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Conversion of Isopropyl Alcohol to Acetone on Irradiated Zinc Oxide*

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Irradiated suspensions of zinc oxide containing isopropyl alcohol form acetone and peroxide provided an adequate concentration of oxygen is present. Initial quantum yields of these products range from 0.25 to 1.50 depending on concentration of alcohol, specific catalyst surface, light intensity, and temperature. The peroxide concentration reaches a limiting value under all conditions, but the acetone accumulates indefinitely.

Detailed investigation shows that the products obtained are the result of reactions of radicals in the liquid phase as well as direct surface reactions. The former are particularly important in pure organic liquids. The data obtained are best explained on the assumption that the energy of radiation at 3650 Å, approximately 80 kcal absorbed by zinc oxide, gives rise to an active form of oxygen which initiates both the surface and liquid phase reactions. Consideration of the various possible reactive forms of oxygen which might be produced under these conditions leads to the conclusion that an excited molecular oxygen anion is the most probable active intermediate. This interpretation is consistent with observations on irradiated zinc oxide reported by other investigators and also previous studies carried out in this laboratory. Lack of sufficient oxygen in the reaction mixture, or the instability of the excited molecular oxygen anion in the gas phase, may account for earlier reports of failure to observe vapor phase conversion of isopropyl alcohol to acetone on irradiated zinc oxide.

These systems may not have practical value for the formation of peroxide, but the photocatalyzed conversion of isopropyl alcohol to acetone in zinc oxide suspensions is a very efficient process. An attractive feature is the fact that it can be carried out at low temperatures without the intervention of undesirable side reactions.

INTRODUCTION

The role of oxygen in catalytic reactions at zinc oxide surfaces has been the subject of numerous investigations in the past ten years (*1–8*). Many catalytic reactions taking place on zinc oxide are light activated. One of these reactions, the formation of hydrogen peroxide from water and oxygen has been extensively studied both in this laboratory and elsewhere (*3, 9–15*). It has been observed that the presence of alcohols in an aqueous suspension of zinc oxide permits a higher steady state concentration of hydrogen peroxide to be reached with simultaneous oxidation of the alcohol (*13*). Hnojevij (*16*) studied the effect of illumination on the dehydrogenation of alcohols by zinc oxide up to 450°C and observed no appreciable effect. Schwab (*4*) has explained this result on the basis that zinc oxide is an *n*-type semiconductor and illumination makes more electrons available in the conduction band. The dehydrogenation of isopropyl alcohol, being a donor type reaction (*18*), will therefore not take place on irradiated zinc

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oxide. However, the formation of hydrogen peroxide involves removal of electrons from zinc oxide; acceptor sites should be created simultaneously, making the dehydrogenation of isopropyl alcohol possible in aqueous suspensions of zinc oxide. Preliminary studies showed that the formation of acetone would take place readily even in illuminated suspenisons of zinc oxide in pure isopropyl alcohol provided there was continuous access of oxygen to the surface. The present studies were therefore undertaken to elucidate the role of oxygen and the function of zinc oxide itself in the photocatalytic conversion of isopropyl alcohol.

METHOD

The light source used in all the experiments was a Hanovia H-4 high pressure quartz mercury arc with a Pyrex envelope to retain all radiation below about 3300 Å. Radiation above 3800 Å is not absorbed by zinc oxide or any of the reactants in the systems studied. The lamp gives a good output at 3650 Å. It was mounted horizontally above a mechanical shaker and provided with an aluminum foil shade to reflect the light downwards.

For measurements of quantum yield the radiant energy at 3650 Å was filtered through a Corning filter, #9863. Light intensity was determined with a calibrated Eppley bismuth-silver thermopile, and also by uranyl oxalate actinometry. The light intensity for the experiments reported in Figs. 1 through 9 was approximately 2×10^{14} photons cm^{-2} sec^{-1} (I_0).

The reaction vessel consisted of a glass tube sealed at one end and provided with a tapered joint at the other end. The complementary half of the ground glass joint served as a cap to seal the tube, and was fitted with a side arm to permit removal of samples. The cap also had a long insert tube, sealed internally to allow bubbling gases through the reaction mixture. The reaction vessel was placed in an outer jacket through which water from a thermostat could be circulated to maintain the reaction system at any desired temperature. The temperature was controlled to ±0.5°C. Two-tenths of a gram of ZnO was taken in the reaction vessel and 30 ml of the liquid under investigation added. After attaching the vessel to its outer jacket with a rubber collar, it was clamped to the platform of the mechanical shaker and shaken at the required temperature for half an hour before irradiation. The reaction vessel was shielded from the lamp for the first 5 min after ignition to permit the lamp to warm up to its maximum output. Samples were removed through the side arm at various intervals for analysis.

