

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Studies. XLVII. Liquid Acetone-Oxygen and Liquid Acetone-Heptane-Oxygen¹

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The photochemical decomposition of liquid acetone proceeds with a very low quantum yield, the products being the same, but the relative amounts different from the reaction in the gas phase. Dissolved oxygen does not completely suppress the formation of ethane and methane, but the quantum yields of oxygenated products are greater than those of methane, ethane and carbon monoxide in the absence of oxygen. Some but not all of the oxygenated products have been identified. The ratio of carbon dioxide to acetic acid is about unity, thus indicating that these two products come either from the same intermediate or from the same sequence of events. Addition of heptane leads, among other things, to the formation of an alcohol (probably by addition of acetone to heptane) and to degradation products of heptane. A brief discussion of the mechanism is given.

I. Introduction

The photochemical decomposition of acetone in the liquid phase, both in the pure state, or when dissolved in various solvents, has been studied by Bowen and co-workers.² Virtually no gaseous products were found, but in hydrocarbon solvents tertiary alcohols were produced.

The quantum yield of acetone decomposition may be lower in the liquid than in the gas phase either due to deactivation of active molecules by collision or due to recombination of radicals because of the "cage" or Franck-Rabinowitch effect. The recombination might be reduced by the presence of dissolved oxygen which would react with the radicals before they can recombine. The products with oxygen present should resemble those found upon exposing gaseous acetone-oxygen mixtures^{3,4} with the possibility that reactions resulting from abstraction of hydrogen atoms from acetone would be of more relative importance.

It was deemed of interest to study the systems of liquid acetone-oxygen and liquid acetone-heptane-oxygen in order to form ideas concerning the behaviors of radicals in the liquid phase. A completely quantitative interpretation of the results is impossible, but certain suggestions may be made concerning the mechanism.

II. Experimental

Substances used were prepared as follows: (a) Acetone was dried by potassium carbonate and fractionally distilled. The center fraction which boiled 57.0-57.6° (uncor.) was collected and stored in a light free container; (b) Biacetyl was obtained from Mr. H. D. Batha (working with Dr. W. D. Walters of this Laboratory); (c) Diacetone alcohol was redistilled from a commercial sample and the fraction boiling 161-163° (uncor.) retained; (d) *n*-Heptane (Phillips "99% pure") was passed through a column of silica gel repeatedly until no change in ultraviolet transmittency could be observed; (e) Tank nitrogen was passed through sodium hydroxide and over heated copper at 400-450°; (f) Oxygen was prepared by heating potassium permanganate.

Preliminary experiments were performed by irradiating

about 220 ml. of liquid in a Pyrex flask with full radiation from a Hanovia type SH Alpine burner. In some instances oxygen was removed by bubbling nitrogen through the liquid. No ultraviolet absorption attributable to biacetyl could be found either in the presence or absence of oxygen. Tests for peroxides by the method of Yule and Wilson⁵ were negative.

Several experiments were also carried out with about 25 ml. of acetone in a small flask irradiated by an AH-6 lamp. Again no absorption due to biacetyl could be found, but a weak absorption extending from about 3300 Å. toward the visible was observed whether or not oxygen was present during irradiation. With oxygen present tests for peroxide were positive, the pH of the solution diluted with water was about 4.9 (compared to 6.3 for unexposed acetone similarly diluted). A fuchsin dye test for aldehydes was positive. Polarographic analysis gave indefinite results.

Some preliminary runs were also made in a vessel with quartz windows and a volume of 16 ml. The results need not be given.

Most of the data were obtained by use of a small quartz cell about 1 cm. in thickness and with windows 2.5 cm. in diameter. This was placed in a horizontal position and exposed to full radiation from a Hanovia Alpine burner placed underneath. The upper surface of the cell was cooled by running tap water over it. The temperature of the liquid being exposed to radiation was within a few degrees of 30°. Between 0.5 and 1.0 ml. of liquid was placed in the cell. The gas-liquid interface was about 5 sq. cm., and thus the opportunity for diffusion of oxygen into the liquid was provided. Slow refluxing of the liquid due to heat from the lamp provided a further surface of contact with the gas phase. All mercury lines from 3130 Å. to the limit of the quartz are completely absorbed by the acetone in the thickness used.

