concentration is high. The fates of the heptyl radicals must be diverse, possibly leading to various ketones and aldehydes with seven carbon atoms or less followed by hydrogen abstraction by RO. The presence of unsaturation in the products indicates loss of a second hydrogen by heptyl radicals and also a splitting of these radicals with the formation of short alkyl radicals. This type of reaction does not occur appreciably in the gas phase at room temperature but may be aided in solution by the longer possible interval between formation of a heptyl radical and collision with another radical or with oxygen.

It is not useful to speculate further on the mechanism of these reactions in the liquid phase. The results are exploratory and qualitative, and some doubt exists as to whether this type of experimentation can lead to quantitative interpretations in the reaction kinetic sense.

Rochester, New York

Photochemical Synthesis of Hydrogen Peroxide at Zinc Oxide Surfaces[1]

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A quantitative study is made of the heterogeneous reaction leading to hydrogen peroxide formation at light activated zinc oxide surfaces in contact with oxygen, and pure water or water solutions of various organic additives (e.g., sodium oxalate, sodium formate, etc.). The rates and quantum yields of peroxide formation are determined over a range of oxygen pressures, flow rates, times of gas saturation, amounts of zinc oxide in the suspension, additive types and concentrations, times of exposure, and intensities and wave lengths of the light. The ratios of reactants and products of the zinc oxide–water–oxygen–sodium oxalate system are determined. From the results the following conclusions are made: (1) The often proposed over-all reaction for the irradiated zinc oxide–pure water–oxygen system, $2H_2O + O_2 \rightarrow 2H_2O_2$ (I) occurs only to a very limited extent, if at all. (2) The presence of an additive increases the peroxide formation, but reaction I is not important. The over-all reaction in the system containing sodium oxalate additive is shown to be: $O_2 + 2H_2O + C_2O_4^- \rightarrow H_2O_2 + 2HCO_3^-$. It is shown that the product hydrogen peroxide is decomposed under certain conditions. In general in the additive-containing system the light-activated zinc oxide catalyzes the occurrence of a normally exothermic reaction.

A number of chemical reactions are promoted in systems containing irradiated zinc oxide. For example, zinc oxide in contact with silver oxide gives silver and oxygen among other products.[2a-d] Also previous investigations have shown that hydrogen peroxide is formed at light-activated zinc oxide surfaces in contact with oxygen, water and miscellaneous compounds.[3a-c] Although no detailed quantitative studies of this heterogeneous reaction have been made, the often proposed over-all reaction[4] of peroxide formation is

$$2H_2O + O_2 \longrightarrow 2H_2O_2. \qquad (1)$$
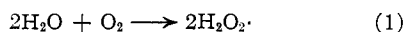
Since reaction (1) involves a large increase in free energy ($\Delta F^\circ_{298} = 25$ kcal./mole H_2O_2) the zinc oxide–water–oxygen system is attractive as a possible converter of light energy to chemical energy. The light absorption region of zinc oxide limits the effective wave lengths for peroxide formation to those less than about 4000 Å. (see Fig. 1). About 4% of the total sun's energy incident at the earth's surface can be effective in promoting this reaction.

With these facts in mind a detailed quantitative study of the zinc oxide system has been made. A report of the results of this investigation is presented here.

In photochemical experiments using only zinc oxide, water and oxygen it was observed that the quantum yield of peroxide formation decreases rapidly to zero as the peroxide concentration increases to about 1×10^{-5} M. However, added peroxide above this concentration is decreased only very slowly when the oxygen-saturated system is irradiated by light absorbed by the zinc oxide. As a result of trace impurities in the zinc oxide there is a good possibility that reactions other than (1) account for the very small yields of peroxide (see reaction (2) reported in the following discussion). Even if reaction (1) does describe the over-all change in the zinc oxide–water–oxygen system, such low yields of hydrogen peroxide make the system unattractive from the standpoint of energy conversion.

