

The Catalytic Action of Binary Metal-Polyphthalocyanine Complexes on the Oxidation of Acetaldehyde Ethylene Acetal

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We wish to report in this communication our recent findings that acetaldehyde ethylene acetal is effectively oxidized with oxygen to ethylene glycol monoacetate in the presence of some metal-phthalocyanine complexes, which may act as catalysts. The catalytic activities of the phthalocyanine complexes are remarkably dependent on the type of complex involved. The acetal is not oxidized with oxygen at 30°C by copper- or iron-phthalocyanine, nor by copper- or iron-polyphthalocyanine. However, the acetal is quickly oxidized with oxygen at 30°C by binary copper-iron-polyphthalocyanine, although the acetal is not oxidized in the presence of the mixture of copper- and iron-polyphthalocyanines.

Similar phenomena have also been observed in the case of iron- and molybdenum-phthalocyanine complexes. The binary complex which contains iron and molybdenum ions together in polyphthalocyanine was active in the oxidation of the acetal with oxygen, but the mixture of iron- and molybdenum-polyphthalocyanines was not active. The meaning of the need for two kinds of metal ions in the complexes is not clearly understood. However, one could speculate that two kinds of metal ions may play different roles in the catalytic oxidation. For example, one kind of metal ion serves to produce the hydroperoxide of the acetal, and the other, to decompose it, while the conjugated system in the complexes would contribute to the electron transfer between two kinds of metal ions.

All of the metal-phthalocyanines used in this investigation were synthesized by a modification of the methods described by Epstein and Wildi,¹⁾ and Drinkard and Bailar.²⁾ Acetaldehyde ethylene acetal was purified by repeated distillation over sodium. The oxidation of the acetal was carried out by stirring 0.05 g. of the catalyst in 5 ml. of the acetal under an atmosphere of oxygen at 30°C.

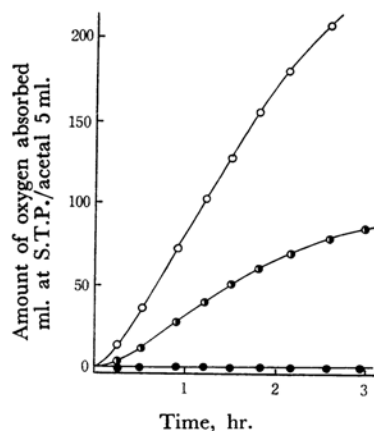


Fig. 1. Effects of metal-polyphthalocyanine complexes on the rate of the oxygen absorption: ○ Cu-Fe-, ○ Mo-Fe-polyphthalocyanines, and ● Cu-, Fe-, Mo-, Cu- and Fe-, Mo- and Fe-polyphthalocyanines.

The amounts of oxygen absorbed and the reaction times were measured by using the equipment described in a previous paper.³⁾ The results are shown in Fig. 1. As the reaction products, ethylene glycol monoacetate and diacetate were identified and were determined by gas chromatography. In the case of binary iron-molybdenum-polyphthalocyanine, the yields of ethylene glycol monoacetate and diacetate, based on the amount of acetaldehyde ethylene acetal, were 41.2% and 1.3% respectively at the reaction time of 3.5 hr.; 58.5% of the acetal was recovered. A detailed report of this experiment will be published later.

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1) A. Epstein and B. S. Wildi, *J. Chem. Phys.*, **32**, 324 (1960).

2) W. C. Drinkard and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 4795 (1959).

3) H. Inoue, Y. Kida and E. Imoto, This Bulletin, in press.