Fugassi valves⁶ were used to separate the cell from the analytical apparatus. After exposure the contents of the cell were cooled with Dry Ice-acetone and the gases removed through a trap placed in supercooled liquid nitrogen at -215°. The acetone in the cell was then distilled to a second trap and the gases uncondensed at -125° again removed. These gases should be O₂, CO, H₂ (if any) and CH₄. These gases were analyzed by previously described methods.^{4,7} A modified Ward still was used to separate other fractions. The C₂ fraction was removed at -165°, the CO₂ fraction at -145°, and the aldehyde fraction at about -125°. The C₂ fraction was analyzed by the method of Blacet and Leighton.⁸

A non-volatile residue was formed only during runs in the absence of oxygen. It was slightly yellow in color and showed infrared absorption somewhat similar to diacetone alcohol.⁹ It was necessary to remove this material between runs by introducing oxygen into the cell and heating. This

(1) This work was supported in part by Contract between the Office of Naval Research and the Department of Chemistry, University of Rochester. The authors wish to express their appreciation to Mr. R. C. Wilkerson, Celanese Corporation of America, Clarkwood, Texas, for performing the mass spectrographic analyses, and to Mr. Carl Whiteman for performing the infrared analyses.

(2) E. J. Bowen, *et al.*, *J. Chem. Soc.*, 1503, 1505 (1934); 1685 (1936).

(3) F. O. Rice and C. E. Schildknecht, *THIS JOURNAL*, **60**, 3044 (1938).

(4) F. B. Marcotte and W. A. Noyes, Jr., *Discussions of the Faraday Soc.*, **10**, 236 (1951); *THIS JOURNAL*, **74**, 783 (1952).

(5) J. Yule and C. Wilson, Jr., *Ind. Eng. Chem.*, **23**, 1254 (1931).

(6) E. Warrick and P. Fugassi, *Ind. Eng. Chem., Anal. Ed.*, **15**, 13 (1943).

(7) For details see P. E. Frankenburg, Ph.D. Thesis, University of Rochester, 1952.

(8) R. Pyke, A. Kahn and D. J. Le Roy, *Anal. Chem.*, **19**, 65 (1947).

(9) See also G. H. Damon and F. Daniels, *THIS JOURNAL*, **55**, 2263 (1933).

film undoubtedly reduced the light transmitted into the cell gradually during the course of these runs.

The degassed liquid could be removed after a run and either titrated for acid, analyzed for aldehydes, studied by infrared or ultraviolet spectrographs, or analyzed by the mass spectrograph.

A rough measure of the quantum yield was obtained by comparing the rate of formation of products obtained from the liquid with that from acetone vapor in the same cell. The relative intensities of the various lines from a mercury arc of this type are known approximately¹⁰ and the absorption coefficients for liquid acetone¹¹ and for acetone vapor¹² are known. The quantum yield of carbon monoxide from the vapor was assumed to be 0.1.¹³ By multiplying the fraction of light absorbed by the relative intensity for each line and summing over the various absorbed lines of the mercury arc, it was estimated that ten times as much radiation was absorbed by the liquid as by the vapor. The calculation led to $\Phi_{CO} \sim 10^{-5}$ for pure liquid acetone, and it is believed this figure is accurate within a factor of 10. A more precise value would have little meaning in the theoretical treatment which follows. The total quanta absorbed per second in liquid acetone were approximately 2×10^{16} .

III. Results

The preliminary runs to determine the nature of the products gave the following results.

Pure Acetone.—No evidence for biacetyl or aldehydes. A compound which absorbs at longer wave lengths in the ultraviolet other than acetone itself is formed. This compound could not be positively identified but may possibly be a polymer of biacetyl.

Acetone-Oxygen.—Tests for peroxides positive. Acid formed. This acid is too weak to be formic acid, but if due allowance is made for the effect of acetone on the apparent ionization constant, it is found to be probably acetic acid. Tests for aldehydes positive. A neutralized sample showed a half-wave potential characteristic of simple aldehydes.

