

Photosensitized Reactions of Toluidines on Zinc Oxide

Investigations on photoinduced reactions of organic substrates on semiconductor oxides like ZnO (*n*-type) are currently receiving much attention because of their relevance to research on PEC cells with organic additives at the illuminated electrode (1, 2). In the presence of illuminated zinc oxide and dissolved oxygen aniline was oxidized to azobenzene (3) with no side products like azoxybenzene being formed (4). The results of the photooxidation of the three toluidines under similar conditions are presented here.

The irradiations were carried out at 365 nm using a Hanovia UVS-500 lamp fixed horizontally above a shaker on the platform of which was mounted a Pyrex cell with two outer jackets used for conducting the reactions. The inner jacket contained 10% CuSO₄ solution while water from a thermostat was circulated through the outer jacket. The cell was shaken at regular intervals to maintain the zinc oxide powder in suspension. Benzophenone actinometry was employed (5) to estimate the quantum efficiency.

The characteristics of the reaction were similar to the reaction of aniline in all respects (3, 4). The products were the corresponding azo compounds and H₂O₂. The azo compounds were identified by uv spectral and polarographic studies on the irradiated solutions. Simultaneous presence of light ($\lambda = 365$ nm), dissolved oxygen, and the zinc oxide were essential for the occurrence of the reaction. Very large amounts of zinc oxide were avoided in systematic experiments to minimize scattering of the light. An optimum amount of zinc oxide, 0.2 g, with 20 ml of the amine solution was used in all the experiments and the results are presented in Table 1.

The amount of the azo compound formed increased with time of irradiation. When parameters like light intensity and amount of zinc oxide were kept constant and the amine concentration was increased the initial rate of formation of azo compound increased.

It has been established that O₂⁻ is formed when the ZnO-O₂(ads) system is illuminated (6-8). In an *n*-type semiconductor like zinc oxide, illumination leads to the formation of ZnO(+) holes and electrons. The electron is captured by the adsorbed O₂ to yield O₂⁻. The amine can bind to the hole and lose an electron to neutralize the hole thereby becoming a cation radical, viz., C₆H₅NH₂⁺. The cation radical can react with O₂⁻ to yield HO₂ and C₆H₅NH· which are the precursors of H₂O₂ and the azo compound. A similar scheme has been proposed for the reactions of alcohols which conforms with the model proposed by Wolkenstein (9).

The sample of ZnO used (M and B) had a surface area of 4.8 m²/g and adsorbed a limiting amount of 0.004 moles of aniline per gram of oxide. Assuming about 5×10^{14} sites per square centimeter of zinc oxide the data correspond to one molecule of aniline adsorbed per site. However, the yield of azo compound is only a small fraction of the adsorbed amine. The relative importance of the competing hole-electron recombination and the paucity of sufficient adsorbed oxygen may be contributing to the inefficiency of the reaction. The reactivity of the amines as reckoned by the initial rates is as follows: *m*-toluidine > *o*-toluidine > aniline > *p*-toluidine. This order is not closely related to the order of the ionization potentials (10). The ionization potentials are in the order: *p*-toluidine (7.48

TABLE I

Amounts of Azo Product Formed (moles $l^{-1} \times 10^6$) in Photooxidation

Amine	Ir radiation time (min)			
	30	60	90	120
Aniline	2.6	3.5	3.5	3.6
<i>o</i> -Toluidine	2.8	4.2	5.1	5.9
<i>p</i> -Toluidine	1.6	2.7	3.0	4.5
<i>m</i> -Toluidine	3.0	4.0	5.9	7.0

Note. Amount of zinc oxide = 0.2 g. Amount of amine = 20 ml of 0.02 *M* amine in ethanol. Light intensity = 2.5×10^{-6} ein. $l^{-1}s^{-1}$.

eV) < *o*-toluidine (7.62 eV) < *m*-toluidine (7.66 eV) < aniline (7.7 eV). It must be noted, however, that as the reaction progresses, the fall in rate is lowest for *p*-toluidine. The unexpectedly low initial reactivity of the *p*-isomer seems to be due to the strong methyl–methyl repulsion between two adjacently adsorbed molecules, whereas in other isomers the major repulsion between two adjacent amines is of the methyl–hydrogen type. This can lead to a lower surface concentration of the *p*-isomer compared to the *meta* and *ortho* isomers as is observed from a study of the adsorption of these compounds on zinc oxide.

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HEMA KASTURIRANGAN
V. RAMAKRISHNAN
J. C. KURIAKOSE

Department of Chemistry
Indian Institute of Technology
Madras 600036
India

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