed that all electrons produced in the solution were brought rapidly to thermal energies and were recaptured by their parent ions,[3] thus eliminating the possible formation of H atoms at large distances from the track. Platzman has calculated the rate at which the secondary electrons lose their last few volts of energy[32] and concludes that they come to thermal energies in the solution only at large distances from the parent ion (of the order of hundreds of A.). These electrons never return to their parent ion but presumably form H atoms or react as H atoms in a very diffuse distribution, approaching uniformity. If some radicals were formed in an essentially uniform distribution, Ganguly and Magee's calculations would be in error, principally at high $-dE/dx$. The experimental value of S would equal the S calculated by Ganguly and Magee plus a constant. Even apart from the calculations, there is no evidence of background of radicals at the larger values of $-dE/dx$ (see Table IV). It may be argued that at the high ion density associated with high $-dE/dx$ the electrons do begin to return to the ion column formed, but the excellent agreement between experiment and the calculations of Ganguly and Magee strongly supports the conclusion of Samuel and Magee.

The increase in G_{-H_2O} and $G_{-H_2O} + G_{H_2} + G_{H_2O_2}$ at high $-dE/dx$ can be explained in terms of the radical distribution in the track. First, G_{HOH} should be greater than $G_{H_2} + G_{H_2O_2}$, since an appreciable number of the radicals are produced in isolated pairs of H and OH which can recombine to H_2O but cannot form H_2 or H_2O_2.[3] At least 40% of the spurs contain only a single pair of radicals. At high $-dE/dx$, these pairs are no longer isolated but are part of a track, so that there is a probability for combination to form H_2 and H_2O_2 and consequently a decreased probability for formation of H_2O. This would lead to an increase in $G_{-H_2O} + G_{H_2} + G_{H_2O_2}$. However, if the radicals in these pairs are separated by 5 Å. or so, the probability[3] of their recombining is small, of the order of 20%. This effect alone cannot account for the observed increase in yield which is 30%. If all of the radicals including the isolated pairs are produced by decomposition of excited water molecules, as suggested by Samuel and Magee, the original pairs of H and OH should be closer than 5 Å. If they are separated by 1 to 2 Å., as seems likely,[33] recombination will be of the order of 50% or more. We may conclude that at low $-dE/dx$ (*i.e.*, for γ-rays) the radical distribution is not random. In any given spur, the initial separation between dissociated water molecules is 5 to 10 Å., while the distance between any pair produced from H_2O is 1 to 2 Å. There would be a strong tendency for the original pair to recombine relative to combination with the other radicals. At high $-dE/dx$ the distance between spur centers is less than the average radius of a spur. For 3.5 Mev. α-particles, the average radical concentration along the track is about 5 M, a factor of 2 higher than the concentration in an isolated spur. Consequently the correlation of the radical pairs is less noticeable, and there will be more random combination leading to increased H_2 and H_2O_2 yields with respect to G_{HOH}.

A corollary of this model is that the total yield of water decomposition is considerably greater than the figure 4.6 indicated in Table V. A large value is quite reasonable, since many other non-aromatic systems have decomposition yields between 5 and 10. Firestone has found $G_{-H_2O} = 11.7$ in the gas phase.[34]

Comparison with Yields in Acid Solution.—In Table IV we have given G_{H_2} and G_H in 0.8 N H_2SO_4 (Schuler and Allen)[4] for comparison with our results. G_{-H_2O} is considerably greater in acid solution, principally because G_H is larger. This increase in yield is caused by the hydronium ion. Na^+ does not produce the effect,[35] and it is independent of the anion.[36]

The yields in acid solution are amenable to the same treatment as above in comparison with Ganguly and Magee's $1 - S$, but the agreement is not quite as good. There are few concentration dependence data available except for γ-rays,[5,23,37] but these studies indicate that G_{H_2} is more sensitive to solute concentration in acid than in neutral solution, while the $G_{H_2O_2}$ sensitivity is about the same. For γ-rays, G_{H_2} extrapolates to the same yield at infinite dilution in both acid and neutral solutions.[34] However, as $-dE/dx$ increases, G_{H_2} in acid solution becomes larger than G_{H_2} in neutral solution, as can be seen in Table IV.

One possible explanation of the pH effect is that acid destroys the correlation between H and OH somewhat, increasing the over-all yield of radicals but also increasing the dimensions of the spur. For γ-rays, these two effects would have to balance to keep the combination yield constant. The increased spur size would also explain the increased scavenger efficiency, since the parameter q is proportional to the square of the average radius of the spur. A possible mechanism for this destruction of the correlation is the occurrence of the reaction $H_3O^+ + e \rightarrow H + H_2O$ instead of the electron returning to the parent ion.

UPTON, L. I., N. Y.

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