All types of commercially available reagent grade zinc oxide as well as the spectroscopically pure (S.P. 500) ZnO supplied by the New Jersey Zinc Co. are photocatalytically active and give similar results. None of the specially prepared photoconducting or charge-accepting and charge-rejecting samples have proven superior. The quantum yield, however, is influenced by the specific surface. The data of Figs. 1 through 6 represent a self-consistent set of experiments using Baker's A. R. ZnO with a specific area of about 4 sq m/g. The initial quantum yield for peroxide formation is approximately 0.4 for 1 *M* isopropyl alcohol irradiated with ZnO at room temperature. Figs. 7 through 11 represent another self-consistent set using S. P. 500 ZnO, area 2.7 sq m/g. Recent tests with Kadox 25, area 9–10 sq m/g, indicate that it would be even better.

For the experiments conducted in the absence of oxygen, nitrogen was bubbled, for about half an hour, through a wash bottle containing the same liquid as was present in the reaction vessel and then through the suspension in the reaction vessel. The current of nitrogen was then shut off, the side arm through which samples were taken stoppered, and the system irradiated. Whenever samples were to be taken the nitrogen was turned on during the withdrawal.

It was found that the initial shaking in the dark for half an hour did not produce any change in the reaction mixture. Results obtained in a pure oxygen atmosphere were the same as in air. The rate of reaction was not affected by shaking rate as long as the zinc oxide was kept in suspension.

Measurements of oxygen uptake were made in Warburg respirometer flasks using the Hanovia H-4 mercury arc lamp in Pyrex shield mounted horizontally above a pair of flasks to give sets of duplicate measurements. The flasks contained 0.2 g of zinc oxide and 3 ml of the liquid reactant.

The peroxide in the reaction mixtures was identified as hydrogen peroxide and titrated quantitatively according to methods previously described (*9, 13*). The ultraviolet spectra of the supernatant liquid obtained after irradiating zinc oxide suspensions in aqueous isopropyl alcohol can be duplicated by preparing mixtures of acetone and hydrogen peroxide of similar concentrations in aqueous isopropyl alcohol.

The acetone was determined by vapor phase chromatography using a 2 ft Carbowax 20*M* column. Preliminary investigation using various columns indicated that acetone was the only major organic product in the reactions where isopropyl alcohol was present. There was in every experiment a very small peak appearing just before acetone. Attempts to identify this trace product have proved unsuccessful. Both formaldehyde and acetaldehyde have the same retention time as this product and we suspect it is one of them. The areas corresponding to this product, except in the experiments at high temperature using aqueous solutions of isopropyl alcohol, have been negligibly small.

The reaction mixture was centrifuged and a 50 μl sample of the supernatant liquid was injected into the carrier gas stream. The recorded output from the flame ionization detector permitted the calculation of the area corresponding to acetone and the concentration was determined from a previously established calibration curve. The injection port temperature was 80°C; the column temperature was 35°C.

RESULTS

The data presented in Figs. 1, 2, and 5 illustrate the effect of alcohol concentration on the formation of peroxide and acetone at 25°C. Figs. 1 and 5 also show that a change in weight of ZnO from 0.1 g to 0.4 g has negligible effect. Figs. 3 and 4 indicate the results when hydrogen peroxide is added initially to a suspension of zinc oxide containing alcohol. There is no change in the rate of formation of acetone, but the peroxide decomposes rapidly and eventually reaches the same equilibrium concentration as would be formed in the absence of added hydrogen peroxide. According to Fig. 4 acetone, in concentration of the order of magnitude that would be formed eventually in these systems, produces peroxide at a slower rate than the isopropyl alcohol.

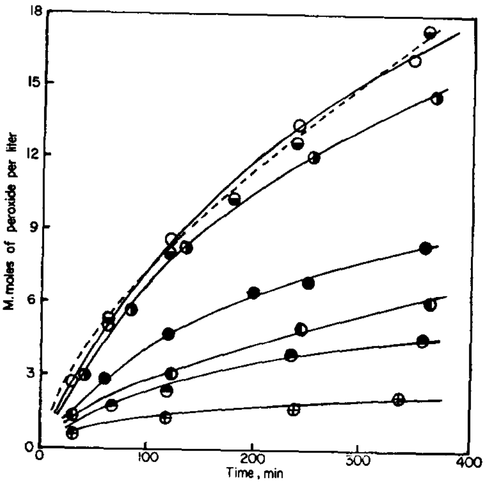

FIG. 1. Influence of the concentration of isopropyl alcohol on the formation of peroxide. Temp 25°C; ⊕ 2×10^{-3} *M* alcohol in water; ◒ 7×10^{-3} *M* alcohol; ◐ 8×10^{-2} *M* alcohol; ● 1 *M* alcohol; ◑ 10 *M* alcohol; ○ 10 *M* alcohol and 0.4 g zinc oxide; ◓ pure alcohol.