Acetone-Heptane-Oxygen.—Some unsaturation. No aldehydes by Fehling solution. Acid (probably acetic) formed. The mass spectrograph showed peaks at masses 143 and 158. A residue remaining after removal of the acetone, heptane and acid showed infrared absorption characteristic of alcoholic hydroxyl.

One experiment with 220 ml. of a 3.6×10^{-3} molar solution of biacetyl in oxygen-free acetone did not indicate any change in absorption spectrum upon irradiation. Thus biacetyl apparently does not disappear by a long chain reaction under these conditions.

An average of six experiments with liquid acetone in the apparatus designed for analysis of gases showed 2.6×10^{-7} mole of CO to be formed per hour. With oxygen pressures above the liquid which varied from about 200 to about 400 mm., the average rate of formation of CO with about the same intensity (14 runs) showed 9.2×10^{-7} mole of CO to be formed per hour. The ratio of these figures is about 3.5. The scatter in results is such as not to indicate a definite trend with oxygen pressure over these limits. Experiments at lower oxygen pressures did indicate a falling off of CO formation, but in these cases the oxygen nearly all disappeared by the ends of the runs, all of which were of 24-hour duration.

Table I shows a summary of ratios of other products to carbon monoxide for the three oxygen-free runs for which all products were determined and for the fourteen runs with oxygen present (see ref. 7 for details of the data).

Two runs were carried out at intensities three- to four-fold higher than in the others. The ratios of products were essentially the same as for the other runs except that CH_4/CO increased to 0.31 and 0.56 (in the second run the oxygen was used up before the end of the run). These experiments indicated that in the zone next to the window where the light entered the cell oxygen was seriously depleted. The temperature of the liquid was undoubtedly somewhat higher for these runs than for runs at lower intensity.

Table II shows similar data for the *n*-heptane-acetone solutions. In each case about 0.5 ml. of *n*-heptane and

TABLE I

RATIOS OF MOLES OF PRODUCTS TO MOLES OF CO

The figure for oxygen consumption is probably the least accurate. Uncertainties are average deviations from the mean.

	Acetone, oxygen- free	Acetone (O ₂ pressure 200-440 mm. above liquid)
Methane	2.3	0.13 ± 0.05
Ethane	0.66	0.13 ± 0.03 (9 runs)
Carbon dioxide	..	3.3 ± 0.6 (8 runs)
Acid	..	3.3 ± 0.6 (5 runs)
Aldehydes	..	0.44 ± 0.16 (8 runs)
Oxygen consumed	..	7.5 ± 1.7 (6 runs)

about 0.1 ml. of acetone were used. The average rate of CO formation was 1.4×10^{-7} mole per hour in the absence of oxygen, and varied from 2×10^{-7} to 4×10^{-7} mole per hour as the oxygen partial pressure over the solution changed from 680 to 66 mm. This would seem to indicate that the rate of CO formation passes through a maximum at low oxygen pressures.

TABLE II

RATIOS OF PRODUCTS TO CARBON MONOXIDE IN ACETONE-*n*-HEPTANE SOLUTIONS

	Oxygen-free	Oxygen present
Methane	2.2 ± 0.4 (4 runs)	1.3 ± 0.3 (5 runs)
C ₂ -Hydrocarbons	0.8 ± 0.2 (4 runs)	0.6 ± 0.04 (5 runs)
CO ₂ + aldehydes	3.3 ± 0.3 (5 runs)
Acid	2.0 ± 0.1 (5 runs)
Oxygen consumed	17.7 ± 1.8 (5 runs)

Mass spectrographic analysis of the "aldehyde-CO₂" fraction from one run gave the following composition: (in mole per cent.) CO₂ (68), CO (0), acetone (2), pentenes (0.7), butenes (9), propenes (16), ethylene (1), formaldehyde (0.2 max.), ethanol (1.9), methanol (0.2).

