

*Photosensitized Oxidation of Isopropylalcohol
in the Presence of Zinc Oxide*

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As reported previously¹⁾, two of us (Y.F. and T.K.) found that photodesorption of oxygen takes place on reduced zinc oxide whereas it turns to irreversible sorption on oxidized sample. This opposite fashion of the photoresponse in the adsorption of oxygen stimulated us to investigate how these phenomena should be associated with the photosensitized oxidation reaction²⁾ known to occur on zinc oxide. Experiments were made, therefore, along with this interest.

The oxidation of isopropylalcohol by oxygen in liquid phase was chosen for the purpose. Commercial zinc oxide powder (guaranteed reagent) supplied by KANTO KAGAKU was outgassed at 480°C for one hour in vacuo. On cooling it was poured into isopropylalcohol. This zinc oxide sample is called here as reduced zinc oxide. On the other hand, the commercial zinc oxide was used without any special pretreatment. The sample is supposed to be in oxidized state, since the d.c. electrical resistance measurement has shown that it possesses a resistance value as large as that of oxidized zinc oxide or is much larger than that of reduced zinc oxide.

A 50 ml. dried isopropylalcohol containing 2 g. reduced or oxidized zinc oxide was put into a round Pyrex flask having three openings, two of which being for thermometer and mercury manometer respectively and the remaining being connected to a reflux condenser and then to a gas burette.

Oxygen was introduced from the gas burette into the flask immersed in 65°C thermostat. The oxidation reaction was allowed to proceed with stirring reactant phase operated by magnetic rod placed in the flask. The apparatus was isolated when working. The rate of oxidation was followed by recording the decrease in the gas volume of the burette at a constant

1) Y. Fujita and T. Kwan, *This Bulletin*, **31**, 380 (1958).

2) For example, see M.C. Markham and K. J. Laidler, *J. Phys. Chem.*, **57**, 363 (1953).

pressure. The partial pressure of oxygen inside the flask was estimated to be 440 mmHg during the reaction.

Irradiation of light was made by Matuda Mercury Lamp SHL 100 UV without filter of any kind but through the window of the thermostat. The reaction product was pipetted and subjected to gas chromatographic and chemical analyses after the measurement of the oxidation rate. The temperature of the oxidation reaction was determined by the thermometer immersed directly in the liquid phase of the reacting system. Illumination caused the temperature of the system to rise less than 2°C.

It was confirmed that without illumination little consumption of oxygen occurs on reduced zinc oxide kept at 65°C. Illumination, however, brought forth distinct consumption of oxygen. On intercepting the light, the consumption occurring steadily was found to cease apparently. Reillumination caused consumption of oxygen again to proceed, so that the photocatalytic oxidation of isopropylalcohol was almost reversible with respect to on or off of the light switch.

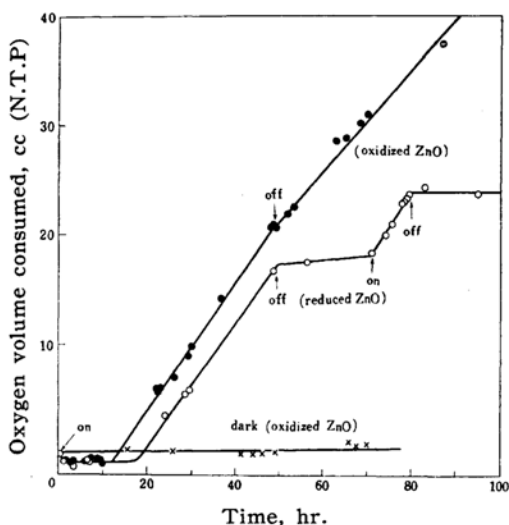
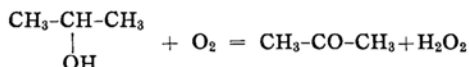


Fig. 1. Oxidation of isopropylalcohol by oxygen on zinc oxide with or without illumination.

T: 65~67°C. P_{O_2} : 440 mmHg.

Now, in the case of oxidized zinc oxide, the photosensitized oxidation reaction took place quite similarly as the case on reduced zinc oxide, while the reaction did not proceed without illumination beyond the period of 70 hr. However, strikingly different behavior was that interception of light still permits the oxidation reaction

to proceed with a speed almost equal to that of illumination. All the rate data for the oxidation of isopropylalcohol are shown in Fig. 1. Gas chromatographic and chemical analyses indicated that the product contains nothing other than acetone and hydrogen peroxide. The oxidation reaction may hence be expressed by



As shown previously¹⁾, adsorbed oxygen due to illumination was unable to desorb from the surface of oxidized zinc oxide on intercepting light whereas photodesorption was almost reversible on the surface of reduced zinc oxide. If it is accepted that the photoresponse of this kind should hold even during the oxidation reaction of isopropylalcohol, the different photocatalytic behavior shown above respectively on reduced and oxidized zinc oxide is to be anticipated. Because the catalyzing surface of reduced zinc oxide varies, when oxygen is present, depending on whether the light is switched on or off whereas the surface of oxidized zinc oxide, once experienced illumination, may maintain its state even during the light is intercepted.

On the other hand, almost identical photocatalytic activity shown by the two zinc oxide samples during the initial stage, including the induction period, and later is unexpected and rather embarrassing. Further work is in progress.

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