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A. A. Krasnovskii and G. P. Brin

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PHOTOCATALYTIC ACTION OF ZnO AND TiO_2 IN REACTIONS PROCEEDING WITH EVOLUTION OF OXYGEN

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The study of reactions in which photochemical evolution of oxygen occurs is of interest in the search for artificial models of individual stages of photosynthesis. Isolated chloroplasts and leaf homogenates retain the ability to carry out the Hill reaction—the photochemical evolution of oxygen from water, coupled with the reduction of ferric iron, quinone, and other compounds. However, reactions of this type have so far not been reproduced in artificial systems. The present communication describes several types of oxidation–reduction reactions, photosensitized by zinc oxide and titanium dioxide, in which oxygen evolution is observed in the presence of a number of oxidants—potassium permanganate, quinone, and ferric iron compounds. The experiments were carried out at 20° in Warburg manometric vessels made of quartz and glass, illuminated from the bottom of the vessel by a PRK-4 mercury-quartz lamp enclosed in a quartz tube 5 cm in diameter. The vessels and the light source were placed in the water bath of a Warburg apparatus. In experiments conducted in quartz manometric vessels, the entire spectrum of the PRK-4 lamp acted, including the mercury lines at 256 and 313 mμ; in glass vessels these lines were retained by the glass, and the groups of mercury lines at 365 and 404 mμ acted.

As is known, zinc oxide and titanium dioxide absorb in the ultraviolet region of the spectrum (the long-wavelength absorption edge is about 400 mμ). In the reactions studied, the components also absorb in this spectral region; therefore, in all cases the direct photochemical action (without a sensitizer) was compared with that in the presence of zinc oxide and titanium dioxide. Experiments in which illumination was carried out in the absence of an oxidant in aqueous media led to slight absorption of oxygen in the case of zinc oxide (which sensitizes the formation of hydrogen peroxide from water and oxygen ([1])). In the presence of titanium dioxide, gas exchange did not change. To test for the possible presence of nonstoichiometric oxygen in zinc oxide, the following experiment was performed: a suspension of zinc oxide in water was placed in a vessel whose side arm contained 10% sulfuric acid. After thermostatting, the acid was added and the gas exchange was followed; no gas evolution was observed over the

Fig. 1

Figure 1: Fig. 1

course of an hour. The possibility of CO_2 evolution was eliminated by placing in the vessel a small cup with alkali. An experiment carried out with freshly ignited zinc carbonate also showed the absence of nonstoichiometric oxygen.

Most experiments were conducted in an atmosphere of nitrogen freed from traces of oxygen by passage through a system of absorbers containing alkaline hydrosulfite. In some experiments the pH was varied by using water acidified and alkalinized to a definite pH with sulfuric acid and a solution of caustic soda. Buffer salts (phosphates) inhibited the reaction.

Photocatalytic decomposition of potassium permanganate. Evolution of oxygen under the action of ultraviolet light on potassium permanganate solutions was discovered in 1913 by Matthews and Dewey (^{2}). This reaction was investigated in the work of Rideal and Norrish (^{3}). Zimmer-

Mann (4) studied the isotopic composition of the oxygen evolved and established that the photochemically evolved oxygen comes from MnO_4^- ions, and not from the water molecule; the photochemical act therefore consists in an intramolecular transfer of an electron from oxygen to the manganese ion. The maximum quantum yield of the reaction was observed at 313 mμ.

We found that the introduction of zinc oxide and titanium dioxide into aqueous solutions of potassium permanganate sensitizes the oxygen-evolution reaction toward longer wavelengths, into the region of the sensitizer' s own absorption (up to 400 mμ). Direct photochemical evolution of oxygen from $KMnO_4$ in glass was insignificant. In the presence of sensitizers (ZnO and TiO_2) in glass vessels, intense evolution of oxygen was observed (Fig. 1), while in quartz vessels there was a considerable acceleration of a reaction that proceeds even in the absence of sensitizers (Fig. 2).

A change in pH within the range from 4 to 10 had little effect on the photochemical evolution of oxygen in potassium permanganate solutions in quartz vessels in the absence of sensitizers, which agrees with the idea of intramolecular electron transfer. However, the pH value has some effect on the ZnO- and TiO_2-sensitized evolution of oxygen, which is probably connected with conditions for blocking active centers on the surface of the photocatalyst.

