

fluoride system probably is due to this phase effect. The several rings opened in the vicinity of one another lead to combinations among themselves and adjacent molecules in the case of the solid aniline hydrofluoride because the free radicals are trapped together for a longer time in the solid than they are in the liquid cage.

The aliphatic amines did not show the complex behavior of aniline and benzene. It seems reasonable that open aliphatic chains will be far less reactive than open aromatic rings. The appreciable yield of the parent molecule lends considerable support to this view. It indicates that a type of direct substitution occurs. The C^{14} atom which was stopped in the collision effectively replaces the atom displaced which carried off the momentum of the incoming C^{14} atom.

For the aliphatic amine salts, the distribution of products is like that expected from the irradiation of the pure solid amine with an increase of the higher molecular weight product observed due to the "phase effect."¹⁶

The higher yield of gaseous products from methylamine hydrofluoride suggests that ethane may be formed by substitution of C^{14} for N^{14} .

The results with the methanol system suggest

oxygen substitution by the C^{14} atoms to give ethane. The higher yield of gaseous products from this system than from methylamine suggests that carbon oxides may make a fair fraction of the gaseous products. Production of labelled aliphatic alcohols seems entirely feasible.

Results given in this paper seem to support in a general way the hot atom theory developed previously.¹⁶⁻¹⁸

It is clear that radiation chemical effects seem not to be serious in this system. A method of synthesis of aliphatic organic compounds by direct pile irradiation seems to have been found.

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(17) W. F. Libby, *THIS JOURNAL*, **69**, 2533 (1947).

(18) F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1940 (1953).

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The Primary Quantum Yield of Hydrogen Peroxide Decomposition¹

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In aqueous hydrogen peroxide-formic acid solutions a chain reaction is initiated by ionizing radiation or by 2537 Å. light absorbed by the hydrogen peroxide. The principal gaseous product is carbon dioxide. This reaction is inhibited by oxygen, and from the quantum yield of oxygen consumption the primary quantum yield of hydrogen peroxide dissociation at 2537 Å. is deduced to be 0.49 ± 0.065 . From this yield and a comparison of the photochemical experiments with those in which the reaction is induced by gamma rays, we calculate a G value of 3.06 water molecules decomposed to radicals per 100 e.v. of absorbed energy. These results suggest that the higher primary quantum yield of Dainton and Rowbottom and the high G value based on it are in error. A mechanism is proposed which fits the experimental data.

Dainton and Rowbottom² have measured at 2537 Å. the limiting quantum yield at high light intensities for aqueous hydrogen peroxide decomposition. By the accepted mechanism the primary quantum yield of hydrogen peroxide dissociation is one-half this limiting yield. These authors found the limiting yield to be 1.9 ± 0.1 and therefore the primary yield to be about 1.0. Next they compared at lower intensities the rates for the chain decomposition of aqueous hydrogen peroxide induced by 3660 Å. light and by CO^{60} γ -rays. Since the initiation rate for light had been determined the rate of radical production by γ -rays followed from the comparison and was estimated as 12.6 ± 1.8 water molecules decomposed per 100 e.v. of absorbed γ -rays at 0°.

Since the G value quoted for water decomposition to radicals is about fourfold that obtained by many workers^{3a} and since Hunt and Taube^{3b} find the limiting quantum yield for aqueous hydrogen peroxide

at 2537 Å. to be 0.98 ± 0.05 at 25° for 0.017–0.186 M H_2O_2 , we thought a redetermination of the primary quantum yield to be important. The system most suitable for this determination appeared to be the aqueous hydrogen peroxide-formic acid chain reaction inhibited by oxygen. The radiation chemistry of this system has been studied by Hart.⁴ His results indicated that, if this system were irradiated with light absorbed by the hydrogen peroxide, then the quantum yield of oxygen consumption would measure the primary quantum yield of hydrogen peroxide dissociation.

Our hopes with respect to this system appear to have been justified, and this paper presents an investigation of the photochemistry of the aqueous hydrogen peroxide, formic acid, oxygen system. The primary quantum yield obtained agrees with that of Hunt and Taube, and this result would decrease by a factor of 2.0 the G value reported by Dainton and Rowbottom.