Figure 6 makes it clear that acetone and water added to a suspension of ZnO in pure isopropyl alcohol have no effect on acetone formation, and a small depressing effect on peroxide accumulation. The effect of the added hydrogen peroxide shows that acetone is certainly not being formed through a secondary reaction of accumulated hydrogen peroxide. Neither does it appear that inhibition caused by accumulated acetone is responsible for the even-

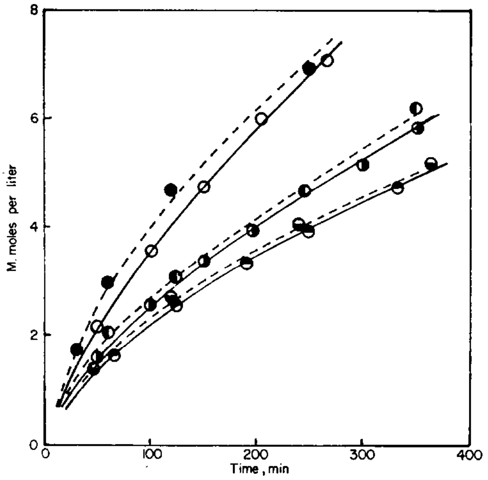

FIG. 2. Comparison of the formation of acetone and peroxide in aqueous isopropyl alcohol. Temp 25°C; ◓ acetone, ◒ peroxide in 7 × 10^{-3} M alcohol in water; ◑ acetone, ◐ peroxide in 8 × 10^{-2} M alcohol in water; ○ acetone, ● peroxide in 1 M alcohol in water.

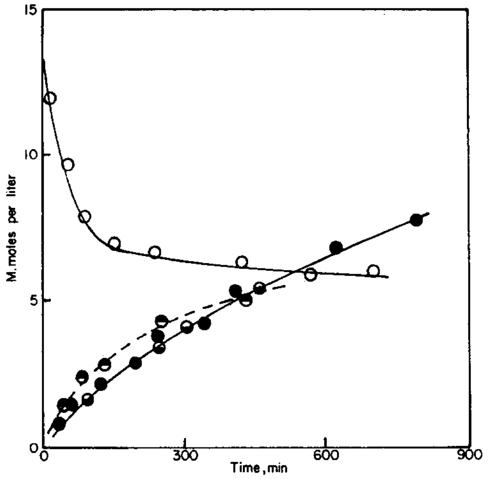

FIG. 3. Influence of hydrogen peroxide on the formation of acetone in 6 × 10^{-2} M isopropyl alcohol in water. Temp 25°C; ● acetone, ○ peroxide in reaction mixture containing initially added hydrogen peroxide; ◒ acetone, ◓ peroxide in reaction mixture not containing any initially added hydrogen peroxide.

tual decrease in rate of formation of peroxide observed in all cases.

The rate of formation of peroxide increases with increasing alcohol concentration up to 10 M. In very dilute solutions it is possible to calculate that this rate has an order of approximately 0.5 with respect to alcohol concentration. The apparent order falls off rapidly at higher concentrations under these conditions of temperature and light intensity (I_0). The concentration of acetone starts out equal to that of peroxide, with alcohol concentrations less than 1.0 M,

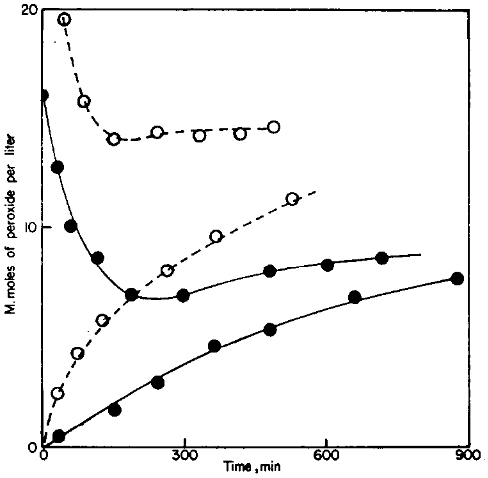

FIG. 4. Comparison of the influence of acetone and isopropyl alcohol on the formation and decomposition of peroxide in aqueous solutions. Temp 25°C; ○ 1 M isopropyl alcohol; ● 2.5 × 10^{-2} M acetone.

