pound (3). However, the deuterium NMR (Figure 1b and d) clearly show the individual deuterium peaks as assigned in the Figure and solved the problems of the proton NMR. The fact that the individual deuterium NMR peaks are from the mono–deuterated compounds on the olefin bonds (2a, 2b, 3) was easily determined by the EIMS (*m/z* 60.0577, 3.2 mmu error). Table 1 shows the yields of each compound from diethyl ether and THF solvents.

It may thus be concluded that in contrast to the previous results,[3,5] 1) the Lewis basicity of solvent is not totally responsible for the *cis* and *trans* reduction route, 2) without adding Lewis acid, a significant amount of hydride transfer to the γ carbon of the triple bond proceeds.
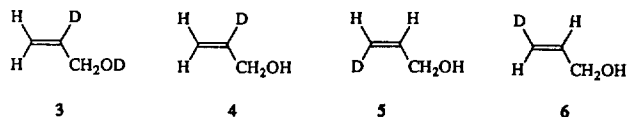
The other interesting results have been observed which is also an additional evidence for a non–specific hydride transfer. When the reduction of alcohol 2 was done by the LiAlD$_4$, the expected deuterium compound 4 and 6% of 5 were obtained after hydrolysis with H$_2$O. The compound 6 was not observed even in diethyl ether.

On the basis of these results, further studies are currently being pursued to unravel the reduction mechanism.

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Catalysis of the Reduction of Dioxygen by N–Hexadecyl–N′–Methyl Viologen(+1) Monomolecular Films at Glassy Carbon Electrodes

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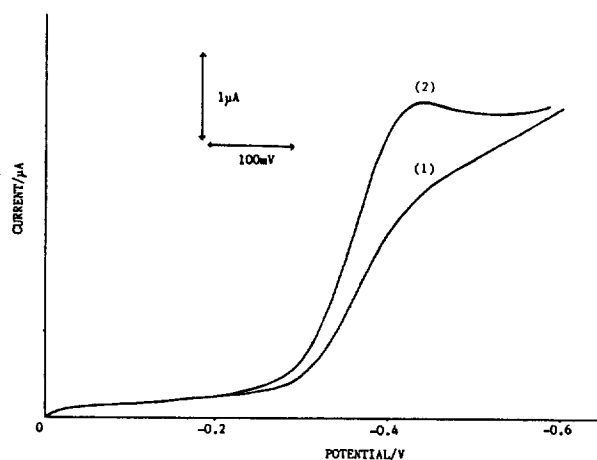**Figure 1.** Voltammetric response at glassy carbon electrode in a 5 μM C$_{16}$MV^{2+} aqueous solution of 0.1M NaCl + 40 mM KH$_2$PO$_4$ + 40 mM CH$_3$COOH (pH 5.3) under nitrogen atmosphere. Electrode area = 0.071 cm^2. Scan rate = 4 mV/s. Potentials are given with respect to saturated calomel reference electrode. Exposure time, (1); 1 min, (2); 10 mins.

Viologens have been extensively used as electron mediators in biological and photoelectrochemical systems[1] and active functional group in electrochromic displays[2]. Recently Anson showed that poly(xylylviologen) catalyzed the electroreduction of dioxygen to hydrogen peroxide[3]. In that study, polymeric viologens were used as a catalytic form because polymeric catalyst coatings on electrode surfaces can provide very high concentrations of redox catalyst sites at positions where they can be easily cycled between oxidation states electrochemically. However, the advantages inherent with polymeric coatings were not apparent in ref. 3 because the rate of the cross reaction between dioxygen and the viologen radical cations proceeded more slowly within the polyelectrolyte film than in homogeneous solution and thus only the outermost monolayer participated in the catalysis. On the other hand, Bard has shown that N–hexadecyl–N′–methyl viologen(+2), C$_{16}$MV^{2+}, forms a monomolecular film on glassy carbon surfaces in the concentration range of 1–20 μM in aqueous solutions of 50 mM NaCl[4]. Therefore, we thought that the monomolecular film formed at glassy carbon could be used as a more effective catalyst for the electroreduction of dioxygen, thereby designing a better electrocatalytic system for activating dioxygen reduction.

Figure 1 shows a voltammetric response at glassy carbon electrode immersed in 5 μM C$_{16}$MV^{2+} aqueous solution of 0.1M NaCl under nitrogen atmosphere. As was shown previously[4], C$_{16}$MV^{2+} strongly adsorbs at glassy carbon surfaces due to the hydrophobicity originating from the long alkyl chain introduced intentionally. When the same experiment was performed under oxygen atmosphere, the current response increased sharply because the reduced form of the viologen, C$_{16}$MV^{1+}, at electrode surfaces catalyzed the electroreduction of dioxygen. Little change from background current was observed with identical experimental conditions of methyl viologen(+2) instead of C$_{16}$MV^{2+}. To investigate the kinetics of the electrode reaction, rotating disk voltammetric techniques were employed[5]. Rotation rates were varied between 700 and 900 rpm, and between 1400 and
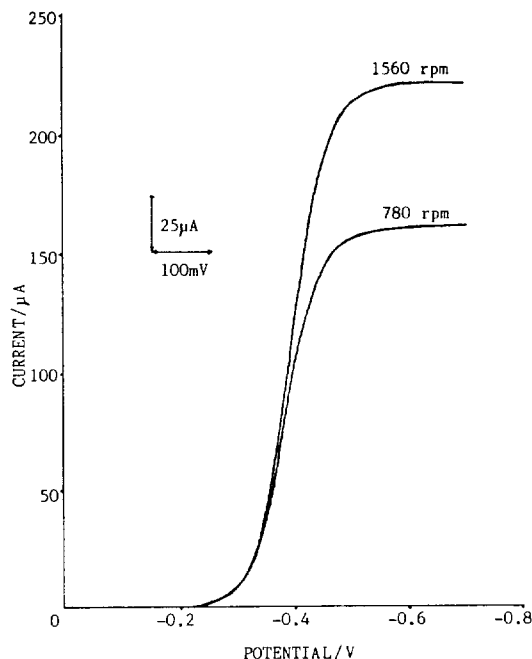
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Figure 2. Rotating disk voltammetric response under oxygen. The experimental conditions are the same as in Figure 1.

Table 1. The pH Dependence of the Half-wave Potential and Limiting Current of the Catalytic Reaction. The Solution Contained $5\,\mu$M $C_{16}MVCl_2$, 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 ($E_p = -0.43$V), 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.

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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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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-