Experimental

For photochemical experiments a fused silica mercury resonance lamp (Type SC-2537, Hanovia Chemical and

(4) E. J. Hart, *ibid.*, **73**, 68 (1951).

(1) Based on work performed under the auspices of the United States Atomic Energy Commission.

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

(3) (a) See Table I, E. J. Hart, *Ann. Rev. Phys. Chem.*, **5**, 139 (1954); (b) J. P. Hunt and H. Taube, *THIS JOURNAL*, **74**, 5999 (1952).

Mfg. Co., Newark, N. J.) was mounted in an enclosure from which the ozone was continually removed. The lamp transformer was supplied from a Sola constant voltage transformer. Used with this lamp was a half thickness Corning filter #9863, transmitting light measured in terms of quanta as 94% 2537 Å., 1% 3130 Å., and 5% 3660 Å. Intensities were measured with an RCA No. 935 phototube combined with the Keithley Instruments Co. (Cleveland, Ohio) model 200A electrometer and model 2008 decade shunt. By mounting the phototube in a holder fitted with ground surfaced fluorite diffusing screens 12 cm. in front of the sensitive surface an area of uniform sensitivity 1×2 cm. on the fluorite was obtained. This combination was calibrated against a Ag-Bi thermopile (Gaertner L234VTBS with fluorite window) using a Gaertner L234-150 quartz monochromator and a constant intensity H-8 mercury arc (Nonex jacket removed). The thermopile calibration was checked against standard lamps from the National Bureau of Standards. An approximate point source and the inverse square law were used to extend the phototube-electrometer calibration to include the highest intensities used in this work. In addition the uranyl oxalate actinometer (0.001 M $\text{UO}_2\text{C}_2\text{O}_4$ and 0.005 M $\text{H}_2\text{C}_2\text{O}_4$) was used periodically to check the phototube-electrometer calibration. With stirred solutions we measured quantum yields of 0.63 and 0.64 at 2537 Å. for this actinometer in comparison with 0.64 and 0.65 reported by Forbes and Heidt.⁵

In the optical arrangement used in most experiments, a fluorite lens 20 cm. from the source focused a reduced image on the diffusing screens 14.5 cm. behind the lens. The reaction cells were placed in a holder immediately behind the lens. For better geometry a 1.4×2 cm. aperture at the source limited the effective area of the lamp. For lower intensities smaller apertures were used, while for higher intensities the mask was removed and the lamp moved closer to the reaction cell. The higher intensities were measured directly with the uranyl oxalate actinometer, since the broad image made the phototube readings a few per cent. low.

Solutions were irradiated in cylindrical fused silica cells with plane polished windows (10 mm. internal length \times 40 mm. internal diameter). Two capillary extensions from opposite sides of the cell, one terminating in a $\frac{3}{20}$ male joint, aided in filling the cells. The cells were baked in air at 500° before each experiment to remove organic impurities. Although the light converged slightly in passing through the cell, it still almost completely filled the cell with a beam of nearly uniform intensity. In any case only the carbon dioxide yields in the presence of oxygen showed a small intensity dependence.

Formic acid (98–100%) (Matheson Co., Inc., East Rutherford, N. J.) was used as received, since the radiolysis behavior of aqueous solutions of the acid was unchanged by distillation through a 30-plate column. Hydrogen peroxide 90% (Buffalo Electrochemical Co.) was diluted as required. With a Beckman model DU spectrophotometer the hydrogen peroxide molar extinction coefficient was measured at 2537 Å. as 18.7 as compared to the literature value of 19.6.⁶ Triply distilled water⁴ was used in all solutions.

The techniques for oxygenating the solutions were similar to those employed by Hart,⁷ with the following modifications. After oxygenation the solution was transferred to a 100-ml. hypodermic syringe fitted with a stopcock and a female $\frac{3}{20}$ joint, so that the cells could be attached to the syringe and filled in turn. During filling, the other capillary of the cell was attached to an oxygen reservoir containing oxygen at the pressure used in oxygenating the solution. This procedure was found necessary to obtain adequate reproducibility of oxygen concentrations.

