Table II. Comparison of Structural Properties of (enH$_2$)MnCl$_4$ and (enH$_2$)CuCl$_4$[13] [a]

	unit cell parameters				M–Cl dist, Å		M–M dist, Å
	a, Å	*b*, Å	*c*, Å	γ, deg	in-layer	out-of-layer	
(enH$_2$)MnCl$_4$	8.61	7.13	7.19	92.7	2.56, 2.58	2.49	5.06
(enH$_2$)CuCl$_4$	8.11	7.16	7.36	92.4	2.29, 2.88	2.29	5.13

[a] The *a* axis corresponds to the tetragonal *c* axis in the undistorted K$_2$NiF$_4$ structure.

out-of-layer. A small in-layer anisotropy may be possible. Plausible Cu–Cl distances are ~2.2–2.3 Å (out-of-layer) and ~2.5–2.6 Å (in-layer). (2) (Figure 9) The copper coordination is an elongated octahedron with the principal axis in-layer and an additional substantial rhombic distortion in the equatorial plane (approximate D_{2h} symmetry). Plausible Cu–Cl distances are ~2.2–2.3 Å (out-of-layer) and ~2.4 and ~2.7–2.8 Å (in-layer).

A definite answer to the question of copper coordination can only come from a diffraction experiment. The very limited range of copper concentrations makes a determination by X-ray diffraction very difficult. The chances are greater if there is a large difference between host and guest geometry. In principle, EXAFS[19] is an ideal method for this purpose, because the structural environment of the guest can be probed without too much perturbation by the host. We are presently engaged in a study of copper coordinations in A$_2$MnCl$_4$ host crystals by EXAFS. In addition high-frequency EPR experiments are planned to separate the overlapping copper(II) and manganese(II) signals.

Acknowledgment. This work was supported by the Swiss National Science Foundation (Grant No. 2.427-0.79). We thank Professor K. Emerson (Montana State University) for first drawing this phenomenon to our attention.

Registry No. (enH$_2$)MnCl$_4$, 68370-07-0; (enH$_2$)CuCl$_4$, 9088-46-4; CsMnCl$_3$·2H$_2$O, 30444-42-9; Cs$_2$MnCl$_4$·2H$_2$O, 31173-79-2; [(CH$_3$)$_3$NH]MnCl$_3$·2H$_2$O, 56115-72-1; [(CH$_3$)$_4$N]MnCl$_3$, 30442-52-5; Cu, 7440-50-8.

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Electrochemistry of (TPP)Mo(O)(OCH$_3$) and (TPP)Mo(O) in Dichloromethane

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The electrochemical reduction of the (5,10,15,20-tetraphenylporphinato)oxomolybdenum(V)–methoxy complex, (TPP)Mo(O)(OCH$_3$), was investigated in TBAP–dichloromethane solution by dc polarography, cyclic voltammetry, coulometry, and controlled-potential electrolysis. Five redox couples were found in the potential range +0.3 to −1.8 V. Two of these couples at −1.15 and −1.53 V corresponded to formation of the five-coordinate anion radical [(TPP)Mo(O)]$^-$ and dianion [(TPP)Mo(O)]$^{2-}$. The other three couples involved six-coordinated complexes of Mo(V) and Mo(IV) containing either ClO$_4^-$ or OCH$_3^-$ as the sixth axial ligand. An overall reduction mechanism involving both covalent and ionic forms of (TPP)Mo(O)(OCH$_3$) and [(TPP)Mo(O)(OCH$_3$)]$^-$ is proposed.

Introduction

In the last several years, the synthesis, structural characterization, and chemical reactivity of molybdenum metalloporphyrins have received considerable attention in the literature. Among several different types of porphyrin complexes, these studies have included porphyrins containing Mo$^{\rm IV}$, Mo$^{\rm V}$, or Mo$^{\rm VI}$ as central metals.[2-12] Our interest in this paper is to report initial results concerning the electrochemistry of Mo$^{\rm IV}$ and Mo$^{\rm V}$ complexes of TPP^{2-}. Until recently there has been no systematic study of molybdenum porphyrin electrochemistry. This is unusual since thermodynamic potentials and electrochemical reactivity should have a direct correlation with the chemical and photochemical reactivity of these complexes.

