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FORMATION OF ENERGY RICH COMPOUNDS AT
LIGHT ACTIVATED SENSITIZER SURFACES

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FORMATION OF ENERGY RICH COMPOUNDS
AT LIGHT ACTIVATED SENSITIZER SURFACES

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ABSTRACT

Study of photosensitized oxidation of isopropyl alcohol to acetone at zinc oxide surfaces irradiated by light at $3650 \overset{0}{\text{\AA}}$, leads to the conclusion that an excited oxygen anion, probably O_2^{*-} , is the photo-activated center formed at the catalyst surface. The alcohol is quantitatively converted to acetone. Hydrogen peroxide accumulates until rates of formation and decomposition become equal. Quantum yields are high. Formation of high molecular weight polymers on irradiation of methyl methacrylate in dilute solutions at zinc oxide surfaces confirms the role of O_2^{*-} . Chain initiation is controlled by oxygen tension and favored by solvents of high dielectric constant and good hydrogen donor properties.

Both formation and decomposition of hydrogen peroxide at irradiated zinc oxide surfaces are inhibited by cyanides and amides. Extensive infrared studies of zinc oxide catalysts pretreated with solutions of cyanides and amides show strongly adsorbed nitrogen-containing frag-

ments indicating that under certain conditions some of these compounds are good electron donors at the catalyst surface.

Knowledge of the effects of oxygen and formamide at irradiated zinc oxide surfaces has been utilized to construct photoelectric cells with electrodes made by coating zinc oxide on platinum mesh. The magnitude of the photoelectric effects at these electrodes depends on the nature of the oxidation-reduction reaction taking place in the dark half cell.

Tests originally undertaken to evaluate the possibility of sensitizing zinc oxide to visible light by adsorbed pigments, have led to the discovery of a unique and efficient photosensitized transformation of carotene in the presence of pheophytin irradiated by red light. Pigment studies and photoelectric effects at irradiated zinc oxide surfaces are being extended under Contract AF19(628)-2768.

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INTRODUCTION

During the past ten or fifteen years many investigations have centered around inorganic photocatalysts and photoconductors, with a view to discovering efficient processes for utilizing or storing solar energy. The need for further study of photochemistry in the liquid and solid state was strongly emphasized in a Symposium held at Endicott House in Dedham, Mass., September 1957; the highlights were published in 1960.(1). Many photocatalytic reactions previously studied in this laboratory had been oxidations of organic substances in aqueous solutions, particularly on zinc oxide, antimony trioxide, and zinc and cadmium sulfides, using light absorbed by the inorganic solid, not by the water, oxygen or organic substance. In most cases the light seems to provide the activation energy necessary to start an oxidation reaction which then proceeds on a thermodynamically spontaneous basis. The rates of most of these reactions are negligibly slow without the photosensitizing solid. In the case of zinc oxide and the rhombic form of antimony trioxide the solids are essentially photocatalysts which can be used repeatedly. In the case of zinc and cadmium sulfides the net result seems to be the oxidation of the sulfides themselves ultimately to sulfates. In prismatic antimony trioxide

irradiation at 3130 Å brings about an internal oxidation-reduction reaction which is reversible in the light.(2-6). Of all these inorganic solids zinc oxide seems to combine the most convenient properties: high quantum yields, absorption in a region of the spectrum readily available to study, good photoconductivity, high specific surface area, and ability to function repeatedly as a catalyst without poisoning.

There had been no thorough study of the course of a photosensitized oxidation reaction in a non-aqueous liquid such as an alcohol, and no systematic study of the optimum conditions for accumulation of hydrogen peroxide and/or organic peroxides. Recent investigations had made it clear that all the oxygen in the hydrogen peroxide formed at irradiated zinc oxide surface in aqueous suspension comes from the air, not from the water.(7). Although useful oxidation products of organic compounds can be obtained in these systems, the only part of the energy stored is in the form of peroxides. The study of the mechanism of the oxidation of isopropyl alcohol to form acetone and hydrogen peroxide at zinc oxide surfaces was undertaken in order to discover effects of conditions on rates of reaction, quantum yields of products, and nature of competing reactions.

During a series of experiments designed to compare photo-oxidation reactions of various aromatic compounds

in irradiated suspensions of zinc oxide, it was observed that hydrogen peroxide produced in presence of acetanilide remained stable indefinitely for prolonged periods of irradiation following the attaining of the maximum concentration. This phenomenon also seemed to merit further study.

Even in the absence of organic material a low steady state level of hydrogen peroxide is formed in these suspensions on exposure to light. The peroxide thus does not appear to be entirely a by-product of oxidation of organic substances. Oxygen evidently can trap electrons at the irradiated surface. In fact formation and decomposition of hydrogen peroxide seems to be completely reversible, since hydrogen peroxide added initially will decompose rapidly on irradiated zinc oxide, the concentration dropping steadily until it reaches the same value as that which would be formed on irradiation of spectroscopically pure zinc oxide in triply distilled water in presence of air.

Oxygen is involved in all the above reactions at irradiated zinc oxide. Observation that irradiated zinc oxide could initiate the polymerization of some vinyl monomers, apparently only in absence of oxygen, suggested the possibility of direct electron transfer to water or monomer at the catalyst surface. Study of the polymerization of methyl methacrylate in these systems was therefore un-

dertaken in order to discover whether substances other than oxygen could undergo direct photoactivation on the surface of the catalyst.

More complete knowledge of electron transfer reactions occurring at the surface of an inorganic photoconductor should lead to more efficient systems for the production of photovoltaic effects. It is hoped that substances can be discovered which absorb light in the visible region of the spectrum and which can be reversibly oxidized and reduced at the photocatalyst surface. Studies of pigments and their participation in energy transfer in these systems are being continued in this laboratory.

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**CONVERSION OF ISOPROPYL ALCOHOL TO ACETONE
ON IRRADIATED ZINC OXIDE**

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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 suspensions 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 $\text{cm}^{-2} \text{sec}^{-1}$ (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 tempera-

ture. The temperature was controlled to $\pm 0.5^\circ\text{C}$. 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 μ l 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.

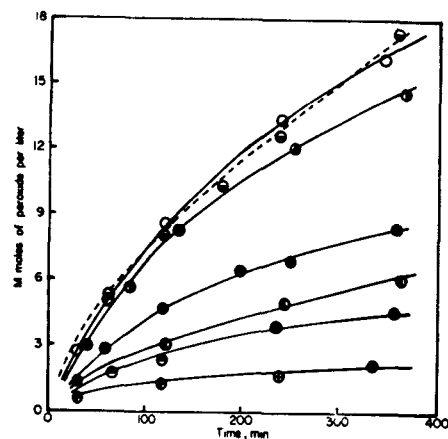


FIG. 1. Influence of the concentration of isopropyl alcohol on the formation of peroxide. Temp 25°C; $\oplus$ 2×10^{-3} M alcohol in water; $\ominus$ 7×10^{-3} M alcohol; $\bullet$ 8×10^{-3} M alcohol; $\bullet$ 1 M alcohol; $\circ$ 10 M alcohol; $\circ$ 10 M alcohol and 0.4 g zinc oxide; $\bullet$ pure 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-

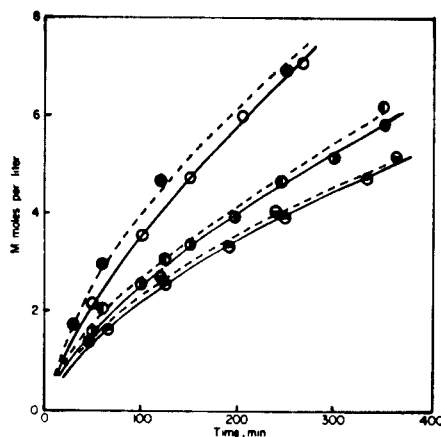


FIG. 2. Comparison of the formation of acetone and peroxide in aqueous isopropyl alcohol. Temp 25°C; ● acetone, ○ peroxide in $7 \times 10^{-3} M$ alcohol in water; ● acetone, ○ peroxide in $8 \times 10^{-3} M$ alcohol in water; ● acetone, ○ peroxide in $1 M$ alcohol in water.

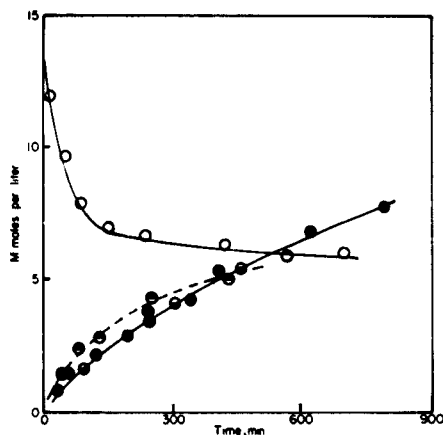


FIG. 3. Influence of hydrogen peroxide on the formation of acetone in $6 \times 10^{-3} M$ isopropyl alcohol in water. Temp 25°C; ● acetone, ○ peroxide in reaction mixture containing initially added hydrogen peroxide; ● acetone, ○ peroxide in reaction mixture not containing any initially added hydrogen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

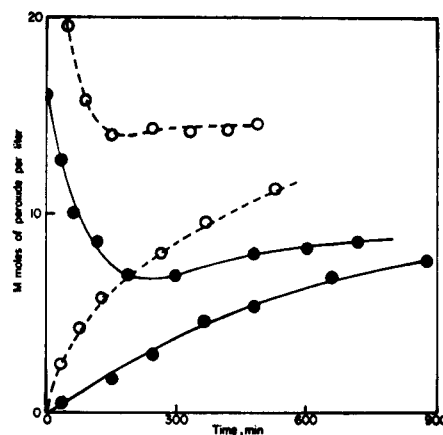


FIG. 4. Comparison of the influence of acetone and isopropyl alcohol on the formation and decomposition of peroxide in aqueous solutions. Temp 25°C; ○ $1 M$ isopropyl alcohol; ● $2.5 \times 10^{-3} M$ acetone.

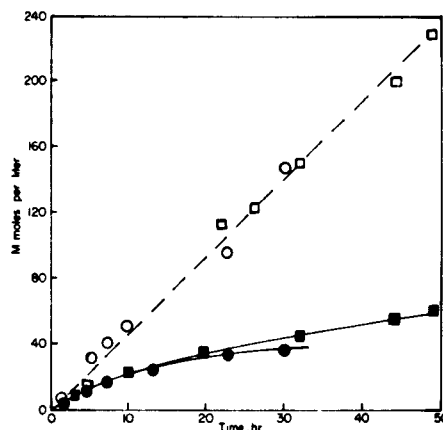


FIG. 5. Influence of the weight of zinc oxide on the formation of acetone and peroxide in pure isopropyl alcohol. Temp 30°C; □ acetone, ■ peroxide with $0.1 g$ zinc oxide; ○ acetone, ● peroxide with $0.4 g$ zinc oxide.

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 $1.0 M$,

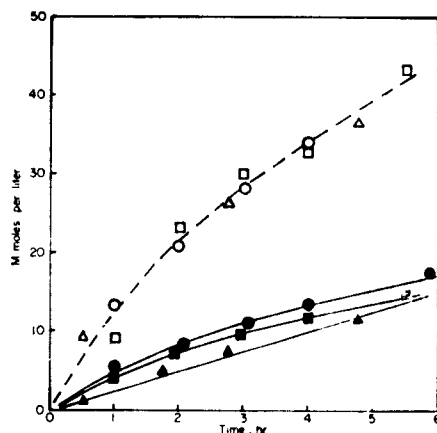


FIG. 6. Influence of small amounts of water and acetone on the formation of acetone and peroxide in isopropyl alcohol. Temp 30°C; ○ acetone, ● peroxide in pure alcohol; □ acetone, ■ peroxide in alcohol containing 0.1 *M* water; Δ acetone, ▲ peroxide in alcohol containing 0.1 *M* acetone.

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.

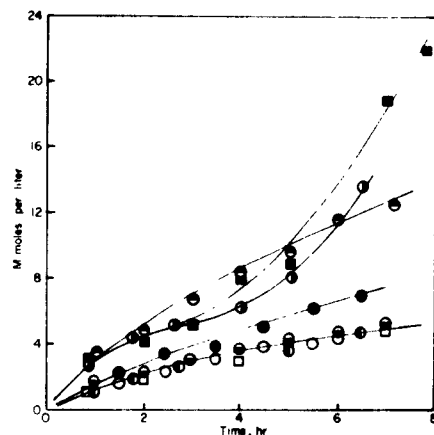


FIG. 7. Effect of temperature on the formation of acetone and peroxide in 1 *M* isopropyl alcohol in water; ■ acetone, □ peroxide at 50°C; ● acetone, ○ peroxide at 40°C; ● acetone, ○ peroxide at 30°C; ● acetone, ○ peroxide at 15°C.

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.

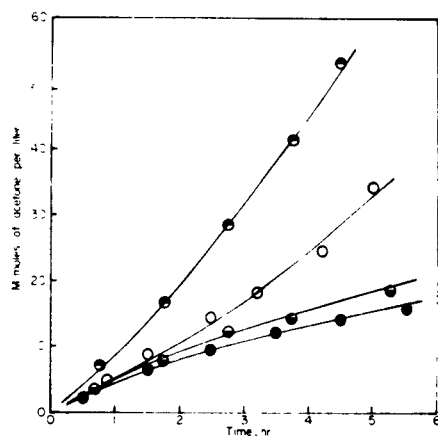


FIG. 8. Effect of temperature on the formation of acetone in pure isopropyl alcohol; ● 50°C; ○ 40°C; ◐ 30°C; ● 17°C.

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 $\cdot\text{O}_2^- + \text{RH} \rightarrow \text{HO}_2\cdot + \text{R}\cdot$ (see below), is 5.7 kcal between 15° and 40°C.

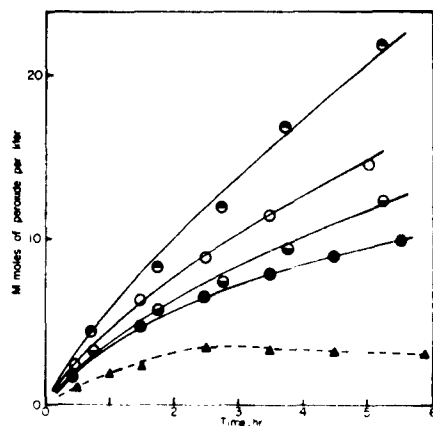


Fig. 9. Influence of temperature on the formation of peroxide in pure isopropyl alcohol; ● 50°C; ○ 40°C; ◐ 30°C; ● 17°C; ▲ 1×10^{-3} M phenol in water at 30°C.

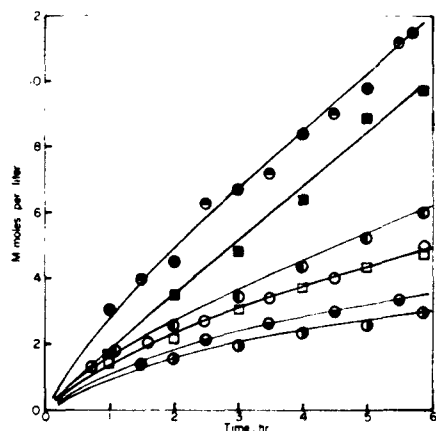


Fig. 10. Effect of light intensity on the formation of peroxide and acetone in 1 M isopropyl alcohol in water. Temp 30°C; □ peroxide, ■ acetone with light intensity ($2 \times I_0$); ○ peroxide, ● acetone (I_0); ◐ peroxide, ◑ acetone ($I_0/2$); ○ peroxide, ● acetone ($I_0/4$).

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 in-

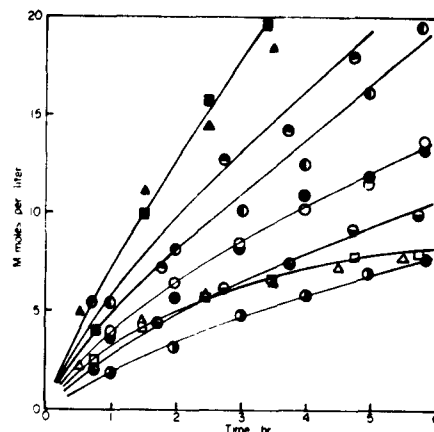


Fig. 11. Effect of light intensity on the formation of peroxide and acetone in pure isopropyl alcohol. Temp 30°C; □ peroxide, ■ acetone with light intensity ($2 \times I_0$); ○ peroxide, ● acetone (I_0); ◐ peroxide, ◑ acetone ($I_0/2$); ○ peroxide, ● acetone ($I_0/4$); ▲ peroxide, ▲ acetone ($2 \times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

tensity 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.

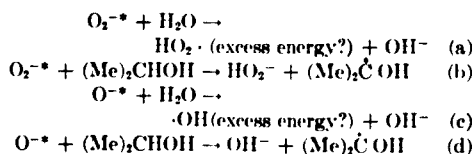
The relatively high quantum yields of both peroxide and acetone in pure isopropyl alcohol suggest the possibility of participation of free radicals. The conversion of isopropyl alcohol to acetone has been effected photochemically using benzophenone as a photosensitizer (21, 22), and by thermal oxidation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

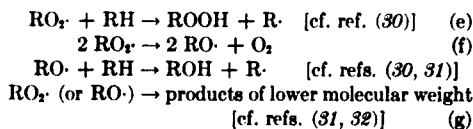


Whether in aqueous solutions or in pure isopropyl alcohol the peroxide and acetone form simultaneously right from the start of irradiation, and the acetone formed is equal to or greater than the peroxide. If O^* is the active intermediate in the case of pure alcohol, both peroxide and acetone must be 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).



