[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

# A Study of the Mechanism of the Photochemical Synthesis of Hydrogen Peroxide at Zinc Oxide Surfaces[1]

BY JACK G. CALVERT, KURT THEURER, GEORGE T. RANKIN AND WILLIAM M. MACNEVIN

RECEIVED OCTOBER 24, 1953

Hydrogen peroxide is formed as near ultraviolet light is absorbed by a suspension of zinc oxide in water saturated with oxygen and containing organic additives. It is demonstrated through the use of $O^{18}$-enriched oxygen and water that the oxygen in the hydrogen peroxide originates entirely from the oxygen gas for systems containing any of the additives studied (sodium formate, phenol, potassium oxalate, toluene, acetanilide) or in additive-free solutions. Decomposition of peroxide product is unimportant for runs of short exposure time for all the additive containing systems, but a small thermal exchange and a larger photochemically initiated exchange between oxygen gas and hydrogen peroxide are observed. The exchange is greatest in the systems exhibiting the lowest peroxide forming efficiency. Tests for hydrogen are negative in the products of the irradiated zinc oxide suspensions in water free from oxygen. Possible reaction mechanisms are considered in view of these data.

Recently three independent quantitative studies have been reported on the photochemical synthesis of hydrogen peroxide in the system zinc oxide–oxygen–water in the presence of various organic additives.[2-4] In explaining the results of these studies, all of the research groups have favored reaction schemes in which the steps leading to peroxide formation are initiated by an electron transfer to a molecule of water or oxygen absorbed on the zinc oxide surface. These mechanisms suggest that the oxygen present in the hydrogen peroxide comes from oxygen gas, and none from water, zinc oxide or the organic additive. The use of water and oxygen gas enriched in $O^{18}$ has been made in the present study to check this point and to aid in the determination of the reaction mechanism.

## Experimental Procedure

**Materials.**—$O^{18}$-Enriched $H_2O$ (1.5%) from Stuart Oxygen Co. was used directly in some experiments together with Linde U.S.P. tank $O_2$ gas (0.20% $O^{18}$). $O^{18}$-Enriched $O_2$ gas was used in most of the experiments. It was prepared in 500-ml. quantities by the electrolysis of the $O^{18}$-enriched $H_2O$ in a system similar to that described by Slack and Ehrke.[5] Pure Na metal was added to the $H_2O$ (under $N_2$) to provide the necessary electrolyte. All chemicals used were reagent grade. In experiments with organic additives, General Chemical Co. B & A reagent grade ZnO was used as received. The ZnO used in the experiments with no additive was washed thoroughly by stirring with conductivity water for successive periods of 15, 30, 60 and 60 min. and treating with fresh water at the end of each period. This procedure removed the soluble material on the ZnO surface (which could act as additive). The same sample of ZnO was used consecutively in the runs without additive.

**Apparatus and Procedure.**—The general method used in the photochemical experiments involved: (1) the irradiation of mixtures of $O^{18}$-enriched $O_2$ gas in a ZnO suspension in an aqueous solution of a given organic additive; (2) the degassing, distillation, and catalytic decomposition of $H_2O_2$ product; (3) the mass spectrometric determination of the abundance of the oxygen isotopes in the $O_2$ used in the run and the $O_2$ evolved from the $H_2O_2$. The photolyses were carried out in a closed all Pyrex glass system consisting of two bulbs, a magnetic pump, a catalyst chamber, a manometer, and connections for $O_2$ gas introduction, a high vacuum line, and a Toepler pump. Photolyses were made at 25 ± 2° in a water-cooled Pyrex bulb which was irradiated using a Hanovia type A burner. The absorption of the Pyrex bulb and the ZnO suspension limited the effective radiation to that in the range 3600 to 4000 Å. Assuming $\Phi_{H_2O_2} = 0.5$ in the $NaO_2CH$ runs,[4] the absorbed light intensity was estimated to be $2 \times 10^{16}$ q./sec. (a lower limit). The intensity was approximately constant during these experiments. The second bulb was used in conjunction with the photolysis bulb in the suspension preparation and degassing, and in the peroxide product distillation and decomposition. For a 15-min. period preceding each experiment and throughout the exposure period the ZnO suspension (0.2 g. ZnO/25 ml. $H_2O$) was stirred magnetically, and $O_2$ (at about 400 mm. pressure) was bubbled through the suspension and circulated (at about 5 ml. (S.T.P)/sec.) by means of the pump. Peroxide product was distilled to the second bulb following the run, degassed, $Ce(HSO_4)_4$ catalyst added, and the solution was stirred for 1 hr. The $O_2$ product was removed with a Toepler pump and collected for analysis.

