The Catalytic Decomposition of Hydrogen Peroxide in a Bromine–Bromide Solution. Effect of Light on the Steady-state Rate

BY ROBERT LIVINGSTON AND E. A. SCHOELD

That exposure to diffuse daylight produces a pronounced decrease in the steady-state concentration of bromine in a hydrogen peroxide–bromine–bromide mixture was remarked in 1923 by Bray and Livingston.[1] On the basis of the mechanism which they adopted for the catalytic decomposition of hydrogen peroxide occurring in these solutions, they predicted that the irradiation of the reaction mixtures with light of constant intensity would not affect the steady-state rate of the decomposition. However, this prediction was not tested experimentally.

More recently[2] it has been suggested that the decomposition of hydrogen peroxide may be a chain reaction in acid as well as in basic solutions. In so far as the halogen–halide catalyzed reactions are concerned, this suggestion appears to be based entirely upon analogy, and is in contradiction to several experimental observations of these reactions.[3]

The measurements presented here substantially check the predictions of Bray and Livingston,[1] and afford definite evidence that the bromine sensitized photochemical decomposition of hydrogen peroxide is not a chain reaction.

Experimental Methods.—The analytical methods for the determination of hydrogen peroxide and bromine in the reacting mixtures were similar to those of Bray and Livingston.[1] The "dark reaction" mixture was kept in a black-coated flask, which was immersed in a large water thermostat, maintained at 35°.[4] The "light-reaction" vessel was a short Pyrex cylinder, with sealed on plane ends. It was provided with a water-sealed glass stirrer, to prevent the development of concentra-

tion gradients due to the photochemical action. The oxygen, evolved during the reaction, escaped through the water seal of the stirrer. This reaction vessel and a similar vessel, which was kept filled with distilled water, were sealed into a flat metal box, which was provided with openings into which the ends of the cylinders fitted. Water from the large thermostat was circulated through this box. Although the ends of the reaction vessel were not jacketed, tests showed that the temperature of the reaction mixture was not more than 0.1° below that of the large thermostat.

In beginning an experiment, a volume of reaction mixture was prepared from stock solutions of hydrogen peroxide and hydrogen bromide, sufficient to fill both the "dark" and "light-reaction" vessels. Both vessels were filled, and the cylindrical cell was irradiated with light of constant intensity. After sufficient time (about three hours) was allowed for steady-state conditions to be attained, samples were removed from each of the reaction mixtures and were analyzed for hydrogen peroxide. After a measured lapse of time, of from one to four hours, samples were again removed from each of the vessels and were analyzed both for peroxide and for bromine.

These measurements made possible the computation of the first order rate constant k of equation 1

$$-d(H_2O_2)/dt = k(H_2O_2) \qquad (1)$$

and the termolecular catalytic rate constant, K of equation 2

$$-d(H_2O_2)/dt = K(H_2O_2)(H^+)(Br^-) \qquad (2)$$

In the computation of K, correction was made for tribromide formation[1] (p. 1262). However, no correction was made for the kinetic salt effect,[5] since in these experiments we were interested primarily in the comparison of the "light" and "dark" rates of initially identical solutions.

The light source used in these experiments was a 500-watt "stereopticon" tungsten-filament lamp provided with a system of condensing lenses and a Corning heat-absorbing neutral-green filter. The light intensity was measured with a galvanometer–surface thermopile system, which was

(1) Bray and Livingston, THIS JOURNAL, **45**, 1264 (1923).

(2) See for example, Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Univ. Press, New York, 1933, p. 211.

(3) If these processes were chain reactions it should be expected that they would be sensitive to the presence of inhibitors, including those substances which are commonly used as hydrogen peroxide preservatives. That this is not the case for the iodine–iodide catalysis was shown by Bohnson, J. Phys. Chem., **25**, 19 (1925); for the bromine–bromide catalysis by Bray and Livingston, reference 1, p. 1260; and for the chlorine–chloride catalysis by Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925).

(4) A lower temperature would have been preferable, but would have required somewhat more elaborate equipment, since these experiments were performed during the summer months, when the average temperature of both air and cooling water was above 25° and the relative humidity was high.

(5) See Livingston, THIS JOURNAL, **48**, 53 (1926).