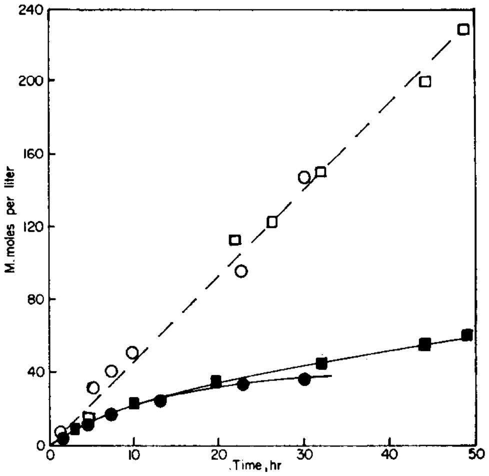

FIG. 5. Influence of the weight of zinc oxide on the formation of acetone and peroxide in pure isopropyl alcohol. Temp 30°C; □ acetone, ■ peroxide with 0.1 g zinc oxide; ○ acetone, ● peroxide with 0.4 g zinc oxide.

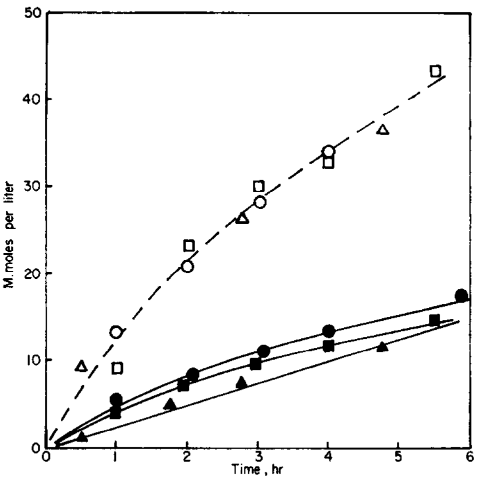

FIG. 6. Influence of small amounts of water and acetone on the formation of acetone and peroxide in isopropyl alcohol. Temp 30°C; ○ acetone, ● peroxide in pure alcohol; □ acetone, ■ peroxide in alcohol containing 0.1 *M* water; Δ acetone, ▲ peroxide in alcohol containing 0.1 *M* acetone.

and temperatures below 25°C. At higher temperatures and higher concentrations of alcohol the acetone increases much more rapidly than the peroxide. On prolonged irradiation the peroxide reaches a limiting value, both in aqueous and pure alcoholic suspensions.

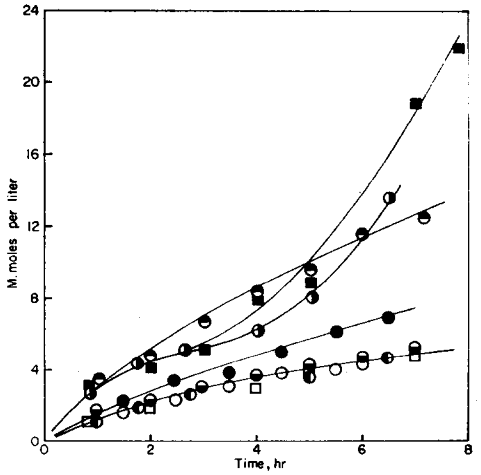

FIG. 7. Effect of temperature on the formation of acetone and peroxide in 1 *M* isopropyl alcohol in water; ■ acetone, □ peroxide at 50°C; ◑ acetone, ◐ peroxide at 40°C; ◓ acetone, ◒ peroxide at 30°C; ● acetone, ○ peroxide at 15°C.

In the former, the rate of formation of peroxide appears to be practically independent of temperature, Fig. 7. The effect of temperature on the acetone formation is complex. At 25°C the rate of formation of acetone appears to remain fairly constant over long periods. Analyses of the reaction products in aqueous systems at 40–50°C show a considerable increase in the aldehydic secondary product noted in the section on experimental methods above. In pure alcohol, Fig. 8, the acetone curves assume an autocatalytic appearance at higher temperatures. The chief difference between the aqueous and nonaqueous systems is the effect of temperature on the peroxide formation; cf. Figs. 7 and 9.