The first electrochemistry of a molybdenum porphyrin was published in 1973 by Fuhrhop, Kadish, and Davis.[2] In this study potentials for 25 representative complexes were reported, which included those for (OEP)Mo(O)(OH) in Me$_2$SO and butyronitrile. A later ESR and electron-transfer kinetic study by Newton and Davis[10] in 1975 gave results for the reduction and oxidation of (TPP)Mo(O)(OH) in four nonaqueous solvents but did not discuss what were considered complex data.

In this study we have limited our discussion to the reactions of (TPP)Mo(O) and (TPP)Mo(O)(OCH$_3$) in CH$_2$Cl containing varying concentrations of supporting electrolyte. Our interest was to determine the effect of the sixth axial ligand OCH$_3^-$ and the possible counterion ClO$_4^-$ on the reversible potentials and to define any existing equilibria which existed in solution. This data would then serve as a needed reference for interpreting the electrochemistry of solutions containing Mo$^{\rm IV}$ and Mo$^{\rm V}$ porphyrins which have been reacted with dioxygen. The electrochemistry of these solutions is complex and is now the object of intense investigation in our laboratories.

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Table I. Stepwise Coulometric Measurements for the Controlled-Potential Reduction of 0.5 mM (TPP)Mo(O) and (TPP)(O)(OCH$_3$) in TBAP-Dichloromethane Solution[a]

compd	metal oxidn state	[TBAP], M	no. of electrons at plateau				
			wave II	wave III	wave IV	wave V	total
(TPP)Mo(O)	Mo^{IV}	0.10		0.99 ± 0.02		0.98 ± 0.02	2.0
(TPP)Mo(O)(OCH$_3$)	Mo^{V}	0.10	1.02 ± 0.02	0.99 ± 0.02	*b*	0.99 ± 0.02	3.0
(TPP)Mo(O)(OCH$_3$)	Mo^{V}	0.10	1.02 ± 0.02	*c*	1.00 ± 0.02	1.00 ± 0.02	3.0

[a] All values represent the average of three measurements with the deviations given as standard deviations of the mean. [b] Wave IV disappeared after complete electrolysis at plateau of wave III. [c] Wave III disappeared after complete electrolysis at plateau of wave IV.

During the course of our studies a recent paper appeared[11] which investigated, in part, similar complexes as we report here. The results, however, are somewhat at variance with what we have observed in our study and will be discussed in the context of our results.

Experimental Section

Methods. Polarography at the classical dropping-mercury electrode (DME) was performed with the aid of an EG and G Princeton Applied Research (PAR) Model 174A polarographic analyzer and Omnigraphic 200 X-Y recorder. Cyclic voltammetric measurements were made with PAR Model 173 potentiostat/galvanostat and Model 178 electrometer probe driven by a PAR 175 universal programmer. An Omnigraphic 200 X-Y recorder was used to record the current-voltage output for sweep rates of 0.02-0.20 V s^{-1}. Current-voltage curves taken at sweep rates between 0.5 and 50.0 V s^{-1} were collected on a Tektronix Model 5111 storage oscilloscope with camera attachment. Coulometric measurements were performed with the Model 179 digital coulometer. A three-electrode system was used in all electrochemical measurements, consisting of the appropriate working electrode (dropping-mercury electrode in dc polarography, Pt-button electrode in cyclic voltammetry, and Pt-mesh in coulometric measurements), a counterelectrode (Pt wire), and reference electrode (saturated calomel electrode SCE). The SCE was separated from the test solution by a fritted supporting electrolyte/solvent bridge.

Materials. The supporting electrolyte TBAP was obtained from Fisher SG, recrystallized from absolute ethyl alcohol and then dried in vacuo at 80 °C. CH$_2$Cl$_2$ was obtained from Fisher SG as technical grade and was distilled from P$_2$O$_5$ and stored in the dark over 4 Å molecular sieves. (5,10,15,20-tetraphenylporphinato)oxomolybdenum(IV), (TPP)Mo(O), and methoxo(5,10,15,20-tetraphenylporphinato)oxomolybdenum(V), (TPP)Mo(O)(OCH$_3$), were obtained by methods identical with those reported previously.[3,12]

Results and Discussion

A typical dc polarogram for the reduction of (TPP)Mo(O) is shown in Figure 1a. Two well-defined reductions are obtained at $E_{1/2} = -1.14$ and -1.50 V. In addition, a small oxidation wave is observable at -0.10 V. These waves are labeled peaks I, III, and V, respectively.