It has been shown that the presence of a small concentration of one of many water-soluble, easily oxidized, organic compounds (often called "stabilizers" or "promoters" and hereafter called "additives") such as sodium formate, potassium oxalate, phenol, etc., in the zinc oxide–water–oxygen mixture increases the rate of peroxide formation greatly.[5] The rate of formation is practically independent of the peroxide concentration up to about 1×10^{-3} M and is only slightly decreased at higher peroxide concentrations. The effect of the concentration of formate and oxalate salts on the quantum yield of peroxide, $\Phi_{H_2O_2}$, is seen in the data of Ta-

(1) This work was supported in part by a contract between the Charles F. Kettering Foundation and The Ohio State University Research Foundation. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(2) (a) V. Kohlschütter and A. d'Almendra, Ber., 54B, 1961 (1921); (b) E. Baur and A. Perret, Helv. Chim. Acta, 7, 910 (1924); (c) A. Perret, J. chim. phys., 23, 97 (1926); (d) A. Goetz and E. C. Y. Iun, Rev. Modern Phys., 20, 131 (1948).

(3) For examples of the numerous studies see: (a) C. Winther, Z. Wiss. Phot., 21, 141, 168, 175 (1921); (b) C. F. Goodeve, Trans. Faraday Soc., 33, 340 (1937); (c) G. Winter, Nature, 163, 326 (1949).

(4) For example see: (a) G. K. Rollefson and M. Burton, "Photochemistry and the Mechanisms of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1946, p. 386; (b) E. I. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 72.

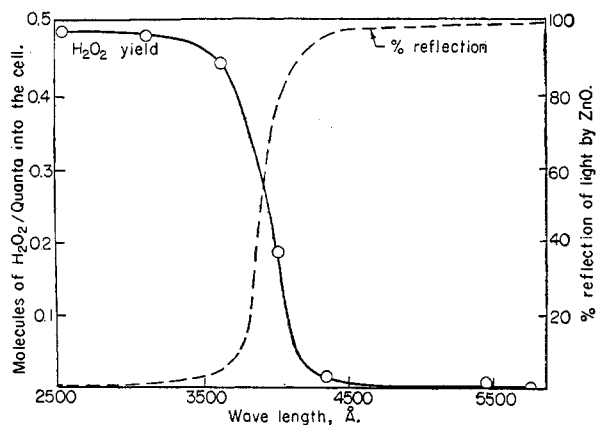(5) C. N. Chari and M. Qureshi, J. Indian Chem. Soc., 21, 97, 297 (1944).

Fig. 1.—Hydrogen peroxide formation and the reflectance of zinc oxide as a function of wave length: additive, $NaCO_2H$ 0.29 M; O_2 flow rate, 15 ml./min.; ZnO, 0.2 g./25 ml. of solution; reflectance data of J. I. Watters and co-workers of this Laboratory using moist ZnO in air.

Fig. 2.—Effect of oxygen pressure on rate of peroxide formation: additive, 0.2 M $NaCO_2H$; O_2 flow rate, 100 ml./min.; 0.2 g. ZnO/20 ml. of solution; intensity approximately constant; wave length of absorbed light, about 3000–4000 Å.

ble I. In view of the great efficiency of peroxide formation in the systems containing additive, a detailed study of the over-all reaction in this system was made. The preliminary results point to the following

TABLE I

QUANTUM YIELD OF PEROXIDE FORMATION IN $ZnO-H_2O-O_2$-ADDITIVE MIXTURES IN 3130 Å. RADIATION

Additive concn., M	Quanta into cell/sec. × 10^{-16}	$\Phi_{H_2O_2}$
(a)	Additive is $NaCO_2CH$	
0.50	1.3	0.51
.50	1.3	.50
.10	1.3	.48
.10	1.3	.46
.01	1.3	.37
.60	3.7	.48
.60	0.75	.52
.60	.52	.52
.30	.11	.48
(b)	Additive is $K_2C_2O_4$	
0.10	1.3	0.20
.01	1.3	.18
.001	1.3	.14

conclusions. (a) In the systems containing additive, zinc oxide is a photosensitizer for peroxide formation as Goodeve concluded.[3b] This is evidenced by the facts that hydrogen peroxide is formed only in the region of light absorption by zinc oxide (see Fig. 1), and no apparent net change in the zinc oxide results since a given sample of zinc oxide may be used repeatedly without change in the quantum efficiency of peroxide formation. (b) The presence of oxygen in the system is necessary for peroxide formation. The effect of oxygen pressure on the rate of peroxide formation is seen in Fig. 2. Baur and Neuweiler[6] came to the same conclusion, but Yamahuzi, Nisioeda and Imagawa claimed that oxygen is not always necessary.[7] (c) The so-called "stabilizers" for hydrogen peroxide formation (sodium formate, etc.) do not act in the sense implied by this

