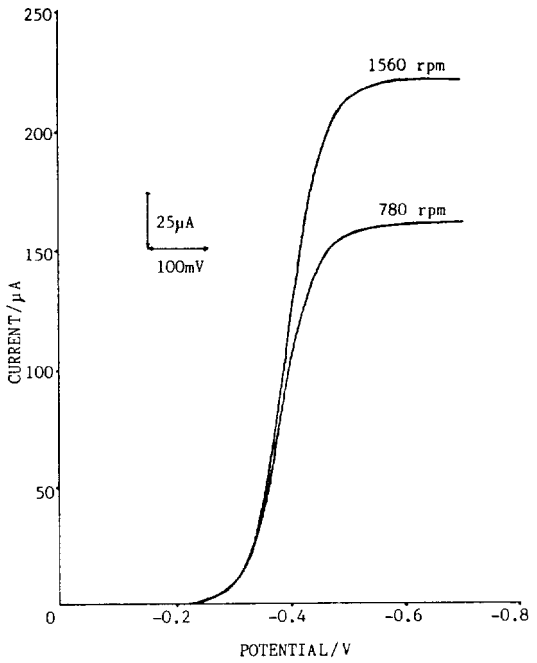

Figure 2. Rotating disk voltammetric response under oxygen. The experimental conditions are the same as in Figure 1.

Table 1. The pH Dependence of the Half-wave Potential and Limiting Current of the Catalytic Reaction. The Solution Contained 5 μM $C_{16}MVCl_2$, 50 mM KH_2PO_4, 40 mM CH_3COOH and 0.1M NaCl

pH	$E_{1/2}$/mV (i_l/μA)	
	780 rpm	1560 rpm
4.5	-392(161)	-404(223)
5.3	-388(161)	-392(225)
6.3	-384(159)	-398(221)
7.1	-384(158)	-394(219)

1800 rpm (Metrohm 628). Figure 2 shows the representative rotation rate dependence of the catalytic reaction. The half-wave potentials of the catalytic waves are much more positive of the peak potentials of Figure 1 (E_p = -0.43V), indicating that the catalytic rate with which the substrate consumes the active form of the catalyst is very large[6]. The reaction rate constant of the catalytic reaction could be determined by the Koutecky-Levich analysis of the rotation rate dependence of the limiting current[7]. The rate constant obtained in the measurements was ca. $10^5M^{-1}S^{-1}$ using $[O_2]$ = 1.0 mM[3] and the catalyst concentration 1.6×10^{-10} mol/cm^2 [4]. This is smaller than ca. $10^6M^{-1}S^{-1}$ obtained by Anson with poly(xylylviologen)[3]. The difference might be attributed to the different reaction conditions and thermodynamic potentials between the polymeric and adsorbed monomolecular layer states. Table 1 shows the pH dependence of the half-wave potentials of the catalytic reaction. Although cation radical viologens(+ 1) are well known to react with dioxygen to produce hydrogen peroxide in aqueous media[8], the electrode reaction shows little pH dependence within the pH region studied

In conclusion, we have shown that the monomolecular films of N-hexadecyl-N'-methyl viologen (+ 1) at glassy carbon catalyze the electroreduction of dioxygen at the rate constant of ca.$10^5M^{-1}S^{-1}$. The catalytic system showed little pH dependence. This point and other mechanistic details will be examined in future studies.

Acknowledgements. This work was supported by the Ministry of Education and in part by the Korea Science and Engineering Foundation. Helpful discussions with Prof. F.C. Anson are greatfully acknowledged.

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Syntheses of Zn(II) Porphyrins with a Long Hydrocarbon Chain: 5-Alkyl-10,15,20-Triphenylporphyrin Zn(II)

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Received January 8, 1990

We have been interested in designing solar energy storage systems, particularly vesicle and microemulsion systems including photosensitizers, electron donors and electron acceptors[1-6]. Photosensitizers, Zn(II) porphyrins with a long hydrocarbon chain (4, and 6, see Figure 1 and 2) were synthesized in our laboratory. The syntheses of these compounds are meaningful because these photosensitizers with nonpolar hydrocarbon chain could be inserted in the vesicle or in the microemulsion interfaces. The porphyrins were prepared in two ways. The first method is that the porphyrin ring was constructed and then a long hydrocarbon chain was attached. The second method is that a long hydrocarbon chain was inserted in the porphyrin ring-formation step.