The two more negative reduction waves have identical diffusion limiting currents and are analyzed as giving reversible one-electron transfers. This is confirmed by coulometry (Table I) and by the theoretically reversible $E_{3/4} - E_{1/4}$ values of -58 to -60 mV. In CH$_2$Cl$_2$, as well as other nonaqueous solvents, these reactions have been characterized as due to reduction of the π-ring system to yield a π anion radical and dianion, as shown by reactions 1 and 2.[10] The oxidation process

$$(\mathrm{TPP})\mathrm{Mo}^{\mathrm{IV}}(\mathrm{O}) + e^- \rightleftarrows [(\mathrm{TPP})\mathrm{Mo}^{\mathrm{IV}}(\mathrm{O})]^- \quad (1)$$

$$[(\mathrm{TPP})\mathrm{Mo}^{\mathrm{IV}}(\mathrm{O})]^- + e^- \rightleftarrows [(\mathrm{TPP})\mathrm{Mo}^{\mathrm{IV}}(\mathrm{O})]^{2-} \quad (2)$$

observed in Figure 1a at -0.10 V is just at the anodic limit of the DME in this solvent system but can be assigned as a metal-centered oxidation to yield [(TPP)Mo^{V}(O)]$^+$.[10] In the presence of ClO$_4^-$ as supporting electrolyte, which is in 100-fold excess of the metalloporphyrin, this electrode reaction may be written as eq 3.

$$(\mathrm{TPP})\mathrm{Mo}^{\mathrm{IV}}(\mathrm{O}) \rightleftarrows [(\mathrm{TPP})\mathrm{Mo}^{\mathrm{V}}(\mathrm{O})]^+\mathrm{ClO}_4^- + e^- \quad (3)$$

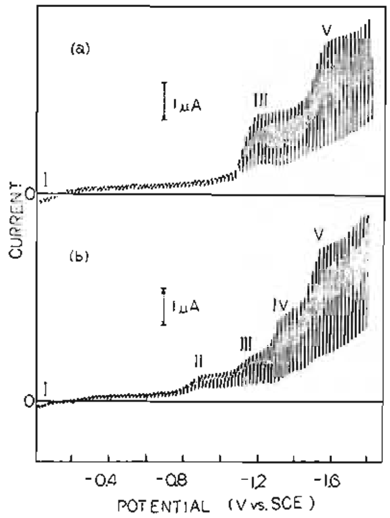

Figure 1. Dc polarograms of (a) 5 × 10^{-4} M (TPP)Mo(O) and (b) 5 × 10^{-4} M (TPP)Mo(O)(OCH$_3$). Both solutions are 0.05 M TBAP in CH$_2$Cl$_2$.

With reactions 1-3 as a basis for comparison, the polarograms of (TPP)Mo(O)(OCH$_3$) were also run. If reduction of Mo^{V} to Mo^{IV} resulted in a concomitant loss of OCH$_3^-$ one would expect to observe three reduction waves with the latter two being at identical potentials as those for the reference compound, (TPP)Mo(O).

A typical polarogram for reduction of (TPP)Mo(O)(OCH$_3$) in CH$_2$Cl$_2$, 0.05 M TBAP is shown in Figure 1b. As seen from this figure, not three but four reduction waves are observed. In addition, a small oxidation wave which is very difficult to define is also observed. These five waves are labeled I to V.

Wave II located at $E_{1/2} = -0.85$ V is slightly irreversible ($E_{3/4} - E_{1/4} = -65$ mV) but gives a diffusion limited current as evidenced by characteristic plots of log i vs. log h which had slopes of 0.47 (the theoretical value is 0.50).[13] This wave is not observed when (TPP)Mo^{IV}(O) is the reactant (see Figure 1a) and may be tentatively assigned as Mo^{V} $\rightleftarrows$ Mo^{IV}. A second reduction wave is observed at $E_{1/2} = -1.14$ V (wave III) and $E_{1/2} = -1.30$ V (wave IV). Wave III is at an identical potential as that observed for reduction of (TPP)Mo(O) (Figure 1a) and is thus tentatively assigned as a reduction of electrochemically produced (TPP)Mo(O) to yield the anion radical [(TPP)Mo(O)]$^-$. The diffusion currents for waves III and IV are approximately equal when the starting porphyrin concentration was equal to 5 × 10^{-4} M (as is illustrated in Figure 1b). However, this ratio was found to be dependent on the concentration of both the metalloporphyrin and the supporting electrolyte and suggests a concentration dependent equilibria between two different Mo^{IV} species.