TABLE I
SUMMARY OF MEASUREMENTS AND COMPUTATIONS

Expt.	Initial concn. $(HBr)_0$	Dark reaction $(H_2O_2)_0$	$\Sigma(Br_2)$	$k_d \times 10^3$	$K_d \times 10^2$	R_d	Light reaction $(H_2O_2)_0$	$\Sigma(Br_2)$	$k_1 \times 10^3$	$K_1 \times 10^2$	R_1	$I_{abs.}$	M/Q	k_1/k_d	K_1/K_d	$\dfrac{(Br_2)_d}{(Br_2)_l}$
1	0.330	0.1517	0.0174	5.71	6.90	0.42	0.1675	0.0172	5.68	6.83	0.41	0	..	0.99	0.99	1.01
2	.165	.1206	.0008	1.90	7.15	.03	.1272	.0005	1.95	7.26	.02	8.7	0.68	1.02	1.01	1.60
3	.322	.0601	.0165	5.59	7.02	.44	.0537	.0154	5.61	6.91	.42	15.1	.08	1.00	0.98	1.07
4	.248	.0829	.0063	3.62	6.70	.42	.0921	.0051	3.69	6.66	.28	17.7	.34	1.02	.99	1.24
5	.320	.1020	.0167	6.02	7.70	.47	.1244	.0158	6.12	7.71	.43	25.3	.50	1.02	1.00	1.06
6	.320	.1112	.0157	5.49	6.90	.43	.1216	.0136	5.77	7.00	.34	25.9	.91	1.05	1.01	1.15
7	.248	.1000	.0061	3.62	6.68	.37	.0981	.0046	3.77	6.74	.30	27.0	.48	1.04	1.01	1.32
8	.320	.1287	.0163	6.16	7.83	.45	.1459	.0151	6.23	7.75	.43	30.0	.34	1.01	0.99	1.08
9	.322	.0265	.0176	5.04	6.45	.49	.0243	.0155	5.17	6.35	.45	32.4	.08	1.03	.98	1.14
10	.248	.0832	.0066	3.92	7.29	.46	.0881	.0044	4.03	7.18	.29	32.9	.26	1.03	.99	1.50
11	.330	.0734	.0167	5.72	6.82	.43	.0781	.0147	5.88	6.78	.33	35.0	.33	1.03	.99	1.14
12	.280	.0869	.0115	4.92	7.70	.52	.0988	.0096	4.90	7.45	.41	38.6	.04	1.00	.97	1.20
13	.330	.1582	.0187	6.05	7.46	.48	.1714	.0157	6.25	7.33	.36	39.2	.70	1.03	.98	1.19
14	.332	.1210	.0160	5.79	7.22	.40	.1314	.0135	6.39	7.63	.33	74.7	1.28	1.10	1.05	1.18
15	.332	.1019	.0171	5.72	6.94	.45	.0910	.0154	6.19	7.63	.44	114.2	0.40	1.10	1.09	1.11
16	.322	.1005	.0158	5.78	7.18	.43	.1110	.0137	6.20	7.43	.33	129.7	.34	1.07	1.04	1.15

calibrated against a U. S. Bureau of Standards standard lamp, in the usual manner. The water jacket, which surrounded both the "light reaction" cell and the similar vessel filled with water, was so arranged that it could be slid along a track to place either cell in the path of the beam of light. The intensity of the light absorbed by the reaction mixture was obtained by comparing the energy transmitted through the two cells, taking into account the difference in transmission of the cells when they were both filled with water, and the effect of the second window of the reaction cell.

Measurements and Computations.—The results of the experiments are summarized in Table I. All concentrations are expressed as moles per liter. In computing the rate constants, k and K, natural logarithms were used and time was expressed in minutes. The symbol $\Sigma(Br_2)$ represents the molar concentration of the total titratable bromine, expressed as Br_2. R is the steady-state function[1], and is defined by the equation $R = (Br_2)/(H^+)^2(Br^-)^2$. $I_{abs.}$ is the intensity of the light absorbed expressed in deflection of the galvanometer in centimeters.

The last three columns compare the results of corresponding measurements in the dark and in the light. Experiment 1 was a "blank," in that the light reaction cell was not illuminated.

In thirteen of the fifteen experiments performed the first order reaction constant, k, was greater for the "light reaction" than for the "dark;" in no case was it less. However, it is noteworthy that this increase in k is about six-fold less than the corresponding change (which is in the oppo-

site direction) in the steady-state concentration of the bromine. The values of the third order rate constant, K, do not exhibit any consistent effect of light. The average value of K_1/K_d is 1.005 ± 0.008, where the error is the average error of the averaged value.[6] These results may be taken as evidence that the only effect of visible light on this system is to increase the specific reaction rate of the reduction of bromine by hydrogen peroxide. To a first approximation equation 2 represents the rate of the light reaction as well as the dark reaction, the increase in the absolute rate being completely accounted for by the increase in the steady-state concentration of the hydrobromic acid.