5-(*p*-methoxy)phenyl-10,15,20-triphenylporphyrin(**1**) was prepared by heating the mixture of pyrrole (1.75 m*l*, 25 mmole), *p*-methoxybenzaldehyde (0.7 m*l*, 6.3 mmole) and benzaldehyde (3 m*l*, 29 mmole) in propionic acid (250 m*l*) at reflux for 2 hrs, and separating the reaction mixture by column chromatography (eluent, chloroform). The red porphy-

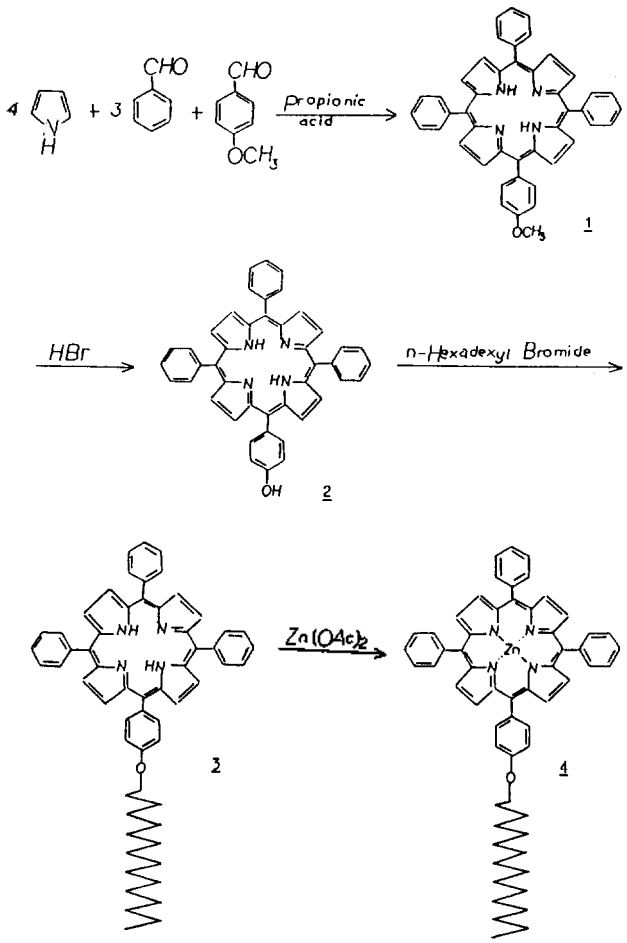

Figure 1. Synthetic scheme of 5-(4-hexadecyloxyphenyl)-10,15,20-triphenylporphyrin zinc complex.

rin band was collected (1.2 g) and then solidified by evaporation of the solvent. The porphyrin mixture was developed on TLC (Merck, silicagel 60 GF, CH_2Cl_2/cyclohexane = 1) to give four main bands (R_f = 0.8, 0.65, 0.50 and 0.40). The compound of R_f = 0.8 was tetraphenylporphyrin because of the same mp and R_f value with those of authentic sample.

The compound of R_f = 0.65 was 5-(*p*-methoxy)phenyl-10,15,20-triphenylporphyrin(1, 300 mg, mp>300 °C). The compound could be identified with visible absorption on 422, 515, 550, 592, and 652 nm, nmr spectra (δ values, $CDCl_3$) of 4.05 (s, 3H, OCH_3), 7.6-8.3 (m, 19H, phenyl) and 8.95 (m, 8H, pyrrole β-proton), and mass spectra, molecular ion peaks at *m/e* 644 (70%) and $(M + H)^+$ at *m/e* 645. The compounds of R_f of 0.50 and 0.40 were not identified. Probably they are di-(*p*-methoxyphenyl)-diphenylporphyrin isomers, because of the slow development of the components on TLC plate. The methoxyphenyltriphenylporphyrin(1, 200 mg, 0.3 mmole) was heated at reflux with hydrogen bromide (1.5 m*l*, 48%) in acetic acid (1.5 m*l*) for 6 hrs. The reaction mixture was developed on TLC (Merck silicagel 600GF) with chloroform/acetone(9/1) to give 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin(2, yield 100 mg, mp>300 °C. The reaction was followedby disappearance of methoxy group on the nmr spectra. The visible absorption band 2 appeared on 422, 510, 550, 592 and 650 nm. NMR spectra of this compound 2($CDCl_3$) appeared on δ, 1.4 (s, 1H, OH), 7.7-8.3 (m, 19H, phenyl) and 8.8(m, 8H, β-pyrr, H). Molecular ion peaks at *m/e* 630(75%) and $(M + 1)^+$(80%) were observed in mass spectra. The Williamson reaction of hydroxy group of the porphyrin 2(100 mg, 0.15 mmole) with *n*-hexadecylbromide (0.2 m*l*) in alkaline alcoholic solution (2 m*l*) under a nitrogen atmosphere gave 5-(4-hexadecyloxyphenyl)-10,15,20-triphenylporphyrin(3, 50 mg). The compound was purified on TLC (R_f = 0.5, mp 67-68 °C). The visible absorption spectra of 3 consists of peaks at 422, 515, 550, 592 and 649 nm. NMR spectra of 3 consists of peaks at δ, 0.9 (t, 3H, CH_3), 1.1 (m, 28H, CH_2), 4.2 (t, 2H, OCH_2), 7.5-8.3 (m, 19H, phenyl), 8.8 (m, 8H, β-pyrrole H). Mass spectra of 3 consists of peaks at M^+/e 855 (mol. ion, 10%), 692 (100% M-163), 663 (20%), 616 (20%), 565 (25%), 523 (70%) and 481 (50%). The metallation of the porphyrin has been done by reaction of the porphyrin derivative (50 mg) with zinc acetate (200 mg) acetic acid for 2 hrs. (yield 40 mg, mp 70-75 °C). UV spectra shows that λ_{max} (benzene) are 415, 550, 592 nm. Disappearance of absorption peaks at 649, and 515 nm of the ligand indicates that the ligand was coordinated. (Anal. Calcd. for $C_{60}H_{60}ON_4Zn$: c, 78.46; H, 6.58; N, 6.10. Found: C, 78.20; H, 6.41; N, 6.02%).

