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INORGANIC MODELS OF THE HILL REACTION

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Isolated chloroplasts and homogenates of green leaves of plants are capable of the photochemical evolution of oxygen from water, coupled with the reduction of externally introduced electron acceptors: ferric iron compounds and other oxidants (the Hill reaction). In this reaction, the chlorophyll-sensitized reduction of ferric iron occurs at the expense of an electron (hydrogen) from water. The Hill reaction includes photochemical and enzymatic stages, and it has not been possible to observe it in chlorophyll solutions. To elucidate the nature of the elementary stages of a reaction of this type, it is desirable to study a simpler model system, in which we used inorganic photocatalysts—electronic semiconductors—in place of chlorophyll.

We have already pointed out that in the zinc oxide–potassium ferricyanide and zinc oxide–quinone systems, upon illumination with near ultraviolet light (in glass vessels), oxygen evolution was observed (*1*). This reaction probably proceeds with the intermediate formation of OH radicals: Korsunovsky (*2*) showed that, upon illumination of an aqueous suspension of zinc oxide in vacuum in the presence of benzene and methylene blue, phenol is formed, which indicates the formation of OH radicals reacting with benzene.

In the present work, the photocatalytic (photosensitizing) action of titanium dioxide, zinc oxide, and tungstic acid on the photoreduction reaction of aqueous solutions of potassium ferricyanide and ferric ammonium alum, accompanied by oxygen evolution, has been studied.

Zinc oxide and titanium dioxide are white and possess strong absorption in the near ultraviolet (up to 400 mμ); the absorption of yellow WO_3 extends further into the blue-violet region.

Dain and Kachan (*3*) discovered oxygen evolution upon illumination of acidic solutions of ferric perchlorate with the light of a mercury-quartz lamp. This reaction took place in the region of the ultraviolet absorption of ferric ions; the maximum effect was observed at 240 mμ. In accordance with this, we observed slight oxygen evolution in a solution of $Fe_2(SO_4)_3(NH_4)_2SO_4$ when the experiment was conducted in quartz vessels. In glass vessels (in which ultraviolet radiation shorter than 365 mμ is retained), we were unable to observe photochemical oxygen evolution in solutions of $K_3Fe(CN)_6$ and $Fe_2(SO_4)_3(NH_4)_2SO_4$, whereas the introduction of photocatalysts led, even under these conditions, to oxygen evolution.

The amount of oxygen evolved was measured by a micromanometric method on a Warburg apparatus in glass and quartz vessels of special form. A number of experiments were carried out in quartz vessels inserted into a glass Petri dish that served as a light filter absorbing the short-wavelength region of the ultraviolet radiation of the mercury-quartz lamp. The vessels were illuminated from the bottom side by a PRK-4 mercury-quartz lamp in a quartz sleeve, immersed in the water bath of the apparatus (Fig. 1). The experiments were carried out in an atmosphere of nitrogen and air. In the former case, the manometric vessel with the reaction mixture was purged with nitrogen purified from traces of oxygen in columns containing an alkaline solution of hydrosulfite.

The following photocatalyst preparations were used: zinc oxide Merck pro anal., muffle zinc white, luminescent zinc oxide;

titanium dioxide Schering Kahlbaum, titanium white (with the anatase structure); tungstic acid Schering Kahlbaum. The iron compounds were reagent grade. In an experiment, usually 0.3 g of photocatalyst and up to 0.5 g of iron salt in 6 ml of water were taken. The total volume of the manometric vessel was about 25 ml. Experiments with illumination were conducted for from 30 to 90 min, with measurement of the kinetics of oxygen evolution.

To judge whether the gas evolved was in fact oxygen, experiments were carried out in a nitrogen atmosphere with a solution of alkaline pyrogallol in the side arm of the manometric vessel. In the presence of alkaline pyrogallol, all the gas evolved under illumination was absorbed.