A Van Slyke blood gas analysis apparatus was used for analysis of CO_2 and O_2 . Because of decomposition of the formic acid-hydrogen peroxide solutions by the basic reagents used in the Van Slyke apparatus, the gas was collected in a tube after the initial equilibration and reintroduced into the Van Slyke apparatus after the chamber had been cleaned. Hydrogen peroxide concentrations were measured by Ghormley's method⁸ in which triiodide ion is

produced and its absorption at 3500 Å. measured. A factor of 38.4 instead of 40.0 was used to calculate hydrogen peroxide concentration from optical density.

Irradiations with Co^{60} γ -rays were carried out as described by Hart,⁴ and dosages measured using a value of 155 Fe^{++} oxidized per 100 e.v.⁹

All experiments were run at room temperature, which ranged from 23.5 to 26.5° for different runs. We consider the average temperature to be 25°.

Results and Discussion

It has been shown by Hart⁴ that the γ -ray induced decomposition of dilute aqueous solutions of hydrogen peroxide and formic acid is a chain reaction and that it is powerfully inhibited by oxygen. On the basis of his results it seemed probable that the chain reaction could also be initiated by light absorbed by the hydrogen peroxide, and that, if oxygen were added to inhibit the photochemical reaction, then the oxygen consumption could be used to measure the primary quantum yield of hydrogen peroxide dissociation. For 0.01 M formic acid in 0.5 mM sulfuric acid Hart found a maximum chain length of 28 at 0.74 mM H_2O_2 as the hydrogen peroxide concentration was varied. It seemed desirable to study the effect of oxygen at concentrations of hydrogen peroxide and formic acid which were known to give long chains. However, at 2537 Å. 0.74 mM hydrogen peroxide absorbs only 3.3% of the incident light in a 1-cm. path, so that the absorbed light is not easily measured precisely. For this reason the hydrogen peroxide and formic acid concentrations were each increased tenfold over those cited as giving the longest chains so that their ratio remained unchanged. The concentrations used in most of our work were ~ 7 mM H_2O_2 and 100 mM HCOOH in 0.001 N H_2SO_4 .

In the uninhibited reaction induced by γ -rays carbon dioxide and a much smaller amount of hydrogen are the only gaseous products. The hydrogen is a measure of the decomposition of water by ionizing radiation and is not found in our photochemical experiments. Carbon dioxide is however found in the photochemical reaction, and if oxygen is added the oxygen is consumed and the carbon dioxide production greatly reduced. In Table I are summarized a number of experiments in which the quantum yields of carbon dioxide production and oxygen consumption were measured. The principal variables studied were oxygen concentration and light intensity. The effects of hydrogen peroxide and formic acid concentrations have been previously studied⁴ for the γ -ray case, and a similar behavior should be expected photochemically. Further, a study of these variables was not considered necessary for the determination of the primary quantum yield of H_2O_2 .

It is evident from Table I that the quantum yield of oxygen consumption is essentially independent of the light intensity or oxygen concentration in the ranges studied. The principal experimental error in ϕ_{O} , probably arises in the filling of cells, since oxygen consumed is measured as the difference in oxygen concentration between the blank cells and the irradiated cell. Since the quantum yield of oxygen consumption was found to be independent

(5) G. S. Forbes and L. J. Heidt, *THIS JOURNAL*, **56**, 2363 (1934).

(6) W. C. Schumb, C. N. Satterfield and R. L. Wentworth, NP-5424 Hydrogen Peroxide Part II Chap. 5-6; Report #43. (Mass. Inst. Tech., 1953).

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

(8) C. J. Hochanadel, *ibid.*, **56**, 587 (1952), or ref. 4.