The *n*-heptane-oxygen mixtures without added acetone showed a slow reaction (undoubtedly due to the presence of some short wave radiation) when exposed under conditions similar to those used with acetone. Average ratios of products to carbon monoxide were found to be as follows: CH₄ (3.8); C₂ (1.3); "aldehyde-CO₂" (2.7); only traces of formaldehyde could be found in the "aldehyde-CO₂" fraction. A mass spectrographic analysis of this fraction from one run gave in per cent.: CO₂ (83.4); CH₂CHCHO (3.8); CH₂CHCH₃ (3.0); CH₃CHO (2.3); CH₂O (0.6). A brown liquid was formed by this fraction on standing. The ultraviolet absorption of the degassed liquid fraction showed a peak at 2700 Å. probably due to small amounts of ketones. *n*-Heptane-oxygen mixtures showed no detectable dark reaction.

It should be remembered in consideration of the above data that due to the difficulty of separating gaseous products from the liquid it was necessary to have appreciable quantities of products to attain a reasonable accuracy. In view of the low quantum yield long exposures were necessary even with the high intensities used.

IV. Discussion

Since approximately 3.6 methyl groups appear as methane and ethane for each carbon monoxide molecule formed from liquid acetone, some carbonyl product such as biacetyl or one of its polymers must be formed. Failure to identify positively the monomer of biacetyl may be due to the small quantity formed and to the fact that it undoubtedly polymerizes to give a colorless polymer. The products of the reaction of pure acetone can be accounted for satisfactorily by reactions similar to those for the gas phase,¹⁴ but the relative amounts are different. This would be expected because of

(10) See W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 45.

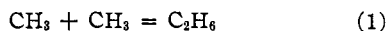
(11) J. Bielecki and V. Henri, *Ber.*, **46**, 3627 (1913).

(12) C. W. Porter and C. Iddings, *THIS JOURNAL*, **48**, 40 (1926).

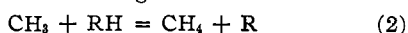
(13) D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

(14) See W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

the low rate of formation of methyl radicals. The reaction



is the only probable source of ethane in the gas phase, and there is no evidence for an additional source in the liquid. Since reaction (1) apparently has a low activation energy and a high steric factor,¹⁵ diffusion should be the rate controlling process in the liquid phase since nearly every collision between methyl radicals should lead to reaction. The main methane forming reaction is



where RH in pure acetone is acetone itself. The activation energy and the steric factor for this reaction in the liquid phase are unknown, but if they are assumed to be the same as in the gas phase,¹⁶ about one collision in 10^{10} will lead to methane formation at 30°. Since the ratio of methane to ethane is about 3.5 in pure acetone, this would indicate a ratio of 10^{10} to 10^{11} to 1 for acetone molecules to methyl radicals during irradiation, or a methyl radical concentration of about 10^{-13} mole/ml. There must be a considerable concentration gradient because of the high absorption coefficient of liquid acetone, and the localized ratio of ethane to methane formation must be greatest near the window through which the radiation enters the cell.

The solubility of oxygen in liquid acetone is not known exactly, but approximately $1/5$ volume of oxygen under standard conditions dissolves in one volume of liquid.¹⁷ If this is true, about 1 molecule in ten thousand will be dissolved oxygen at a pressure of $1/3$ atmosphere. If the steric factor for removal of methyl radicals by oxygen is the same in the liquid as in the gas phase⁴ (2×10^{-4}), neither methane nor ethane should be formed when dissolved oxygen is present. The fact that methane and ethane are formed in presence of oxygen might lead one to assume that the steps leading to their formation are quite different, at least as regards rates, in the liquid from the gas. Since, however, the ratio of ethane to methane is increased in presence of oxygen (from 1:5 to 1:1), it is much more logical to assume that the rate of radical formation is so high near the window as to deplete the oxygen seriously. Indeed, the absorption is so high that if one molecule of oxygen disappears per quantum, all oxygen would disappear in one second within 1 mm. of the window. Thus the oxygen would be effective in removing methyl radicals only at a distance from the window, *i.e.*, in the region where methane formation is greatest in the absence of oxygen.

The foregoing discussion indicates that attempts to determine the true radical reaction constants from these data would not be fruitful. Indeed, it would be very difficult and perhaps impossible to design experiments which could be used for this purpose in the liquid phase.

(15) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951); see also R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951).