Illumination of aqueous solutions of ferric ammonium alum in quartz vessels in nitrogen led to a small evolution of oxygen, in agreement with the work of Dane and Kachan (^3). In glass this effect was not observed (see Fig. 2). In an air atmosphere, gas evolution could not be observed either in quartz or in glass. In the presence of TiO_2 and WO_3, the evolution of oxygen in quartz increased; in glass, oxygen evolution of similar magnitude was also observed. Thus, in experiments in glass vessels, sensitization of the reaction to the near ultraviolet (365 and 404 mμ) was observed; in the absence of a photocatalyst this did not lead to a direct photoreaction of the iron salt. Experiments in the presence of TiO_2 and WO_3 in air and in nitrogen gave identical results: what is essential is that in reactions with ferric ammonium alum, the presence of oxygen in the atmosphere does not exert an inhibiting effect. Zinc oxide has basic properties and therefore reacts with ferric ammonium alum, losing its photochemical activity.

Fig. 1. Diagram of illumination of manometric vessels: *1*—thermostat bath of the Warburg apparatus, *2*—manometric quartz vessel, *3*—glass light filter, *4*—

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Illumination of aqueous solutions of potassium ferricyanide in nitrogen did not lead to evolution or absorption of gas, whereas in an air atmosphere vigorous absorption of oxygen was observed, more intense in quartz than in glass. The mechanism of this effect requires more detailed investigation. The following explanation of this phenomenon may be proposed. The act of absorption of a light quantum in the complex $Fe^{2+}(CN)_6$ consists in transfer of an electron from the addend $(CN)^-$ to the central iron atom (⁀4); in this process Fe^{2+} and the radical CN are formed, which can be oxidized by oxygen to CNO. A water molecule enters the complex $Fe^{2+}(CN)_5 \cdot H_2O$, which is oxidized by oxygen:

$$Fe^{2+}(CN)_5 \cdot H_2O + \tfrac{1}{2}O_2 \rightarrow Fe^{3+}(CN)_5 \cdot H_2O + 2OH^-.$$

In the complex $Fe(CN)_5 \cdot H_2O$, upon absorption of a light quantum, electron transfer again occurs, followed by incorporation of a second water molecule into the complex, and so on, with the final formation of $Fe(OH)_3$ as a result of alkalinization of the medium during oxidation of Fe^{2+} and the successive departure of CN^- from the complex.

In the presence of photocatalysts in nitrogen, oxygen evolution was observed in quartz and glass, the least in the presence of TiO_2. In air, in the presence of TiO_2 and ZnO in quartz, gas absorption was observed (less than in the absence of photocatalysts), probably because of the light-screening action of the photocatalysts, whereas in glass in the presence of ZnO oxygen evolution was observed, in agreement with data published by us earlier ([1]). The same effect, but weaker, was observed in the presence of WO_3. With TiO_2, oxygen absorption was observed; in these experiments, apparently, there is a superposition of the screening and photochemical actions.

Table 1

Evolution (+) and absorption (—) of oxygen in μl over 30 min ± (5 μl) upon illumination of the system photocatalyst—aqueous solution of ferric compounds

Photocatalyst	$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4$, quartz	$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4$, glass	$K_3Fe(CN)_6$, quartz	$K_3Fe(CN)_6$, glass
In nitrogen				
–	+20	0	0	0
ZnO	–	–	+91	+90
TiO_2	+50	+37	+32	+12
WO_3	+100	+100	+95	+70
In air				
–	0	0	−645	−250
ZnO	–	–	−70	+89
TiO_2	+53	+27	−82	−165
WO_3	+100	+84	+6	+27

Note. The data were obtained with reactive samples of photocatalysts; titanium and zinc whites were less active. The photocatalysts were taken in an amount of 0.3 g, $K_3Fe(CN)_6$ 0.015 g, $Fe_2(SO_4)_3(NH_4)_2SO_4$ 0.5 g.

