reaction rate in a chain reaction as is obtained with a known photochemical initiation rate. Putting the data of expt. 16 in eq. 17 and using $q = 0.49$ one obtains $k_2/k_5 = 5.42$. (This may be compared with the value of 7.2 obtained by Hart.)[4] This value of $k_2/k_5 = 5.42$ is next put into eq. 18 with the data of expt. 81. Since the chains are so long in expt. 81, one can set the intercept G_H of eq. 18 equal to $(G_H + G_{OH})/2$ with very little error, and solving find $(G_H + G_{OH})/2$ equals 3.21.

The G Value for Radical Production by γ-Rays.—Dainton and Rowbottom[2] give a value of $G_R = (G_H + G_{OH})/2$ for H_2O decomposed to radicals of 12.6 ± 1.8 water molecules/100 e.v. Since they used a value of 19.9 Fe^{++} oxidized/100 e.v. in the ferrous sulfate dosimeter, the γ-ray intensity was underestimated and G_R may be corrected by the factor 15.5/19.9 to give $G_R = 9.83 \pm 1.40$. We accept the Hochanadel–Ghormley value of 15.5 Fe^{++}/100 e.v.[9] As noted by Dainton and Rowbottom their G_R will be reduced if the primary quantum yield of H_2O_2 decomposition is less than 1.0. Using our value of $q = 0.49$, G_R becomes 4.86 ± 0.69. Since the radiolyses of ref. (1) were done at 0° it is better to correct G_R using Hunt and Taube's 0° value of $q = 0.38$, and then $G_R = 3.74 \pm 0.53$.

While Dainton and Rowbottom compared the γ-ray initiated chain-reaction rate with the rate initiated by 3660 Å. light, their primary quantum yield of peroxide decomposition, q, was measured at 2537 Å., the wave length used in our work. Their value was measured in 0.1 M H_2O_2, while our value was obtained in 7 mM H_2O_2 and 0.1 M HCOOH. However, the ratio of $[k_2(OH)(HCOOH)/k_5(OH)(H_2O_2)]$ is 5.42 from our work if the HCOOH and H_2O_2 are both 0.1 M and the OH concentrations are equal. This shows HCOOH is a better scavenger than H_2O_2 for OH radicals, and our lower value of q cannot be attributed to failure of the primary OH's to react.

We conclude from the above discussion that $(G_H + G_{OH})/2$ is approximately 3 for γ-rays as found by numerous workers.[3a] This conclusion is also supported by the results of Table II of this paper.

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The Primary Quantum Yield in the Photolysis of Hydrogen Peroxide at 3130 Å. and the Primary Radical Yield in the X- and γ-Radiolysis of Water

BY F. S. DAINTON

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The kinetics of the polymerization of acrylamide in deaerated aqueous solutions (a) initiated by X- or γ-rays in the presence or absence of ferric perchlorate, and (b) initiated by 3130 Å. light using either H_2O_2 or $FeOH^{++}$ as photosensitizers, are outlined. It is shown that the data are consistent only if the primary quantum yield for the photolysis of H_2O_2 in aqueous solution using 3130 Å. light has the value 0.6 OH radical per quantum. Assuming that this quantum efficiency does not increase with increasing wave length, this result, combined with the measurements of Dainton and Rowbottom,[1] leads to an upper limit for the primary radical yield $(G_H + G_{OH})$ in the X- or γ-radiolysis of water of 6 ± 0.4.

Four years ago, Dr. J. Rowbottom and the author[1] showed that the mechanisms of the radiolysis and photolysis of aqueous solutions of hydrogen peroxide differed only in the primary acts, which may be written

