CHEMISTRY LETTERS, pp. 855-858, 1993.

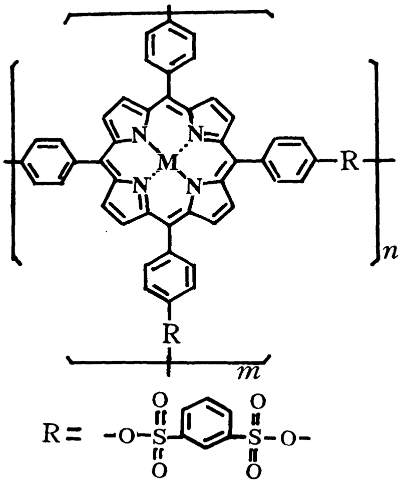
Synthesis of Polymeric Metalloporphyrin and Their Catalytic Activity in the Oxidation

Rong Min WANG* and Yun Pu WANG

Department of Chemistry, Northwest Normal Universty, Lanzhou 730070, China

The polymeric porphyrin has been prepared by interfacial polymerization of tetrakis(*p*-hydroxylphenyl)porphyrin with *m*-benzene-disulfo chloride. The spectra and catalytic behaviours of its complexes with transition metal (Cu, Zn) have been studied. The cupric complex exhibits higher catalytic activity in oxidation of ethyl benzene, cyclohexene and isobutyl alcohol by O_2 without any solvent.

Cytochrome P-450 plays as important role in metabolizing biomolecules and Xenobiotics.$^{1)}$ This enzyme can catalyze the oxidation of various substrates by the introduction of one oxygen atom into a substrate from molecular oxygen. Recently many attempts have been done to apply low-molecular-weight Fe(Ⅲ)-, Mn(Ⅲ)-, and Cr(Ⅲ)-tetraarylporphyrine derivatives$^{2-5)}$ or polymer bound metalloporphyrin$^{6-8)}$ in mimicking the reactivity of cytochrome P-450. So far, to our knowledge, very few studies were carried out using polymeric metalloporphyrin which improves the catalytic behaviour of the system by preventing the formation of inactive porphyrin *μ*-oxo-dimers. In this paper, the polymeric porphyrin (H_2 PTBSOPP) which is linked by *m*-benzene-disulfonate to form two-



M=H_2(H_2PTBSOPP)

M=Zn, Cu (MPTBSOPP)

dimensional arrangements and its complexes with cupper and zinc have been synthesized and the catalytic preperties of CuPTBSOPP have been studied.

The polymeric porphyrin (H_2PTBSOPP) was synthesized as follows: THPP9) (0.27 mmol) was dissolved in 10 ml of 1.25 (mol/l) NaOH (without Na_2CO_3), 30 mg of the phase transfer catalyst was added, and then stirred for 10 min. To this solution added dropwise 1 ml of the solution of *m*-benzene-disulfo chloride (0.62 mol/l) in drying $CHCl_3$ with sharply stirring. The crude product was isolated by filtration and washed separately by water, alcohol and chloroform for several times. A polymeric film of H_2PTBSOPP was obtained with yield of 72% after drying. Complexations of H_2PTBSOPP with $M(OAc)_2 \cdot nH_2O$ ($Cu(OAc)_2 \cdot H_2O$, $Zn(OAc)_2 \cdot 2H_2O$) were performed in the mixture of H_2O-C_2H_5OH. The value of pH was adjusted to 4—5 by dilute HOAc. The reaction mixtures were refluxed for 6 h with stirring. Products were filtered and washed separately by H_2O and C_2H_5OH. Yields of 80% or better of MPTBSOPP were obtained after drying.

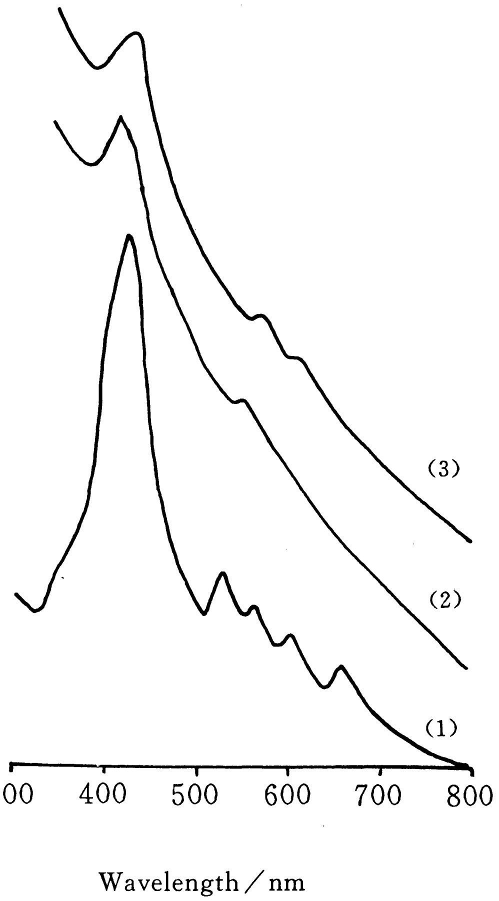
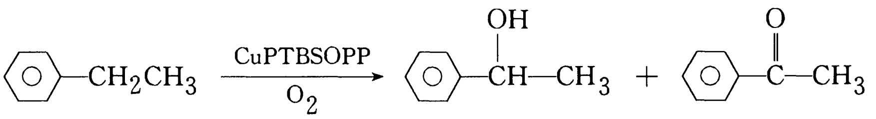


Fig. 1. UV/VIS spectra (in KBr) of H_2PTBSOPP(1), CuPTBSOPP(2), and ZnPTBSOPP(3).