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 $\text{HO}_2\cdot$ 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, $\text{HO}_2\cdot$ and $(\text{Me})_2\dot{\text{C}}\text{OH}$ 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_m) 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 $\text{O}_2\cdot^*$ is formed in very high concentration at the surface, leading to nearly complete surface coverage with $\text{HO}_2\cdot$, peroxide ions lose electrons to the electron-deficient zinc oxide, leading to formation of $\text{HO}_2\cdot$ 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 $\text{HO}_2\cdot$ 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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Mechanism of the Photo-Initiated Polymerization of Methyl Methacrylate at Zinc Oxide Surfaces

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MECHANISM OF THE PHOTO-INITIATED POLYMERIZATION OF METHYL METHACRYLATE AT ZINC OXIDE SURFACES¹

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Detailed investigation of the photosensitized polymerization of methyl methacrylate in suspensions of zinc oxide in various solvents, irradiated by near ultraviolet light at 365 m μ , demonstrates conclusively that surface-adsorbed oxygen is essential to chain initiation. Polymers of high molecular weight, ca. 10^6 , are obtained with oxygen-free solutions, and untreated zinc oxide surfaces. Zinc oxide reduced under hydrogen, or heated to remove surface oxygen during evacuation, results in greatly suppressed polymerization. Presence of oxygen in solution yields a larger number of chains initiated, but lower molecular weight. Excess oxygen inhibits polymerization completely. Comparison of polymerizations in various solvents indicates that solvents having high dielectric constants coupled with good proton-donating or hydrogen-bonding characteristics favor chain initiation via excited oxygen on the surface. This photo-activated oxygen is formed on the surface of zinc oxide during irradiation and the polymer chains initiated by it continue to grow for some time in the dark. Evidence that the excited oxygen may be an anion initiator stems from the observation that methyl methacrylate and acrylonitrile polymerize readily in these systems, but styrene not at all. Electron spin resonance spectra show that both oxygen and water adsorbed in the dark are able to trap all the conduction electrons in heated, evacuated zinc oxide, but light is necessary for initiation of polymerization. Ultraviolet light at 365 m μ therefore is believed to produce an excited oxygen, probably anion radical, at the surface of the zinc oxide.

Introduction

Formation of hydrogen peroxide in dilute aqueous suspensions of zinc oxide containing organic material is the characteristic effect of irradiation at 365 m μ .²⁻⁴ Organic substances vary considerably in their ability to promote peroxide formation. An essential condition is rapid entrainment of air or vigorous shaking to bring molecular oxygen in continuous contact with the photocatalytic surface of the zinc oxide. In the absence of organic matter a low steady-state level of peroxide is formed, indicating a reversible reaction. Proposed mechanisms for the formation of peroxide have postulated intermediate free radicals from either oxygen or water.

Observation that irradiated zinc oxide could initiate polymerization of some vinyl monomers in dilute aqueous solution, apparently only in absence of air, suggested possible direct dissociation of water at the catalyst surface. The present studies were undertaken to clarify the mechanism of initiation of polymerization in these systems, particularly the effects of previous treatment of the catalyst, removal of oxygen from the solution, and the influence of the solvent.

Experimental

Apparatus and Materials.—The 365 m μ line of a Hanovia high pressure quartz mercury arc was used as the exciting light. Radiation above 380 m μ is not absorbed by zinc oxide or any of the materials in these systems. Shorter wave lengths, below 330 m μ , are filtered out by using Pyrex reaction vessels and a thick Pyrex shield over the arc. Thus the only light absorption is by zinc oxide at 365 m μ .

A simple water-jacketed Pyrex tube with provision for transferring samples under nitrogen was used for preliminary comparison of relative efficiencies (in promoting polymerization) of solvents and types of photocatalysts. For studies of the rate of polymerization a similar, but larger, vessel was designed, using standard Pyrex creosote flasks for the inner vessel and employing a magnetic stirrer. It soon was discovered that both nitrogen stirring and mag-

netic stirring interfered with the growth of polymer chains. A 250-ml. Pyrex flask of the erlenmeyer type with a large surface on which the catalyst could be distributed for light absorption proved to be most convenient.

Materials.—Methyl methacrylate, inhibitor-free, was supplied by courtesy of Monsanto Chemical Co., Springfield, Mass. Formamide, N,N-dimethylformamide and N-methylformamide were Matheson Coleman & Bell highest purity, 99% or better. Absolute methanol was ACS reagent grade. Spectroscopically pure zinc oxide and zinc sulfide were obtained from the New Jersey Zinc Company. This company also supplied samples of zinc oxide specially prepared to be (1) photoconducting, (2) charge-accepting and (3) charge-rejecting. When no other type is specified the term zinc oxide will refer to the spectroscopically pure sample, which however gives the same results as ordinary analyzed reagent grade commercially available zinc oxide.

Measurement of Molecular Weights of Polymers.—A specially constructed viscometer was designed for intrinsic viscosity measurements to determine approximate molecular weights of polymers dissolved in benzene. A reservoir bulb of large cross-section made possible progressive dilutions without intermediate emptying and refilling of the viscometer. Values of K and a used were, respectively, 7.45×10^{-4} and 7.575×10^{-1} .

Dielectric Constants.—Dielectric constants of solvent mixtures were measured with a Sargent Oscillometer calibrated with the pure liquids.

Usual Experimental Conditions.—Unless otherwise stated all data in tables were obtained using 0.15 g. of zinc oxide, 50 ml. of water and 1 ml. of methyl methacrylate. The usual temperature was 30°. The suspension was allowed to settle giving a uniform distribution of zinc oxide on the bottom of a 250-ml. erlenmeyer flask. The system then was evacuated, irradiated for 2.5 hours, and allowed to stand 18 hours in the dark before adding dilute sulfuric acid to terminate the reaction.

Electron Paramagnetic Resonance Measurements.—These studies were carried out by irradiating specially prepared zinc oxide samples with the Hanovia H-4 lamp described above in the cavity of a Varian, 100 Kc. spectrometer, through the courtesy of Dr. P. H. Bray's laboratory, Physics Department of Brown University.

Results and Discussion

The extent and characteristics of polymerization of methyl methacrylate in dilute solution, initiated by light absorbed by a photocatalytic solid, are influenced by the following factors: (1) the nature and pre-treatment of the photocatalyst; (2) the concentration of oxygen present in solution or supplied during irradiation; (3) physical conditions of irradiation such as quantity of photocata-

(1) This work was carried out under Contract No. AF 19(604)-7224, with the Geophysics Research Directorate, Air Force Cambridge Research Laboratories, Air Force Research Division.

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lyst, stirring, duration of irradiation, temperature; (4) time and temperature of standing after irradiation before termination; (5) the nature and concentration of the monomer; (6) the nature of the solvent.

(1) **Nature and Pre-treatment of the Photo-catalyst.**—The study of the kinetics and mechanism of photo-catalytically initiated polymerization of methyl methacrylate has been carried out with spectroscopically pure zinc oxide. A few preliminary experiments with various photocatalytic solids indicate that zinc sulfide is also a good initiator for these polymerizations.

Of the various preparations of zinc oxide tested, both the ordinary analytical reagent grade of zinc oxide and the specially prepared charge-accepting zinc oxide also showed good ability to initiate polymerization. The photoconducting and charge-rejecting zinc oxides were much less effective. These latter two samples have been prepared in such a way as to contain more excess zinc and possess better thermal conductivity. The charge-accepting zinc oxide is a poorer conductor. Since it gives off hydrogen sulfide on treatment with dilute acid, it must contain zinc sulfide. At any rate higher conductivity does not appear to be favorable to initiation of polymerization at the photocatalyst surface.

In every case adsorbed oxygen was found to be necessary for initiation of polymerization. Zinc oxide reduced under hydrogen is not effective. Table I shows the effect of pre-treatment of the zinc oxide.

TABLE I
EFFECT OF PRE-TREATMENT OF CATALYST AND
SUSPENSION

Treat- ment of ZnO	Treatment of suspension	Polymer wt., g.	Mol. wt. $\times 10^{-4}$	Min. no. chains $\times 10^{-11}$
Heated	Evacuated	0.3240	2.167	0.906
Unheated	Evacuated	.3724	1.981	1.139
Unheated	Not evacuated	.2077	0.543	2.317

Discussion I.—Heating the zinc oxide under vacuum increases the molecular weight of the polymer but reduces the number of chains. It seems that this effect is not due to sintering, since heating produces the same effect on 0.15 g. of zinc oxide as on 0.25 g. A decrease in surface area would not be expected to reduce the efficiency of 0.25 g. of heated zinc oxide to less than that of 0.15 g. of unheated zinc oxide.

(2) **Effect of Oxygen Present in Solution.**—Comparison of the evacuated and non-evacuated suspensions in Table I shows that the more oxygen there is in the system the less the molecular weight, and the greater the number of chains initiated. The total weight of polymer is least when the system is not evacuated, and greatest when the zinc oxide is not heated and the system is evacuated. It would appear from these results that oxygen is required for the initiation process, but too much oxygen in solution serves as an inhibitor. Table II gives more complete data on the effect of oxygen on the course of the polymerization.

Discussion II.—With increase in time of irradiation there are more chains initiated whether the

TABLE II
EFFECT OF TIME OF IRRADIATION

Irradiation time, hr.	Polymer wt., g.	Mol. wt. $\times 10^{-4}$	Min. no. chains $\times 10^{-11}$
System evacuated			
0.5	0.0867	1.923	0.273
1.5	.2963	1.469	1.222
2.0	.3525	1.816	1.176
2.5	.3724	1.981	1.139
System not evacuated			
0.5	0.0326	...	...
1.0	.0912	0.432	1.278
1.5	.1456	.543	1.624
2.5	.2077	.543	2.317
5.5	.3798	.589	3.908

system is evacuated or not; the molecular weight remains about the same. The initiating species must be formed during the period of irradiation. The inhibiting effect of extra oxygen can be compensated for by longer irradiation as far as total amount of polymer is concerned, but in the presence of excess oxygen the molecular weight always remains low, and the number of chains increases.

(3) **Physical Conditions of Irradiation.**—For best results the zinc oxide should be spread uniformly over a large surface. In a 250-ml. erlenmeyer flask, containing 1 ml. of methyl methacrylate in 50 ml. of water, 0.15 g. of zinc oxide gave maximum polymerization. Results are remarkably reproducible, producing polymers of high, uniform average molecular weight. Under these conditions 2.5 hr. irradiation is sufficient for maximum amount of polymer provided polymerization is allowed to go to completion in the dark as described below. It is very important to allow the solution to remain undisturbed during polymerization as the data of Table III clearly show.

TABLE III
EFFECT OF STIRRING

Conditions	Polymer wt., g.	Mol. wt. $\times 10^{-4}$	Min. no. chains $\times 10^{-11}$
No stirring	0.3724	1.991	1.139
Stirred every $\frac{1}{2}$ hr. during irradiation	0.3637	1.096	2.010
Vigorous stirring with mag- netic stirrer	trace	...	...

Discussion III.—Vigorous stirring during irradiation prevents polymerization. Occasional stirring decreases the molecular weight but also results in a larger number of chains formed. Stirring therefore appears to favor chain termination. The influence of temperature during irradiation can be seen best in Table IVB where it is compared with the effect of temperature in the dark period following irradiation.

(4) **Time and Temperature Variables.**—

Discussion IV.—During the period of irradiation the total weight of polymer formed is almost the same whether the system is evacuated or not. Even after the period of irradiation, chains seem to be initiated. In an evacuated system the period after irradiation results in increased weight

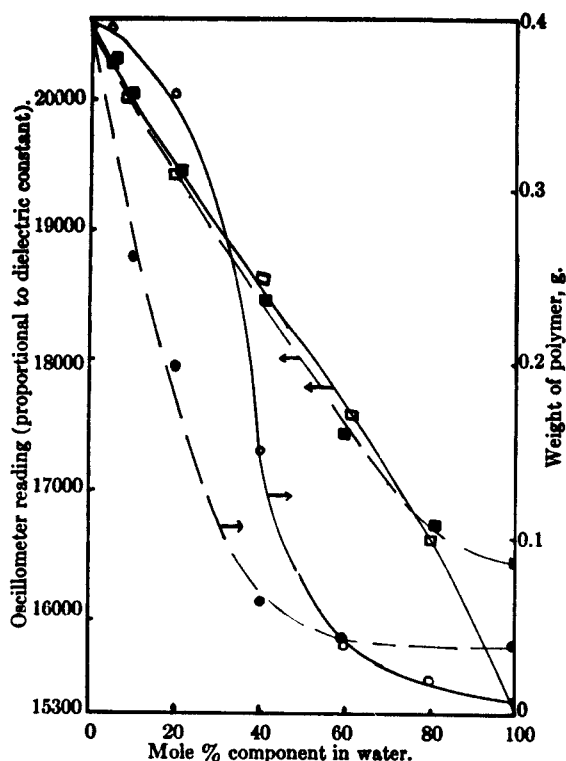


Fig. 1.—Influence of mixtures of solvents on extent of polymerization of methyl methacrylate at irradiated zinc oxide surface, showing relationship to dielectric constant of mixture: ●, weight of polymer and ■, dielectric constant, in mixtures of *N,N*-dimethylformamide and water; ○, weight of polymer and □, dielectric constant, in mixtures of methanol and water. 0.15 g. ZnO, 1 ml. methyl methacrylate, 50 ml. solvent, irradiated 2.5 hr., acid added to terminate polymerization after 18 additional hr. in the dark.

TABLE IVA

EFFECT OF DARK PERIOD ON POLYMER GROWTH

Total time before adding acid, hr.	Polymer wt., g.	Mol. wt. $\times 10^{-3}$	Min. no. chains $\times 10^{-17}$
System evacuated			
2.5	0.1539	1.310	0.712
6.0	.3205	1.413	1.375
21.0	.3724	1.981	1.139
System not evacuated			
2.5	0.1476	0.678	1.275
21.0	0.2077	0.543	2.317

of polymer chiefly through increased average molecular weight. In a non-evacuated system the average molecular weight remains about the same; only the apparent number of chains initiated increases.

The effect of raising the temperature is to increase the weight of polymer formed, both during and after the period of irradiation. In the evacuated systems the average molecular weight remains around 1.5×10^4 ; the apparent number of chains initiated again appears to increase during the dark period. These effects are much smaller in the non-evacuated systems, with average molecular weights of 0.5×10^4 , and a large number of

chains already formed at the end of the 2.5 hours irradiation.

TABLE IVB
EFFECT OF TEMPERATURE

Total time before adding acid, hr.	Temp., °C.	Polymer wt., g.
System evacuated		
2.5	20	0.183
2.5	30	.264
2.5	40	.283
21.0	20	.288
21.0	30	.390
21.0	40	.529
System not evacuated		
2.5	20	0.139
2.5	30	.148
2.5	40	.222
21.0	20	.188
21.0	30	.208
21.0	40	.250

These results could mean any of the following: (1) More polymer chains are really initiated in the dark; this condition could be realized only if the photo-reactive oxygen formed by light on the zinc oxide surface is a very stable free radical or excited species which takes a long time to react with monomer molecules; (2) The monomer molecules which have reacted with the photo-activated oxygen need time to grow to a detectable size which can be precipitated and filtered out of the reaction mixture after adding acid to dissolve the zinc oxide.

It already has been shown that vigorous stirring results in apparently complete suppression of polymerization. Nevertheless, the oxygen must have been photo-activated on irradiating the zinc oxide in the stirred vessel also, and monomer molecules must have come in contact with the surface more frequently. Chain propagation therefore seems to be a slower process than chain initiation or termination. The effect of stirring seems to be largely chain termination, whereas the increase in temperature seems to affect the extent of chain propagation and thus the number of chains counted in the analytical process. This interpretation is strengthened by considering the effect of increasing monomer concentration.

(5) The Nature and Concentration of the Monomer.—

TABLE V

EFFECT OF CONCENTRATION OF METHYL METHACRYLATE

Vol. methyl methacrylate, ml.	Polymer wt., g.	Mol. wt. $\times 10^{-3}$	Min. no. chains $\times 10^{-17}$
0.5	0.1439	0.750	1.103
1.0	.3724	1.981	1.139
2.0	.4515	2.565	1.067

Discussion V.—Increases in both temperature and concentration yield higher total weights of polymer. In the case of increasing concentration the effect is to increase molecular weight only, whereas the temperature affected

primarily the apparent number of chains initiated. The usual experimental condition, 1 ml. of methyl methacrylate in 50 ml. of water, already exceeds slightly the solubility of methyl methacrylate in water. The addition of more methyl methacrylate cannot increase the concentration of monomer in solution, but only serves to maintain a saturated solution for a longer period of time, and thus keep up a steady rate of addition to growing chains, thereby increasing the average molecular weight. The rise in temperature increases both the solubility of monomer and the rate of diffusion. Once a layer of polymer has formed on the surface of zinc oxide, the diffusion of monomer to add to initiated chains becomes increasingly difficult. Some chains apparently fail to reach a detectable size unless the temperature is increased, or polymerization is allowed to continue for a long time in the dark.

Both acrylonitrile and methyl methacrylate have been found to polymerize readily in these systems. Styrene does not polymerize to any measurable extent when irradiated in a suspension of zinc oxide in water. Since styrene is known to be susceptible to polymerization only by free radicals or cations,⁶ it is possible that the photo-initiator may be an anion. These considerations prompted an investigation of the nature and role of solvents favorable to these polymerizations.

(6) The Role of the Solvent.—

TABLE VI
EFFECT OF DIELECTRIC CONSTANT

Solvent (dielectric constant)	Polymer wt. g.	Mol. wt. $\times 10^{-4}$	Min. no. chains $\times 10^{-11}$
CH ₃ OH (33)	0.01	...	...
HCON(CH ₃) ₂ (37)	.0417	...	...
H ₂ O (80)	.3681	1.694	1.316
HCONH ₂ (109)	.4620	0.543	5.153
HCONH(CH ₃) (190)	.0249	...	...

Discussion VI.—Methyl methacrylate is much more soluble in the three amides (formamide, N-methylformamide and N,N-dimethylformamide) and in methanol, than in water. One might have thought that dielectric constant was the most important property of the solvent for this polymerization, except that there is very little polymerization in N-methylformamide which has the highest dielectric constant of all. Figure 1 illustrates the effect of mixture of solvents.

The drop in weight of polymer is much greater on adding small amounts of N,N-dimethylformamide to water than on adding methanol. Independent studies in this Laboratory have shown that the rate of oxidation of methanol is greater than that of the amides in irradiated aqueous suspensions of zinc oxide. Therefore it is improbable that the inefficiency of the polymerization in these solvents is due to competing reactions of oxidation of the solvent on the zinc oxide surface. Addition of either N-methylformamide or N,N-dimethylformamide to formamide lowers the extent of polymerization almost equally. These facts indicate that neither the dielectric constant nor the solubility is the unique determining property. The ability of the solvent to furnish protons or

form hydrogen bonds seems to be one of the most influential characteristics.

N-Methyl groups in the amides serve to prevent intermolecular association, thus allowing the unshared electron pair on the nitrogen to bind its own protons more strongly and increasing the nucleophilic character. The suitability of formamide as a solvent for the photo-initiated polymerization appears to be related to its more electrophilic nature.

When methanol is added to water it increases the solubility of methyl methacrylate as would N,N-dimethylformamide. Water, however, is a good proton donor, and methanol is more akin to water than N,N-dimethylformamide in its electron attracting properties. Therefore methanol in small concentrations causes a smaller decrease in polymer yield than N,N-dimethylformamide. The higher the concentration of methanol or dimethylformamide the smaller the molecular weight of the polymer.