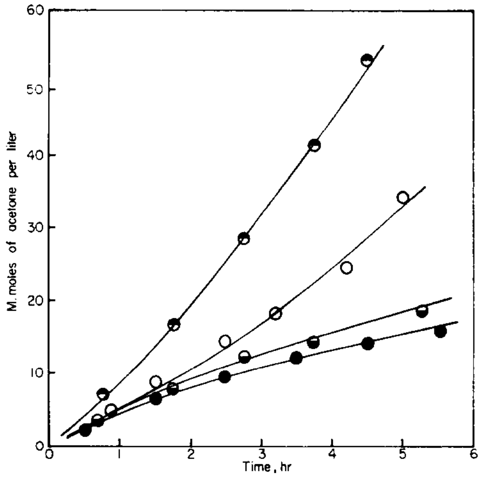

FIG. 8. Effect of temperature on the formation of acetone in pure isopropyl alcohol; ◓ 50°C; ○ 40°C; ◒ 30°C; ● 17°C.

Since the data of Figs. 7 through 11 show that the reaction products are complex functions of temperature and light intensity, and that different mechanisms evidently come into prominence under varying conditions, there is only one case where a straightforward increase in rate with increasing temperature makes it possible to calculate an activation energy, and that is in the case of peroxide formation in pure alcohol. The apparent activation energy, which may correspond to the process $\cdot O_2^- + RH \rightarrow HO_2\cdot + R\cdot$ (see below), is 5.7 kcal between 15° and 40°C.

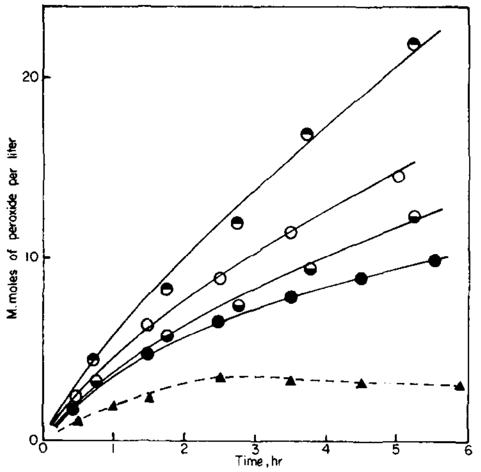

FIG. 9. Influence of temperature on the formation of peroxide in pure isopropyl alcohol; ◓ 50°C; ○ 40°C; ◒ 30°C; ● 17°C; ▲ 1 × 10^{-3} M phenol in water at 30°C.

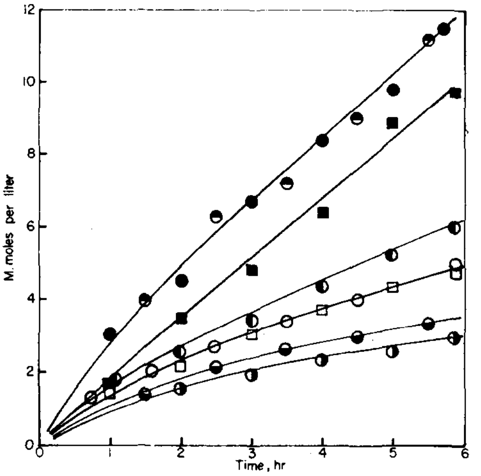

FIG. 10. Effect of light intensity on the formation of peroxide and acetone in 1 M isopropyl alcohol in water. Temp 30°C; □ peroxide, ■ acetone with light intensity (2 × I_0); ○ peroxide, ● acetone (I_0); ◒ peroxide, ◓ acetone ($I_0/2$); ◑ peroxide, ◐ acetone ($I_0/4$).

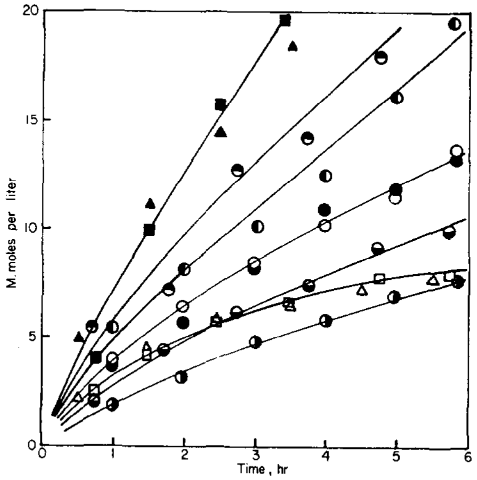

FIG. 11. Effect of light intensity on the formation of peroxide and acetone in pure isopropyl alcohol. Temp 30°C; □ peroxide, ■ acetone with light intensity (2 × I_0); ○ peroxide, ● acetone (I_0); ◒ peroxide, ◓ acetone ($I_0/2$); ◑ peroxide, ◐ acetone ($I_0/4$); △ peroxide, ▲ acetone (2 × I_0) reaction carried out in an atmosphere of pure oxygen.