Both waves III and IV yield limiting currents which are proportional to concentration between 1.5 and 9.5 × 10^{-4} M (TPP)Mo(O)(OCH$_3$) (see Figure 2a). However, wave III is present only at concentrations of (TPP)Mo(O)(OCH$_3$) below 9.5 × 10^{-4} M and disappears at higher concentrations.

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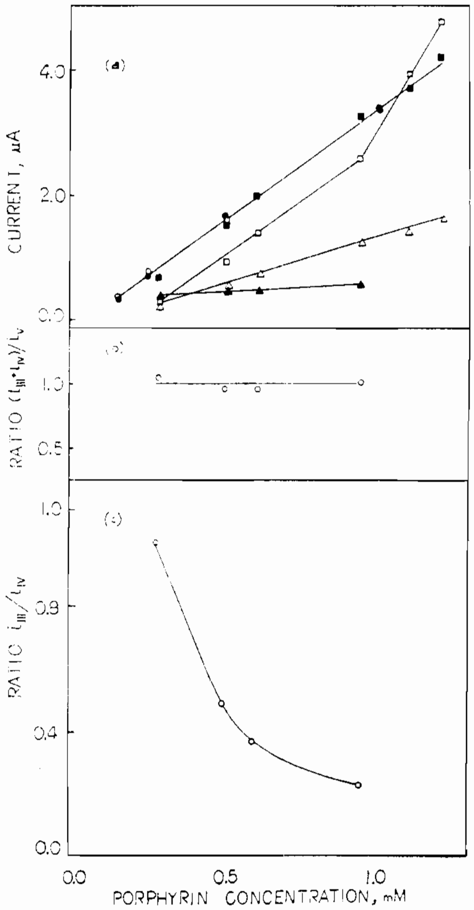


Figure 2. Porphyrin concentration dependence of (a) polarographic limiting currents for waves II–V of (TPP)Mo(O) and (TPP)Mo(O)(OCH_3) (currents were measured as the limiting currents at the plateau for waves III (○) and waves V (●) of (TPP)Mo(O) and waves II (△), III (▲), IV (□), and V (■) of (TPP)Mo(O)(OCH_3)), (b) ratio of $(i^{III} + i^{IV})/i^{V}$ for (TPP)Mo(O)(OCH_3), and (c) ratio of i^{III}/i^{IV} for (TPP)Mo(O)(OCH_3).

In addition, at concentrations about 9.5×10^{-4} M an inflection is observed in the plot of i_l vs. concentration for wave IV (Figure 2a) and the current increases faster than that observed for a simple increase in concentration. This result also indicates there exists an equilibrium between the species being reduced in waves III and IV and that the increased concentration has shifted the equilibrium toward wave IV.

Analysis of plots of log i_l vs. log h were made for waves III and IV in order to test for diffusion control. This was done at a constant drop time of t = 2 s so that the theoretical slopes would be 0.50 for diffusion control and 0.67 for kinetic control of the wave.[13] In this case, possible kinetic control of the reaction might be a rate-controlled partial dissociation of the complex preceding the electron-transfer step.

Wave III yielded diffusion-controlled plots with slopes of 0.50 ± 0.02. On the other hand, a slope of 0.69 ± 0.02 was obtained for wave IV, in excellent agreement with the theoretical value of 0.67.[13] This suggests a rate-controlling dissociation of the counterion before electron transfer to yield $[(TPP)Mo(O)]^-$. If this were the case, both the products of waves III and IV should be identical and the sum of the currents should be identical. This is exactly what was observed in our study.