$$\text{Photolysis}\quad H_2O_2 \xrightarrow{h\nu} \phi_{OH}OH$$

$$\text{Radiolysis}\quad H_2O \xrightarrow{\gamma} G_HH + G_{OH}OH$$

The ratio $(G_H + G_{OH})/\phi_{OH}$ was found to be 12.6 ± 1.8 for Co^{60} γ-rays and 3665 Å. based on a value of 20 for $G_{Fe^{+++}}$ in aerated 0.8 N sulfuric acid. ϕ_{OH} was determined for 2537 Å. light by Lea's method[2] and found to be 1.9 ± 0.1. Assuming that ϕ_{OH} does not vary with wave length and taking $\phi_{OH}^{3665} = 2$ these data lead to a value of $G_H + G_{OH}$ of 25.2, which, when corrected for the now generally accepted value of $G_{Fe^{+++}} = 15.6$, becomes 19.7, just over three times larger than the values obtained by other methods.[3] This serious discrepancy disappears if ϕ_{OH}^{3665} is ∼0.6. It is highly improbable that ϕ_{OH}^{3665} exceeds ϕ_{OH}^{2537} and the value of 0.98 for the latter obtained by Hunt and Taube,[4] together with the considerable accumulated evidence[5] that quantum efficiencies of unity are rarely attained in liquid systems strongly suggests that our early value is too large. Repeated careful perusal of our earlier data having failed to reveal any errors, it was decided to measure ϕ_{OH} at some wave length exceeding 2537 Å. by a different method, arising out of two other investigations recently completed in this laboratory. Full experimental details will be given elsewhere. Through the kindness of Dr. Max Matheson we were allowed to see the manuscript of the preceding paper[6] and it seemed entirely desirable to publish a brief statement concerning ϕ_{OH}^{3130}, the method of its determination, and the implication which the revised value has for the conclusions to be drawn from our earlier work[1].

Collinson, Dainton and McNaughton[7] have

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[1] F. S Dainton and J. Rowbottom, *Trans. Faraday Soc.*, **49**, 1160 (1953).

[2] D. E. Lea, *ibid.*, **45**, 81 (1949).

[3] For a summary of these see E. Collinson, *Ann. Rep. Progr. Chem.*, **51**, 82 (1955).

[4] A. C. Hunt and H. Taube, THIS JOURNAL, **74**, 5999 (1952).

[5] See for example H. Rutenberg and H. Taube, *ibid.*, **72**, 5561 (1950); **73**, 4426 (1951); F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

[6] J. L. Weeks and M. S. Matheson, *ibid.*, **78**, 1273 (1956).

[7] E. Collinson, F. S. Dainton and G. S. McNaughton, *J. Chim. Phys.*, **52**, 556 (1955), and to be published.

studied the action of X- and γ-rays on aqueous solutions of acrylamide over a very wide range of concentrations in the presence and absence of ferric perchlorate. Acrylamide is a very efficient radical acceptor[8] and in aqueous solutions readily undergoes polymerization to a high molecular weight but water soluble product at rates which are uninfluenced by change of pH over a wide range. In pure aqueous solution the dose rate exponent is half and the monomer exponent unity. All the kinetics can be accommodated in the simple polymerization scheme

$$\text{Initiation} \quad \text{H (or OH)} + m_1 \longrightarrow m_1^* \qquad (1)$$

$$\text{Propagation} \quad m_1 + m_j^* \xrightarrow{k_p} m_{j+1}^* \qquad (2)$$

$$\text{Mutual termination } m_j^* + m_i^* \xrightarrow{k_t} \text{dead polymer} \qquad (3)$$

Experimental criteria exist which may be used to indicate whether all the initial radicals are captured by acrylamide. When this is the case the expression for the rate of polymerization (R_p) is

$$R_p = \left(\frac{(G_H + G_{OH})I}{k_t}\right)^{1/2} k_p(m_1) \qquad (4)$$

where I is the dose rate in hundreds of electron volts per liter per second. When ferric perchlorate is added two additional termination reactions can occur, namely

$$m_j^* + \text{Fe}^{+++}\text{H}_2\text{O} \xrightarrow{k_t'} P_j\text{OH} + \text{H}^+ + \text{Fe}^{++} \qquad (5)$$

$$m_j^* + \text{Fe}^{+++}\text{OH}^- \xrightarrow{k_t''} P_j\text{OH} + \text{Fe}^{++} \qquad (6)$$