The results obtained at various light intensities are summarized in Figs. 10 and 11. In aqueous systems the initial rate of formation of peroxide remains constant for the two highest light intensities and thereafter diminishes. Under the same conditions the initial rate of formation of acetone at first increases with decreasing light intensity and then gradually decreases again. In pure isopropyl alcohol, Fig. 11, the initial rates of formation of peroxide follow the same pattern as those of acetone in aqueous systems. The rate of formation of acetone in pure alcohol decreases with the initial decrease of light intensity, then increases at slightly lower light intensity, and finally decreases again at the lowest light intensity used. The quantum yield for acetone and peroxide formation, on ZnO of area approximately 4 sq m/g, Fig. 1, in 1 M isopropyl alcohol at 25°C is 0.4. The quantum yield for formation of acetone in pure isopropyl alcohol at 30°C, Fig. 6, is about 1.5. The initial yields on ZnO of smaller surface area, Fig. 8, are about half this value and increase sharply between 40° and 50°C. The rate of formation of peroxide in a ZnO suspension containing 10^{-3} M phenol, a system that has been extensively studied (*9, 12*) and found to have a quantum yield of 0.3 on this same ZnO, is included in Fig. 9 for comparison. The initial quantum yield of peroxide in pure isopropyl alcohol at higher temperature is seen slightly to exceed 1.0.

Measurements of oxygen uptake show

that the ratio of oxygen absorbed to peroxide formed in irradiated suspensions of zinc oxide containing isopropyl alcohol is always greater than one. Without irradiation there is no oxygen uptake in these systems. A few experiments were carried out in a nitrogen atmosphere at temperatures of 30° and 50°C with suspensions of zinc oxide in aqueous as well as pure isopropyl alcohol. In all cases a long period of induction, of the order of 3 hr, was followed by an extremely slow rate of formation of acetone. No measurable amounts of peroxide were formed. At low temperatures, in air, oxygen consumption ceases as soon as the light is turned off. At higher temperatures, around 50°C, the oxygen uptake initiated by irradiation continues at a slower rate in the dark. This observation is in agreement with the results of Komuro *et al.* (*17*).

DISCUSSION

According to the interpretation of several investigators (*3, 8, 11, 19, 20*) the formation of hydrogen peroxide at irradiated zinc oxide surfaces involves the reduction of molecular oxygen. This process must create electron-deficient sites on zinc oxide at which alcohol can be dehydrogenated. Thus the addition of two electrons to molecular oxygen to form peroxide, and the removal of two electrons (or hydrogen atoms) from isopropyl alcohol to form acetone, may be visualized as complementary processes accounting for the apparent equivalence of acetone and peroxide formed in the experiments summarized in Fig. 2.

Furthermore, although the formation of hydrogen peroxide from oxygen is an acceptor reaction, the reverse decomposition of hydrogen peroxide can take place by both acceptor and donor type mechanisms. Competition between alcohol and hydrogen peroxide for donor sites might be postulated to account for the higher equilibrium concentrations of hydrogen peroxide observed in the presence of alcohol. The results of Figs. 3 and 4, with addition of hydrogen peroxide initially, show that this explanation is certainly incomplete. In addition, the complexities arising with high concentrations of alcohol, and with variations in the temperature and light intensity, serve to elucidate the nature of the active intermediates and the conditions under which quantum yields can be varied considerably.

The relatively high quantum yields of both peroxide and acetone in pure isopropyl alcohol suggest the possibility of participation of free radicals. The conversion of isopropyl alcohol to acetone has been effected photochemically using benzophenone as a photosensitizer (*21, 22*), and by thermal oxidation at 380°–440°C (*23*). Hydrogen peroxide is formed during these reactions whenever sufficient oxygen is present. The radical $(\mathrm{Me})_2\,\dot{\mathrm{C}}\,\mathrm{OH}$ and hydroxyisopropyl hydroperoxide have been postulated as the probable intermediates.