(9) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

TABLE I
QUANTUM YIELDS IN AQUEOUS HYDROGEN PEROXIDE, FORMIC ACID (100 mM) SULFURIC ACID (0.5 M), AND OXYGEN AT 25°

Expt. no.	Initial (O), mM	(H ₂ O ₂), mM	Av. I absorbed (moles/l. sec.) (× 10 ⁸)	Irrad. time, (sec.) (× 10 ⁻⁴)	$\left[\frac{(\text{H}_2\text{O}_2)}{\text{av. I abs.}} \right]^{1/2}$ (× 10 ⁻³)	Quantum yields ϕ_{CO_2}	ϕ_{O_2}
1	0.0301	7.17	1.299	0.138	7.43	2.67	0.38
2	.0283	7.12	1.648	0.180	6.57	2.30	.50
3	.0741	0.79 ^a	0.174	4.989	6.74	1.87	.35
4	.100	7.27	1.344	0.492	7.35	2.00	.46
5	.178	7.02	1.312	1.011	7.32	1.89	.46
6	.639	6.99	1.556	3.090	6.70	2.05	.40
7	.646	7.14	1.788	3.264	6.32	1.79	.58
8	1.014	7.35	1.329	4.662	7.44	1.68	.48
9	0.355	6.44	74.7 ^b	0.0300	0.929	1.04	.46
10	.391	6.78	11.51 ^b	0.204	2.43	1.43	.55
11	.395	6.86	1.106	2.124	7.89	2.16	.42
12	.413	7.10	1.276	1.929	7.46	2.19	.51
13	.583	6.92	0.435	11.50	12.62	2.24	.36
14	.364	6.61	0.121	20.18	23.37	3.86	.38
15	.390	6.82	0.128	23.19	23.10	3.73	.52
16	0	6.80	1.276	0.0860	7.30	39.0	..

0.465 ± 0.065
Av. of 4-15

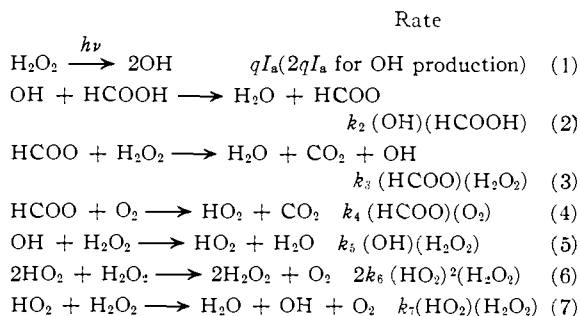
^a 10 mM HCOOH. ^b Measured with uranyl oxalate actinometer.

of oxygen concentration (and the quantum yield of carbon dioxide formation nearly so) it was possible to run the experiments to about 30% consumption of oxygen without affecting the rate, and this high fractional consumption of oxygen minimized this error in ϕ_{O_2} . However, even with the careful technique used the standard deviation in oxygen concentration for all blank cells for experiments 4-15 in Table I is 2.81%. A deviation of 2.81% in the original oxygen concentration of the irradiation cell from the average blank cell concentration would introduce an error of the order of 9-10% in ϕ_{O_2} for 30% oxygen reacting. It is also apparent that if oxygen concentration only is varied (expts. 1, 2, 4-8, and 11, 12) then ϕ_{CO_2} is not appreciably affected, except possibly at the very lowest oxygen concentration (30 micromolar in expts. 1 and 2). In experiments 9 to 15 where absorbed light intensity is varied the quantum yield of carbon dioxide production increases with decreasing intensity. However in experiment 3 where hydrogen peroxide and formic acid concentrations are also reduced, the effect of reduced light intensity on ϕ_{CO_2} seems to be cancelled.

In a typical experiment of Table I the fraction of incident 2537 Å. light absorbed was about 24%. About 87% of the absorbed light was absorbed by hydrogen peroxide, 8% by formic acid and 5% by the water. In the calculation of quantum yields the absorbed light was taken as the total absorbed by the hydrogen peroxide and the formic acid. Since Fricke and Hart¹⁰ conclude that the photochemical activity of water as determined by its action on methanol ceases above 2000 Å., this exclusion of the light absorbed in the water may be justified. Also the absence of H₂ in the products of the photochemical experiments indicates water is not being decomposed. For 1.0 M HCOOH plus 0.379 mM O₂ (no H₂O₂) the quantum yields of CO₂ production and O₂ consumption were both measured as 0.85 at 2537 Å. Assuming additivity of

oxygen consumption and using 0.85 for ϕ_{O_2} due to HCOOH absorption, then ϕ_{O_2} due to absorption by the peroxide is revised from 0.465 in Table I to 0.43. This small correction will be ignored in the subsequent discussion. If the fate of the radicals from the photoactivated HCOOH is similar to the fate of those from photoactivated H₂O₂, then the over-all kinetics will be unchanged by the small amount of initiation due to the HCOOH light absorption. In any case any deviations due to this source should be small.