The quantum yield, M/Q, was computed with the aid of the following assumptions. The average wave length of the absorbed light was assumed to be 5300 Å. This value was chosen upon the basis of a qualitative consideration of the energy distribution of the light from a tungsten filament and of the absorption curve for bromine. Although the average wave length of the absorbed light is undoubtedly a function of the concentration of bromine, it is quite probable that the present assumption does not introduce an error of more than 20%. The rate of the purely photochemical reaction was assumed to be equal to $(k_1 - k_d)(H_2O_2)$. The quantum yield was computed by means of the expression

$$(k_1 - k_d)(H_2O_2) \, VNh\nu/S \cdot I_{abs.}$$

Where (H_2O_2) is the average concentration of hy-

(6) The corresponding average of k_1/k_d is 1.037 ± 0.006. This value is given only for purposes of comparison, since the ratio k_1/k_d is undoubtedly a function of the intensity of the absorbed light.

drogen peroxide during an experiment, V is the volume of the "light reaction" vessel, N is Avogadro's number, $I_{abs.}$ is the average intensity of the absorbed light expressed as galvanometer deflection in centimeters, $h\nu$ is the energy of a photon of λ 5300 Å., and S is the sensitivity of the galvanometer thermopile system in ergs per minute per cm. deflection. This expression will give the true value of the quantum yield only if it is directly proportional to the concentration of the hydrogen peroxide.[7] However, if the quantum yield were independent of the concentration of hydrogen peroxide, the error introduced by the use of this approximate relation would be less than the average error of the experimental determination of the quantum yield. The average value of the quantum yield (so computed) is 0.4.[8] It is noteworthy that this value is less than unity, and

(7) Even for this case the method is an approximate one, since $k_d(H_2O_2)$ does not properly represent the rate of the thermal reaction which is taking place in the illuminated solution. Although this quantity may be readily corrected for the differences in the steady-state concentrations of H⁺, Br⁻ and Br₂ in the "light" and "dark" reacting mixtures, the corrected values of the quantum yield do not differ greatly from the approximate values given in Table I. Therefore, for the sake of simplicity and brevity only the approximate method is presented here.

(8) The value of M/Q for experiment 14 appears to be out of the range of the random distribution of errors and has been excluded from the average.

is therefore not in agreement with any chain mechanism of the reaction. More exact measurements of the effect of light on the steady-state rate and function (preferably at a lower temperature and at lower concentrations of peroxide) must be available before a detailed discussion of the mechanism of the photochemical process will be justifiable.

Summary

1. The steady-rate of the decomposition of hydrogen peroxide in bromine–bromide solutions has been measured in the dark and in the light, under otherwise comparable conditions. Although light increases the absolute rate of the reaction, within the limits of experimental error the rate for either the dark or light reaction may be represented by the equation $V = K(H_2O_2)(H^+)(Br^-)$. The increase in the absolute rate is satisfactorily accounted for by the increase in the steady-state concentration of hydrobromic acid.

2. The quantum yield for the bromo sensitized decomposition of hydrogen peroxide has been computed (with the aid of certain simplifying assumptions), and has been shown to have an average value less than unity.

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The Action of Magnesium on Homonuclear Dibromodiphenyls

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The study of the action of magnesium on homonuclear dibromo aromatic hydrocarbons has thus far been confined to the compounds m- and p-dibromobenzene,[1] 3,4-dibromotoluene, sym-tribromotoluene, 1,3-dimethyl-4,6-dibromobenzene,[2] and 1,2 and 1,4-dibromonaphthalenes.[3] In the case of p-dibromobenzene, which has been rather extensively investigated, it was first believed that in the presence of two atoms of magnesium[4] only one atom of bromine is capable of reacting. Later investigations, however, showed that in an inert atmosphere a part of the second atom[5] of magnesium will react to form a di-Grignard, but this re-

(1) Salkind and Rogovina, J. Russ. Phys.-Chem. Soc., 59, 1013 (1927).
(2) Salkind, J. Gen. Chem. (U. S. S. R.), 1, 193 (1931).
(3) Salkind, Ber., 67, 1031 (1934).
(4) Pink, J. Chem. Soc., 123, 3418 (1923).
(5) (a) Quelet, Bull. soc. chim., 41, 933 (1927); (b) Gilman, Beaber and Jones, Rec. trav. chim., 48, 597 (1929).

action never reaches completion. Thus it has been found that with both p- and m-dibromobenzene, 87% of the original two atoms of magnesium enters the reaction; 3,4-dibromotoluene, 83%; 1,3-dimethyl-4,6-dibromobenzene, 49.6% of the total bromine; sym-tribromotoluene, no reaction; 1,4-dibromonaphthalene, 72% magnesium; 1,2-dibromonaphthalene, 75.5% magnesium. It is worthy of note that in the few cases where unsymmetrical dibromides have been investigated, in only one instance (1,2-dibromonaphthalene) have results been obtained that would indicate which of the bromine atoms is more readily attacked by the magnesium.

The object of the present investigation has been to determine the extent to which certain homonuclear dibromodiphenyls react with two atoms of magnesium, and in the case of unsymmetrical de-