Since isopropyl alcohol does not undergo any transformation on zinc oxide in the dark, or on irradiated zinc oxide in the absence of oxygen, both light and oxygen are essential for the reaction. There are several species of oxygen which might be formed at the photocatalyst surface, and which must be considered as possible active intermediates: O_2^*, O_2^{-*}, O_2^-, O^*, O, O^{-*}, O^-. Calvert *et al.* (*11*) suggested that the effect of light absorbed by the zinc oxide was to transfer an electron to an oxygen molecule adsorbed at the surface, leading to formation of O_2^-. Recent studies (*7, 8, 24*) demonstrate that adsorbed oxygen has already trapped electrons at the zinc oxide surface in the dark, forming O^- ions. Since isopropyl alcohol undergoes no reaction on zinc oxide with light, O^- cannot be considered as the active species. Barry and Stone (*7*) report rapid exchange of isotopic oxygen on zinc oxide at room temperature in the dark. This exchange must take place through dissociated oxygen, and hence atomic oxygen can also be excluded as the active intermediate. Thus one or more of the four excited species or O_2^- must be responsible for initiating the processes leading to the formation of peroxide and acetone.

Any satisfactory explanation of the initial effects of light activation in these processes must account for the formation of hydrogen peroxide, even though with low efficiency, in suspensions of zinc oxide in pure water. Reactions of O_2^* or O^* with water must lead to the formation of $\cdot OH$ radicals from the water, and would predicate the presence of some oxygen originating from the water in the hydrogen peroxide formed. The fact that Calvert *et al.* (*11*) find that the oxygen in the peroxide comes entirely from molecular oxygen, makes O_2^* and O^* unlikely active species, at least in suspensions of zinc oxide in liquid water, although desorbed oxygen in an excited state may play a part in high temperature vapor phase reactions (*25*).

Without making any distinction between O_2^{-*} and O_2^- as far as the initial reactions are concerned, the reactions of the remaining possible active species with water and alcohol may be tabulated as follows:

$$O_2^{-*} + H_2O \rightarrow HO_2\cdot\ \text{(excess energy?)} + OH^- \qquad \text{(a)}$$

$$O_2^{-*} + (Me)_2CHOH \rightarrow HO_2^- + (Me)_2\dot{C}\,OH \qquad \text{(b)}$$

$$O^{-*} + H_2O \rightarrow \cdot OH\text{(excess energy?)} + OH^- \qquad \text{(c)}$$

$$O^{-*} + (Me)_2CHOH \rightarrow OH^- + (Me)_2\dot{C}\,OH \qquad \text{(d)}$$

Whether in aqueous solutions or in pure isopropyl alcohol the peroxide and acetone form simultaneously right from the start of irradiation, and the acetone formed is equal to or greater than the peroxide. If O^{-*} is the active intermediate in the case of pure alcohol, both peroxide and acetone must be formed through the hydroperoxide of the radical $(Me)_2\dot{C}$ OH. This implies that the acetone observed is due to the decomposition of the hydroxyisopropyl hydroperoxide in the chromatographic column. Under the conditions of analysis employed this decomposition is unlikely. Further, the type of reaction envisaged here involves the least probable reaction of the radicals postulated, as subsequent discussion will show. It may be suggested that O^{-*} abstracts a proton from the isopropyl alcohol giving rise to an $\cdot OH$ radical and an alcohol anion-radical which may react to form acetone at the electron-deficient zinc oxide. However, from the mechanism suggested for the catalytic dehydrogenation of isopropyl alcohol (*4, 18, 26*) it seems more likely that the isopropyl alcohol will transfer a hydrogen atom rather than a proton.

The active form of oxygen which provides the most satisfactory explanation for all the observed results is a molecular anion. Oxygen is known to have a large capture cross section for electrons with energies in the region of 2–3 ev (*27*), forming O_2^{-*} which is unstable unless some of the energy is removed by collision, which occurs readily in the liquid phase. The excitation energy is supposed to be partly electronic and partly vibrational, and the stabilized O_2^- resulting from collisions may not be in its ground state. There is evidence also for a very low energy form of O_2^- near the ground state of O_2. Since reactions in zinc oxide suspensions only occur on irradiation, it is unlikely that the latter form of O_2^- initiates the reactions. The formation of HO_2^- results in measurable peroxide directly. The radicals $HO_2\cdot$ and $\cdot OH$ can both lead to hydrogen peroxide formation by dimerization. The radical $HO_2\cdot$, particularly if it contains excess energy, may also form hydrogen peroxide by hydrogen abstraction from an organic molecule.

Under the experimental conditions addition of oxygen to the hydroxyisopropyl radical formed in the initial step would lead to a radical of the type $RO_2\cdot$. The reactions of $RO_2\cdot$ radicals have been summarized by Noyes (*28*) and Bach (*29*).