**Analysis of $H_2O_2$ Product.**—Recent studies of the catalytic decomposition of $H_2O_2$ and oxidation of $H_2O_2$[6] prove that the $O_2$ evolved from aqueous solutions of $H_2O_2$ is derived entirely from the $H_2O_2$. Furthermore there is very little isotopic fractionation observed in solutions of $H_2O_2$

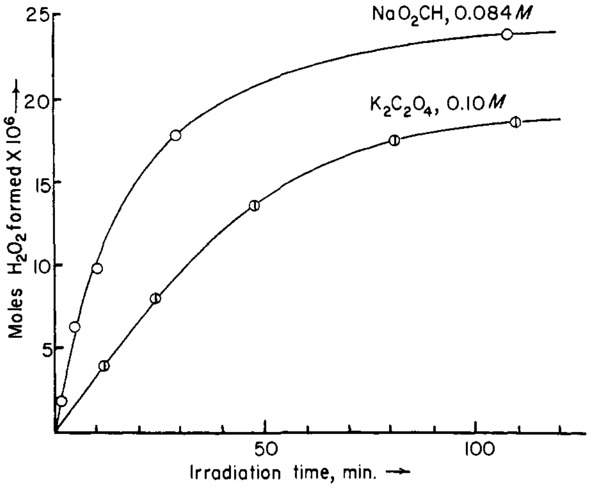

Fig. 1.—Moles of $H_2O_2$ formed in the $ZnO–H_2O–O_2$–additive system *vs.* irradiation time: $O_2$ pressure, 400 mm. at 20°; flow rate of $O_2$ about 5 ml. (S.T.P.)/sec.; ZnO, 40 mg./8 ml. $H_2O$; wave lengths, 3600–4000 Å.; absorbed intensity, about $2 \times 10^{16}$ q./sec.

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[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, Chicago, Illinois, September 6–11, 1953.

[2] I. Veselovskii and D. M. Shub, *Zhur. Fiz. Khim.*, **26**, 509 (1952).

[3] M. C. Markham and K. J. Laidler, *J. Phys. Chem.*, **57**, 363 (1953).

[4] T. R. Rubin, J. G. Calvert, G. T. Rankin and W. M. MacNevin, THIS JOURNAL, **75**, 2850 (1953).

[5] C. M. Slack and L. F. Ehrke, *Rev. Sci. Instruments*, **8**, 39 (1937).

[6] (a) A. E. Cahill and H. Taube, THIS JOURNAL, **74**, 2312 (1952); (b) C. A. Bunton and D. R. Llewellyn, *Research* (*London*), **5**, 142 (1952); (c) M. Dole, DeF. P. Rudd, G. R. Muchow and C. Comte, *J. Chem. Phys.*, **20**, 961 (1952).

TABLE II

SOME TYPICAL DATA FROM ISOTOPIC STUDIES OF THE PHOTOCHEMICAL FORMATION OF $H_2O_2$ IN THE $ZnO-H_2O-O_2$-ORGANIC ADDITIVE SYSTEMS WITH ADDED $H_2O_2$

| | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) |
|---|---|---|---|---|---|---|---|---|---|
| | | | Moles $H_2O_2$ × $10^5$ | | Ratios of masses 34/32 | | | | |
| Run no. | Irradiation time, min. | Method of $H_2O_2$ addn. | Added start run | Formed calibration run | $H_2O_2$ added | $O_2$ start run | $O_2$ end run | $O_2$ from $H_2O_2$ | Theoretical ratio[a] |
| Additive $NaO_2CH$, 0.084 *M* | | | | | | | | | |
| 15[b] | 0(60) | Added | 1.0 | 1.0[c] | 0.0040 | .... | 0.0298 | 0.0039 | 0.0040 |
| 17 | 110 | Added | 2.5 | 2.5 | .0040 | 0.0303 | .0303 | .0292 | .0170 |
| 20 | 3.03 | Photo | 0.526 | 0.526 | .0308 | .0040 | .0040 | .0167 | .0173 |
| Additive $K_2C_2O_4$, 0.10 *M* | | | | | | | | | |
| 22[b] | 0(60) | Added | 1.0 | 1.0[c] | 0.0040 | .... | 0.0314 | 0.0062 | 0.0040 |
| 32 | 3.0 | Photo | 0.098 | 0.098 | .0040 | 0.0296 | .0302 | .0199 | .0167 |
| Additive MePh, satd. | | | | | | | | | |
| 33[b] | 0(30) | Added | 0.5 | 0.5[c] | 0.0040 | .... | 0.0308 | 0.0039 | 0.0040 |
| 35 | 5.0 | Photo | .17 | .17 | .0303 | 0.0040 | .0040 | .0118 | .0170 |
| Additive PhOH, 0.01 *M* | | | | | | | | | |
| 36[b] | 0(60) | Added | 0.5 | 0.5[c] | 0.0040 | .... | 0.0311 | 0.0044 | 0.0040 |
| 38 | 5.0 | Photo | .29 | .29 | .0312 | 0.0040 | .0040 | .0152 | .0174 |
| Additive PhNHAc, 0.01 *M* | | | | | | | | | |
| 39[b] | 0(68) | Added | 0.5 | 0.5[c] | 0.0040 | .... | 0.0308 | 0.0057 | 0.0040 |
| 41 | 5.0 | Photo | .19 | .19 | .0040 | 0.0315 | .0313 | .0208 | .0175 |
| No organic additive present | | | | | | | | | |
| 42[b] | 0(120) | Added | 1.0 | 1.0[c] | 0.0040 | .... | 0.0305 | 0.0040 | 0.0040 |
| 43[d] | 15.0 | Added | 0.28 | 0.28 | .0040 | 0.0304 | .0302 | .0222 | .0170 |

[a] Ratio was calculated assuming no decomposition or exchange of $H_2O_2$. [b] Run was a thermal run; the sample was mixed with $O^{18}$-enriched $O_2$ in the dark at 25 ± 2° for the period of time indicated in the parentheses. [c] Moles of $H_2O_2$ remaining after thermal run. [d] Run 43 was made using 100 ml. suspension volume (8–11 ml. used in all other runs) and about five-times larger irradiated area than in the other runs. $P_{O_2}$, 300 mm. (about 400 mm. in all other runs).

undergoing complete decomposition under a variety of conditions. These results were utilized in the isotopic analysis of the $H_2O_2$ in the present work. The isotopic compositions of the $O_2$ from the $H_2O_2$, the $O_2$ introduced into the system, and that in the system at the end of the run were determined by measurement of the 34 and 32 mass peaks using a General Electric mass spectrometer. The error in the mass ratio 34/32 as determined for the $O_2$ samples from the $H_2O_2$ was about ±5% (because of the small sample size, 30–300 μl.), while that for the ratios for the start and finish $O_2$ samples was about ±0.5%. The amount of $H_2O_2$ formed in the series of rate experiments shown in Fig. 1 was determined (following removal of the ZnO by centrifugation) by $Na_2S_2O_3$ titration of the $I_2$ liberated in an acid-KI-$(NH_4)_6Mo_7O_{24}$ solution using starch indicator.

## Experimental Results

The isotopic studies are summarized in Tables I and II.[7] In Table I the effects of the different additives, exposure time and isotopic composition of the $O_2$ gas and the $H_2O$ on the composition of the oxygen in the peroxide are given. In one run (no. 5) $H_2O$ containing 1.5% $O^{18}$ and normal $O_2$ gas were used. In the other runs $O^{18}$-enriched $O_2$ gas and normal $H_2O$ were the starting materials. Within the experimental error there is an equality between the ratios of mass 34 to mass 32 in the $O_2$ gas at the start of the run, $O_2$ remaining at the end of the run, and $O_2$ from the peroxide product. This equality exists in all additive systems used and even in the system without additive.