(16) A. F. Trotman-Dickinson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951); see also A. J. C. Nicholson, *THIS JOURNAL*, **73**, 3981 (1951).

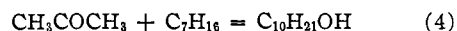
(17) F. Fisher and G. Pfeiderer, *Z. anal. Chem.*, **124**, 61 (1922).

Certain conclusions about mechanism are, nevertheless, possible. Both methane and ethane production are considerably reduced by the presence of dissolved oxygen, and yet carbon monoxide production has increased threefold. Carbon dioxide and acid (acetic) become the main products as they are in the gas phase³ at high oxygen pressures. The number of radicals formed has, therefore, increased by a factor of ten or more due to the presence of oxygen. If some of the methyl radicals are removed by reaction with oxygen, the acetyl radical will be given greater opportunity to dissociate. As judged by the data in Table I the methyl radicals do not form mainly formaldehyde but seem to give carbon monoxide. The steps may be similar to those given earlier.⁴ The constancy of the ratio of carbon dioxide to acid indicates, however, that carbon dioxide is not formed mainly from methyl radicals. The acetyl radical is suggested strongly as the intermediate. One might write



In the gas phase this reaction could be exothermic enough to lead to dissociation of the methyl glyoxal with formation of acetic acid and HCO.³ The OH could abstract hydrogen from acetone with the formation of acetyl and water. Methyl glyoxal is fairly easily oxidized to acetic acid and carbon dioxide.¹⁸ It is suggested that this is the path which leads to carbon dioxide and acetic acid as the main products in the ratio of about 1 to 1.

The presence of heptane leads to many changes in the reaction. In oxygen-free acetone-*n*-heptane mixtures the presence of the peak of mass 158 and the alcoholic infrared band indicate strongly the addition reaction



The mechanism of this reaction is probably similar to others discussed by Kharasch.¹⁹ The peak at 143 may be due to an ion produced from this alcohol by loss of a methyl radical.

The ratio of methane to C₂ hydrocarbons in heptane solution with oxygen present is greater than in the acetone-oxygen system. One must be careful in drawing conclusions from this fact due to the different distributions of radicals which must exist in the two cases and also to the difference in oxygen solubilities. Nevertheless the trend is in agreement with work in the gas phase²⁰ to the effect that the activation energy for abstraction of hydrogen atoms by methyl radicals is lower for aliphatic hydrocarbons with three or more carbon atoms than it is from acetone. It is significant that the ratio of CO₂:acid in heptane is still about 1/1 although the ratios of these products to carbon monoxide has dropped as compared to the acetone-oxygen system. Acetyl radicals may, if formed, tend to abstract hydrogen atoms from heptane to form acetone and heptyl radicals unless the oxygen

(18) H. A. Spoehr and H. W. Milner, *THIS JOURNAL*, **56**, 2068 (1934).

(19) M. S. Kharasch and H. C. Brown, *ibid.*, **62**, 454 (1940); **64**, 329, 1621 (1942).

(20) E. W. R. Steacie and A. F. Trotman-Dickenson, *J. Chem. Phys.*, **18**, 1097 (1950); *THIS JOURNAL*, **72**, 2310 (1950).

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.

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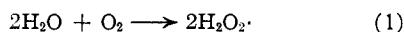
Photochemical Synthesis of Hydrogen Peroxide at Zinc Oxide Surfaces¹

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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, $2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{H}_2\text{O}_2$ (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: $\text{O}_2 + 2\text{H}_2\text{O} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{H}_2\text{O}_2 + 2\text{HCO}_2^-$. 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 reaction⁴ of peroxide formation is



Since reaction (1) involves a large increase in free energy ($\Delta F_{298}^\circ = 25$ 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.

(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'Almeida, *Ber.*, **54B**, 1961 (1921); (b) E. Baur and A. Perret, *Helv. Chim. Acta*, **7**, 910 (1924); (c) A. Perret, *J. chim. phys.*, **33**, 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.

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 $1 \times 10^{-5} M$. 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 $1 \times 10^{-3} M$ 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, $\Phi_{\text{H}_2\text{O}_2}$, is seen in the data of Ta-

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