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \quad \text{[cf. ref. (30)]} \qquad \text{(e)}$$

$$2\,RO_2\cdot \rightarrow 2\,RO\cdot + O_2 \qquad \text{(f)}$$

$$RO\cdot + RH \rightarrow ROH + R\cdot \quad \text{[cf. refs. (30, 31)]}$$

$$RO_2\cdot\ (\text{or } RO\cdot) \rightarrow \text{products of lower molecular weight} \quad \text{[cf. refs. (31, 32)]} \qquad \text{(g)}$$

Since in the presence of water, hydroxyisopropyl hydroperoxide is unstable (*30*) most of the peroxide in the aqueous systems must arise directly from $HO_2\cdot$ and HO_2^- (a, b) by temperature independent reactions, cf. Fig. 7. The activation energy requirements of (e), (f), and (g), make it seem probable that at low temperatures acetone results chiefly from further dehydrogenation of the radical $(Me)_2\dot{C}$ OH at the irradiated surface.

At higher temperatures other processes leading to the formation of acetone become important, as evidenced by changes in rates of formation and distribution of products as well as by oxygen uptake studies. In water solutions the effect of increasing temperature is to enhance the reactions (f) and (g). Reaction (f) leads to a *gem*-dihydroxy compound which might be expected to undergo immediate dehydration yielding acetone. Reaction (g), which gives rise to the unidentified secondary product and possibly fresh radicals, apparently involves a slightly higher activation energy than (f). The new secondary radicals may explain the rapid rise in rate of acetone formation in the later stages of the reaction at 40° and 50°C. The difference in extent of secondary products formed in pure alcohol and in water solutions may thus be attributed to the relative importance of reaction (g) in the latter, where the radicals encounter alcohol molecules less frequently.

In pure alcohol reaction (e), which involves an activation energy, must also become important. Any hydroperoxide formed in pure alcohol at 40°–50°C would be unstable in water and addition of dilute sulfuric acid prior to analysis for peroxide would result in almost complete conversion to hydrogen peroxide.

Variation of light intensity seems to affect primarily the rate of immediate production of radicals at the photocatalyst surface. The complex changes in rates of formation of peroxide and acetone observed in Figs. 10 and 11 can be explained by shifts in balance between reactions directly at the surface and those taking place through radical chains in the liquid phase.

In water solution at very high light intensity $HO_2\cdot$ radicals produced in high concentration at the surface would undergo extensive dimerization to form hydrogen peroxide, while an almost equivalent amount of acetone would be produced by direct dehydrogenation of alcohol on the catalyst. As the light intensity is decreased, the rate of formation of peroxide is affected very little at first, but there is an increase in rate of production of acetone as more peroxide is formed via reaction (b) with initiation of organic radicals in the liquid phase. Finally as the light intensity is decreased still further the rates of formation of both peroxide and acetone eventually decrease.

In suspensions of zinc oxide in pure isopropyl alcohol, HO_2^- and $(Me)_2\dot{C}OH$ radicals are the expected primary products at the surface. Extensive dehydrogenation to form acetone should take place directly at the surface at very high light intensities. One would expect nearly equivalent amounts of peroxide and acetone to be formed in this case also. At the intermediate light intensity (I_0) this is approximately the result observed. At the highest light intensity used, however, there is observed a slight depression of the rate of appearance of peroxide and a large increase in rate of appearance of acetone. Apparently if O_2^{-*} is formed in very high concentration at the surface, leading to nearly complete surface coverage with HO_2^-, peroxide ions lose electrons to the electron-deficient zinc oxide, leading to formation of $HO_2\cdot$ radicals, increased hydrogen abstraction from alcohol in the liquid phase, and an over-all decrease in net hydrogen peroxide concentration. Simultaneously there is a large increase in acetone formation through increased radical chain reactions, (f), as well as due to dehydrogenation at the electron-deficient sites produced in greater concentrations at the high light intensity. One will recall that at 30°C there is considerable increase in acetone formation (Fig. 7), but very little increase in peroxide. This is evidence that hydroxyisopropyl hydroperoxide is not an important intermediate under these conditions.

At lower light intensities in suspensions in pure isopropyl alcohol, there is noticeable decrease in peroxide formed, owing to lower rates of formation of HO_2^- at the surface. The rate of formation of acetone rises slightly at first as radical chains in the liquid phase more than compensate for decreased dehydrogenation to form acetone at the surface.

ACKNOWLEDGMENT

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