Consequently the rate of polymerization falls and the dose rate exponent rises to the limiting value of unity as increasing concentrations of ferric salt are employed. In the region where the dose rate exponent is unity the rate expression is

$$R_p = \frac{(G_H + G_{OH})Ik_p[m_1]}{(k_t'[\text{Fe}^{+++}] + k_t''[\text{FeOH}^{++}])} \qquad (7)$$

and whenever a chain is terminated a ferric ion is reduced to ferrous ion so that

$$(G_H + G_{OH})I = \text{d}[\text{Fe}^{++}]/\text{d}t \qquad (8)$$

Measurements of the rate of ferrous ion formation during polymerization thus enable $G_H + G_{OH}$ to be found, and studies of the effect of hydrion concentration permit the ratio k_t'/k_t'' to be evaluated. We find that at 25° $G_H + G_{OH} = 6.3$, $k_t''/k_t' = 5$ and $k_p/k_t' = 6.0$. By substituting for $G_H + G_{OH}$ in equation (4), $(k_p/k_t^{1/2})^{25°}$ is found to be 4.7 $\text{l.}^{1/2}$ $\text{mole}^{-1/2}$ $\text{sec.}^{-1/2}$.

If, instead of X- or γ-ray initiation, the ion-pair complex FeOH^{++} is used as a photo initiator, the initiation mechanism becomes reactions (9) and (10)

$$\text{FeOH}^{2+} + h\nu \longrightarrow \text{FeOH}^{2+*} \longrightarrow \text{Fe}^{2+} + \text{OH} \qquad (9)$$

$$\text{OH} + m_1 \longrightarrow m_1^* \qquad (10)$$

and is followed by reactions (2), (5) and (6). Tordoff and Dainton[9] have measured rates of polymerization and of ferrous ion production as functions of acidity, monomer concentration and intensity of 3130 light and have shown that the relation

$$R_p = AI_{\text{abs}}[m_1]/([\text{Fe}^{+++}] + B[\text{FeOH}^{2+}]) \qquad (11)$$

holds, from which may be calculated values of $k_t''/k_t' = 5.6$ and $k_p/k_t' = 7.0$. The good agreement between the values is strong presumptive evidence that, as would be expected, k_p and k_t would have the same values in the photochemical as in the radiation initiated polymerization. If, instead of FeOH^{++}, hydrogen peroxide is employed as a photoinitiator, there is a wide range of conditions over which the rate of polymerization is proportional to the first power of the monomer concentration and to the square root of the absorbed light intensity. The appropriate rate expression is thus

$$R_p = \left(\frac{\phi_{OH}\, I_{\text{abs}}}{k_t}\right)^{1/2} k_p[m_1] \qquad (12)$$

and substituting the value of $k_p/k_t^{1/2} = 4.7$ $\text{l.}^{1/2}$ $\text{mole}^{-1/2}$ $\text{sec.}^{-1/2}$ and the observed R_p and I_{abs} when 3130 Å. light is used, ϕ_{OH}^{3130} at 25° is found to be 0.6.

Three comments may be made on this value. Firstly, it is rather less than that obtained by both Hunt and Taube[4] and by Matheson and Weeks.[6] This difference may reflect a genuine dependence of ϕ_{OH} on wave length or may merely be due to experimental error. Secondly, ϕ_{OH}^{3665} is unlikely to exceed 0.6 and hence Dainton and Rowbottom's data can be used to fix an upper limit of $G_H + G_{OH} = 19.7 \times 0.6/2 = 6 \pm 0.4$ for Co^{60} γ-rays, and an outstanding anomaly in the radiation chemistry of aqueous systems is thereby eradicated. Thirdly, lifetime values determined by using intermittent radiation enable $k_t\phi_{OH}$ and $k_t(G_H + G_{OH})$ to be obtained for each of the H_2O_2 photosensitized and γ-ray initiated systems, respectively, thus permitting a check to be made on $(G_H + G_{OH})/\phi_{OH}^{3130}$. As yet we have made measurements only on the photochemical system.

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[8] F. S. Dainton and T. J. Hardwick, to be published.

[9] F. S. Dainton and M. Tordoff, to be published.