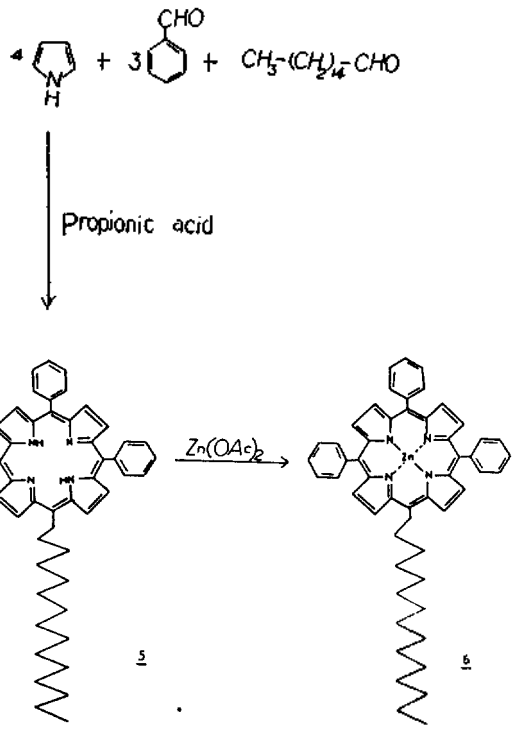

Figure 2. Synthetic scheme of 5-pentadecyl-10,15,20-triphenyl zinc complex.

5-pentadecyl-10,15,20-triphenylporphyrin(5) was synthesized by heating hexadecanal (3.66 g, 15.2 mmole), pyrrole (4.23 m*l*, 60 mmole) and benzaldehyde (4.64 m*l*, 46 mmole) in propionic acid (300 m*l*) at reflux for 2 hrs. The reaction mixture was eluted on neutral alumina column (70-230 mesh) with methylene chloride. The red porphyrin bands were collected and dried by evaporation (0.91 g). The mixture was developed on TLC plate (silicagel 60GF) with mixture solvent (CH_2Cl_2: cyclohexane = 1:1.3) to give four bands (R_f = 0.89, 0.84, 0.77, 0.69). The compound of R_f = 0.77 was 5-pentadecyl-10,15,20-triphenylporphyrin (343 mg, mp

62–65 °C). The peaks of visible absorption spectra of **5** appeared at 420, 515, 550, 593, and 650 nm. The nmr spectra of **5** showed peaks at (δ, $CDCl_3$) 0.88 (t, 3H, CH_3), 1.25 (s, 28H, CH_2), 7.6–8.4 (15H, phenyl hydrogen), 8.7–8.9 (6H, pyrrole β-proton), 9.3–9.5 (2H, pyrrole β-proton). (Anal. Calcd. for **5**($C_{53}H_{56}N_4$): C, 84.90; H, 7.53; N, 7.49, Found: C, 84.73; H, 7.56; N, 7.28%). The band of R_f = 0.69 was tetraphenylporphyrin (307 mg). The porphyrin derivative (**5**, 100 mg) was metallized by heating it with zinc acetate (400 mg) to boiling for 2 hrs. The complex was purified on TLC (silicagel 60GF, methylene:cyclohexane = 1:3). The yield of zinc porphyrin derivative (**6**) was 99 mg (mp 72–75 °C). This method is quite straightforward. The visible spectra of **6** showed that λ_{max} are 423, 551, 589 nm. The absorption band of porphyrin derivative (**5**) on 650 nm disappeared in the absorption spectra of zinc porphyrin derivative (**6**). The absorption of **6** on 551 and 589 nm is characteristic for zinc porphyrin compound[7]. (Anal. Calcd. for $C_{53}H_{54}N_4Zn$: C, 78.36; H, 6.69; N, 6.89. Found: C, 78.63; H, 6.68; N, 6.87%). Hexadecanal was prepared by oxidation of hexadecanol with CrO_3-pyridine complex.