Formamide itself gives rise to a low molecular weight polymer, similar to that obtained in water when the system is not evacuated. The number of chains initiated in formamide is more than double that in water. Irradiation of pure zinc oxide in formamide results in a decrease in absorption of the irradiated formamide at 290 m μ as shown by difference spectra *vs.* unirradiated formamide as the blank. The same effect in the spectrum can be obtained in limited degree by addition of hydrogen peroxide to formamide.

Electron paramagnetic resonance studies show that the solvent may influence the properties of zinc oxide even in the dark. Good conduction signals are obtained from zinc oxide only after heating and evacuation. Signals obtained in the dark from these samples are very little altered on irradiation at 365 m μ . Introduction of either oxygen or water completely obliterates this conduction electron signal, which is not restored on irradiation. These effects are in striking confirmation of observations in the infrared spectral measurements being conducted in the laboratories of the National Research Council, Ottawa.⁷ The electron paramagnetic resonance effects certainly merit further study. To the present, only a very slight increase in the conduction electron signal has been observed on irradiating an oxygen-covered zinc oxide surface in contact with water.

Summary and Conclusions

The data outlined above lead to the following general interpretation of the mechanism of the photo-initiated polymerization of methyl methacrylate at zinc oxide surfaces.

The photo-initiator formed at the surface of zinc oxide is certainly a form of oxygen. The polymerization process initiated in the light is completed in the dark.

The light must produce an excited state of oxygen, not merely an electron-transfer to oxygen, since electron paramagnetic resonance studies show that oxygen has indeed already trapped all the conduction electrons of the zinc oxide, even in the dark. Furthermore, samples of zinc oxide spe-

(6) D. C. Pepper, *Quart. Revs. (London)*, **8**, 88 (1954).

(7) J. H. Taylor and C. H. Ainberg, *Can. J. Chem.*, **39**, 535 (1961).

cially made to be good conductors do not favor the polymerization.

The fact that styrene will not polymerize in these systems whereas monomers containing electrophilic groups such as acrylonitrile and methyl methacrylate polymerize readily seems to suggest that the photo-activated oxygen may be anionic in character, possibly a radical-anion, such as excited $\cdot O_2^-$. Styrene is less soluble in water than methyl methacrylate, but the failure to observe polymerization of styrene is not due to limited solubility, since it will not polymerize when the solvent is formamide, in which styrene has a much greater solubility.

The polymerization must not be anion-propagated, even though it may be anion-initiated, because the process has many features characteristic of free radical chain polymerizations. Vigorous stirring increases chain termination. If the reac-

tion mixture is not disturbed reproducible polymers of high average molecular weight are obtained in evacuated systems. Oxygen present in solution shortens the chain length. Solubility of monomer and rate of diffusion are important factors.

The role of the solvent is incompletely understood. Neither dielectric constant nor solubility of the monomer is a unique determining characteristic. Ability to donate protons, or to solvate and stabilize the chain-initiator through hydrogen-bonding, seems to be an important feature.

An excited oxygen radical-ion may be able to fulfill all these requirements. It would initiate polymerization only of monomers susceptible to anion-initiation. Since it also has a free-radical character, neutralization of the anion character of the initiated polymer chain by a solvent which can furnish protons would still leave an ordinary free radical chain propagation process.

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Effects of Amides on Photochemical Processes at Zinc Oxide Surfaces

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EFFECTS OF AMIDES ON PHOTOCHEMICAL PROCESSES AT ZINC OXIDE SURFACES¹

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Amide residues exert a stabilizing influence on hydrogen peroxide at irradiated surfaces of zinc oxide in aqueous suspension, whether the peroxide has been formed in the system by the photocatalyzed oxidation of the amide itself, or whether hydrogen peroxide has been added to the system before irradiation. In the former case the rate of oxygen uptake and the final steady-state concentration of hydrogen peroxide are related to the number of oxidizable C-H bonds in the amide. In the latter case the level of hydrogen peroxide that can be maintained is governed by both the initial concentration of added peroxide and the nature of the amide. Formamide gives rise to a surface-inactivating residue immediately on irradiation in contact with zinc oxide, and therefore stabilizes high concentrations of added peroxide, but produces very little peroxide itself. Acetanilide both produces and maintains high concentrations of hydrogen peroxide. Other amides studied include N-methylformamide, N,N-dimethylformamide, and urea. Effects of several nitrogen-containing compounds are compared with those of the amides.

Introduction

When an aqueous suspension of zinc oxide is irradiated with light in the near ultraviolet a small amount of hydrogen peroxide is formed. The presence of organic material in the system greatly increases the yield of hydrogen peroxide. Previous studies² using phenol as the organic additive showed an optimum rate of peroxide formation at a phenol concentration of $1 \times 10^{-3} M$. With this initial concentration of phenol, hydrogen peroxide builds up to a maximum concentration of $4 \times 10^{-3} M$ in about two hours, and then gradually decreases until it reaches the steady-state concentration that would be formed at an irradiated zinc oxide surface in pure water. The first detectable oxidation products of the phenol are catechol and hydroquinone. After a few hours there is no further indication of an aromatic ring in the system, and evolution of carbon dioxide suggests exhaustive oxidation of the phenol.

During a series of experiments designed to compare reactions of various aromatic compounds in irradiated suspensions of zinc oxide, it was observed that hydrogen peroxide formed in the presence of acetanilide remained stable indefinitely for prolonged periods of irradiation following the attaining of the maximum concentration. This phenomenon is illustrated in Fig. 1.

Meanwhile, studies of the photosensitized polymerization of methyl methacrylate in aqueous suspensions of zinc oxide³ had indicated that oxygen is essential to the initiation process, contrary to the earlier suggestion that polymerization in the absence of oxygen proved that oxygen might not be necessary for photochemical reaction at zinc oxide surfaces.⁴ Several simple amides such as formamide, N-methyl-, and N,N-dimethylformamide are good solvents for oxygen. Their dielectric constants are, respectively, 109, 190, and 37. While formamide is a good solvent for the photosensitized polymerization, neither N-methylformamide nor N,N-dimethylformamide are.

The object of the present research was to study in detail the behavior of amides in these systems, in order to understand better the chemical effects produced by light at the surface of zinc oxide. Data are presented on the formation of hydrogen peroxide in the presence of various amides. In some cases it has been possible to identify intermediates. Measurements of oxygen uptake have been made in both aqueous and non-aqueous systems.

Experimental

The apparatus and method of procedure for the investigation of peroxide formation were the same as described.⁴ The Hanovia H-4 high pressure quartz mercury arc lamp was used throughout with a Pyrex jacket to retain all radiation below 320 m μ . Rapid entrainment of air supplied oxygen to the system and kept the zinc oxide in suspension. The air was washed through distilled water before entrainment. For each study 0.1 g. of zinc oxide and 25-30 ml. of solution were used. Samples of 1 or 2 ml. were withdrawn periodically and analyzed for peroxide by addition of iodide to the acidified solution and titration with standard thiosulfate. All chemicals used were Analytical Reagent grade.

Ultraviolet analyses were performed with a Beckman DK-2 ratio recording spectrophotometer. Infrared analyses were made on a Perkin-Elmer Infracord. Samples of the irradiated solution, from which zinc oxide had been removed by centrifugation, were prepared for infrared analysis by evaporation to dryness, dissolving the residue in chloroform, addition of potassium bromide, and vacuum evaporation of the chloroform.

Measurements of oxygen uptake were made in Warburg respirometer flasks using the Hanovia H-4 mercury lamp in its Pyrex shield mounted horizontally above a pair of flasks to give sets of duplicate measurements. The temperature was maintained at 25° in these experiments as well as in the tests for peroxide formation. The flasks contained 0.2 g. of zinc oxide and 3 ml. of liquid reactant. A few measurements were carried out with potassium hydroxide solution in the center well to check on carbon dioxide evolution.

Concentrations of oxidation products of acetanilide were estimated by making the centrifugate from the irradiated suspension alkaline with 1 M sodium hydroxide and extracting the unreacted acetanilide into chloroform. The sodium hydroxide layer, containing the hydroxyacetanilides, then was neutralized with 1 M hydrochloric acid and analyzed on the spectrophotometer. Standards were prepared according to the same procedure. The chloroform layer was evaporated to dryness under vacuum and the residue of acetanilide redissolved in water for spectrophotometric measurements.

Hydroxylamine hydrochloride and hydrazine sulfate were neutralized with sodium hydroxide before adding zinc oxide and irradiating. The effects of the salts produced by the neutralization were tested in separate measurements of decomposition of hydrogen peroxide and were found to be negligible. For example, curve 6 of Fig. 7 shows that

(1) This work was carried out under Contract AF 19 (604)-7224, with the Geophysics Research Directorate of the Air Force Cambridge Research Laboratories, Air Force Research Division.

(2) M. C. Markham, M. C. Hannan, and S. W. Evans, *J. Am. Chem. Soc.*, **76**, 820 (1954).

(3) J. C. Kuriaiose and M. C. Markham, *J. Phys. Chem.*, **65**, 2232 (1961).

(4) M. C. Markham and K. J. Laidler, *ibid.*, **57**, 363 (1953).

the decomposition of hydrogen peroxide is the same in the presence and absence of added sodium chloride. Highest purity grades of redistilled aniline, methylamine hydrochloride, ammonia, and propionitrile were used, all at concentration $10^{-3} M$, without further treatment. KCN was neutralized with HCl to obtain a solution of cyanide at pH 7.

Results

Suspensions of Zinc Oxide Containing Acetanilide.—Under the conditions used, the initial rate of formation of hydrogen peroxide in suspensions of zinc oxide containing acetanilide appears to be limited chiefly by the available light intensity at the catalyst surface. Moving the reaction vessel farther from the lamp reduces the reaction rate, but by a factor less than that predicted by the inverse square law. On the other hand, substituting oxygen for air does not increase the rate. The initial rates of formation of peroxide in solutions of acetanilide 0.001 M or higher apparently are independent of concentration. With the limiting concentration of 0.02 M , due to the solubility of acetanilide in water, there is a definite inhibition. Kinetic studies show that the reaction is zero order with respect to acetanilide between 0.001 and 0.010 M . The steady-state level reached by the hydrogen peroxide, however, is dependent on the initial acetanilide concentration, but in no simple numerical ratio, as shown in Fig. 1. The products of the reaction maintain a high concentration of peroxide in the system for long periods of irradiation. In some cases the time of irradiation has been extended to 40 hr. with no appreciable decrease in the peroxide concentration. The effect of temperature on these systems is slight. Activation energies of a few kilocalories can be measured in the initial stages.

Ultraviolet spectra reveal that the chief oxidation product of acetanilide is the *o*-hydroxyacetanilide. The formation of the hydroxy derivatives and the disappearance of acetanilide were studied in the initial reaction stages for several different initial concentrations of acetanilide. Results of the 0.001 M initial concentration of acetanilide are typical, and are shown in the following table.

TABLE I

FORMATION OF PRODUCTS AND DECOMPOSITION OF ACETANILIDE IN AQUEOUS SUSPENSIONS OF ZINC OXIDE AT 365 $m\mu$ AND 0.001 M INITIAL CONCENTRATION OF ACETANILIDE

Time (min.)	Concn. acetanilide, M ($\times 10^4$)	Concn. <i>p</i> - and/or <i>m</i> -hydroxyacetanilide, M ($\times 10^4$)	Concn. <i>o</i> -hydroxyacetanilide, M ($\times 10^4$)	Concn. hydrogen peroxide, M ($\times 10^4$)
0	10.0	0.00	0.00	0.00
5	7.2	.47	0.86	1.90
10	5.3	.48	2.31	4.25
15	3.6	.44	3.24	6.05
20	2.2	.30	4.05	9.75

* *p*- and *m*-hydroxyacetanilides are not distinguished here. In any case there is not much of either. By analogy with the oxidation products of phenol in these systems, we expect more of the *para* derivative and very little *meta*.

The fact that the *ortho* derivative builds up to a much higher concentration than the *para* and/or *meta* might be taken as an indication that the latter are preferentially adsorbed at the zinc oxide surface and therefore react at a faster rate. In the dark it has not been possible to detect any appreciable adsorption of either the parent acetanilide or

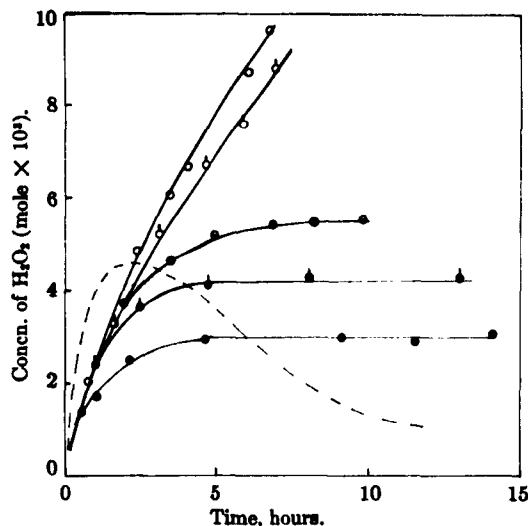


Fig. 1.—Effect of concentration of acetanilide on the formation of hydrogen peroxide: —, phenol (0.001 M); ●, 0.0005 M ; ●, 0.001 M ; ●, 0.002 M ; ○, 0.005 M ; ○, 0.01 M .

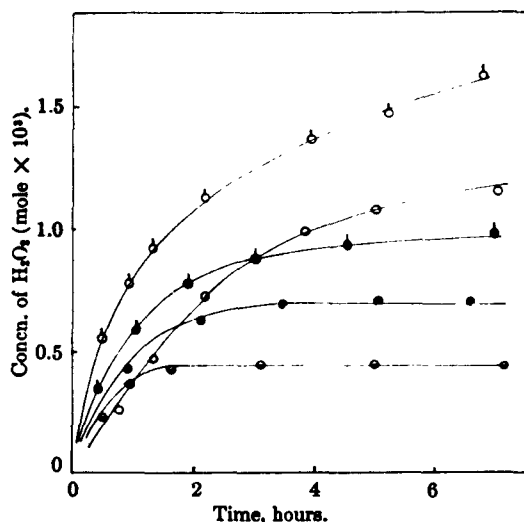


Fig. 2.—Effect of various amides on the formation of hydrogen peroxide: ●, formamide; ●, acetamide; ●, *N*-methylformamide; ○, water; ○, *N,N*-dimethylformamide.

the hydroxy-derivatives on the surface of zinc oxide suspended in water. It cannot be ruled out, however, that there might be some difference on irradiation. Nor does the *p*-hydroxyacetanilide appear to form peroxide faster at an irradiated zinc oxide surface. Independent studies of the rate of formation of hydrogen peroxide in irradiated suspensions containing 0.001 M *o*-hydroxyacetanilide or *p*-hydroxyacetanilide show that, when irradiated in equal initial concentrations, these compounds produce hydrogen peroxide at equal rates, and both produce it twice as fast as acetanilide solutions of equal concentration. It seems possible nevertheless that when hydroxy compounds are present simultaneously in smaller amounts there may be competition for the surface. It is noteworthy that

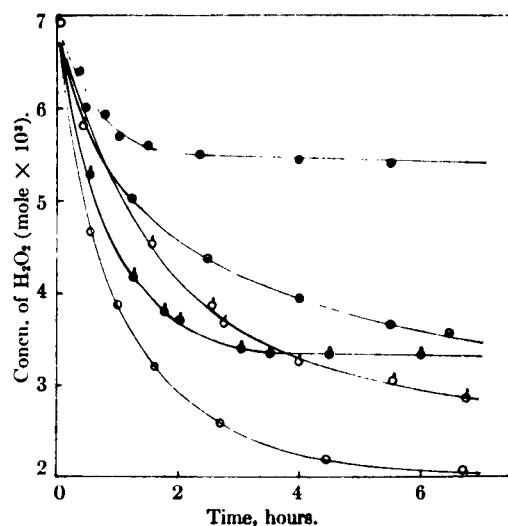


Fig. 3.—Effect of various amides on the decomposition of hydrogen peroxide: ●, formamide; ■, acetamide; ▲, N-methylformamide; ○, water; △, N,N-dimethylformamide.

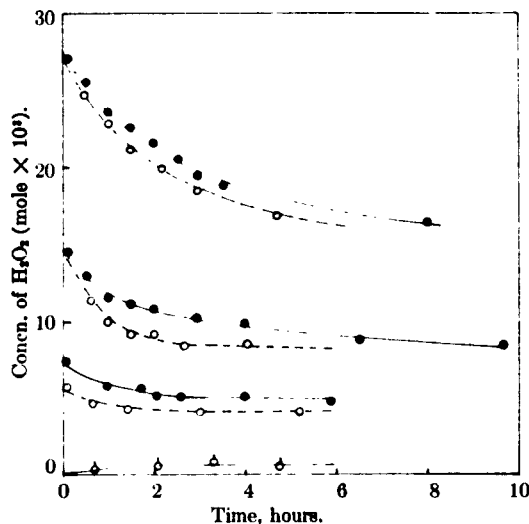


Fig. 4.—Effect of initial concentration of formamide and hydrogen peroxide on the steady-state concentration of hydrogen peroxide: ○, 0.001 *M* formamide; ●, 0.002 *M* formamide.

during the initial stages of oxidation in these irradiated suspensions of zinc oxide, 0.001 *M* *p*-hydroxyacetanilide forms a pink oxidation product, suggesting formation of an *o*-quinoid structure, whereas *o*-hydroxyacetanilide under the same conditions forms a yellow product, indicative of a *p*-quinoid structure. Since the *p*-quinone would be more stable than the *ortho*-, it is possible that the apparent persistence of the *o*-hydroxyacetanilide features in the spectra are due in part to the *p*-quinoid oxidation product. The corresponding *o*-quinone oxidation product of the *p*-hydroxyacetanilide would be expected to undergo rapid auto-oxidation. In fact the measured ratios of oxygen consumed to peroxide formed in these systems always are somewhat greater than 1:1.

Infrared studies of the products of irradiation of suspensions of zinc oxide containing acetanilide confirm those in the ultraviolet in indicating the presence of both *o*- and *p*-hydroxyacetanilides in the early stages of the reaction. After a few hours, when no more indication of an aromatic ring can be found in the ultraviolet spectra, infrared spectra also show the disappearance of aromatic ring vibrations. In fact, the only persistent features in the infrared spectrum after several hours or irradiation are small vibrations in regions characteristic of simple aliphatic amides. The only other final products seem to be hydrogen peroxide and carbon dioxide. One might expect the amide residue to be either acetamide or formamide. The differences in the infrared spectra for small amounts of these amides are not sufficiently unambiguous to permit a decision regarding the nature of the residue on this basis alone. It therefore was decided to carry out a comparative study of several amides in their abilities to take up oxygen and produce hydrogen peroxide, or maintain hydrogen peroxide added initially in irradiated aqueous suspensions of zinc oxide.