In Table II[7] some typical experiments are presented in which $H_2O_2$ was added to the suspension before the run. Runs marked with a superscript *b* are non-irradiated thermal experiments which are otherwise identical to the photochemical runs. Known amounts of $H_2O_2$ solution were placed in the suspension at the start of each run either by addition of a measured quantity of a standard $H_2O_2$ solution (runs marked "Added in column (2) of Table II) or by the photochemical formation of a known quantity of $H_2O_2$ (runs marked "Photo" in column (2) of Table II). Calibration runs preceded each experiment to establish the quantity of $H_2O_2$ expected in the run (data of column (4) of Table II). In the calculation of the theoretical ratios of column (9) of Table II, it is assumed that no decomposition of added $H_2O_2$ or $O_2$–$H_2O_2$ exchange occurs, and that the isotopic composition of the $H_2O_2$ formed in the light is equal to that of the $O_2$ present in the system. (This point is demonstrated in the runs of Table I.)

In another series of experiments the relative initial rates of peroxide formation were determined with each additive at a concentration near that for maximum efficiency. The relative rates are: (a) $NaO_2CH$ (0.3 *M*), 1.00; (b) PhOH (0.001 *M*), 0.38; (c) $K_2C_2O_4$ (0.1 *M*), 0.28; (d) PhNHAc (0.001 *M*), 0.23; (e) MePh (satd.), 0.21; (f) No intentional organic additive, 0.03. These relative rates should be compared with the amount of $O_2$–

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[7] Table I and the unabridged Table II have been deposited as Document number 4182 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance check or money order payable to: Chief, Photoduplication Service, Library of Congress.

$H_2O_2$ exchange which occurred in the various additive systems. From the data of Table II it is calculated that the percentages of peroxide ($0.5 \times 10^{-5}$ mole in 11 ml. $H_2O$) which underwent thermal exchange with $O_2$ (400 mm.) in 1 hr. for the different additive systems are: (a), 0%; (b) 1.5%; (c) 2.5%; (d) 6.5%. In the various systems a photochemically initiated oxygen–peroxide exchange occurred in added $H_2O_2$ when an equal quantity of peroxide was formed photochemically in its presence. These percentages are: (a) 0% (runs 18–21); (b) 19.2, 16.2% (runs 37, 38); (c) 24.0, 22.3, 15.4, 27.0, 24.0% (runs 28–32); (d) 38.0, 24.0% (runs 40, 41); (e) 28.8, 39.6% (runs 33, 34). An inverse correlation between peroxide forming efficiency and $O_2$–$H_2O_2$ exchange is observed.

**Tests for $H_2$ Product in Irradiated $O_2$-free ZnO–$H_2O$ Suspensions.**—In one experiment a Pyrex bulb containing 200 ml. of ZnO suspension in conductivity $H_2O$ was degassed thoroughly using a high vacuum pump. The suspension was stirred (magnetically) and irradiated for a period of 60 hr. at a distance of 15 cm. from a Pyrex-jacketed A-H6 lamp. There was no significant quantity of gaseous product which was non-condensable at liquid $N_2$ temperature, and $H_2$ could not be detected by mass spectrometric analysis of this product. Chemical analysis showed that a negligible quantity of $H_2O_2$ was present in the solution. In another experiment toluene vapor was circulated through an $O_2$-free ZnO–$H_2O$–PhMe suspension and irradiated for 21 hr. in the apparatus used for the isotopic studies. It has been demonstrated that toluene does not inhibit but promotes $H_2O_2$ formation in the ZnO–$H_2O$–$O_2$ system. A small amount of non-condensable gas present at the end of the run was analyzed for $H_2$ mass spectrometrically. $H_2$ could not be detected. (Presumably the small amount of gas present at the end of the run was $N_2$ since this gas was used to flush the system free from $O_2$ and probably was not removed completely by the degassing procedure used.)