The ratio of currents for peaks III–IV decreased with increasing concentration of (TPP)Mo(O)(OCH_3) (Figure 2c), but in all cases the sum of the currents were equal. In addition, the total current i^{III} and i^{IV} was approximately equal to that observed for wave V so that the ratio $(i^{III} + i^{IV})/i^{V}$ was constant. This is seen in Figure 2b. Wave V was observed at $E_{1/2}$ = −1.50 V and was independent of either the concentration of supporting electrolyte or the starting species. It is also at the same potential for formation of the dianion from the anion radical according to reaction 2.

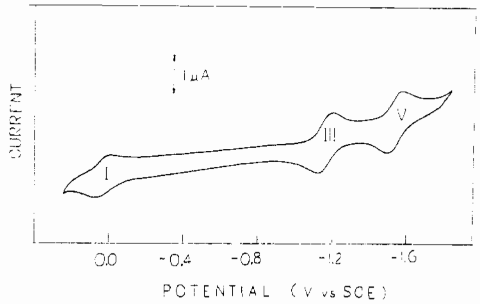


Figure 3. Cyclic voltammogram for 5×10^{-4} M (TPP)Mo(O) in 0.05 M TBAP (CH_2Cl_2, scan rate 0.1 V/s, continuous scan, cathodic peak I not observed on first scan).

On the basis of polarographic results it appears that waves III and V are due to a five-coordinate complex in which OCH_3^- is not axially bound while IV is due to a form of Mo^{IV} containing a bound OCH_3^- group. The more negative wave IV might be assigned as due to reduction of the negatively charged $[(TPP)Mo(O)(OCH_3)]^-$.

Controlled-potential electrolysis was performed on the plateau of waves II–V in order to verify the equilibrium between peaks III and IV. These results are shown in Table I. When the starting complex was (TPP)Mo(O), values of n = 0.99 ± 0.02 and 0.98 ± 0.02 were measured under conditions of controlled-potential reduction at −1.15 and −1.55 V, respectively. On the other hand, when (TPP)Mo(O)(OCH_3) was the starting material, three single-electron-transfer steps could be observed. The first reduction gave an n = 1.02 ± 0.02 and was always observed when controlled-potential reduction was performed on the plateau of wave II (E = −0.95 V). The addition of a second electron was observed on stepping from the plateau of wave II to either the plateau of wave III (E = 1.15 V) or to the plateau of wave IV (E = −1.30 V), again indicating an equilibrium between the reducible species. Finally, stepping to a reduction at the plateau of wave V (E = −1.55 V) yielded addition of a third electron. These results are summarized in Table I.

On the basis of these polarographic and coulometric results, waves III and V can be assigned as represented by reaction 1 and 2 and wave I as represented by reaction 3. Wave II and wave IV both seem to involve covalently complexed OCH_3^- and can be assigned as reactions 4 and 5 where $[(TPP)Mo^{IV}(O)]^0OCH_3^-$ represents a partially ionic compound.

$$(TPP)Mo^{V}(O)(OCH_3) \xrightleftharpoons{e^-} [(TPP)Mo^{IV}(O)(OCH_3)]^- \quad \text{wave II} \qquad (4)$$

$$\begin{tikzcd}
{[(TPP)Mo^{IV}(O)(OCH_3)]^-} \arrow[r, shift left] & {[(TPP)Mo^{IV}(O)]^0OCH_3^-} \arrow[l, shift left] \arrow[d, shift left, "e^-"'] & \text{wave IV} \quad (5) \\
& {[(TPP)Mo^{IV}(O)]^- + OCH_3^-} \arrow[u, shift left] &
\end{tikzcd}$$

In order to confirm the assignments of reactions 1–5, reduction and reoxidation of (TPP)Mo(O) and (TPP)Mo(O)(OCH_3) were also investigated as a function of scan rate and concentration by the technique of cyclic voltammetry. A typical cyclic voltammogram of (TPP)Mo(O) in CH_2Cl_2–0.05 M TBAP is shown in Figure 3. In the range of potentials between +0.3 and −1.8 V vs. SCE, three well-defined waves were obtained with continuous scan. The first at +0.02 V corresponded to an oxidation of the starting complex and has been identified as yielding $[(TPP)Mo^{V}(O)]^+$.[11] This wave is slightly shifted from that observed at the DME and the reaction has already been characterized as being represented by reaction 3. The remaining reactions were reductions at −1.15