Comparative Study of Effects of Simple Aliphatic Amides at Irradiated Zinc Oxide Surfaces.—Besides acetamide and formamide other simple amides tested were: N-methylformamide, N,N-dimethylformamide, and urea. Figure 2 shows the rates of formation of hydrogen peroxide by several amides, as compared with water. It is evident that these substances produce peroxide much more slowly than acetanilide. Also there is evidence of some relation between the number of oxidizable methyl groups and the amount of hydrogen peroxide formed.

Figure 3 shows the effect of the same amides, also at 0.001 *M* concentration, in governing the extent of decomposition of hydrogen peroxide initially present at a concentration slightly higher than that which was formed by 0.001 *M* acetanilide. The amides appear almost in inverse order from that in Fig. 2, but peroxide decomposes fastest of all in pure water. Urea was found to have no effect on either the formation or maintenance of hydrogen peroxide in these systems, and so is not included in the figures. It appears that the other amides all are capable of producing some product that inhibits the extent of decomposition of hydrogen peroxide at irradiated zinc oxide surfaces. The inverse order of the amides in Fig. 2 and 3 may be due to the fact that the methyl groups on the nitrogen are capable of delaying the formation of this final product more than the methyl attached to the carbon as in acetamide.

In Figure 4 there are further studies with formamide, showing that doubling the concentration of formamide has very little effect on the final steady-state concentration of a given initial concentration of hydrogen peroxide. Doubling the hydrogen peroxide concentration, however, raises the steady level of hydrogen peroxide appreciably in the presence of a given amount of formamide.

Figure 5 shows the effects of 0.001 *M* formamide and 0.001 *M* acetanilide solutions with respect both to formation and decomposition of hydrogen

peroxide. Acetanilide not only preserves hydrogen peroxide added initially, but increases the concentration. Apparently the rate of decomposition of hydrogen peroxide at the surface is balanced and more than compensated by its rate of formation in the presence of acetanilide.

Oxygen absorption measurements were made with zinc oxide suspended in pure formamide, N-methylformamide, and N,N-dimethylformamide, as well as decimolar solutions of two of these. The results are presented in Fig. 6. The rate at which oxygen is taken up is highest for dimethylformamide and decreases through N-methylformamide and formamide. In water solution, too, dimethylformamide shows a higher rate of oxygen uptake than formamide, but the differences are much smaller. These results show the same trend as the rates of peroxide formation in Fig. 3. The presence of a larger number of C-H bonds increases the rate of oxygen uptake as well as the rate of peroxide formation.

In water solution dimethylformamide gives a rate of oxygen uptake lower than that with pure amide, while in the case of formamide the rate apparently is higher in aqueous solution. With potassium hydroxide in the center well of the Warburg flasks to absorb carbon dioxide, it becomes apparent that the rate of oxygen uptake by pure formamide really is higher, and that carbon dioxide is evolved right in the initial stages. Dimethylformamide shows no appreciable carbon dioxide formation in the first hour of irradiation. Formamide, having only one oxidizable C-H bond, gives rise to the final decomposition products immediately on irradiation, and these evidently inhibit peroxide formation and oxygen uptake. Water takes up oxygen less readily than the amides, hence aqueous solutions of the amides show a decrease in rate of oxygen uptake.

Comparative Study of Effects of Nitrogen-Containing Compounds other than Amides.—In order to obtain further information as to the probable nature of the amide residue, several nitrogen-containing compounds, at concentrations 10^{-3} M, were tested for their effects on inhibiting the decomposition of hydrogen peroxide in irradiated zinc oxide suspensions. The results are shown in Fig. 7. Curve 1 shows the effect of potassium cyanide, pH 9.8. Cyanide ion completely prevents the decomposition of hydrogen peroxide. Since zinc hydroxide fails to decompose hydrogen peroxide on irradiation, and the suspension at pH 9.8 contains appreciable hydroxide ion, it is not certain whether this effect is due to cyanide alone. Curve 2 shows the effect of adjusting the pH of the cyanide suspension to 7.1. There is a slight initial decomposition, but the cyanide ion certainly shows a strong inhibition of the decomposition of hydrogen peroxide. Curve 3, showing the effect of formamide, is included for comparison.

The effects of aniline and ammonia are indicated in curve 4, and that of hydrazine in curve 5. These compounds permit appreciable decomposition of hydrogen peroxide to take place before a stable concentration is attained. By comparison with water (or salts), shown in curve 6, the preceding com-

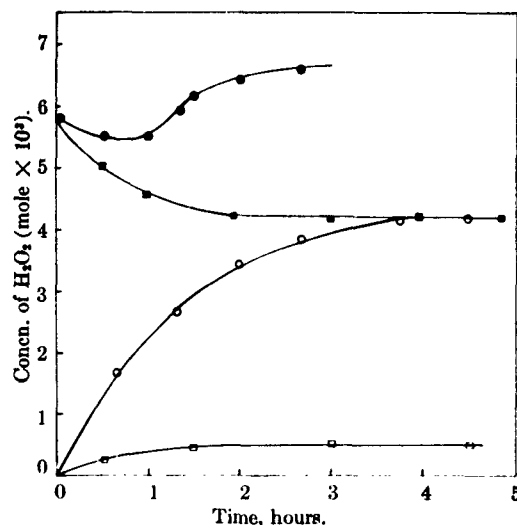


Fig. 5.—Comparison of the effects of 0.001 M formamide and acetanilide on the formation and decomposition of hydrogen peroxide: O, ●, acetanilide; ■, □, formamide.

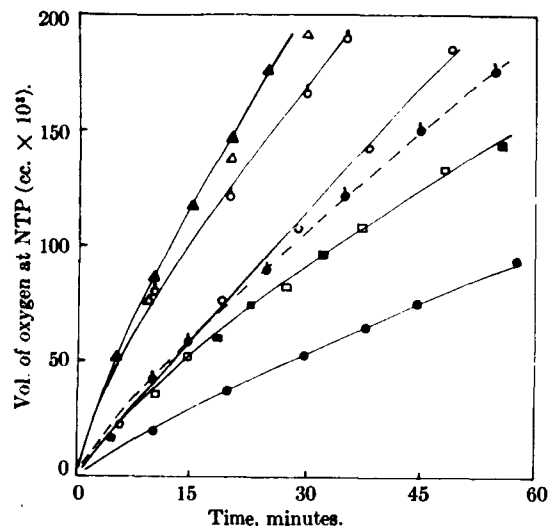


Fig. 6.—Effect of amides on oxygen uptake: ●, formamide; ○, formamide + KOH; ■, 0.1 M formamide; □, 0.1 M formamide + KOH; △, N,N-dimethylformamide; ▲, N,N-dimethylformamide + KOH; ●, 0.1 M N,N-dimethylformamide; ○, N-methylformamide.

pounds all show some inhibition. The pH of the methylamine hydrochloride was 6.0.

Surprisingly hydroxylamine and propionitrile, curve 7, are accelerators of the decomposition of hydrogen peroxide. It seems likely that these compounds give rise to free radicals which enhance the decomposition of the peroxide. In stabilizing the hydrogen peroxide in irradiated suspensions of zinc oxide the role of the organic additive appears to be the contribution of electrons to the catalyst. According to this picture it is unlikely that propionitrile can give rise to a cyanide ion, and therefore it does not show the same inhibition as potassium or hydrogen cyanides. Similarly hydroxylamine would not be expected to produce hydroxide ions in these systems.

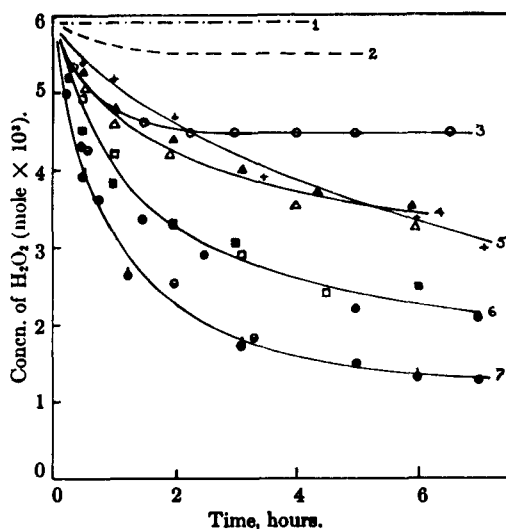


Fig. 7.—Comparison of the effect of various nitrogen-containing compounds on the decomposition of hydrogen peroxide: curve 1, potassium cyanide; 2, hydrogen cyanide; 3, formamide; 4, ammonia, Δ , aniline; 5, hydrazine; 6, $\bullet$, no additive, $\square$, methylamine hydrochloride, $\blacksquare$, sodium chloride; and 7, $\odot$, hydroxylamine, $\bullet$, propionitrile.

Conclusions

Results show that the persistence of hydrogen peroxide in irradiated suspensions containing acetanilide is due to an amide residue which apparently is strongly adsorbed on the surface, and able to exclude both oxygen and hydrogen peroxide. This residue does not reach an effective concentration on the surface until after the oxidation of the ring has permitted the accumulation of a relatively high concentration of hydrogen peroxide.

Formamide on reaction at an irradiated zinc oxide surface is converted directly to the final products and at least one of these must be remaining on the surface and acting as an inhibitor for further reaction. Since the other amides have to go through several intermediate steps before they give rise to products similar to those formed from formamide, the inhibiting action prevails only at a later time. Meanwhile considerable quantities of oxygen are taken up and the rate of this uptake must be related to the number of oxidizable linkages available in the molecule. The same explanation accounts for the effect of the amides in producing hydrogen peroxide in these systems. Urea, either because it is not adsorbed or not oxidized, has no effect. Since the inhibited surface no longer can participate in the oxygen-hydrogen peroxide exchange, the remaining hydrogen peroxide is stable indefinitely on continued irradiation.

The inhibiting residue must be the nitrogen-containing part of the amide group, perhaps forming a complex with the zinc at the catalyst surface, since large amounts of carbon dioxide are produced during the initial stages of the surface inactivation by formamide. Hydrogen peroxide added initially decomposes at the surface until the inhibiting product accumulates in sufficient quantity by the oxida-

tion of the amide. This conclusion is justified by Fig. 4, which shows that for a given initial concentration of formamide any desired steady-state concentration of hydrogen peroxide can be maintained provided the initial concentration is sufficiently high. During the initial period the decomposition of hydrogen peroxide follows an apparent second-order rate law. On the surface of zinc oxide a given amount of formamide always requires a definite amount of time for the formation of the nitrogen-containing residue, which inhibits the formation and decomposition of hydrogen peroxide. The higher the initial concentration of peroxide, the greater will be the per cent. decomposition during this time. The amide residue from 0.001 *M* formamide evidently is sufficient to produce a nearly covered surface, because doubling the concentration of formamide has practically no effect on the final level of peroxide. There is evidently an equilibrium with the aqueous phase because the zinc oxide can be filtered or centrifuged and used again for a period in a fresh solution.

The inhibiting residue evidently is not an ordinary zinc-ammonia complex, since ammonia is not able to inhibit directly. However, the fact that ammonia and hydrazine eventually do prove to be inhibitors of the decomposition of hydrogen peroxide proves that a simple nitrogen-containing residue can account for the effects of the amides. Aniline and ammonia, in spite of a large difference in basicity (K_b , ammonia, 1.8×10^{-5} ; K_b , aniline, 3.8×10^{-10}), require about the same amount of time to give rise to inhibiting fragments which tentatively might be considered to contain electron-deficient nitrogen. Apparently hydroxylamine produces both radicals which can accelerate peroxide decomposition and also a surface-adsorbed fragment which leads to the maintenance of a steady-state concentration even lower than that in pure water. Certainly the inhibiting residue from the amides would not be expected to be a cyanide ion, since this ion cannot even be formed from propionitrile in this system.

The probability that the inhibiting fragment formed at the irradiated zinc oxide surface can be an electron-deficient nitrogen group is of interest to the various theoretical explanations of photochemical processes at zinc oxide surfaces. If in accordance with the interpretations of several investigators of surface reactions at irradiated zinc oxide,⁵⁻⁸ the effect of light is to reduce an adsorbed oxygen molecule which subsequently reacts to form hydrogen peroxide in aqueous suspensions, the zinc oxide will be left in an electron-deficient state. The now positively charged zinc oxide is neutralized by regaining an electron from an oxidizable substrate. This process may lead to an electron deficient nitrogen-containing fragment which becomes strongly adsorbed on zinc oxide.

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IV. INFRARED STUDIES OF NITROGENOUS RESIDUES AND THEIR EFFECTS ON PHOTOCATALYTIC PROPERTIES OF ZINC OXIDE

INTRODUCTION

Effects of amides and other simple nitrogen-containing compounds on the photocatalytic formation and decomposition of hydrogen peroxide at zinc oxide surfaces have been reported recently from studies carried out in this laboratory.¹ Formamide and cyanides are particularly effective in inhibiting decomposition of hydrogen peroxide in these systems. It was postulated that an electron-deficient nitrogen-containing residue was remaining as a strongly adsorbed fragment on the zinc oxide surface. It was the object of the present study to examine the pretreated zinc oxide catalysts by infrared absorption spectroscopy, in the hope of identifying the nature of the adsorbed species present on the surface, and where possible to investigate the mechanism of the desorption process.

Experimental

The ultraviolet light source in these experiments was a Hanovia H-4 high pressure mercury arc lamp, fitted with a Pyrex shield to retain radiation below 3200 Å. Neither zinc oxide nor any of the additives used in this study absorb visible light. Thus the effective wavelength is 3650 Å which is strongly absorbed by zinc oxide. The lamp was mounted horizontally over a mechanical shaker on which the reaction vessel was mounted. An aluminum reflector

was placed over the light source to focus the light onto the reaction vessel, which was water-cooled, and kept at 15-20° C.

The zinc oxide used was Kadox - 25, supplied by the New Jersey Zinc Co. This grade of zinc oxide has a surface area of approximately 10 m²/g.

Infrared absorption measurements were made on a Perkin Elmer Infracord. Samples of treated zinc oxide were prepared for analysis by centrifuging out of suspension, drying under reduced pressure and pelletizing under pressure in a conventional K Br die, Model MK 3, Perkin Elmer Co. Kadox - 25 adheres tenaciously to the bare die face and the pellet cannot be removed without shattering. To overcome this difficulty circular pieces of various types of paper, foil, and plastic sheet were placed over the die faces. Glazed weighing paper, Carl Schleicher & Schnell Co., No. B-2, was most satisfactory.

All chemicals were certified Reagent Grade. Solutions of hydrogen cyanide were prepared by titrating 0.01 M potassium cyanide to pH 7 with dilute hydrochloric acid. As tested in separate experiments, the potassium chloride produced has no effect on processes at zinc oxide surfaces. The usual time of shaking the zinc oxide with solutions of various additives was 30 minutes.

The study of rates of desorption of nitrogenous residues at constant aqueous tension was carried out at 80°, 90°, 100°C in an enclosed, thermostatically controlled chamber. The

aqueous tension was maintained as follows: 80°C, 355 mm, the normal vapor pressure of water; 90°C, 341 mm, and 100°C, 383 mm, by the use of saturated solutions of sodium nitrate and sodium iodide respectively.

Results

Examination of Residues Left on Zinc Oxide Surfaces by Formamide.

When suspensions of zinc oxide in dilute aqueous solutions of formamide are shaken under ultraviolet light in the presence of oxygen or air, and the zinc oxide is subsequently removed by centrifuging, washed, dried, and prepared for infrared analysis, the most pronounced feature in the absorption spectrum is a sharp peak at 4.5μ (Fig. 1A). Pure formamide has no absorption maximum in this region, which is characteristic of $C \equiv O$, $-C \equiv N$, and $-C \equiv C-$, but the peak shows up rapidly via photochemical transformations at the surface of zinc oxide, even from 10^{-4} M solutions of formamide. Kadox itself has good transparency between 3 and 9μ , except for absorption bands at 6.7 and 7.2μ , usually ascribed to adsorbed CO_2 .² During adsorption of formamide and desorption of products, these peaks shift to about 6.2 and 7.4μ .

The absorption maximum at 4.5μ does not arise from formamide in contact with zinc oxide in the dark. Oxygen is required as well as light. The peak can readily be removed from the surface by heating for a few hours at 110°C or by repeated washing with hot water. (Fig. 1B). During the desorption process infrared spectra reveal transient peaks

at 5.9μ , suggestive of the reappearance of the $=C=O$ stretching vibration of formamide, and at $8.2 - 8.7\mu$, a peak often encountered in conjunction with the absorption at 4.5μ due to adsorbed cyanate. (Cf. Fig. 5A). These fleeting intermediates occur under conditions not strictly reproducible, and they may easily be overlooked. The magnitude of the 4.5μ absorption peak resulting from irradiation under an oxygen-containing atmosphere is directly proportional to the concentration of formamide from 10^{-4} to $10^{-2}M$. There is no effect on the general background transmission of Kadox.

Cyanide Residues on Zinc Oxide Surfaces. Several attempts to find traces of adsorbed carbon monoxide by infrared spectrophotometry on zinc oxide samples, prepared and exposed to carbon monoxide under various conditions, resulted in failure. Carbon monoxide was therefore eliminated as a possible source of the peak at 4.5μ resulting from formamide as described above. Carbon monoxide adsorption has been detected by special techniques³, but apparently would not be a stable product under conditions used to treat zinc oxide in these experiments. Cyanides were therefore examined next as possible products of formamide decomposition at zinc oxide surfaces.

When zinc oxide is shaken with aerated dilute solutions of potassium cyanide in the dark, there is no appreciable change in the infrared spectrum. Under ultraviolet irradiation for 30 minutes a sharp peak appears at 4.5μ , even

from solutions as dilute as $5 \times 10^{-5} \text{M}$. (Fig. 2A). Absorption is proportional to concentration of potassium cyanide over a wide range of concentrations. Oxygen is necessary for appearance of the peak. Desorption occurs readily on heating the sample at 110°C in a drying oven under ambient atmospheric conditions, and follows a course similar to that shown in Fig. 1B.

