

# PHOTOOXIDATION OF WATER BY DYES ON THE SURFACE OF SEMICONDUCTORS

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**Abstract**

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**PHYSICAL CHEMISTRY**

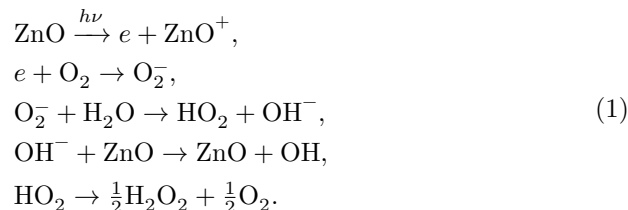
**G. A. KORSUNSKII**

**PHOTOOXIDATION OF WATER BY DYES  
ON THE SURFACE OF SEMICONDUCTORS**

*(Presented by Academician A. N. Terenin, 19 XI 1956)*

In a recently published work by T. S. Glikman and M. E. Podlinyaeva (<sup>1</sup>), on the basis of kinetic studies of the photoreduction of thiazine dyes on zinc oxide, a suggestion was made concerning the direct participation of water in this photoreaction as an oxidation substrate. Starting from the same premises, although somewhat different from those expressed by the authors of the article, we investigated the photoreduction reaction of methylene blue on zinc oxide, titanium dioxide, and cadmium sulfide, using the method of hydroxylation of benzene to detect hydroxyl radicals.

At present the following mechanism is accepted for the photooxidation of water on zinc oxide in the presence of oxygen (<sup>2</sup>):



Discharge of the hydroxyl ion at a positively charged center of a semiconductor microcrystal ( $\text{ZnO}^+$ ), formed as a result of electron capture by an oxygen molecule, leads to the formation of a hydroxyl radical. Possessing high oxidizing ability, the latter either reacts with the radicals  $\text{HO}_2$  and hydrogen peroxide present, leading to a decrease in the yield of peroxide, or, in the presence of organic reducing agents, to oxidation of the latter (<sup>3</sup>). Even the benzene molecule, stable with respect to oxidation, interacting with hydroxyl is converted into phenol, diphenyl, and higher oxy-derivatives, which has been observed in various photo- and radiochemical reactions associated with the appearance of free hydroxyl (<sup>4</sup>).

Transfer of an electron from zinc oxide to water directly, without the participation of an intermediate carrier such as, for example, oxygen, although in principle possible, since the electron affinity of water is of the same order as

Fig. 1. Vacuum tube for irradiating suspensions

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that of oxygen <sup>(5)</sup>, has nevertheless never been observed in the further decomposition of water into OH and H with the release of the latter in molecular form, as proposed by V. I. Veselovskii <sup>(2)</sup> (apparently because of the greater probability of reverse reactions). However, besides oxygen, other electron carriers with a sufficiently high oxidizing potential may be used, such as, for example, dyes. Many dyes of the most diverse classes possess the ability to capture an electron and undergo subsequent photoreduction to the leuco compound.

In our experiments, zinc oxide from Kahlbaum, chemically pure, with grain sizes of  $1\ \mu$ , was used. 100 mg of powder was placed in the lower end of two

Tungberg tubes, into which 10 ml of methylene blue solution of concentration  $1.5 \cdot 10^{-4}\ M$  in a saturated aqueous solution of benzene ( $\sim 10^{-2}\ M$ ) was poured (see Fig. 1). The tubes were sealed to a vacuum apparatus and evacuated to a pressure of  $1-5 \cdot 10^{-5}$  mm Hg with fourfold freezing and thawing. The tubes were then sealed off, and one of them was irradiated for 1 hour with a PRK-2 mercury lamp through light filters transmitting the mercury line at  $366\ m\mu$ ; complete bleaching of the dye occurred. After irradiation, water from the methylene blue solution was distilled in vacuum into the upper end of the tube by immersing it in liquid air and carefully heating the lower end. The tubes were opened and the distillate was poured through branch *a* into the cuvette of an SF-4 spectrophotometer, while distillate from the unirradiated tube was poured into the comparison cuvette. The absorption spectrum of the distillate, shown in Fig. 2, coincides with the spectrum of phenol shown in the same figure\*.

**Fig. 1.** Vacuum tube for irradiating suspensions

Phenol formation can occur only by the addition of OH groups to benzene, the source of which is water either directly or through the formation of zinc hydroxide <sup>(1)</sup>. However, as will be shown below, phenol is also formed on semiconductors that exhibit acidic properties in aqueous solution; therefore, in neutral solutions, in our opinion, direct participation of water is more probable.