(6) E. Baur and G. Neuweiler, *Helv. Chim. Acta*, **10**, 901 (1927).

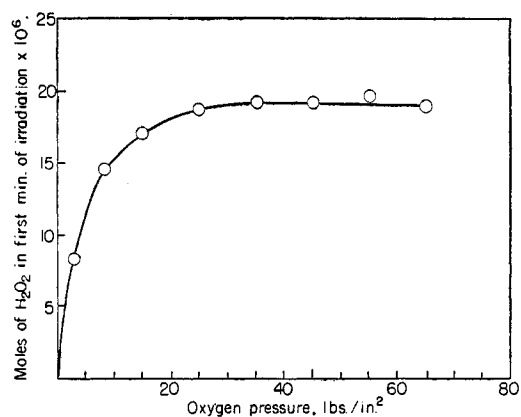(7) K. Yamahuzi, M. Nisioeda and H. Imagawa, *Biochem. Z.*, **301**, 404 (1939).

designation. Although the rate of peroxide formation is increased greatly when those compounds are present in the irradiated system, peroxide decomposition is also very rapid in zinc oxide–water–additive mixtures in which the oxygen supply is low. (d) The so-called "stabilizers" are actually reactants and undergo oxidation simultaneous with the peroxide formation as suggested by Baur and Neuweiler. Experiments have shown that oxalate and formate ions are oxidized to carbonate; phenol is oxidized in part to catechol. The quantitative relationships between the reactants and products are summarized in Table II for the system containing potassium oxalate additive. The results are consistent with the occurrence of the over-all reactions (2) and (3).

$$2H_2O + O_2 + C_2O_4^{--} \longrightarrow H_2O_2 + 2HCO_3^- \quad (2)$$
$$2H_2O_2 \longrightarrow O_2 + 2H_2O \quad (3)$$
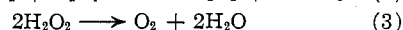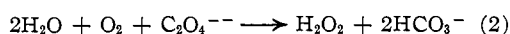
Assuming these reactions occur simultaneously, the values of the mole ratios of oxygen uptake to peroxide found and of oxalate used to peroxide

TABLE II

RATIOS OF REACTANTS AND PRODUCTS IN IRRADIATED MIXTURES OF $ZnO-H_2O-O_2-K_2C_2O_4$

| Irradiation time, min. | Molecular ratios | | |
	$\dfrac{O_2 \text{ used}}{H_2O_2 \text{ found}}$	$\dfrac{O_2 \text{ used}}{\text{Oxalate used}}$	$\dfrac{\text{Oxalate used}}{H_2O_2 \text{ found}}$
(a)	0.002 M $K_2C_2O_4$ solution		
2	1.30	1.25	1.03
4	1.56	1.29	1.21
	1.50	1.13	1.33
6	1.57	1.04	1.51
	1.54	0.95	1.63
16	2.37	.82	2.88
	2.36	.74	3.18
(b)	0.02 M $K_2C_2O_4$ solution		
0.5	1.30	1.22	1.07
2	1.33	1.09	1.22
	1.25	0.96	1.30
5	1.27	.99	1.28
	1.24	.99	1.25
36	2.65	.65	4.06
	1.81	.69	2.64