Effect of pH on Cyanide Adsorption. A solution of potassium cyanide has a pH between 9 and 10. On adding hydrogen chloride to change the pH to 7 the cyanide is largely converted to hydrogen cyanide. Agitation of zinc oxide in a solution of hydrogen cyanide 0.01 M results in appearance of a peak at 4.5μ , both in the dark and under ultraviolet, but with considerable reduction of the general transmission of zinc oxide in the infrared region. (Fig. 2B). This phenomenon is associated with an increase of electrons in the conduction band.³ At a concentration of 0.01 M hydrogen cyanide leaves a marked peak at 4.5μ on zinc oxide both in presence and absence of oxygen, and with or without irradiation. At 0.001 M concentration the peak is undetectable in absence of oxygen and light.

In contrast to the formamide and potassium cyanide residues adsorbed on zinc oxide, the peak at 4.5μ resulting from adsorption of hydrogen cyanide is quite stable to heat. Continued heating causes a further reduction of the general infrared transmission. (Fig. 4). There is no elimination of

the peak, except in the case of peaks formed in very dilute solutions, 0.001 M, under oxygen and ultraviolet.

Adsorption of Cyanate Ion on Zinc Oxide. Suspensions of zinc oxide in dilute solutions of potassium cyanate result in formation of a very strong peak at 4.5μ , whether in presence or absence of oxygen and/or light. (Fig. 2C). There is no accompanying reduction of background transmission as in the case of hydrogen cyanide. Again, the absorption is proportional to concentration of cyanate over a wide range, 10^{-5} - 10^{-2} M. The cyanate peak can readily be removed by heating the zinc oxide, but the rate of desorption is strongly influenced by water vapor pressure. The effect is illustrated in the series of desorption tests, carried out on portions of the same sample of zinc oxide pretreated with 0.01 M potassium cyanate, and shown in Fig. 5. In two hours of heating at $105 - 110^{\circ}\text{C}$ in a vented tube containing Drierite, there is little desorption. On heating for two hours in the same tube containing a vial of saturated sodium chloride solution to provide a constant high relative humidity, there is complete desorption. Desorption at 110°C at ambient atmospheric conditions shows an intermediate rate whereas there is much less effect on heating for two hours under vacuum at 200°C . Desorption is accompanied by evolution of ammonia. Tests for desorbed cyanide, although very sensitive, have repeatedly and consistently proved negative.

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Examination of Zinc Oxide for Residues from Related

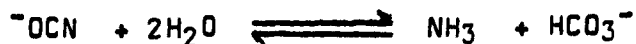
Compounds. A number of other simple compounds related to cyanide, ammonia and amides, have been examined for ability to produce adsorbed residues on zinc oxide surfaces at comparable concentrations and under similar conditions. There was no observable peak at 4.5μ , and no outstanding change in the absorption of Kadox from 10^{-3} - 10^{-2} M solutions of any of the following, in the dark or in the light: formic acid, formaldehyde, ammonia, acetonitrile, or methyl amine. In 30 minutes, under air and ultraviolet light N methylformamide and N, N' dimethylformamide also failed to produce peaks at 4.5μ .

A series of experiments was carried out under conditions of approximately constant aqueous tension to measure rates and activation energies of desorption of residues left on zinc oxide by: 1) cyanate, 0.1 M, in the dark; 2) 0.1 M formamide and 3) 0.1 M potassium cyanide in light and air. Within the limits of experimental accuracy results show comparable temperature effects on rates of desorption in all three cases.

Discussion and Conclusions

The results of this study show that cyanate ion is readily adsorbed on zinc oxide even in the dark and in absence of oxygen, and is easily detectable at low concentrations by a strong characteristic peak at 4.5μ . This peak is desorbed with formation of ammonia by mild heating in the

presence of adsorbed water vapor. The following transformation evidently takes place on the surface:



The ammonia is driven off the surface by heating even at 110°C in an oven under ambient conditions. The bicarbonate remains on the surface as indicated by the absorption at 6.2 μ and 7.4 μ . (Cf. Taylor and Amberg²; and Eischens³.)

Neither cyanate nor bicarbonate have any appreciable effect on the conduction electrons. Not only do they fail to donate electrons to deficient sites on the zinc oxide surface, but they also fail to displace oxygen which already has trapped electrons at the surface.⁴ Special tests show that cyanate ion, although strongly adsorbed at room temperature, has very little effect on the decomposition of hydrogen peroxide at irradiated zinc oxide surfaces.

Cyanide ion and formamide are apparently adsorbed with loss of electrons at the zinc oxide surface, and with subsequent conversion to cyanate. The relative humidity has the same general effect on desorption of the peaks at 4.5 μ , formed by the cyanide ion and formamide in presence of air and ultraviolet light, as on the peak formed by cyanate in the dark. Ammonia evolution accompanies desorption in both cases. Creation of electron deficient sites by irradiation seems to be essential for adsorption, and stable fragments are produced at the surface only in presence of oxygen.

Cyanide ion and formamide are evidently in equilibrium at zinc oxide surface, with a common mode of adsorption and

desorption. These observations are in agreement with those of Schwab and Leute.⁵



At pH 7 HCN behaves very differently in contact with zinc oxide. The fact that HCN lowers the background transmission of zinc oxide so markedly must mean either: 1) that HCN is donating electrons directly to the conduction band of zinc oxide, or 2) that HCN displaces oxygen from the surface of zinc oxide and thus releases to the conduction band electrons which had been trapped by oxygen at the surface. Migration of a hydride ion or hydrogen atoms into the surface are possibilities since the process is intensified by heating. Ambient humidity does not have the same effect on adsorbed HCN as on adsorbed cyanide ion or cyanate.

Interpretation of these studies in relation to the effects of these nitrogen-containing compounds on decomposition of hydrogen peroxide at irradiated zinc oxide surfaces, indicates that inhibition of peroxide decomposition is due chiefly to adsorption at electron-deficient sites created by irradiation, and not directly to displacement of oxygen. Hydrogen peroxide decomposes on irradiated zinc oxide just as rapidly under nitrogen as under oxygen. Since oxygen reduction and hydrogen peroxide oxidation are reversible at the surface competitive loss of electrons by cyanides and formamide inhibits oxidation of hydrogen peroxide. In spite of the similarities in the infrared spectra cyanate is not oxidized at the surface and therefore does not retard

decomposition of hydrogen peroxide. Since the peak at 4.5μ for cyanide ion and formamide appears only in presence of light and air, it must be due to formation of cyanate, with inhibition of peroxide decomposition occurring during the oxidation process. This interpretation is supported by the similar activation energies of desorption and the effect of humidity on the adsorbed residues from cyanate ion, cyanide ion and formamide. The adsorption of hydrogen cyanide follows a different mechanism, leading to a similar absorption at 4.5μ , but superimposed on a background with a greatly lowered infrared transmission.

LEGENDS FOR FIGURES

- Fig. 1. A. Solid curve, infrared spectrum of Kadox 25 as supplied by the New Jersey Zinc Co.; dotted curve, infrared spectrum of Kadox after shaking 30 min. with 0.01 M aqueous formamide, in presence of air and light at $365m\mu$.
- Fig. 1. B. Rate of desorption of formamide residue at 4.5μ in Fig. 1. A., on heating in an oven at 110°C .
- Fig. 2. A. Infrared spectrum of zinc oxide treated with 0.01 M solution of potassium cyanide: solid curve, in light at $365m\mu$; dotted curve, in dark.
- Fig. 2. B. Infrared spectrum of zinc oxide treated with 0.01 M. solution of hydrogen cyanide, pH 7, in the dark.
- Fig. 2. C. Infrared spectrum of zinc oxide treated with 0.01 M solution of potassium cyanate, in the dark.
- Fig. 3. Infrared spectra of zinc oxide treated with 0.01 M HCN in presence of air and light for 30 min., and then heated in an oven at 110°C for: solid curve, 0 hours; broken line, 20 hours; dotted curve, one week.
- Fig. 4. Effect of heating in oven at 110°C on peak produced at 4.5μ by treating zinc oxide with 0.01 M solution of potassium cyanate in the dark.
- Fig. 5. Effect of water vapor pressure on removal of peak produced at 4.5μ by treating zinc oxide with potassium cyanate solution in the dark: A.) original peak B.) same sample after heating at 110°C in a vented tube with constant humidity provided by a saturated solution of sodium chloride, solid curve; after heating at 110°C in a vented tube containing drierite, dotted curve C.) same sample after heating at 110°C in an oven at ambient conditions D.) after heating under vacuum at 210°C . All samples in B., C., D. heated for two hours