The concentration of the phenol formed is approximately half the concentration of the dissolved dye, which corresponds to the photoreaction:

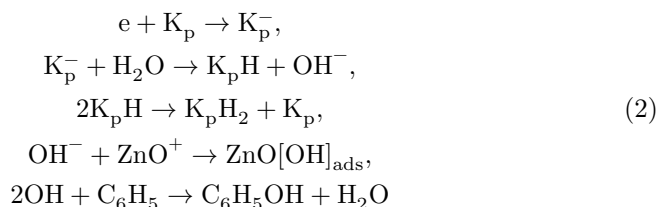


Fig. 2. Absorption spectra of the distillate of suspensions of zinc oxide and titanium dioxide in an aqueous-benzene solution of methylene blue after irradiation in vacuum: 1—ZnO suspension, 2—TiO<sub>2</sub> suspension, 3—phenol  $8 \cdot 10^{-5} M$

Figure 2: Fig. 2. Absorption spectra of the distillate of suspensions of zinc oxide and titanium dioxide in an aqueous-benzene solution of methylene blue after irradiation in vacuum: 1—ZnO suspension, 2—TiO<sub>2</sub> suspension, 3—phenol  $8 \cdot 10^{-5} M$

(K<sub>p</sub>—dye molecule).

**Fig. 2.** Absorption spectra of the distillate of suspensions of zinc oxide and titanium dioxide in an aqueous-benzene solution of methylene blue after irradiation in vacuum:

1—ZnO suspension, 2—TiO<sub>2</sub> suspension, 3—phenol  $8 \cdot 10^{-5} M$

Experiments with titanium dioxide were carried out in a similar way (of domestic manufacture, grade unknown, grain size  $2-3 \mu$ ), which, as is known, sensitizes the photoreduction of methylene blue in aqueous solution<sup>(6)</sup>. In this case we also detected phenol (Fig. 2), which indicates the same mechanism of the photoreaction as in the case of zinc oxide. Indeed, after irradiating in air a suspension of titanium dioxide in an aqueous solution of benzene, separating the powder by centrifugation, and recording the absorption spectrum of the solution, we detected phenol in approximately the same amount as for zinc oxide (Fig. 3).

On the other hand, when an aqueous suspension of titanium dioxide was irradiated, hydrogen peroxide was never detected, which gave A. A. Krasnovskii grounds to consider it inactive under aqueous conditions<sup>(6)</sup>. Since the processes of formation of hydrogen peroxide and hydroxyl are closely interrelated, we assumed that the absence of peroxide in the irradiated suspension

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\* The same results are obtained when the solution is distilled in air after centrifugation. In both cases phenol passes off with the water vapor.

TiO<sub>2</sub> is explained by its dark decomposition on the surface of the semiconductor. Experiments showed that hydrogen peroxide of concentration  $1.5 \cdot 10^{-4} M$  in an amount of 10 ml, when shaken in the dark for 30 min with 100 mg of titanium dioxide, decomposes completely, whereas when shaken with the same amount of zinc oxide the peroxide concentration does not change.

The third semiconductor tested by us was cadmium sulfide from Kahlbaum, pure, with grain sizes of  $0.5-1 \mu$ . It is known that upon illumination of an aqueous suspension of cadmium sulfide with ultraviolet or blue light in the presence of oxygen, hydrogen peroxide is formed in fairly high yield<sup>(7)</sup>, which was also confirmed in our experiments. Nevertheless, the yield of phenol proved

Fig. 3

Figure 3: Fig. 3

to be several times lower than for ZnO and TiO<sub>2</sub> (Fig. 3). We explained this by the interaction of hydroxyl radicals with hydrogen sulfide, formed as a result of partial hydrolysis of CdS. In this case one may expect oxidation of hydrogen sulfide to sulfuric acid, which was indeed confirmed by a qualitative reaction for the SO<sub>4</sub>' ion by adding a solution of a barium salt. Control experiments established that hydrogen peroxide of the same concentration as is formed upon illumination, shaken with cadmium sulfide, gives no BaSO<sub>4</sub> precipitate in the filtrate and, consequently, is not the oxidant of hydrogen sulfide.

Fig. 3. Absorption spectra of the filtrate of suspensions of zinc oxide (1), titanium dioxide (2), and cadmium sulfide (3) in aqueous-benzene solution, illuminated in the presence of air

Illumination of a cadmium sulfide suspension in an aqueous or aqueous-benzene solution of methylene blue in vacuum for a long time (up to 5 h) leads to slight bleaching of the dye. The dye adsorbed on the surface of the semiconductor bleaches especially poorly (about 60-70% adsorbed). Tests for the formation of phenol or sulfuric acid gave a negative result, which apparently is explained by a different bleaching mechanism. It is possible that the substrate of oxidation is hydrogen sulfide, whose reducing ability with respect to the dye is higher than that of water.

In conclusion I express my gratitude to Academician A. N. Terenin for his constant attention to the present work.

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