found must lie between 1 and ∞, while the values of the ratio of oxygen uptake to oxalate used must be in the range 0.5–1.0. The qualitative agreement of these values with the experimental results in Table II is in accord with the occurrence of (2) and (3). The data of Table II were obtained by intense irradiation of mixtures in a Warburg apparatus under experimental conditions preventing rapid and continuous replenishment of the oxygen reactant in the zinc oxide suspension. As indicated in conclusion (c), hydrogen peroxide is decomposed rapidly in the irradiated zinc oxide–water–additive system when oxygen is in short supply in the mixture, and consequently decomposition of peroxide (presumably given by the over-all reaction (3)) was important. This interpretation is substantiated by the results of one experiment in which the reaction mixture was continually saturated with oxygen, as was the case in the quantum yield and oxygen pressure studies; in this case the ratio of peroxide formed to oxalate lost was unity within the experimental error ($\pm 10\%$). The effect of irradiation time on the ratios given in Table II is consistent with this interpretation. Added proof for reaction (2) was obtained in a single experiment in which the mole ratio of carbonate formed to oxalate used was 1.8 ± 0.2. This ratio is consistent with the expected value of 2.0. (e) A slow but definite thermal reaction analogous to reaction (2) occurs in non-irradiated zinc oxide–water–oxygen–additive mixtures. (f) In view of the foregoing results and conclusions the attractiveness of the zinc oxide–water–oxygen mixtures as a converter of light to chemical energy is greatly decreased. Only in the presence of an additive has this system a high quantum efficiency and the ability to produce large quantities of peroxide. Under these conditions the light activated zinc oxide crystals merely catalyze the occurrence of a normally exothermic reaction (reaction (2) in the case of oxalate additive).

Definite conclusions regarding the mechanism of peroxide formation cannot be made on the basis of these preliminary results; however, an electrolysis mechanism similar to that originally proposed by Baur and Neuweiler[6,8] for zinc oxide photosensitized reactions may be operative here. It may be significant that the photoconducting region of zinc oxide[9] has a close correspondence to the region of zinc oxide light absorption and peroxide formation. Also the maximum quantum yield of peroxide formation for the many experimental conditions used (different additives, reactant concentrations, etc.) was 0.5, obtained in experiments at low light intensities and with formate additive (see Table I). Then it is attractive to assume that electrons made mobile by light activation may reduce molecular oxygen absorbed at certain crystal sites, and simultaneous oxidation of additive may occur at electron deficient regions in the crystal. With this assumption the expected theoretically maximum possible quantum efficiency of peroxide formation is 0.5. The catalysis of peroxide decomposition by reducing agents acting as electron donors is well

known; so in terms of the simple Baur picture it is not surprising that the peroxide is decomposed more rapidly the lower the oxygen supply in the irradiated zinc oxide–additive mixtures. In this case a large number of donor positions will be available for peroxide. However, Kistiakowsky[10] concluded from the fact that the ratio of oxidized to reduced substances is never stoichiometric in the data of Baur, that Baur's electrolysis theory loses its simplicity and much of its power to predict the course of events. It is our belief that the experimental conditions were not ideal in Baur's work and in the present work to test properly the Baur mechanism. With Kistiakowsky's objection in mind a redetermination of the ratios of reactants and products is being made for the photochemical reaction in the zinc oxide–water–oxygen–additive system under conditions providing rapid oxygen replenishment during exposure. Preliminary data indicate that reaction (3) becomes much less important under these conditions.

Experimental

Materials.—All chemicals used were reagent grade. ZnO from different companies often had different peroxide forming efficiencies; the General Chemical Co. B & A reagent grade ZnO gave consistent results and was one of the most efficient. All of the results reported in this work were determined using this material. In all experiments either ordinary distilled water or special conductivity water was used. In the system containing additive no difference in peroxide forming efficiency was observed using the two types of purified water. The oxygen used was Linde U.S.P. gas. Before introduction to the reaction mixture the gas was bubbled through concentrated H_2SO_4 and then water.