The results of Table I are all consistent with the following mechanism



Steps (1), (5), (6) and (7) are the reactions involved in the photodecomposition of pure aqueous hydrogen peroxide using the termination step proposed by Hart and Matheson¹¹ to account for the rate dependence of the γ -ray initiated reaction on hydrogen peroxide concentration in the range 0.03-1.0 M. Hart has previously proposed (2) and (3) as the chain carrying steps in the aqueous H₂O₂-HCOOH radiolysis, attributed termination at higher H₂O₂ concentrations to step (5),⁴ and accounted for oxygen inhibition by step (4).⁷ Hart also considered a termination reaction of HCOO + impurity as operating at low peroxide concentrations. This step would be negligible for our con-

(10) H. Fricke and E. J. Hart, *J. Chem. Phys.*, **4**, 418 (1936).

(11) E. J. Hart and M. S. Matheson, *Disc. Faraday Soc.*, No. 12, 169 (1952).

centrations, assuming our materials are of equal purity to those used by Hart.

By the usual steady state assumptions the above mechanism yields the following expressions for the quantum yields of carbon dioxide formation and oxygen consumption

$$\phi_{\text{CO}_2} = \frac{\left[1 + \frac{k_3(\text{H}_2\text{O}_2)}{k_4(\text{O}_2)}\right] \left\{2q + \frac{k_7}{(2k_6)^{1/2}} \left[\frac{2q(\text{H}_2\text{O}_2)}{I_a}\right]^{1/2}\right\}}{1 + \left[1 + \frac{k_3(\text{H}_2\text{O}_2)}{k_4(\text{O}_2)}\right] \frac{k_5(\text{H}_2\text{O}_2)}{k_2(\text{HCOOH})}} \quad (8)$$

$$\phi_{\text{O}_2} = \frac{q - \left\{q + \frac{k_7}{(2k_6)^{1/2}} \left[\frac{2q(\text{H}_2\text{O}_2)}{I_a}\right]^{1/2}\right\} \left[1 + \frac{k_3(\text{H}_2\text{O}_2)}{k_4(\text{O}_2)}\right] \frac{k_5(\text{H}_2\text{O}_2)}{k_2(\text{HCOOH})}}{1 + \left[1 + \frac{k_3(\text{H}_2\text{O}_2)}{k_4(\text{O}_2)}\right] \frac{k_5(\text{H}_2\text{O}_2)}{k_2(\text{HCOOH})}} \quad (9)$$

From eq. 10 of ref. (4) we calculate k_5/k_2 is 0.138, therefore for $(\text{H}_2\text{O}_2)/(\text{HCOOH}) \cong 0.07$ as in our work, $k_5(\text{H}_2\text{O}_2)/k_2(\text{HCOOH})$ is $\ll 1.0$. Also, if one assumes that $k_3(\text{H}_2\text{O}_2)/k_4(\text{O}_2)$ is of the order of one or less, since both the quantum yields of Table I are nearly independent of oxygen concentration, then eq. 8 and 9 reduce to

$$\phi_{\text{CO}_2} = \left[1 + \frac{k_3(\text{H}_2\text{O}_2)}{k_4(\text{O}_2)}\right] \left\{2q + \frac{k_7}{(2k_6)^{1/2}} \left[\frac{2q(\text{H}_2\text{O}_2)}{I_a}\right]^{1/2}\right\} \quad (10)$$

$$\phi_{\text{O}_2} = q \quad (11)$$

Equation 10 is further reduced to eq. 12 if $k_3(\text{H}_2\text{O}_2)/k_4(\text{O}_2)$ is $\ll 1.0$ so that the quantum yield of carbon dioxide formation is largely independent of oxygen concentration as found in Table I.

$$\phi_{\text{CO}_2} = 2q + \frac{k_7}{(2k_6)^{1/2}} \left[\frac{2q(\text{H}_2\text{O}_2)}{I_a}\right]^{1/2} \quad (12)$$