Fig. 1

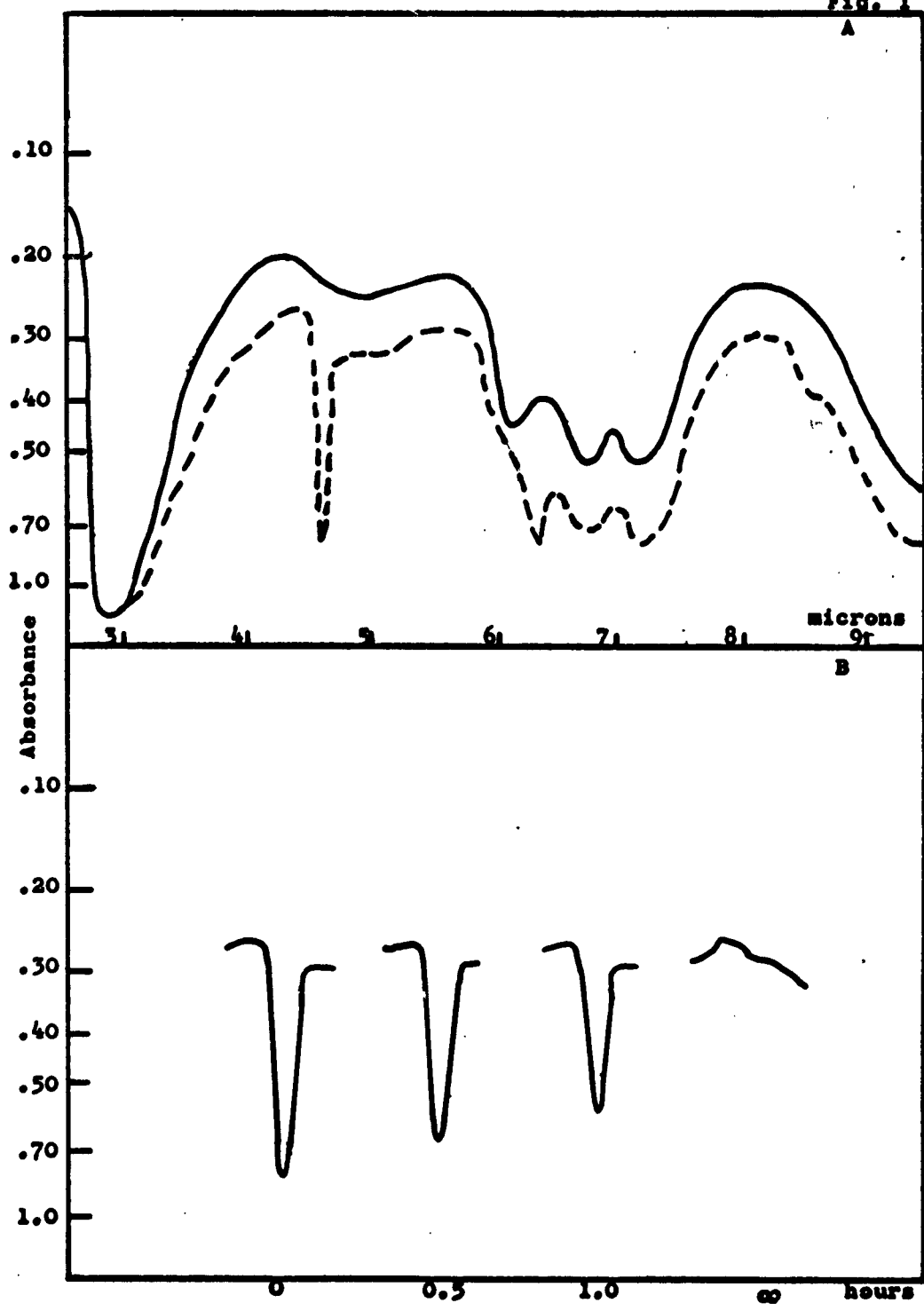


Fig. 2

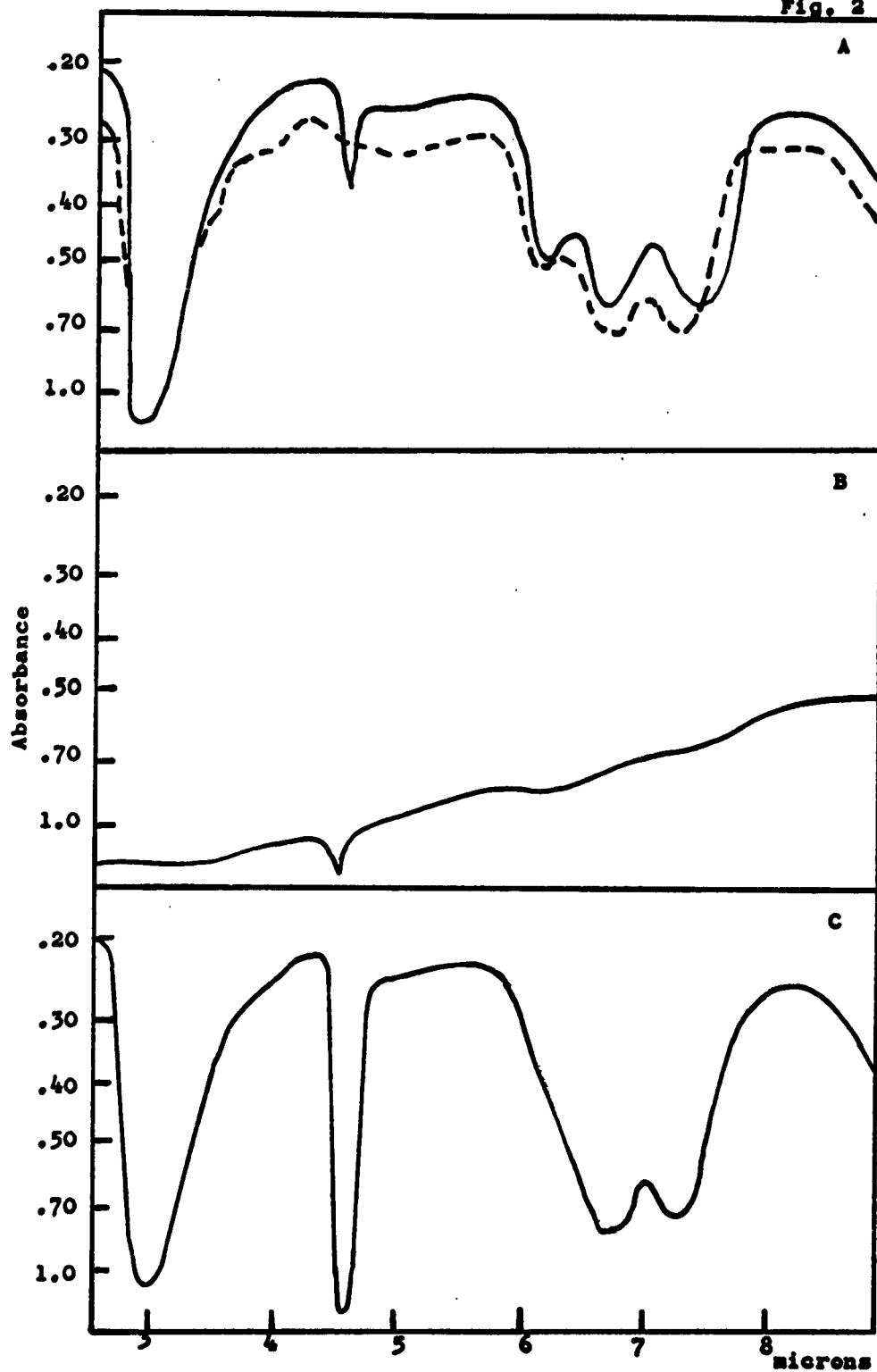


Fig. 3

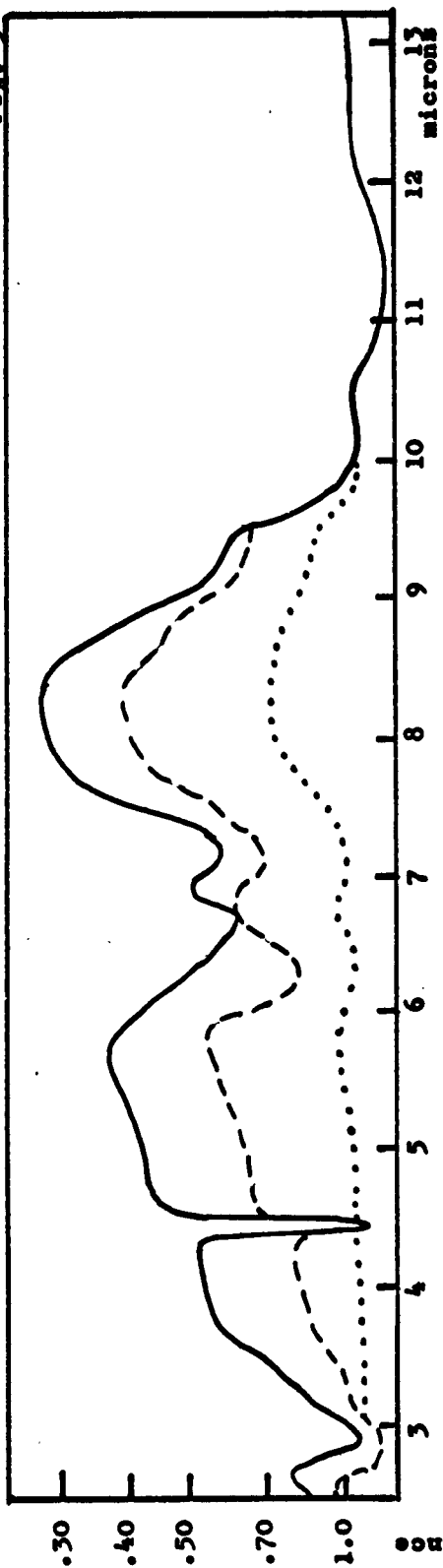


Fig. 4

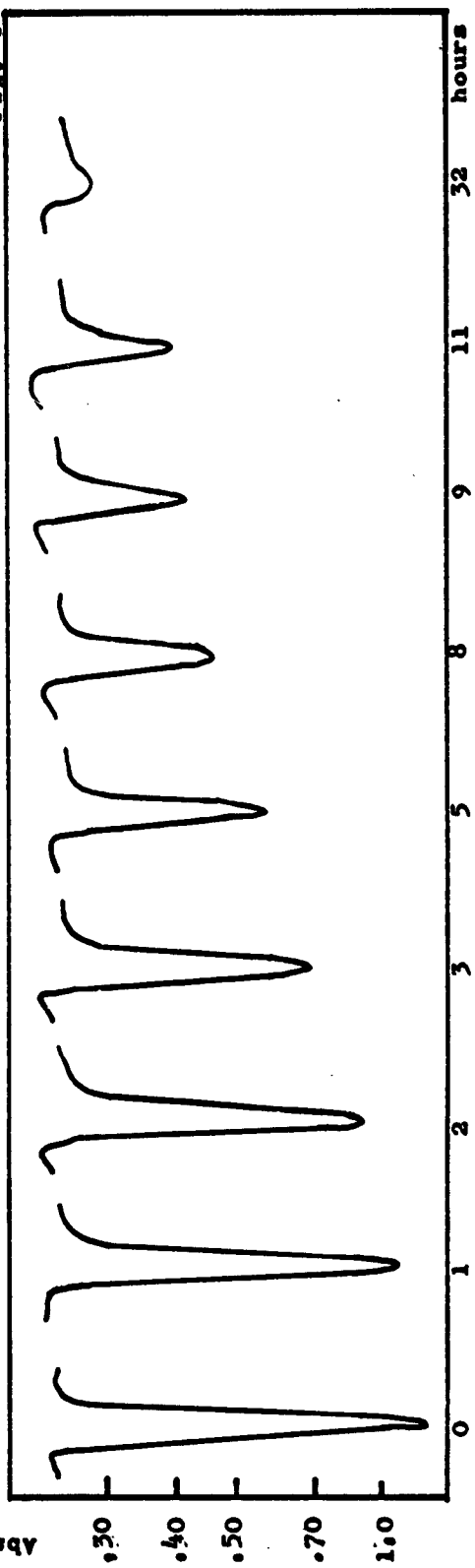
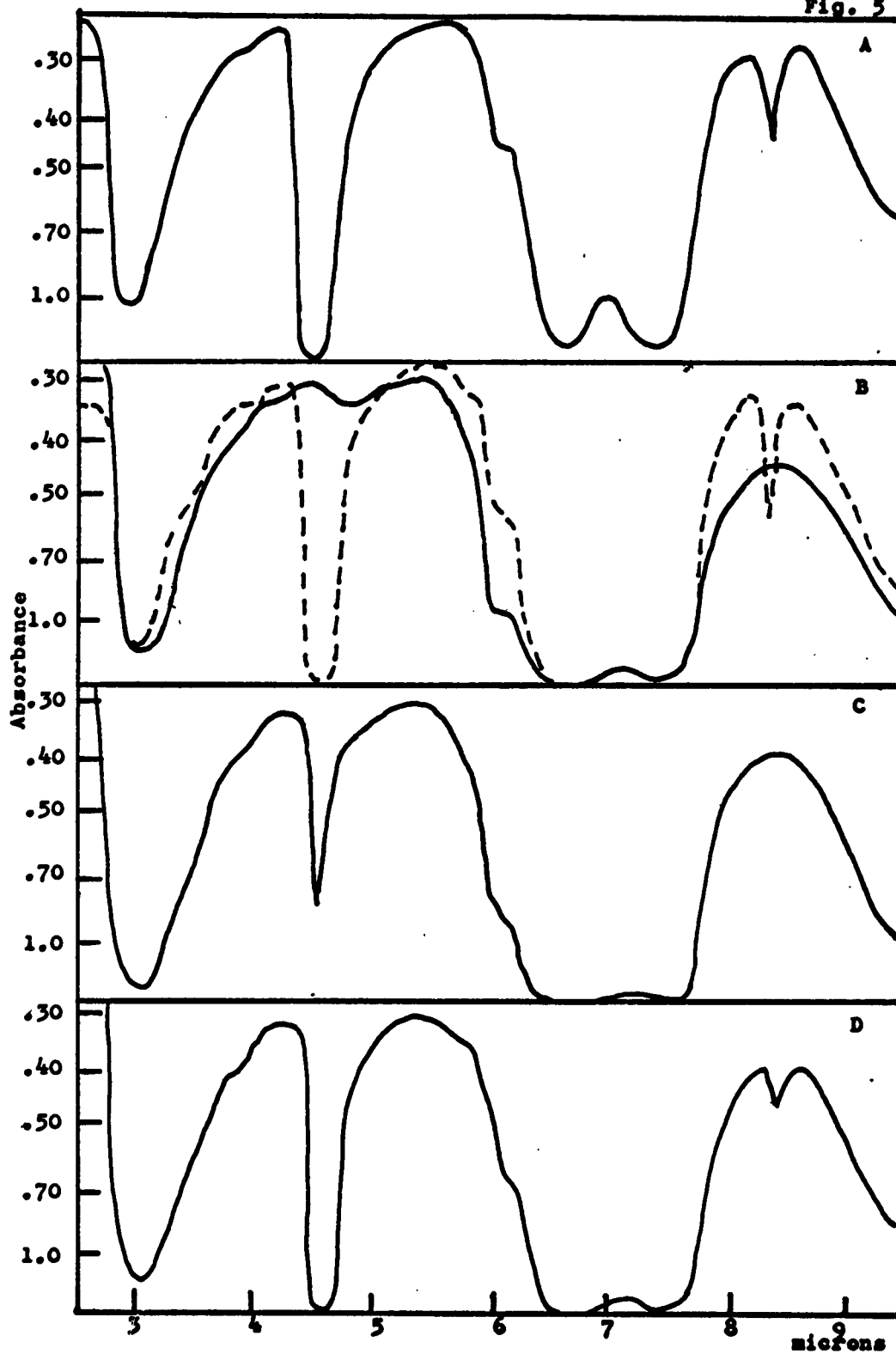


Fig. 5



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V. PHOTOELECTRIC EFFECTS AT ZINC OXIDE ELECTRODES

INTRODUCTION

Knowledge of the efficiency of electron transfer processes at irradiated zinc oxide surfaces, as discussed in the preceeding sections, suggests that useful electrical work should be derivable from photoelectric cells containing zinc oxide electrodes. Zinc oxide is well-known as a photoconductor. Electron spin resonance studies carried out by Kokes¹ agree with tests made in this laboratory in demonstrating that oxygen traps electrons at zinc oxide surfaces. The electron spin resonance signal from ordinary zinc oxide samples is practically zero. On evacuation even at room temperature an appreciable amount of oxygen is removed from the surface and a conduction electron signal is immediately observable. The same interpretation explains effects on transparency observed in infrared absorption studies. Accumulation of small steady state amounts of hydrogen peroxide in irradiated aqueous suspensions of zinc oxide free from organic additives also demonstrates a reversible oxidation-reduction of oxygen in these systems. Formamide produces effects exactly opposite to those caused by oxygen at zinc oxide surfaces. Adsorption of formamide slightly increases the electron spin resonance signal and lowers the transmission of zinc oxide to infrared radiation. In Section III of this report it was demonstrated that formamide inhibits peroxide formation and decomposition at irradiated surfaces of zinc oxide.

Reported quantum yields^{2,3,4} for photochemical processes at zinc oxide surfaces are high. Since zinc oxide absorbs only in the near ultraviolet region of the spectrum, it seems important to look for dyes and pigments which can be adsorbed at the surface and sensitize zinc oxide to light in the visible region of the spectrum. Rose Bengal has been used to sensitize zinc oxide to green light in the Electrofax photoreproduction method.⁵ Oster⁶ has reported reversible bleaching of Rose Bengal and other dyes on zinc oxide in green light. Terenin⁷ has reported induced photo emf effects in zinc oxide by porphyrin and chlorophyll type pigments in light which only the pigment absorbs.

The idea of a photoelectric effect on zinc oxide in aqueous suspensions is not new. Baur proposed this explanation of observed photo-oxidation-reduction reactions at irradiated zinc oxide surfaces many years ago.^{8,9} However there has been no systematic reinvestigation of photovoltaic effects in these systems in the light of new understanding of photoconductors and photochemical surface effects.

The foregoing considerations have suggested certain avenues of approach which appeared to be profitable starting points. The results of a few investigations are reported in this section. The work is being continued under Contract AF19 (628)-2768.

EXPERIMENTAL

The light source used in these experiments was a Hanovia H-4 high pressure mercury arc lamp with a Pyrex envelope to retain radiation below 330 $m\mu$. Heat absorbing glass, supplied by the American Optical Company, was used to filter out infrared. Radiation in the green region of the spectrum was obtained from this source by using a 0.05 M potassium chromate solution as a filter. A Corning filter was used for selective transmission (approximately 50%) of radiation in the neighborhood of 365 $m\mu$. A calibrated Eppley thermopile was used with a 1 mv SR500 Sargent recorder for measurements of light intensity.

The zinc oxide test electrode was prepared by applying a paste of zinc oxide (unless otherwise stated, Kadox 25, supplied by the New Jersey Zinc Co.) to a cylindrical platinum gauze electrode and drying in the oven at 110°C. In a few experiments as noted below, a similar electrode kept in the dark was used as a reference electrode. In most of the experiments a bare platinum spiral electrode was used in the dark half-cell.

The half-cells were made to specifications by Fisher Scientific Co., (Fig. 1), and designed to permit passage of gases over the electrodes. Voltages were measured and compared on several different instruments because the cell was suspected of having a high resistance to the passage of the photocurrent. The side arms of the half-cells were filled with agar saturated with KCl and connected through a solution

of 0.1 N KCl. KCl was used as a supporting electrolyte unless special buffers were used. The agar salt bridge presents certain difficulties in these systems and in many cases the bridge resistance appears to increase with time. Dark current measurements of resistance on a vacuum tube voltmeter were not considered to be true representations of the photo-resistance, because the current flowing under the latter conditions must cross grain boundaries from the irradiated zinc oxide to the platinum gauze. Under applied voltage in the dark some of the platinum comes in direct contact with the electrolyte and part of the resistance is eliminated. Photo-emf measurements on the Model 232 EICO vacuum tube voltmeter, the Patwin research model Polarograph and the Bausch and Lomb VOM-5 recorder were comparable. Measurements on a Beckman Model G pH meter were about 10% higher.

Photo currents were measured on the VOM-5 recorder. Continuous records of the output of the photocells were made on an Esterline Angus recorder with a 2 ma full scale deflection.

All chemicals used were certified reagent grade. Attempts have been made to anodize zinc and use the oxide-coated metal itself as the illuminated electrode, but without success.

RESULTS

Effects of Oxygen. Two ZnO/Pt electrodes immersed in 0.1 M KCl in separate half-cells develop a small potential difference, which slowly disappears, when oxygen is bubbled over

one electrode and nitrogen over the other. On irradiation of the nitrogen-covered electrode at $365\text{m}\mu$ a photo emf of about 800-900 mv is produced. The potential difference falls off slowly when the light is turned off. The effects are remarkably reproducible and appear to be quite reversible. The cell can be cycled over several light-dark periods. The fact that a bare platinum electrode surrounded by a suspension of zinc oxide in the illuminated half-cell results in much lower potentials seems to indicate that contact with the platinum during absorption of light is necessary. Kadox 25 was used because of its large surface area for contact with gases, but photoconducting zinc oxide gives similar photo emf measurements and larger photo currents. Tests on doped zinc oxide are incomplete at this time and are undergoing further study. The dark zinc oxide electrode can be replaced by a bare platinum spiral.

Substitution of p-Benzquinone for Oxygen. Since p-benzoquinone has about the same oxidation-reduction potential as oxygen, and can be made to specified concentration, several tests were made substituting p-benzoquinone at the dark platinum electrode. The pH of the solution at a saturated p-quinone dark electrode appears to have little effect on the potential difference generated, but does affect the reversibility or drop in potential when the light is turned off. The photo-voltage drops most rapidly on cessation of irradiation when a low pH, approximately 3 in a chloroacetate buffer, is maintained in the quinone half-cell. Figs. 2 and 3

illustrate these effects for pH 3 and 9 respectively. The quinone solution darkens while the cell is running, the effect being most marked at pH 9 and scarcely noticeable at pH 3. In alkaline solution the absorption spectrum indicates polymerization via quinone ion-radicals to melanoid products. At pH 3 loss of absorption at $420\text{m}\mu$ and shifting of the ultraviolet maximum from 295 to $285\text{m}\mu$ indicates reduction to hydroquinone. Oxygen is excluded by passing nitrogen through both half-cells.

Effect of Formamide at the Irradiated Zinc Oxide Electrode.

The fact that formamide appears to donate electrons to irradiated zinc oxide, as shown in Section V of this report, suggests that there may be some advantage in adding it to the illuminated half-cell. Formamide produces no change in the photo emf, but does seem to increase the reversibility of the system, and to prolong the useful output. An extensive study has been carried out on the cell:

Pt, ZnO (N ₂); 0.1 M KCl, formamide //	0.1 M KCl,
(illuminated)	sat'd quinone; Pt (N ₂)
	(dark)

Table I. TIME STUDY OF OUTPUT OF CELL

<u>Concentration</u>		<u>Max. Photocurrent (ma)</u>	<u>Rate of fall of Photocurrent (ma/hr)</u>
<u>p-Benzoquinone (mg/ml)</u>	<u>Formamide (M)</u>		
0.50	0.10	0.40	0.0167
0.55	0.10	0.39	0.0161
1.36	0.10	0.38	0.0036
1.70	0.10	0.43	0.0080
1.82*	0.10	0.36	0.0035
2.55	50 mole %	0.42	0.0022
1.55	"pure"	0.24	0.0040
1.50	0.001	0.36	0.0080
4.00	0.01	0.41	0.0020
2.05	0.10	0.36	0.0070
1.60	1.00	0.45	0.0013
<u>special solutions</u>			
2.40 isopropanol..	0.10	0.12	0.0005
1.80 methanol.....	0.10	0.44	0.0015
2.00 n-propanol...	0.10	0.39	0.0028
2.00 ethanol.....	0.10	0.42	0.0011

*Higher concentrations of p-quinone in aqueous systems caused breakdown of the agar bridge.

Effect of Nature of Electron-Acceptor at the Dark Electrode.

A few preliminary tests on substitution of naphthaquinone and anthraquinone for p-benzoquinone at the dark electrode indicated that the photo emf was strongly dependent on the reduction potential of the electron-acceptor at the dark electrode. Photo currents in turn seem to be related to the potential difference produced by illumination. The data summarized in Table II were obtained with the indicated solutions under nitrogen in the dark half-cell, and with 0.1 M formamide in 0.1 M KCl under nitrogen at the irradiated zinc oxide electrode.

Table II. RELATION OF PHOTOEFFECTS TO DARK REACTION

Half-cell reaction (dark electrode, N ₂ , 0.1 M KCl)	Standard E ₀ (volts)	Photo EMF (volts)	Photo Current (ma)
Ce ⁺⁴ --Ce ⁺³ (ceric bisulfate, 0.1M)	1.61	1.75	1.15
Fe ⁺³ --Fe ⁺² (FeCl ₃ , 0.1M)	0.77	1.10	0.75
p-Q--p-QH ₂ (0.02M, chloroacetate buffer, pH 3)	0.70	0.95	0.45
O ₂ --O ₂ ⁻ (sat'd sol.)	0.68	0.90	0.42
1-2 N-Q--1-2 NQH ₂ (sat'd sol., 50% EtOH, 50% chloro- acetate, pH 3)	0.56	0.82	0.38
1-4 NQ--1-4 NQH ₂ "	0.48	0.61	0.20
AQ--AQH ₂ "	0.15	0.32	0.10

DISCUSSION

There is no doubt that oxidation-reduction reactions induced by irradiation of zinc oxide at 365mμ can be converted to useful electrical work. Photo emf's higher than any previously reported can be effected by proper selection of the dark half-cell. Reduction of complex cobalt ions, which might be reversible by admitting oxygen, offers interesting possibilities. Formamide is effective in maintaining a continuous supply of electrons. Doped zinc oxides offer promise of producing higher currents.

When it comes to the question of evaluating the efficiency of the processes, there are several problems. 1.) So far most of the tests have been made on zinc oxide systems absorbing light at 365mμ. Sensitizing dyes have been shown to produce an increment in the visible region of the spectrum, but so far these effects have been small compared to those produced in the ultraviolet. Further tests are being carried out with the dyes.

Some measurements have been made of the quantum yields, and the best results have been of the order of 10 - 20% in electrical ergs as compared to 100% ergs of radiant energy at $365\text{m}\mu$ falling on the electrode. Measurements give relative values of $\text{ergs cm}^{-2}\text{sec}^{-1}$.

2.) Some of the cells tested have been run continuously for 100 hours with about 10% drop in photo-current and voltage during that period. The agar bridge is the seat of the most serious difficulties in maintaining a constant output over a long period. p-Quinone in particular has a tendency to migrate into the bridge and cause channelling. Use of special types of cells to minimize diffusion may help.

3.) The fact that voltages read higher on the model G pH meter designed for use with the glass electrode, must mean that the irradiated zinc oxide electrode has a very high resistance. Better contact between zinc oxide grains and the platinum gauze might help. A conducting plastic containing metallic silver has been tried, but proved unsatisfactory. It seems to be extremely difficult to anodize zinc. Perhaps a zinc-aluminum alloy of the type used in special solders would be anodizable. The high resistance is no problem if only a high photo emf is desired. For efficient conversion of light energy to work good photocurrents would also be necessary.

The fact that the photo-currents increase in these cells in proportion to the emf is puzzling. It seems that electrons with high kinetic energies are produced by the light, and that

the more nearly the energy of the electron fits the reduction potential of the material in the dark half-cell, the more efficient the transfer of electrons becomes.