Analysis Procedure. (a) Hydrogen Peroxide.—The presence of oxalate in known mixtures containing H_2O_2 vitiated the analytical results for H_2O_2. $CaCl_2$ was added and CaC_2O_4 and ZnO solids were separated by centrifugation. Negligible quantities of peroxide remained on the solid after one washing. The H_2O_2 in the solution was determined quantitatively by the $Na_2S_2O_3$ titration of the iodine liberated by acid, KI and $(NH_4)_6Mo_7O_{24}$. No analytical difficulties were encountered in the peroxide–sodium formate solution. **(b) Oxygen Uptake.**—Oxygen used was determined manometrically using a Warburg apparatus and the procedure of Umbreit, Burris and Stauffer.[11] **(c) Oxalate Used.**—Standard $KMnO_4$ titrations were made to determine the original oxalate concentration and the final sum of the oxalate and peroxide concentrations in an aliquot from the irradiated mixtures separated from ZnO solid. In another aliquot portion from the irradiated mixture the peroxide was determined by the method described in (a), and the final oxalate concentration was determined from these data. **(d) Carbonate Formed.**—CO_2 was liberated from an aliquot portion of an irradiated mixture by acidification. It was removed from the solution quantitatively using N_2 carrier gas and absorbed in standard $Ba(OH)_2$ solution which was titrated with acid to determine the loss of base.

Apparatus and Procedure. (a) Quantum Yield Studies. —The light source was a Hanovia Type A burner operated with 3 amp. current at 150 v. d.c. from a Nobitron regulated supply. A Farrand Model 300 UV monochromator was used to isolate the desired wave length of radiation in the experiments summarized in Fig. 1. A chemical filter system[12] was used in some experiments to obtain higher inten-

(8) E. Baur, Z. Elektrochem., **34**, 595 (1928).

(9) (a) E. Mollwo, Z. physik. Chem., **198**, 258 (1951); (b) H. Weiss, Z. Physik, **132**, 335 (1952).

(10) G. B. Kistiakowsky, "Photochemical Processes," Reinhold Publ. Corp., New York, N. Y., 1928, p. 159.

(11) W. W. Umbreit, R. H. Burris and J. F. Stauffer, "Manometric Techniques and Tissue Metabolism," Burgess Publishing Co., Minneapolis, Minn., 1951.

(12) R. E. Hunt and W. Davis, Jr., THIS JOURNAL, **69**, 1415 (1947)

sities of 3130 Å. radiation (data of Table I). The photolysis cells were made from fused quartz test-tubes containing an optically flat quartz window fused into the side wall. Light intensities obtained from the monochromator were measured with an Eppley line thermopile together with a high sensitivity galvanometer calibrated with standard radiation lamps provided by the N. B. S. The intensities refer to the quanta/sec. striking a fixed area of the zinc oxide suspension. Uranyl oxalate actinometry[13] was employed to measure the intensity of the beam from the chemical filter system. Light intensities were measured before and after each run. The mixture in the photolysis cell containing 0.20 g. of ZnO/25 ml. of solution was stirred magnetically to form a fairly uniform suspension and was continually saturated with oxygen by bubbling the gas through the solution at atmospheric pressure for a 5-min. period before irradiation and during the run. Flow rates of about 15 and 100 ml./min. were used for experiments at low and high light intensities, respectively. The peroxide yield was independent of both the flow rate of oxygen (at flow rates above 10 ml./min.) and the time of initial oxygen saturation (at periods above 5 min.) for the light intensities used in the quantum yield work (1 × 10^{13} to 1 × 10^{15} quanta/sec.). Other conditions being equal, amounts of ZnO above 0.2 g./25 ml. of solution gave no increase in peroxide quantum yield, evidencing complete light absorption. The H_2O_2 product was analyzed as described. The absorption coefficient of zinc oxide at wave lengths less than 4000 Å. is extremely great, so the reasonable assumption was made in the calculation of the quantum yields given in Table I that all quanta entering the cell were absorbed by the ZnO. Correction for the dark reaction was made, assuming the photochemical and thermal rates to be additive. In the case of the oxalate solutions the corrections were most serious; they amounted to as much as 20% of the net amount