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The Effect of Medium on the α-Effect (Part 2)

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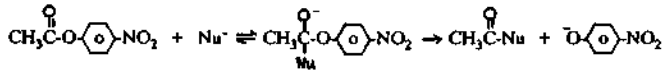
Received January 8, 1990

The term α-effect has been given to the enhanced nucleophilicity which is often observed in reactions of nucleophiles containing an atom with nonbonding electrons adjacent to the reaction center.[1] Numerous studies have been performed to explain the cause of the α-effect,[2] and the following have been most frequently suggested as the origin of the α-effect: destabilization of the ground-state,[3] stabilization of the transition-state,[4] intramolecular general acid-base catalysis,[5] polarizability,[1] and solvent effect.[6,7] However the origins for the α-effect are not completely understood yet. Particularly, the role of solvent on the α-effect has been the subject of controversy.[6,7]

Recently a systematic study has revealed that the α-effect is significantly dependent on solvent for the reactions of *p*-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate (1) as the α-nucleophile, in comparison with *p*-chlorophenoxide (2) as the corresponding normal-nucleophile in DMSO-H_2O mixed solvents.[8] A similar conclusion has also been drawn from the same reactions run in CH_3CN-H_2O mixtures of varying compositions.[9]

In order to investigate the role of solvent on the α-effect by an independent method, a series of reactions of PNPA with aryloxides and the oxymate (1) has been carried out in aqueous solutions of hexadecyltrimethyl ammonium bromide (CTAB).



Nu⁻ : $CH_3C(O)C(Me)=NO^-$ (1)

Such a bimolecular reaction causes usually significant rate enhancement, which is generally believed due to the result of bringing the two reactants together in a small volume of the surfactant aggregate.[10] Furthermore it has been very well known that the enhanced reactivity observed in reactions performed in aqueous CTAB solutions shows a good correlation with hydrophobicity of reactant.[11] Thus the present study would give us relative strength of solvation energy of the anionic nucleophiles in H_2O by investigating relative interaction between the reactants and surfactant aggregate.

The kinetic results for the reaction of PNPA with anionic nucleophiles in various concentrations of CTAB solutions are summarized in Table 1 and plotted in Figure 1. It is illustrated in Figure 1 that the reactivity increases sharply as the surfactant concentration increases up to a certain point as expected for the reactions of anionic nucleophiles in cationic surfactant solutions.[10] However the effect of CTAB on reactivity of *p*-$CNPhO^-$ is very small. The observed rate constants for *p*-$CNPhO^-$ in carbonate buffer solutions containing CTAB are almost identical to the one for carbonate buffer solution alone. This indicates that the contribution of *p*-$CNPhO^-$ to the observed rate constant is negligible, and such a low reactivity of *p*-$CNPhO^-$ could be attributed to the low basicity.

The rate enhancements for the other phenoxides are in the order of *p*-$EtPhO^-$ > *p*-$MePhO^-$ > *p*-$ClPhO^-$ > PhO^- in most region. Although the basicities of the three phenoxides except *p*-$ClPhO^-$ are very similar each other, their reactivities are very different in the presence of CTAB. Moreover, *p*-$ClPhO^-$ is generally more reactive in CTAB solutions than PhO^- although the former is less basic than the latter. This clearly indicates that basicity alone can not be a measure of nucleophilicity for the present system. Thus the Bronsted type of equation can not be used to correlate basicity with nucleophilicity for bimolecular reactions in presence of CTAB.

It has been reported that the interaction of phenoxides with surfactant aggregate decreases in the order of *p*-$EtPhO^-$ > *p*-$MePhO^-$ > PhO^-.[12] It is quite consistent with the present kinetic data, i.e. the phenoxide which interacts more strongly with CTAB shows more significant rate enhancement in CTAB solution or vice versa. Thus the higher rate enhance-