## Discussion

**Hydrogen Peroxide Formation in Irradiated Zinc Oxide–Water–Oxygen–Organic Additive Systems.**—The experiments described in this study establish several points. (1) The oxygen in the peroxide product originates entirely from the oxygen gas (compare columns (4), (5) and (6) of Table I[7]); none comes from the water, zinc oxide or organic additive. It is established that the formation of peroxide from hydroxyl radicals formed from water, $H_2O \rightarrow H + OH$ (or from oxygen gas or zinc oxide through the occurrence of reactions: $O_2 \rightarrow 2O$ or $ZnO \rightarrow Zn + O$ followed by $O + H_2O \rightarrow 2OH$) must be unimportant in this sytem. (2) The plateau region of the rate curve at long exposure times (see Fig. 1) is the result of the establishment of a photostationary state of peroxide in the formate solutions and probably in the solutions of the other additives; inhibition of peroxide formation by the action of the $HCO_3^-$ product cannot explain the apparent exchange observed in run 17 of Table II. (3) The results with sodium formate additive (Table II) show that in the runs of short duration (where peroxide concentration remains relatively low) there is neither a destruction of added hydrogen peroxide nor a thermal exchange nor a photochemically initiated exchange reaction between peroxide and oxygen gas. It is probable that the quantum yields observed with this additive represent primary quantum efficiencies of peroxide formation.[4] (4) With all additives tested other than sodium formate a rapid photochemically initiated exchange and a slower thermal exchange occur between oxygen gas and hydrogen peroxide (see Table II). The amount of exchange observed using the different additive systems increases with the decreasing efficiency of the additive systems for peroxide formation.

**Hydrogen Peroxide Formation in the Irradiated Zinc Oxide–Water–Oxygen–Additive-free System.**—The data of runs 14 (Table I),[7] 42 and 43 (Table II) show the oxygen present in the hydrogen peroxide formed in this system originates entirely in the oxygen gas. Thus the often suggested over-all reaction for this system[8]

$$2H_2O + O_2 \longrightarrow 2H_2O_2 \qquad (1)$$

cannot be correct. This conclusion is in accord with the work of Markham and Laidler[3] in which it was shown that one molecule of oxygen disappears for every peroxide molecule formed in the additive-free system. The observation that a given zinc oxide sample shows some loss of peroxide forming efficiency after continued use may indicate that the zinc oxide crystal undergoes a change (perhaps an oxidation to $Zn(OH)(O_2H)$ as Markham and Laidler have suggested) simultaneous to peroxide formation. However, because of the high efficiency of even trace quantities of different compounds in promoting peroxide formation in this system, one cannot eliminate the possibility that the observed activity of the so-called "additive-free" systems for peroxide formation is the result of the unintentional introduction of oxidizable material into this system and the occurrence of reactions analogous to (2) and (3). These have been shown to be the important reactions in the oxalate[4,9] and formate[9] additive systems, respectively.

$$2H_2O + C_2O_4^{=} + O_2 \longrightarrow H_2O_2 + 2HCO_3^- \qquad (2)$$

$$H_2O + HCO_2^- + O_2 \longrightarrow H_2O_2 + HCO_3^- \qquad (3)$$

**Mechanism of the Reaction.**—The reaction mechanisms suggested by the recent studies of Veselovskii and Shub,[2] Markham and Laidler,[3] and Rubin, Calvert, Rankin, and MacNevin[4] are in general compatible with these results. The suggested mechanisms utilize the photoexcitation of electrons in zinc oxide and interaction of these electrons with the adsorbed molecules, either water or oxygen. There are many reasons for the attractiveness of such a scheme. For example, it is in accord with the fact that the photoconductivity in

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[8] 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.

[9] C. B. Vail, J. P. Holmquist and L. White Jr., THIS JOURNAL, **76**, 624 (1954).

zinc oxide, the photochemical formation of hydrogen peroxide in aqueous zinc oxide–oxygen suspensions, and light absorption by zinc oxide all occur in the same wave length region. The equivalence of oxidation and reduction[4,9] and the observed maximum quantum yield of peroxide formation[4] (0.5 in 0.3–0.5 *M* $NaO_2CH$ solutions) are also consistent with such a scheme. Veselovskii and Shub[2] and Rubin, *et al.*,[4] have suggested an "electrolysis" mechanism similar to that originally proposed by Baur and Neuweiler[10,11] for the zinc oxide photosensitized reactions. A reduction of adsorbed molecular oxygen by a photoexcited electron

$$O_2 + e^- \longrightarrow O_2^- \qquad (4)$$

followed by peroxide forming reactions such as 5 and 6

$$O_2^- + H_2O \rightleftharpoons HO_2 + OH^- \qquad (5)$$

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

may occur simultaneous to oxidation of the organic molecules at the electron deficient regions in the crystal. Therefore, the reaction 7 may occur in the oxalate solutions.