Equation 11 is in agreement with our conclusion that the quantum yield of oxygen consumption is independent of the light intensity or initial oxygen concentration. Further, according to eq. 11 the quantum yield of oxygen consumption is equal to q , the quantum yield for the primary decomposition of aqueous hydrogen peroxide. Our value (the average of expts. 4 to 15) is 0.465 ± 0.065 in reasonable agreement with the 25° value of 0.49 ± 0.025 found by Hunt and Taube,^{3b} but not in agree-

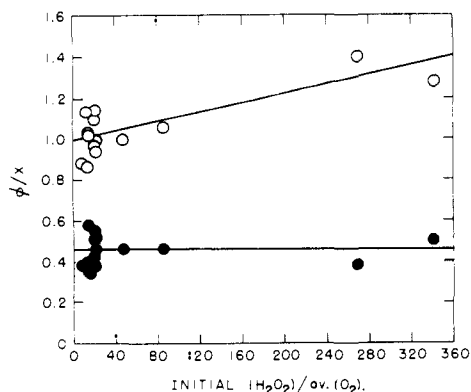


Fig. 1.—Quantum yields as a function of O_2 concentration: \circ , ϕ_{CO_2} ; $\{x = 2q + k_7/(2k_6)^{1/2} [2q(\text{H}_2\text{O}_2)/I_a]^{1/2}\}$; \bullet , ϕ_{O_2} ; $\{x = 1\}$.

ment with the value of 1.0 used by Dainton and Rowbottom.²

The carbon dioxide quantum yields of Table I were treated by a method of successive approximations. First, ϕ_{CO_2} for experiments 4 to 15 was plotted against $[(\text{H}_2\text{O}_2)/I_a]^{1/2}$. For these experiments the effect of oxygen appears to be small, so that eq. 12 is valid and the plot should give a straight line. Within experimental error the points over the 600-fold range of intensities do fit a straight line which is arbitrarily passed through the intercept $2q = 2\phi_{\text{O}_2}(\text{av.}) = 0.93$. The slope by least squares is 1.32×10^{-3} using moles, liters, and seconds. Next, eq. 10 was assumed and

$$\phi_{\text{CO}_2} / \left\{2q + \frac{k_7}{(2k_6)^{1/2}} \left[\frac{2q(\text{H}_2\text{O}_2)}{I_a}\right]^{1/2}\right\}$$

was plotted against $(\text{H}_2\text{O}_2)/(\text{O}_2)$ as shown in Fig. 1, using the above slope and intercept to evaluate the term in brackets. The intercept was set at 1.0 as required by eq. 10, and a straight line drawn to fit the two points at lowest oxygen concentration. The slope, k_3/k_4 , is 1.11×10^{-3} , showing how much more reactive the formate radical is toward O_2 than toward H_2O_2 . Because of this inhibitor efficiency, very low oxygen concentrations are required to measure k_3/k_4 with consequent uncertainties in the value measured. We believed $k_3/k_4 = 0.0011 \pm 0.0005$ expresses a fair estimate of the uncertainty.

As a further step the values of $q = 0.465$, $k_3/k_4 = 1.11 \times 10^{-3}$, $k_7(2q/2k_6)^{1/2} = 1.32 \times 10^{-3}$, (obtained above) and $k_2/k_5 = 5.42$ (calculated later) were put into eq. 9 to calculate a small correction to q . The revised average value is $q = 0.49$ in better agreement with Hunt and Taube. Finally, eq. 10 was again assumed and $\phi_{\text{CO}_2}/[1 + k_3(\text{H}_2\text{O}_2)/k_4(\text{O}_2)]$ plotted against $[(\text{H}_2\text{O}_2)/I_a]^{1/2}$ using k_3/k_4 as given above. In this plot (Fig. 2) all experiments now fit a straight line within experimental error. The slope of the line then is given by $(0.98)^{1/2} k_7/(2k_6)^{1/2}$ where k_7 and $2k_6$ are, respectively, the prop-