Fig. 1. Photosensitized, by ZnO and TiO_2, evolution of oxygen from potassium permanganate solutions upon illumination with a PRK-4 lamp in glass vessels at 20° (5 mg $KMnO_4$, 30 mg ZnO or TiO_2, and 10 ml water).
1 –$KMnO_4$ + ZnO; 2 –$KMnO_4$ + TiO_2; 3 –$KMnO_4$; 4 –ZnO; 5 –TiO_2; 6 –$KMnO_4$ + ZnO, solution of alkaline pyrogallol in a side arm

That the evolved gas is in fact oxygen was shown by experiments carried out in an atmosphere of nitrogen in the presence of an oxygen absorber—a 2% solution

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

of pyrogallol in a 10% solution of NaOH (1 ml of this solution was placed in a side arm of the vessel while nitrogen was flowing). During the experiment the oxygen was absorbed; the results are shown in Fig. 1. Control experiments with ZnO and TiO_2 in water without $KMnO_4$ showed no evolution of oxygen.

Fig. 2. Same as in Fig. 1, in quartz vessels

On the basis of experiments by A. N. Terenin and E. K. Putseiko (5), which showed sensitization of the photoconductivity of ZnO by adsorbed dyes, we attempted to use similar adsorbates in order to sensitize the reaction to the visible region of the spectrum. These experiments, however, did not lead to positive results. We also attempted to sensitize, to the red region of the spectrum, the decomposition of $KMnO_4$ in acetone and pyridine solutions of chlorophyll, but these experiments likewise were not successful, nor was the attempt to sensitize the decomposition of aqueous $KMnO_4$ solutions with colloidal chlorophyll and crystals of magnesium and copper phthalocyanines, which possess photosensitizing action in the oxidation of ascorbic acid (6).

Since ZnO sensitizes the formation of hydrogen peroxide ([1]), it would seem that oxygen evolution could proceed "in the bulk" through the interaction of H_2O_2 with $KMnO_4$. However, this mechanism is contradicted by the fact that the reaction also proceeds in the absence of oxygen no less, and even more, efficiently, and that titanium dioxide, which is not capable of sensitizing the formation of H_2O_2, is nevertheless active in the decomposition of potassium permanganate.

Photosensitized evolution of oxygen in the presence of potassium ferricyanide. The experiments were carried out in glass vessels in a nitrogen atmosphere. The ratio between ZnO and $K_3Fe(CN)_6$ strongly affects the efficiency of the process. At a high concentration of $K_3Fe(CN)_6$, ZnO is screened from the action of light. The optimal ratios under our experimental conditions were 500 mg ZnO and 15 mg $K_3Fe(CN)_6$ in 10 ml of water. Experiments were also carried out in the presence of absorbents—alkali and alkaline pyrogallol. In the presence of alkali alone, gas exchange did not change.

Fig. 3. Photosensitized by ZnO oxygen evolution from $K_3Fe(CN)_6$ solutions under illumination with a PRK-4 lamp in glass vessels at 20° in a nitrogen atmosphere (15 mg $K_3Fe(CN)_6$, 500 mg ZnO, and 10 ml of water). 1 – $K_3Fe(CN)_6 + ZnO$; 2 –$K_3Fe(CN)_6$; 3 –ZnO; 4 –$K_3Fe(CN)_6 - ZnO$ (1 ml of 2% pyrogallol solution in 10% NaOH; 9 ml of water was removed in the side arm of

the vessel in this case).

It is seen from Fig. 3 that the gas evolved is absorbed by pyrogallol and therefore is oxygen. In 30 min of illumination, up to 100 mm^3 of oxygen is evolved, which is about 0.1 mole per 1 mole of $K_3Fe(CN)_6$. In the presence of titanium dioxide under these conditions it was not possible to observe oxygen evolution.