The reaction studied, like the Hill reaction, should obey the balance equation:

$$2Fe^{3+} + H_2O \rightarrow 2Fe^{2+} + 2H^+ + \tfrac{1}{2}O_2.$$

To verify the validity of this relationship, longer experiments (1.5 hours) were carried out with titration of Fe^{2+} in the reaction mixture with 0.1 N $KMnO_4$ before and after illumination.

Table 2 compares the volume of oxygen evolved with the volume of oxygen calculated from the amount of Fe^{2+} formed, on the basis of stoichiometry of the reaction. From Table 2 a satisfactory agreement of these values is evident.

Fig. 2. Photocatalytic evolution of oxygen in aqueous solutions of ferric complexes in a nitrogen atmosphere (0.3 g TiO_2 or WO_3; 0.5 g $Fe_2(SO_4)_3(NH_4)_2SO_4$ and 6 ml water): 1 –sensitization of the reaction by WO_3; 2 –sensitization by TiO_2; 3 –sensitization by TiO_2 in the presence of alkaline pyrogallol in a side arm; 4 –iron salt without photocatalyst; 5 –photocatalysts without iron salt. C –illumination, T –darkness.

On the mechanism of the photocatalytic reaction

In studying the photochemical evolution of oxygen in aqueous solutions of cerium perchlorate, Dain and Kachan [3] showed that the introduction of quartz powder into the solution led to an increase in the amount of photochemically formed oxygen. In the experiments, quartz played the role of a catalyst promoting the recombination of primarily formed hydroxyl radicals.

Table 2

Oxygen evolution during the photoreaction (in μl). Illumination for 1.5 hours. Amount of photocatalyst 0.3 g, $Fe_2(SO_4)_3(NH_4)_2SO_4$ 0.5 g and $K_3Fe(CN)_6$ 0.015 g. Nitrogen atmosphere

System	In Warburg apparatus	By Fe^{++} formation
$Fe_2(SO_4)_3(NH_4)_2SO_4$+WO_3	353	336
$Fe_2(SO_4)_3(NH_4)_2SO_4$+TiO_2	150	180
$K_3Fe(CN)_6$+ZnO	90	100

In our experiments, the introduction of quartz powder or aluminum oxide into the iron salt solution during illumination in glass had no noticeable effect on oxygen evolution. These experiments indicate that the mechanism of action of ZnO, TiO_2, and WO_3 differs from the action of SiO_2 and Al_2O_3, which do not absorb in the near ultraviolet. It should be assumed that the light absorbed by the photocatalyst is used to carry out the reaction. The following hypothetical reaction mechanism may be proposed. Molecules of the iron compound and molecules of water (hydroxyl ions) are adsorbed on the surface of the photocatalyst, and electron transfer occurs between them, probably through the photoconductivity band of the photocatalyst—semiconductor. The hydroxyl radicals formed on the surface recombine with evolution of oxygen.

The elementary processes may be represented in the form of the scheme:

1. Photoreduction of Fe^{3+} at an electron-donor center of the photocatalyst surface: $Fe^{3+} + e \to Fe^{2+}$.
2. Photooxidation of water (or hydroxyl ion) at an electron-acceptor site of the photocatalyst surface

$$H_2O - e \to H_2O^+ \to H^+ + OH$$

or

$$OH^- - e \to OH.$$

3. Recombination of hydroxyl radicals on the surface of the photocatalyst and evolution of oxygen

$$2OH \to H_2O + {}^1/{}_2O_2.$$

The overall process: $Fe^{3+} + {}^{1}/{}_{2}H_2O \rightarrow Fe^{2+} + H^+ + {}^{1}/{}_{4}O_2$ corresponds to the Hill reaction, with the difference that in a suspension of chloroplasts the reaction proceeds in the visible region of chlorophyll absorption, whereas in the models studied by us the reaction is sensitized to the near ultraviolet region of the spectrum.

In the heterogeneous model systems studied, the photocatalyst (semiconductor) plays the role of a pigment—sensitizer that absorbs light—and of a catalyst promoting the evolution of oxygen from the primary products of the photooxidation of water and thereby preventing the occurrence of reverse reactions of the primary photoproducts.

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