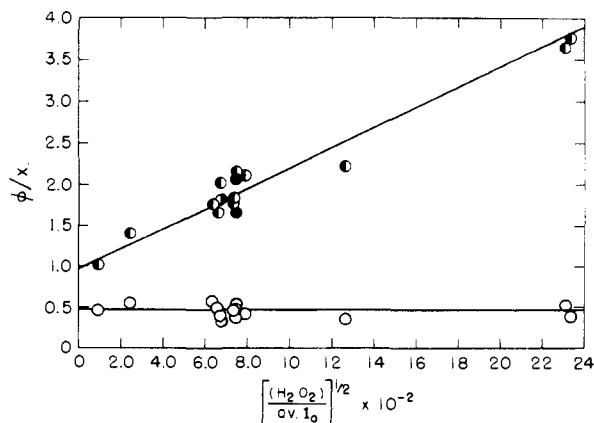


Fig. 2.—The quantum yields of carbon dioxide production and oxygen consumption as a function of light intensity

\bullet = expt. 1 and 2, Table I }
 \circ = expt. 3 }
 \bullet = other }
 \circ = ϕ_{O_2} ; $\{x = 1\}$. }
 $\phi_{\text{CO}_2} / \left[1 + \frac{k_3(\text{H}_2\text{O}_2)}{k_4(\text{O}_2)}\right]$

TABLE II

CO₂ AND (-ΔO₂) YIELDS IN AQUEOUS HYDROGEN PEROXIDE, FORMIC ACID (100 mM), SULFURIC ACID (0.5 mM) AND OXYGEN

Expt. no.	Initial (O ₂), mM	Initial (H ₂ O ₂), mM	E. v./cc. sec. abs. (× 10 ⁻¹⁴)	Total e. v. absorbed (× 10 ⁻¹⁹)	H ₂ /100 e. v.	CO ₂ /100 e. v.		(G _H + G _{OH})/2, Obsd.
						Estd.	Obsd.	
82	0.383	7.12	0.833	3.40	0.77	10.23 ^a	10.11	2.65 ^b
83	0.385	7.21	36.5	3.08	0.77	4.46 ^a	5.21	3.33 ^b
81	0	7.11	0.833	0.129	5.02	247.8	3.21 ^c

^a From eq. 15. ^b From eq. 16. G_{O₂} = (G_H + G_{OH})/2. ^c From expt. 16 in eq. 17 and expt. 81 in eq. 18.

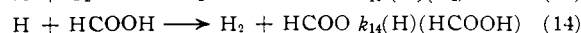
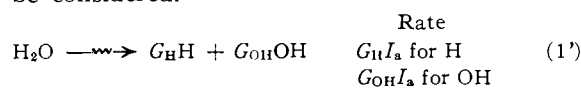
agation and termination constants for the free radical chain decomposition of pure aqueous hydrogen peroxide. From the line of Fig. 2, $k_7/(2k_6)^{1/2}$ is 1.21×10^{-3} sec.^{-1/2} which may be compared with 2.31×10^{-3} obtained by Hart and Matheson¹¹ in the radiolysis of pure aqueous hydrogen peroxide. Considering the degree of reproducibility of rates of decomposition obtainable with pure H₂O₂ solutions the agreement is acceptable.

Replacing step (6) by (6')



would not affect eq. 11 and therefore would not affect the calculated primary quantum yield. Equation 10 would be modified by replacing (H₂O₂)^{1/2} in the second bracket by (H₂O₂). As most of our experiments were run at the same peroxide concentration, φ_{CO₂} would generally plot linearly against either [(H₂O₂)/I_a]^{1/2} or (H₂O₂)/I_a^{1/2} with the exception of expt. 3 at one-tenth the usual peroxide concentration. This φ_{CO₂} would be far away from the line of the other experiments for a plot against (H₂O₂)/I_a^{1/2}. This result indicates termination by step (6) is correct.

γ-Ray Induced Experiments.—If the chain reaction of HCOOH + H₂O₂ is initiated by γ-rays reaction (1) of the photochemical mechanism is replaced by (1') and the additional steps (13) and (14) must be considered.



Since for our conditions $k_{13}/k_{14} \approx 1500$ from ref. (12), at our oxygen concentrations step (14) must be considered. We can assume as before that reactions (3) and (5) may be neglected for high oxygen and formic acid concentrations. With these assumptions we obtain for the inhibited reaction

$$G_{\text{CO}_2} = G_{\text{OH}} + G_{\text{H}} \left[\frac{1}{1 + \frac{k_{13}(\text{O}_2)}{k_{14}(\text{HCOOH})}} \right] + \frac{k_7}{(2k_6)^{1/2}} \left[\frac{(G_{\text{H}} + G_{\text{OH}})(\text{H}_2\text{O}_2)}{I_a} \right]^{1/2} \quad (15)$$

and

$$G_{\text{O}_2} = \frac{G_{\text{H}} + G_{\text{OH}}}{2} \quad (16)$$

where the G's are molecules per 100 e. v. and I_a is absorbed intensity in 100 e. v. units.