LEGENDS FOR FIGURES

- Fig. 1. Half-cell for zinc oxide electrode: A) gas outlet, B) agar salt bridge, C) gas inlet, D) platinum electrode coated with zinc oxide
- Fig. 2. Effect of intermittent light-dark periods on photo emf developed at a zinc oxide electrode vs p-benzoquinone at pH 3
- Fig. 3. Effect of intermittent light-dark periods on photo emf developed at a zinc oxide electrode vs p-benzoquinone at pH 9
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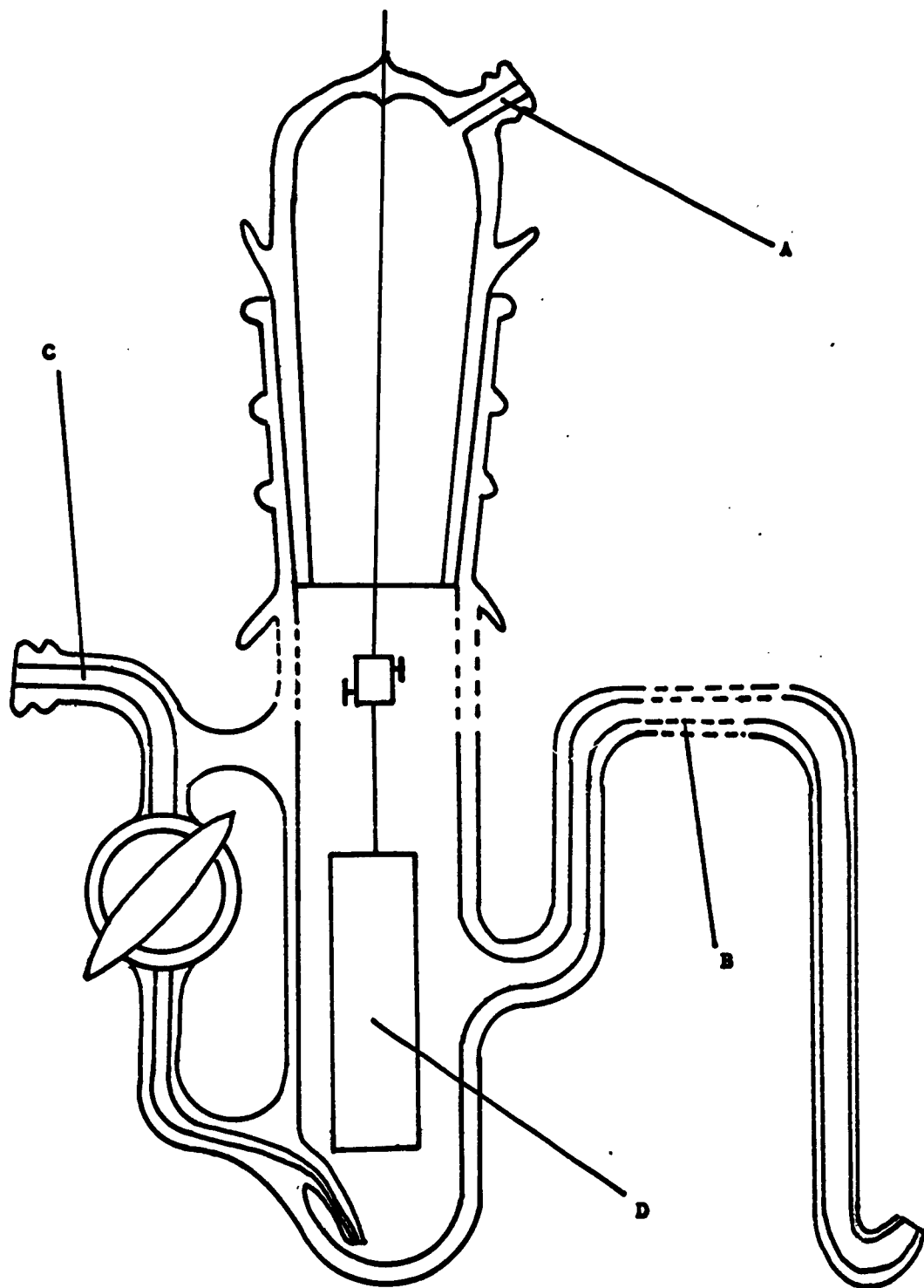
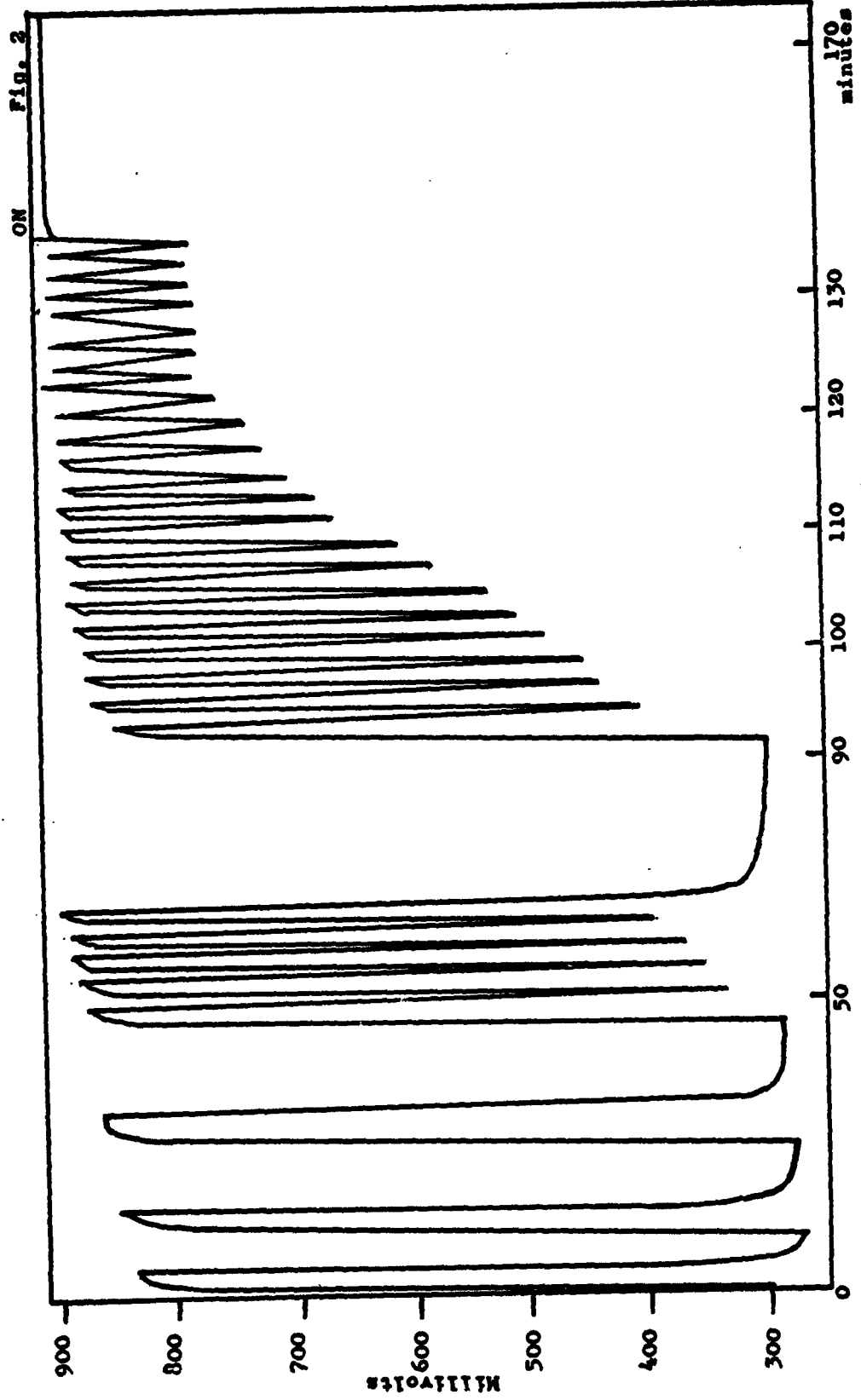
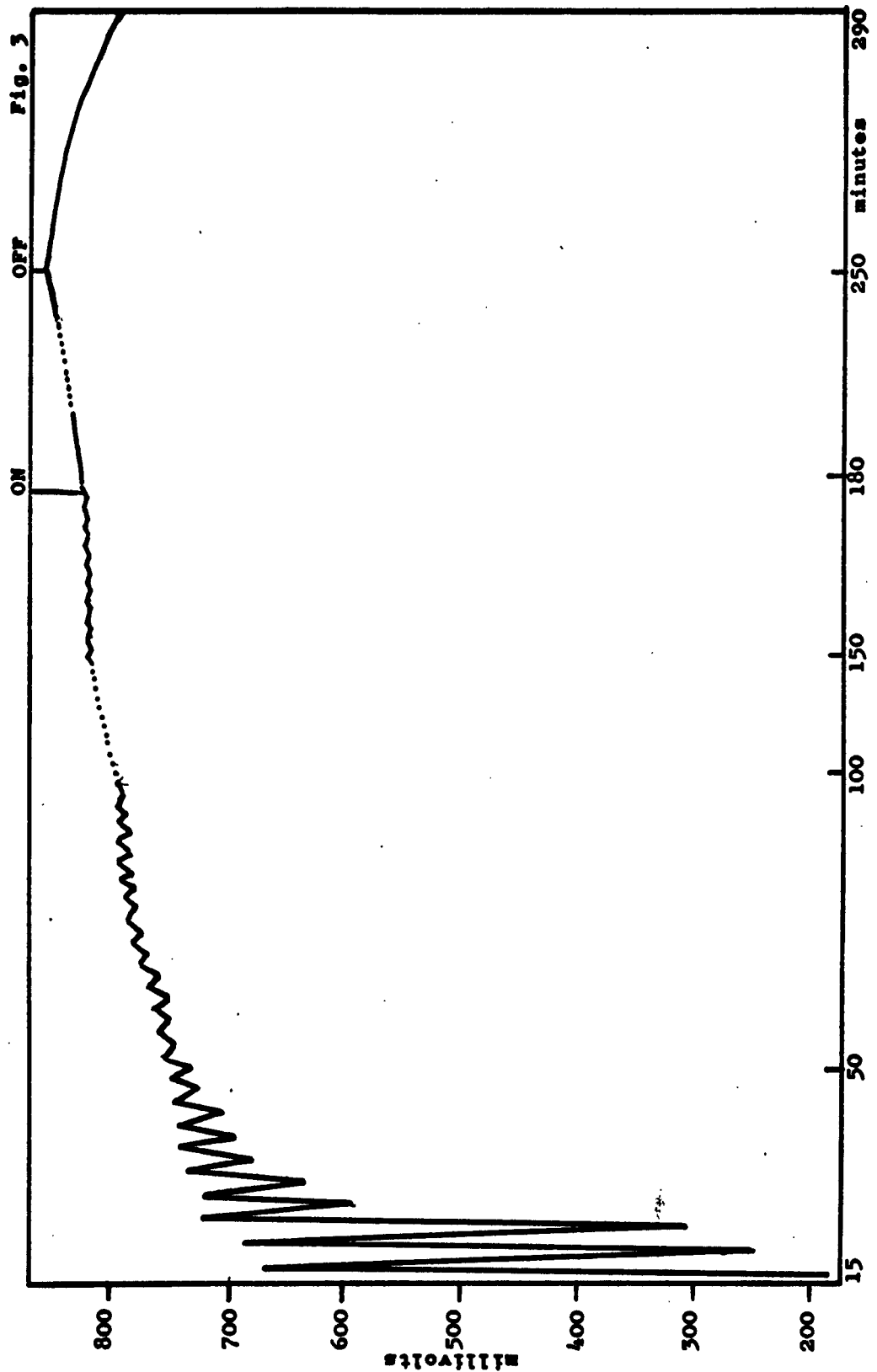


Fig. 1





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VI. STUDIES OF ENERGY TRANSFER BETWEEN PHEOPHYTIN AND CAROTENE IN RED LIGHT

INTRODUCTION

With the intention of following up Terenin's¹ work on the use of chlorophyll and pheophytin to sensitize zinc oxide to red light, experiments were undertaken in the summer of 1960 to gain experience in preparing and separating photosynthetic pigments from green plants. Chlorophylls and carotenoid pigments were prepared by extraction from spinach and separation on sugar columns. Subsequent tests of the ability of adsorbed chlorophyll to produce photovoltages on irradiation of zinc oxide electrodes with red light, have shown a small effect, about 200 millivolts, but the effects are so much smaller than those obtained from zinc oxide in the ultraviolet, as described in Section VII of this report, that the study has been temporarily suspended until more basic knowledge of photoelectric effects at the semiconductor surface are obtained.

Meanwhile interest in Krasnovsky's "pink" chlorophyll² and Garrilova's sensitized photo-oxidation-reduction reactions³, suggested the possible value of these systems for energy storage.

Early experiments indicated that on irradiation in red light of solutions containing "chlorophyll" and carotene, with various additives, the peaks at 450 m μ and 478 m μ characteristic of carotene, always "disappeared" rapidly from the reaction mixture. The 660-670 m μ peak supposedly belonging to chlorophyll "a" sometimes decreased, and some-

times remained about the same. More careful examination of pigment preparations indicated that in some cases the chlorophyll preparations contained pheophytin also. On irradiation of pure beta carotene with pure pheophytin in red light, the carotene, otherwise perfectly stable to red light, was used up rapidly (Fig 1.). When pure beta carotene was irradiated in red light with purified chlorophyll "a", both carotene and chlorophyll "a" were used up, as evidenced by rapid decrease in absorption not only of the carotene at 450, 475 $m\mu$, but also of the chlorophyll maxima at 660-665 and 423 $m\mu$, as shown in Fig. 2.

Survey of the literature showed a similar observation by Claes and Nakayama.⁴ The authors postulated a photosensitized isomerization of carotene. However isomers of carotene should still absorb in the same general region of the spectrum, and did not seem to be a satisfactory explanation. A series of experiments was undertaken to investigate the kinetics of the reaction and to try to obtain more definite information about the carotene conversion product. These experiments have been continued intermittently during the past two years.

EXPERIMENTAL

Except for early tests with pigments extracted from spinach and separated on sugar columns, all results reported in this section were made with 100% pure beta carotene obtained from Fisher Scientific Co. and maintained in an evacuated tube. Pheophytin "a" of good purity was obtained from

Bios Laboratories. Tests of chlorophylls "a" and "b" from Bios Laboratories showed large amounts of pheophytin, and are unsuitable for these tests without further purification. Best preparations of pure chlorophyll "a" and "b" were obtained according to the directions of Jacobs.⁵ Solvents used were Fisher Spectranalyzed n-Hexane and Methanol.

The light source was a 500 watt projection lamp with a Cenco No. 87309C filter having a maximum at 625 m μ and a half-band width from 605 to 790 m μ . In the blue region a No. 87309A filter was used having a maximum at 410 m μ and a half-band width from 370 to 460 m μ .

A calibrated Eppley thermopile with a Pyrex window was used with a sensitive galvanometer (5×10^{-3} μ amps/mm) for light intensity measurements. Pyrex Erlenmeyer flasks with evacuable ground glass tops were used for irradiation of macro quantities. For kinetic studies and continuous spectral recording without opening the reaction vessel, mixtures were irradiated in standard quartz spectrophotometer cells with ground glass tops. A piece of Tygon tubing was fitted over the neck of the cell and connected to a vacuum stopcock. The cell could be evacuated and irradiated without removal from the cell holder of the Beckman DK-2 spectrophotometer. The Tygon tubing caused much difficulty, especially in cases where hexane was used as solvent, probably from some refluxing of hexane during evacuation. A peak at 275 - 277 m μ , mistaken at first for a reaction product, proved to be easily reproducible by dipping Tygon tubing in hexane.

Analytical problems have been surmounted only recently by the advent of thin-layer chromatography, coupled with the use of radioactive carotene as a tracer. Reaction mixtures and products, formerly separated by column chromatography under nitrogen pressure, in a process that was time-consuming and gave poor resolution, can be neatly and rapidly separated in 15 minutes on thin-layer plates. The adsorbent used was Silica Gel G, with a mixture of petroleum ether and acetone, 5:1, as the developer. The order of R_f numbers is approximately the same as in the column chromatography. Beta carotene travels with the solvent front in the unirradiated mixtures; oxidized carotene products, obtained from auto-oxidized carotene, separate farther down on a vertical plate, with the most oxidized species trailing farthest behind the solvent front. Pheophytin separates as one chief band (bright red fluorescence under ultraviolet light) about half-way up the plate, with two faint satellite blue fluorescent bands. Chlorophyll moves only very slowly under these conditions. Presumably this order could be reversed on alumina plates.

In order to track down the colorless carotene conversion product on the developed thin-layer plate, it was decided to use C^{14} labeled carotene as a tracer. A convenient method of obtaining C^{14} labeled carotene by addition of C^{14} acetate to the mold, phycomyces blakesleeana, has been carefully worked out by Krause and Lilly⁶ at the University of West Virginia. Dr. Lilly kindly supplied a culture. His work was easily reproduced in this laboratory.

RESULTS

The kinetics of the disappearance of carotene in the presence of pheophytin in red light have been investigated in both hexane and methanol as solvents and found to be directly proportional to the first power of the concentration of both pheophytin and carotene, and to the square of the light intensity.

$$\frac{-d(\text{Car})}{dt} = \frac{-d A_{s478}}{dt} = k I^2 (\text{Car}) (\text{Ph})$$

The rate constant is much larger in methanol than in hexane. The quantum yield in methanol is approximately 0.5. The reaction proceeds smoothly under a vacuum, a little more rapidly than in air. The rate is decreased by stirring, suggesting the probability of some alignment of the carotene and pheophytin molecules for most efficient energy and/or hydrogen transfer.

The only prominent features in the absorption spectra taken during the reaction are the decrease in absorption at 450 and 478 $m\mu$, and the slight increase at 377 and 400 $m\mu$.

Early attempts to isolate the product absorbing at 377 and 400 $m\mu$ by column chromatography on sugar, under nitrogen, were positive only once. The product had a spectrum resembling either 7-7' dihydro beta carotene or possibly cryptoxanthin or zeaxanthin. Since the latter two compounds are oxidation products of beta carotene, and the reaction is taking place under vacuum, it does not seem likely that they can be the correct assignment. Pheophytin is recoverable with its spectrum essentially unchanged. Neither carotene nor pheophytin

have pronounced characteristics in the ultraviolet region before irradiation. There is some indication of an increase around 270 - 280 $m\mu$ after irradiation, and a large increase around 225 - 230 $m\mu$, but again no sharp maximum.

When C^{14} labeled carotene was used in the reaction mixture, and the irradiation products separated on the thin-layer plates, all of the radioactivity was found at the solvent front where unreduced carotene would have been. The radioactive product is colorless and shows a row of opaque white spots (whiter than the wet silica gel) at the solvent front.

Pheophytin is recoverable from an adsorbed layer about halfway up the plate. Since it is known from an independent study in our laboratories that cryptoxanthin and zeaxanthin have much lower R_f values than carotene under similar conditions, the evidence again points to the conclusion that the radioactive product is a hydrocarbon-like substance, probably a reduced carotene.