Photosensitized evolution of oxygen in the presence of quinone. Upon illumination of aqueous quinone solutions in glass and quartz vessels, we were unable to observe direct photochemical evolution of oxygen. Introduction of zinc oxide or titanium dioxide into glass vessels led to gas formation upon illumination in a nitrogen atmosphere. However, a considerable part of the gas was absorbed by the alkali solution, whereas alkaline pyrogallol absorbed 20–30% more gas (Fig. 4). Thus, in the photoreaction a mixture of carbon dioxide and oxygen is evolved in approximately a 2 : 1 ratio. In control experiments with zinc oxide alone, quinone alone, and the absorbing solutions alone, no gas evolution was observed. Introduction of hydroquinone into quinone suppressed oxygen evolution. In the presence of air, photosensitized oxidation of quinone and hydroquinone was observed. Probably, in the reaction without air, the OH radicals formed initially lead to partial destructive oxidation of quinone or of the semiquinones formed as intermediates. This side reaction is very efficient, and, apparently, only a smaller part of the OH radicals manages to recombine with evolution of oxygen on the surface of zinc oxide.

On the mechanism of the reaction. In the excitation region, both photocatalysts and oxidants absorb. Therefore, in the systems studied there is no sensitization in the "pure" form, and one should speak of the photocatalytic action of zinc oxide and titanium dioxide, although in control experiments in glass vessels the direct photochemical action was insignificant. The following types of mechanism for these reactions may be envisaged: 1) the elementary process proceeds in the bulk, and the photocatalyst "selects" photoproducts, preventing the rapid reversibility of the primary stages; 2) molecules adsorbed on the surface of the catalyst photoreact upon excitation in the region of their own absorption; 3) the photocatalyst

absorbs light and leads to photosensitized oxidation–reduction of the reacting molecules adsorbed on its surface. To resolve these questions it is necessary to measure the "action spectrum" of the reactions studied. In our opinion, the most probable mechanism is one according to which photochemical electron transfer proceeds through the semiconductor catalyst, since reactions of this type also occur with substances that do not absorb in the region of the exciting light (^{1}).

Zinc oxide and titanium dioxide are semiconductors; upon illumination of them, charge separation occurs—an electron and a hole. Under the action of light on the sensitizer surface, the formation of electron-donor and electron-acceptor centers is possible (^{7}). The probable elementary stages of the reaction consist in the uptake of an electron by the electron-acceptor component (MnO_4^-, quinone, Fe^{+++}) and the donation of an electron by the electron-donor com-

Fig. 4

Figure 4: Fig. 4

ponent (OH—H_2O) into the "hole," with intermediate formation of hydroxyl radicals. In the experiments of G. A. Korsunovskii (^{8}) it was shown that, upon illumination of an aqueous suspension of zinc oxide in vacuum in the presence of benzene and the electron-acceptor dye methylene blue, phenol is formed. This indicates the formation of hydroxyl radicals reacting with benzene (^{9}).

On the basis of our experiments it should be assumed that the primary photoproducts (probably hydroxyl radicals) can recombine on the surface of the photocatalyst with evolution of oxygen. The mechanism of the reactions described by us requires more thorough study.

Fig. 4. Photosensitized ZnO evolution of oxygen from quinone solutions in glass vessels upon illumination with a PRK-4 lamp at 20° in a nitrogen atmosphere (15 mg quinone, 500 mg ZnO, and 10 ml water).
1 –quinone + ZnO; 2 –quinone + ZnO + KOH in the side arm; 3 –quinone + ZnO + solution of alkaline pyrogallol in the side arm; 4 –quinone; 5 –ZnO.

In conclusion it should be pointed out that the photocatalytic action of zinc oxide and titanium dioxide differed for the various preparations of these compounds. It is known that the activity of photocatalysts of this type depends on the specific surface area, structure, and microadmixtures of heavy metals (^{7}).

In the experiments we used zinc oxide pro anal. from Merck (I), four samples of muffled zinc whites (II), and ZnO obtained by ignition of chemically pure $ZnCO_3$ at 700° (III), pure titanium dioxide Schering-Kahlbaum (IV), and titanium white with the anatase structure (V). In the reaction of oxygen evolution from $KMnO_4$, the activity was high for all the photocatalyst preparations studied. In the reaction with $K_3Fe(CN)_6$, the most active were the ZnO samples (I), less active (II), and inactive (III). The figures present experiments with ZnO (I) and TiO_2 (IV).

Institute of Biochemistry named after A. N. Bach
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.