Table II. Half-Wave Potentials vs. SCE for 0.5 mM Oxomolybdenum(IV) and Oxomolybdenum(V) Complexes in Dichloromethane Containing TBAP as Supporting Electrolyte[a]

compd	metal oxidn state	[TBAP], M	$E_{1/2}$, V: I	II[b]	III	IV[c]	V	ref[e]
(TPP)Mo(O)	Mo^{IV}	0.05	0.02[d]		−1.15		−1.53	tw
$(TPP)Mo(O)(OCH_3)$	Mo^V	0.05	~0.02	−0.74	−1.14		−1.49	11
$(TPP)Mo(O)(OCH_3)$	Mo^V	0.05	0.02	−0.89	−1.15	−1.26	−1.50	tw
$(TPP)Mo(O)(OCH_3)$	Mo^V	0.20	0.02	−0.86	−1.10	−1.26	−1.40	tw
$(TPP)Mo(O)(OCH_3)$	Mo^V	1.00	−0.02	−0.81	−1.06		−1.47	tw

[a] All values are for single-scan measurements. [b] Cathodic peak potential. This peak splits into two peaks by using continuous-scan rates greater than 0.5 V s^{-1}. [c] Based on $E_{p,c} = -1.33$ and $E_{p,a} \simeq -1.19$ V. [d] Oxidation process. [e] tw = this work.

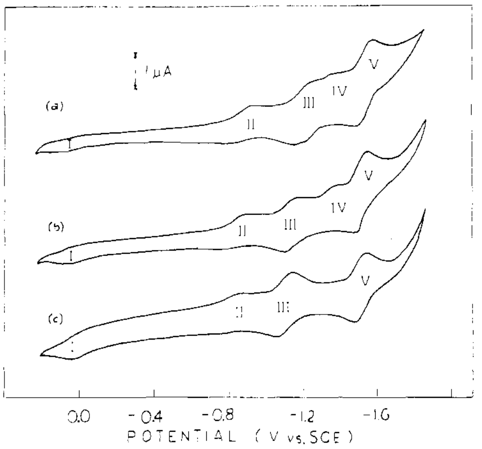


Figure 4. Cyclic voltammograms for 5×10^{-4} M $(TPP)Mo(O)(OCH_3)$ in different concentrations of TBAP: (a) 0.05 M, (b) 0.2 M, and (c) 1.0 M (scan rate 0.1 V/s, continuous scan, cathodic peak *I* not observed on first scan).

V and −1.53 V respectively and have been assigned as formation of the anion radical and dianion (reaction 1 and 2).[10] The potential difference of 0.38 V between the half-wave potentials is slightly below the average value of 0.42 ± 0.03 V observed by Felton and Linschitz[14] for a large series of tetraphenylporphyrin complexes.

Both of the ring reduction potentials agree with those obtained by classical polarography in this study but are cathodically shifted by 190–210 mV from those reported by Newton and Davis using cyclic voltammetry in the same solvent (−0.96 and −1.31 V, respectively).[10] No explanation for this shift is evident. In Me_2SO, (OEP)Mo(O)(OH) undergoes two ring reductions at the π-ring system to yield the anion radical and dianion.[2] The potentials for these reactions are −1.30 and −1.72 V, which compare to −0.98 and −1.34 V for (TPP)Mo(O)(OH) obtained by Newton and Davis[10] in the same solvent. Since potential differences between reduction of TPP^{2-} and OEP^{2-} complexes are usually of the order of 200 mV[15] and these are of the order 320–380 mV, it would appear that the potentials of Newton and Davis are generally shifted in an anodic direction.

Reduction potentials for $(TPP)Mo(O)(OCH_3)$ were measured in CH_2Cl_2 containing various concentrations of supporting electrolyte. When the supporting electrolyte was 0.05 M, five reduction and either four or five oxidation peaks were obtained with all but the last peak being irreversible. Half-wave potentials and peak potentials obtained by cyclic voltammetry for the reduction of $(TPP)Mo(O)(OCH_3)$ in CH_2Cl_2–0.05 M TBAP are presented in Table II, and a cyclic voltammogram obtained under the same experimental conditions is displayed in Figure 4a.