$$C_2O_4^= \longrightarrow 2CO_2 + 2e^- \qquad (7)$$

Markham and Laidler do not rule out an oxygen reduction mechanism, but they have suggested tentatively that the primary process may be the transfer of a photoexcited electron in zinc oxide to an adsorbed water molecule

$$H_2O + e^- \longrightarrow H_2O^- \qquad (8)$$

and peroxide formation may result from the sequence of reactions 9, 10 and 6.

$$H_2O^- \longrightarrow OH^- + H \qquad (9)$$

$$H + O_2 \longrightarrow HO_2 \qquad (10)$$

An oxidation of organic material by OH radicals (presumably formed following 9 at the $(ZnO)^+$ surface $(ZnO)^+—OH^- \rightarrow ZnO{\cdot}OH$) was suggested.

Neither the oxygen nor the water reduction mechanism can be considered as unique in the explanation of all of the studies which have been made, but several points seem to favor the oxygen reduction scheme. The apparent ease of electron capture by molecular oxygen ($O_2 + e^- \rightarrow O_2^- +$ 15.8 kcal., in the gas phase[12]) and the observed efficiency of the quenching of the fluorescence of zinc oxide by oxygen together with the lack of influence of water in this respect[13] are facts which favor the molecular oxygen reduction theory. However the equilibrium (5), where $\Delta F^0$ is estimated to be about 18.5 kcal.,[14] is somewhat unfavorable for $HO_2$ formation. In an aqueous zinc oxide suspension where the *p*H is about 7 the ratio of the concentration of $O_2^-$ to that of $HO_2$ at equilibrium would be about 57,000:1.

The two schemes suggested differ in one important respect. Hydrogen atoms are expected in irradiated aqueous zinc oxide suspensions according to the water reduction mechanism and the reaction 9,[2,3] while they are not expected assuming the "electrolysis" mechanism and oxygen reduction. A few experiments made in the present study aid in the differentiation between these mechanisms. Tests for hydrogen product were made in extensively irradiated, oxygen-free zinc oxide–water and zinc oxide–water–toluene systems. The absence of detectable quantities of hydrogen in the products seems to indicate that the occurrence of reaction 9 in these systems is unlikely. If water reduction occurs as suggested in reaction 8 then one must postulate that reactions 9 and 10 are closely coupled; therefore oxygen is necessary to promote reaction 9.[15] Although the results are not entirely conclusive the evidence at hand appears to favor an "electrolysis" mechanism involving oxygen reduction and simultaneous oxidation of organic additive.[2,4]

Definite conclusions regarding the exchange kinetics are impossible since the exchange results show considerable variation between runs with a given additive, but it appears that the exchange involves a heterogeneous reaction whose rate is roughly proportional to the number of absorbed quanta. The data from the thermal runs with $K_2C_2O_4$ additive (22–26 of Table II[7]) do not show any simple variation in rate with change in $H_2O_2$ concentration.

**Acknowledgment.**—Grateful acknowledgment is made to the C. F. Kettering Foundation which sponsored this study, to Prof. T. R. Rubin with whom the authors participated in several valuable discussions in regard to the reaction mechanism, to Mr. Eugene Mezey and Mr. Emerson Garver who helped in the design and construction of the apparatus used, and to Mr. Harold D. McBride who performed many of the peroxide chemical analyses.

COLUMBUS, OHIO

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

[11] E. Baur, *Z. Elektrochem.*, **34**, 595 (1928).

[12] M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949).

[13] V. Gachkovskii and A. Terenin, *Bull. acad. sci. U.R.S.S. Classe sci. math. nat., Ser. Chim.*, 805 (1936).

[14] M. G. Evans, N. S. Hush and N. Uri, *Quart. Revs. (London)*, **6**, 186 (1952).

[15] The authors' assumption that hydrogen atom production should lead to hydrogen gas has been questioned by one of the referees. He has pointed out that if reaction 9 occurs on the zinc oxide surface then the reaction, $ZnO + 2H \rightarrow H_2O + Zn$, may follow, and hydrogen would not be an expected product, assuming either mechanism. This may be the case; however, extensive irradiation of the oxygen-free system produced no noticeable change in the appearance of the zinc oxide and no significant quantities of oxygen and hydrogen peroxide. These products and some color change in the zinc oxide might be expected if zinc oxide reduction is important and the subsequent reoxidation of zinc is slow in this system.