In Table II a few experiments with γ-ray initiation are summarized. The peroxide and formic acid concentrations were similar to those used in the majority of the photochemical experiments.

Experiments 82 and 81 were run with a γ-ray intensity expected to give a rate of initiation approximately equal to that used in most of the photochemical experiments, while expt. 83 was run at the highest intensity available in order to get as low a yield of CO₂ per 100 e. v. as possible. We consider first only expts. 82 and 83 with added oxygen. In the last column the radical pair yields/100 e. v., that is (G_H + G_{OH})/2, are given as estimated from oxygen consumption by eq. 16. These may be compared with (G_H + G_{OH})/2 = 3.08, when G_H = 3.19 H/100 e. v. and G_{OH} = 2.96 OH/100 e. v.¹³ at our measured pH of 3.

Equation 15 is similar in form to the corresponding eq. 12 for the photochemical case. However, the limiting yield of G_{CO₂} at infinite intensity is not much greater than G_{O₂} and is calculated to be 3.37 from eq. 15. This result follows, since in the limit of no chain reaction the OH's but not the H's cause CO₂ formation. In expt. 83 at the higher intensity the CO₂ yield is definitely less than twice the O₂ yield. In the 7th and 8th columns of Table II the estimated and observed yields of CO₂ molecules per 100 e. v. are given. The estimated values were obtained from eq. 15 using G_H and G_{OH} as given above from ref. (13) and $k_7/(2k_6)^{1/2}$ from the slope of the line in Fig. 2.

The H₂ yields in Table II were calculated from the very small net amounts of inert gas in the irradiation cells and are quite approximate. From eq. 11' ref. (12) G_{H₂} of 0.85 would be expected for expts. 82 and 83.

Experiments without Added Oxygen.—In the absence of added oxygen, no oxygen in the photolysis of aqueous HCOOH + H₂O₂ can be detected. One may thus make the additional assumption of a steady state for oxygen. The mechanism then gives

$$\phi_{\text{CO}_2} = q \frac{k_2(\text{HCOOH})}{k_3(\text{H}_2\text{O}_2)} \quad (17)$$

For the γ-radiolysis if one assumes all H's react with HCOOH so that reaction (14) occurs but not reaction (13), then eq. 18 is obtained

$$G_{\text{CO}_2} = G_{\text{H}} + \frac{(G_{\text{H}} + G_{\text{OH}})}{2} \frac{k_2(\text{HCOOH})}{k_3(\text{H}_2\text{O}_2)} \quad (18)$$

From ref. (12) $[k_{13}(\text{O}_2)/k_{14}(\text{HCOOH})] = \sim 1.5 \times 10^{-2}$ for 0.1 M HCOOH and for oxygen concentrations 10⁻⁶ molar (our limit of detection for oxygen).

By comparing the experiments without added inhibitor (expt. 16 Table I with expt. 81 Table II), one can follow the essential procedure of Dainton and Rowbottom to determine the radical pair yield. In this procedure one finds the intensity of absorbed ionizing radiation necessary to give the same

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

(13) E. J. Hart, *ibid.*, **76**, 4198 (1951).

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 Rowbottom² 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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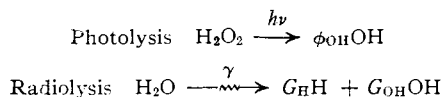
The Primary Quantum Yield in the Photolysis of Hydrogen Peroxide at 3130 Å. and the Primary Radical Yield in the X- and γ -Radiolysis of Water

BY F. S. DAINTON

RECEIVED JANUARY 13, 1956

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 author¹ 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



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 method² 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 evidence⁵ 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 paper⁶ 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 work¹.

Collinson, Dainton and McNaughton⁷ have

(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.

(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).