On elution of the carotene product with methanol and examination of the ultraviolet spectrum, a new peak is found at 255 - 270 $m\mu$, which was not present in the irradiated mixture before thin-layer chromatography (Fig. 3). There is absolutely no evidence for maxima at 377 and 400 $m\mu$ either in the radioactive carotene peak nor from any other fraction eluted from the thin-layer plate. The only related spectrum found in the literature⁷ is that of the quinones containing carotenoid side chains, such as ubiquinone, plastoquinone, and the quinone called Q-254. All of these quinones are

reducible by sodium borohydride, with characteristic shifts in the ultraviolet toward longer wavelengths on reduction. The result of borohydride reduction on the quinone-like product eluted from the thin-layer plate in these experiments is shown in Fig. 3.

DISCUSSION

The evidence for identification of the reaction product of beta carotene on irradiation with red light in the presence of pheophytin is still circumstantial. It appears that the carotene is being reduced in this photosensitized reaction. Hydrogen may come either from the solvent, or from the phytol side chain of the pheophytin. The basic constancy of the pheophytin spectrum during irradiation indicates no change in the porphyrin ring. It is not known whether there is a single reduced carotene product, or whether prolonged irradiation can result in increased reduction. The solvent appears to be important, because the reaction proceeds about four times faster in methanol than in hexane.

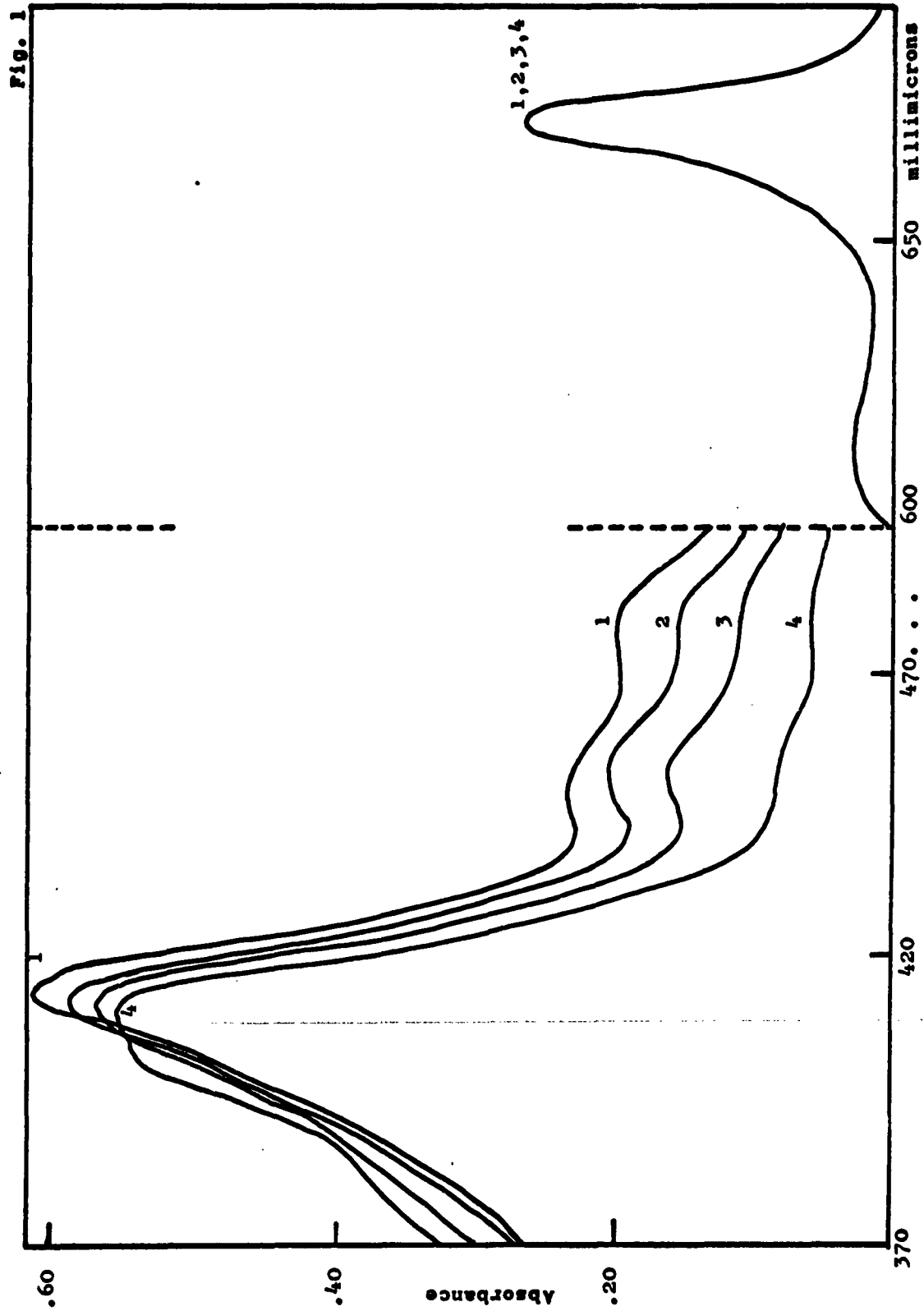
If a reduced carotene is produced during irradiation, oxidation to a quinone must occur subsequently either in the chromatography on silica gel, which is a relatively polar adsorbent, or on elution into methanol. It would be interesting to repeat these experiments, maintaining the plates under a nitrogen atmosphere during chromatography and elution.

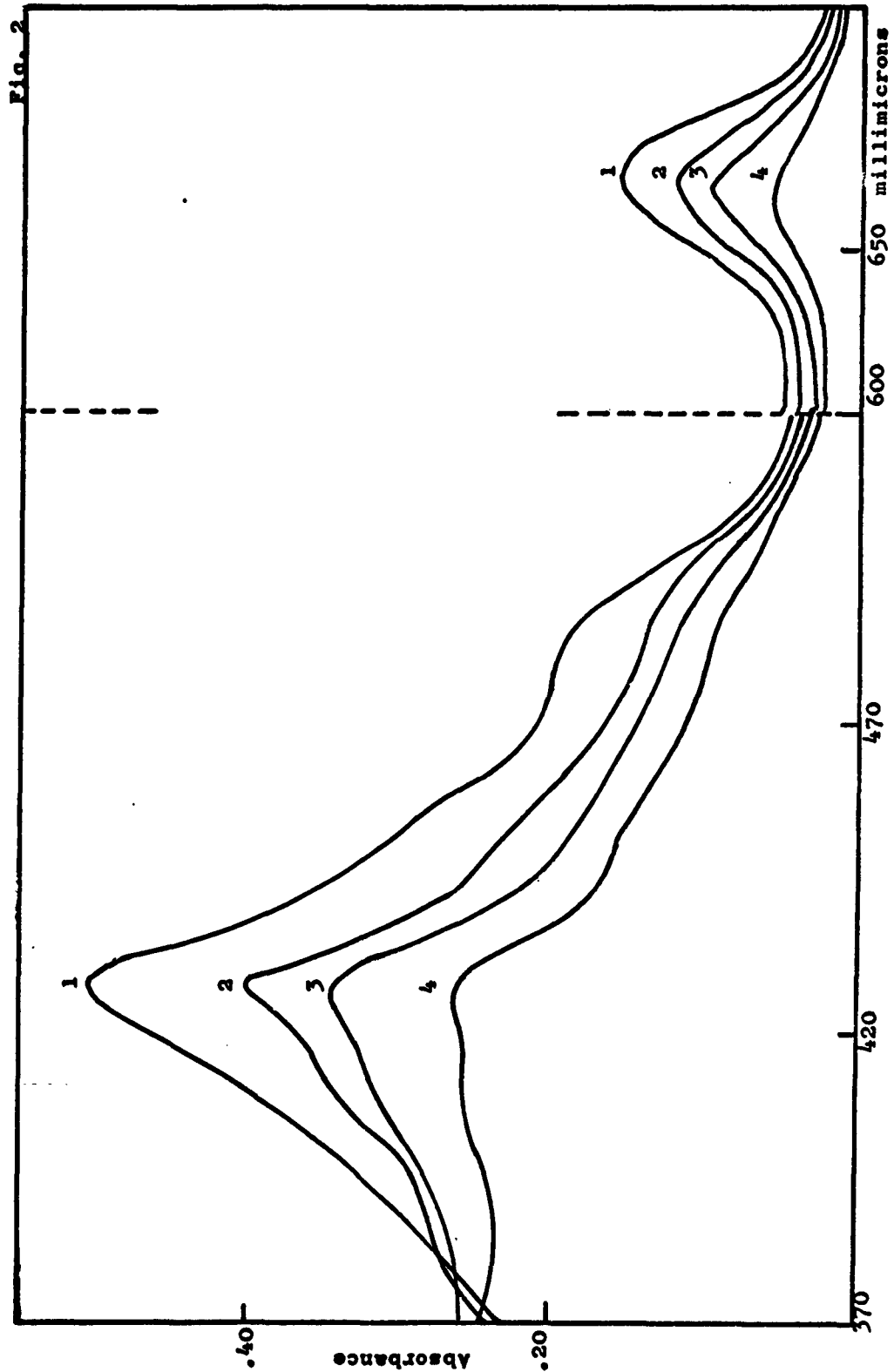
The extent of reduction of carotene may differ in hexane and methanol, and the quinonoid products formed may not always be the same. Much confirmation of this work is needed.

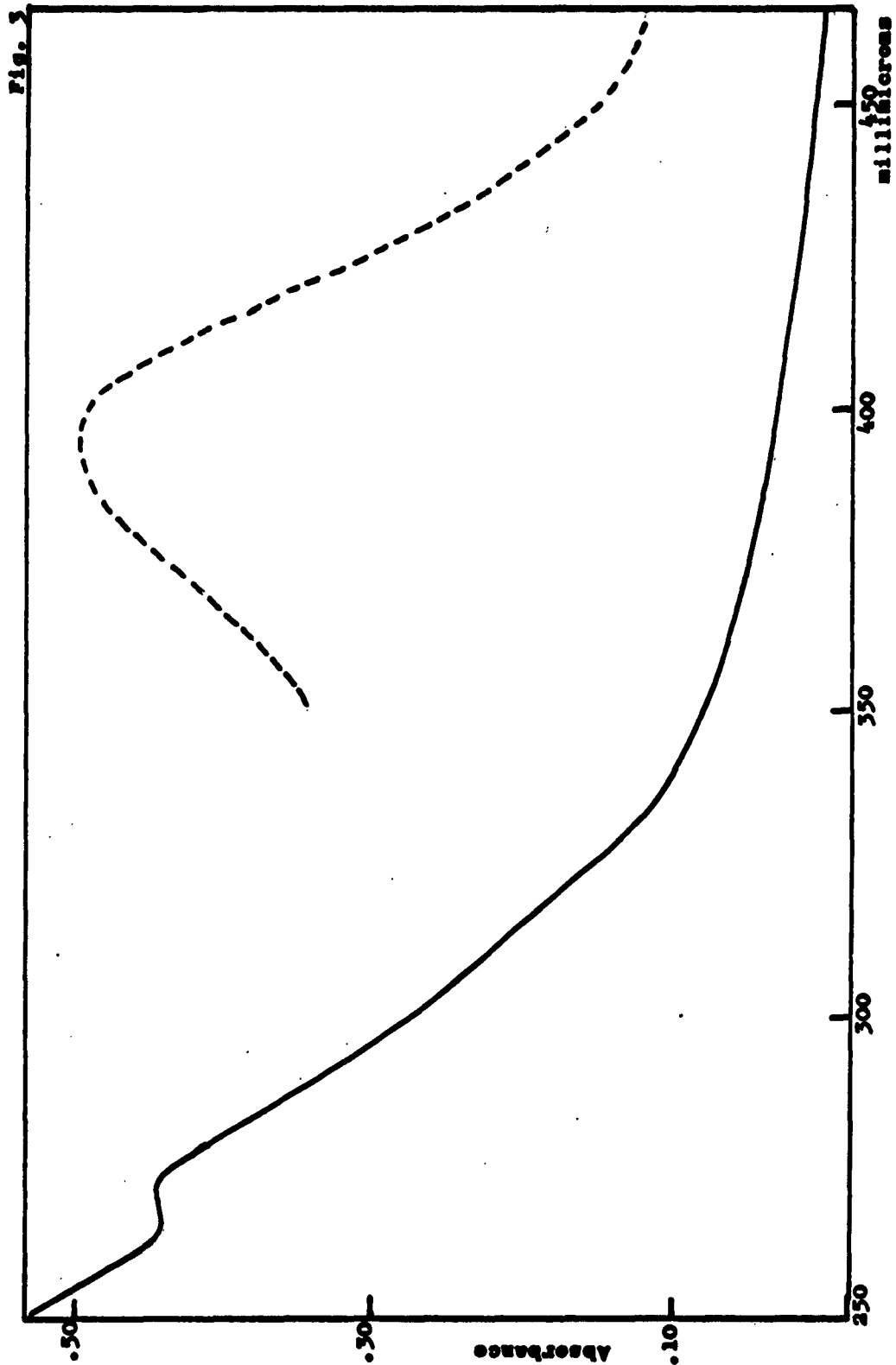
It will also be of interest to compare carotene conversion products formed on irradiation by red light in the presence of chlorophyll with those formed when pheophytin is the "sensitizer". The rate of reaction in methanol-hexane mixtures may also shed interesting light on the course of the reaction. Carotene and its conversion product are more soluble in hexane than in methanol, so it may be possible to produce larger quantities of products for infrared analysis. In the light of the discussion of the importance of Q-254 to electron transport in photosynthesis, it certainly seems desirable to complete this study.

LEGENDS FOR FIGURES

- Fig. 1. Rate of disappearance of carotene absorption at 478 and 450 $m\mu$ in presence of pheophytin, irradiated with red light; hexane solvent; 1) original 2), 3), 4) after 15, 30, 60 min. irradiation respectively
- Fig. 2. Rate of disappearance of carotene absorption at 478 and 450 $m\mu$ in presence of chlorophyll, irradiated with red light; methanol solvent; 1) original 2), 3), 4) after 15, 30, 60 min. irradiation respectively. Note disappearance of chlorophyll peaks at 662 $m\mu$ and 425 $m\mu$ also.
- Fig. 3. Absorption spectrum of carotene conversion product (formed on irradiation with pheophytin in red light) on desorption from thin layer chromatography plate in methanol: solid curve before, and broken curve after addition of sodium borohydride.







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DISCUSSION AND CONCLUSIONS

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 reaches a steady-state concentration the magnitude of which varies with conditions, but the acetone accumulates as long as isopropyl alcohol remains. These systems may not have practical value for the formation of peroxide, but the photocatalytic 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. 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 data obtained are best explained on the assumption that the energy of irradiation at 3650 Å, approximately 80 kcal. absorbed by the 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 formed under these conditions leads to the conclusion that an excited molecular oxygen anion is the most probable active intermediate.

This conclusion is supported by the study of the photo-

sensitized polymerization of methyl methacrylate in suspensions of zinc oxide in various solvents irradiated by light at 3650 Å. Surface-adsorbed oxygen appears to be essential to chain initiation. Polymers of high molecular weight, about 10^6 , are obtained with oxygen-free solutions, but untreated zinc oxide surfaces. Zinc oxide reduced under hydrogen, or heated to remove oxygen during evacuation, results in greatly suppressed polymerization. Presence of low concentrations of oxygen in solution yields a larger number of chains initiated, but lower molecular weight. Excess oxygen inhibits polymerization completely. Comparison of polymerization in various solvents indicates that solvents having high dielectric constants coupled with good proton-donating or hydrogen-bonding characteristics favor chain initiation, e.g. water and formamide. Electron spin resonance spectra show that both oxygen and water adsorbed in the dark are able to trap conduction electrons in heated evacuated zinc oxide. Formamide however increases the conduction electron signal and may be acting through a different mechanism on irradiated zinc oxide. The role of formamide in photosensitized polymerization, and observations on peroxide accumulation in zinc oxide suspensions containing amides, prompted further investigation of these effects. Amide residues exert a stabilizing influence on hydrogen peroxide at irradiated zinc oxide surfaces, whether the peroxide has been formed in the system by the photocatalyzed oxidation of the amide itself, or whether hydrogen peroxide has been added

to the system before irradiation. In the former case the rate of oxygen uptake and the final steady state concentration of hydrogen peroxide are related to the number of oxidizable C-H bonds in the amide. In the latter case the level of hydrogen peroxide that can be maintained is governed by both the initial concentration of the added peroxide and the nature of the amide itself.

Infrared studies of adsorbed residues from amides and other nitrogen-containing compounds indicate that both cyanides and cyanates can be produced from amides at irradiated zinc oxide surfaces, depending on oxygen tension in the suspension. Both are strongly adsorbed; cyanates are more effectively adsorbed at low concentrations, and also more readily desorbed on increasing the temperature.

Knowledge of specific effects at photocatalytic zinc oxide surfaces has been utilized in the construction of photo-voltaic cells. The properties of some of these cells, producing photo-voltages up to 1.7 volts, are described briefly. The study is being extended under Contract AF 19(628)-2768.

Preliminary studies on the use of pigments to sensitize zinc oxide and other photoconductors to light in the visible region of the spectrum, has resulted in the discovery of a unique reaction between pheophytin and carotene. Red light absorbed by the pheophytin results in rapid loss of carotene in the system, with no observable change in the pheophytin.

The reaction appears to be a reduction of carotene, accompanied by a rearrangement which results, on reoxidation, in formation of a quinone having a carotenoid side chain. This study is also being continued under Contract AF19 (628)-2768.

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PUBLICATIONS

Under Partial or Total Sponsorship of this Contract

"Mechanism of the Photo-Initiated Polymerization of Methyl Methacrylate at Zinc Oxide Surfaces", by Joseph C. Kuriacose and M. Clare Markham; J. Phys. Chem., 65, 2232 (1961)

"Effects of Amides on Photochemical Processes at Zinc Oxide Surfaces", by M. Clare Markham, Joseph C. Kuriacose, JoAnn DeMarco and Carol Giaquinto; J. Phys. Chem., 66, 932 (1962)

"Conversion of Isopropyl Alcohol to Acetone on Irradiated Zinc Oxide", by Joseph C. Kuriacose and M. Clare Markham; J. Catalysis, 1, 498 (1962)

Air Force Cambridge Research Laboratories, Bedford, Mass.
Rpt. No. AFCRL-63-608
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Unclassified Report
The 3 bound-in reprints are: Conversion of Isopropyl alcohol to Acetone; J. Catalysis, 1, 498-507 (1962)
Mechanism of photo-initiated

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- I. AFCRL, Project 6694, task 669402
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