In their UV/VIS spectra, the polymeric porphyrin and its complexes exhibit typical absorptions of porphyrin. The soret band of the ligand(H_2PTBSOPP) hypsochromic shift in CuPTBSOPP and hyperchromic shift in ZnPTBSOPP. Compared with the ligand, the number of the absorption peak of metal complexes decreases because of increasing symmetry of porphine ring (Fig. 1). In the IR spectra of polymeric metalloporphyrins, the characteristic absorption bands of ν_{NH} (3314 cm^{-1}) and δ_{NH}

(966 cm^{-1}, 734 cm^{-1}) of the ligand are not observed, and the characteristic absorption peaks of complexes$^{10)}$ are detected at 1001 cm^{-1} for CuPTBSOPP and 996 cm^{-1} for ZnPTBSOPP. The absorption of $\nu_{S=O}$ appears in 1375 cm^{-1} and 1180 cm^{-1} for the ligand and complexes. The polymeric ligand(H_2PTBSOPP) and its metal complexes have also been characterised by thermal analysis, scanning electron microscope and fluorescence spectra.

In order to investigate the catalytic reactivities of polymeric metalloporphyrins in oxidation reaction, we first examined the oxidation of ethyl benzene with O_2. The reaction were carried out



under 1 atm of O_2 without use of any solvent or coreductant. The oxidation happens on the α-carbon of ethylbenzene. The reaction products were determined and analyzed by using Shimadzu QP-1000A GC/MS system and GL-16A gas chromatograph with a 5 m×3 mm OV-17 column. Affording corresponding ketone and alcohol with the conversion of 9.5% in 3 h (Fig. 2) and the selectivity to total ketone and alcohol is more than 80%.

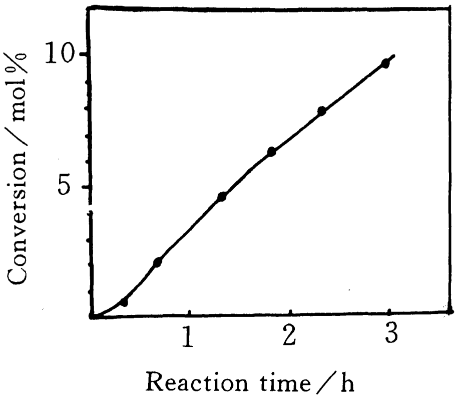


Fig. 2. The oxidation of ethylbenzene by O_2 at 125 °C. Sub. 20 mmol; Cat, CuPTBSOPP, 0.005 mmol.

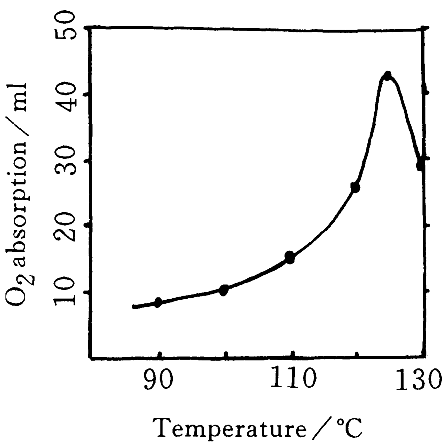


Fig. 3. The relationship between activity of CuPTBSOPP and temperature Sub. phC_2H_5; Cat, ca. 0.005 mmol; 3 h.

No activity of ZnPTBSOPP or the monomeric cupper-porphyrin complex (CuTHPP) has been found in oxidation of alkylbenzene. The activity of CuPTBSOPP in oxidation of methylbenzene is very low. The activity of CuPTBSOPP in oxidation of ethylbenzene is affected by temperature (Fig. 3).

We next examined the oxidation of cyclohexene (20 mmol) catalyzed by CuPTBSOPP (7.0 mg). The reaction was carried out under 1 atm O_2 without the use of any solvent. The conversion of cyclohexene was 86 (mol%) in 11 h. It had also been found that isobutyl alcohol could be oxidized by O_2 catalyzed by CuPTBSOPP.

References

1) "Cytochrome P-450: structure, mechanism and biochemistry," ed by P. R. Ortiz de Montellano, Plenum Press, New York (1986).
2) D. Mansuy, *Pure Appl. Chem.*, **59**, 759(1987).
3) D. Mansuy, *Pure Appl. Chem.*, **62**, 741(1990).
4) F. Montanari, S. Banfi, and S. Quici, *Pure Appl. Chem.*, **61**, 1631(1989).
5) P. E. Ellis, Jr. and J. E. Lyons, *Coord. Chem. Rev.*, **105**, 181(1990).
6) D. Wohrle and J. Gitzed, *Makromol. Chem., Rapid Commun.*, **9**, 229(1988).
7) T. Mori, J. Santa, and M. Hirobe, *Tetrahedron Lett.*, **26**, 5555(1985).
8) A. W. Van der Made, J. W. H. Smets, R. J. M. Nolte, and W. Drenth, *J. Chem. Soc., Chem. Commun.*, **1985**, 1204.
9) THPP: meso-tetra(*p*-hydroxylphenyl)porphyrin.
10) D. W. Jhomas and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5111(1959).

(Received January 18, 1993)