(13) (a) W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930); (b) G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

of H_2O_2 formed in the long experiments necessary at the very low light intensities. The data of Fig. 1 were obtained at different intensities of incident radiation, but all intensities were below 4 × 10^{14} quanta/sec. In this range the quantum yield of H_2O_2 formation at 3130 Å. (and probably at the other wave lengths) is independent of the incident intensity as shown in Table I. At the conditions used in this research the quantum yield decreases at intensities above 1 × 10^{16} quanta/sec. At 1 × 10^{17} quanta/sec. the net quantum yield of H_2O_2 formation in the region of 3130–3660 Å. is about 0.3 (0.6 M NaO_2CH solution and O_2 flow rate of 100 ml./min.). (b) **Effect of Oxygen Pressure on Peroxide Yield.**—A water-cooled, Pyrex-jacketed General Electric A-H6 arc, operated on a stabilized a.c. voltage, was used as the light source. ZnO (0.20 g.) in 20 ml. of 0.2 M NaO_2CH solution was stirred magnetically in a heavy Pyrex test-tube connected to a high pressure oxygen flow system. Oxygen was bubbled through the mixture at 100 ml./min. at the pressures indicated in Fig. 2 for a preliminary period of 5 min. and then irradiated for a period of 1 min. The intensity was approximately constant during this series of runs. H_2O_2 was determined as before. (c) **Reactant and Product Ratio Determination.**—A water-cooled A-H6 arc was suspended in the constant temperature bath of the Warburg apparatus. A 0.10-g. sample of ZnO, 7.00 ml. of solution and several glass beads were placed in a Warburg reaction flask. The solution was saturated with O_2 and pure O_2 was placed over the solution and in the connecting and manometer tubes. The shaking of the irradiated system provided by the Warburg apparatus supplied the means of mixing. The usual procedures were utilized to determine the amount of oxygen uptake. Following irradiation and separation of the ZnO, aliquots of the solution were analyzed as described for H_2O_2 and oxalate. Usually duplicate simultaneous runs were made.

COLUMBUS, OHIO

The Differential Diffusion Coefficient of Rubidium Chloride in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND MILTON BLANDER

RECEIVED FEBRUARY 9, 1953

The differential diffusion coefficient of rubidium chloride between 0.001 and 0.01 M concentrations at 25° has been determined by the conductometric method previously employed in this Laboratory. Good agreement with the prediction of the Nernst–Onsager and Fuoss equations has been obtained.

Determinations of the differential diffusion coefficients of potassium chloride from 4 to 30°,[1,2] sodium chloride[3] and lithium chloride[3] at 25° in water at concentrations less than 0.01 M have achieved three purposes. They have supplied definite objective evidence for the validity of the Nernst equation for the diffusion coefficient of an electrolyte at infinite dilution. This result lends confidence to an analogous limiting equation for the self-diffusion coefficients of ions at infinite dilution.[4] Secondly, the concentration dependences of these diffusion coefficients confirm the validity of the thermodynamic term which results from the general theory of irreversible processes.[5] Finally, the re-

sults seem to indicate that the mobility term of the theory[6,7] which corrects for the effect of electrophoresis on the limiting ionic mobilities is of the right order of magnitude and sign. The proof of this contention requires a high order of accuracy in the determination of the diffusion coefficients and one hesitates to give a final verdict until a large amount of evidence is available. As a further contribution to this subject, the diffusion coefficient of rubidium chloride from 0.0015 to 0.011 M concentration has been measured by the conductometric method. These determinations form the subject of the present communication.

Theoretical Considerations

The concentration and temperature dependences of the diffusion coefficient of 1–1 electrolytes

(1) H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 737 (1947); **71**, 1460 (1949).

(2) H. S. Harned and C. H. Blake, Jr., *ibid.*, **72**, 2265 (1950).

(3) H. S. Harned and C. L. Hildreth, Jr., *ibid.*, **73**, 650 (1951).

(4) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945); H. S. Harned and L. J. Gosting, THIS JOURNAL, **73**, 159 (1951); J. H. Wang, *ibid.*, **74**, 1611, 1612 (1952).

(5) L. Onsager, *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931).

(6) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932); H. S. Harned, *Chem. Revs.*, **40**, 461 (1947).

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y.