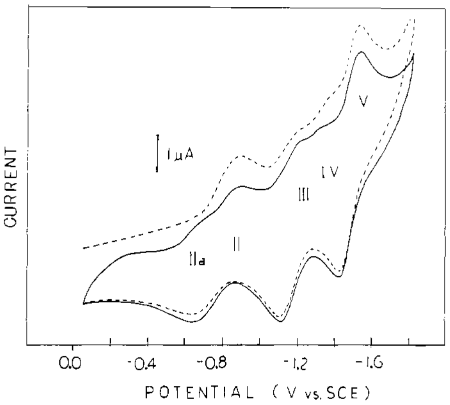
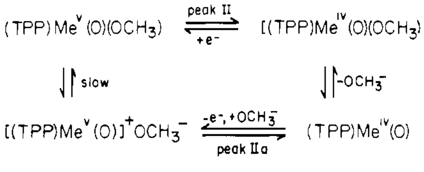


Figure 5. Cyclic voltammogram for 5×10^{-4} M $(TPP)Mo(O)(OCH_3)$ in 0.05 M TBAP–CH_2Cl_2 solution: dashed line, first scan; solid line, second scan (scan rate 0.5 V/s).

Scheme I



A reversible reduction and reoxidation occurs for (TPP)-$Mo(O)(OCH_3)$ at 0.02 and at −1.50 V. Currents for the latter process are substantially larger than those for the former. These are labeled peaks I and V in Figure 4. In addition, three additional cathodic peaks were obtained at $E_{p,c}$ = −0.89 V (peak II), −1.18 V (peak III), and −1.33 V (peak IV). At low scan rates peak II had what appeared to be a broad reoxidation peak at ∼−0.78 V while those for peaks III and IV were better defined and gave overlapping reoxidation peaks at −1.12 and ∼−1.19 V.

Experiments were performed for a series of constant porphyrin concentration in which the supporting electrolyte was increased systematically from 0.05 to 1.0 M in CH_2Cl_2. With increasing concentration of TBAP (from 0.05 to 1.0 M), peak I increased in height, as the potential shifted anodically by about 80 mV. At the same time peak III also increased in height and shifted in the anodic direction while peak IV decreased continuously and practically disappeared at 1.0 M TBAP concentration (see Figure 4b, c). Peak II also decreased somewhat with increasing supporting electrolyte. No significant current changes were found for peak V with increasing concentration of TBAP. These results imply an equilibrium between peaks I and II and also between peaks III and IV which involves ClO_4^- as a counterion.

Similar evidence for an equilibrium between peaks I and II is presented by the cyclic voltammograms as a function of scan rate. When the scan rate was equal to, or higher than, 0.5 V s^{-1}, a splitting of cathodic peak II (labeled peak II and IIa in Figure 5) is observed on the second or continuous-potential scan. The new cathodic peak IIa appeared at a po-

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(15) Fuhrhop, R.-H. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978.

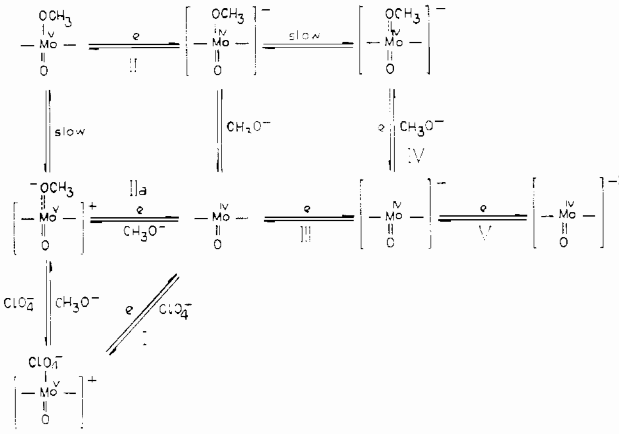

Figure 6. Reduction mechanism of (TPP)Mo(O)(OCH_3) in CH_2Cl_2–TBAP. The roman numerals I–V refer to the reactions given in Figures 1, 4, and 5.

tential of $E_{p,c}$ = –0.68 V. With increasing scan rate peak II decreased and peak IIa increased in current, indicating a further equilibrium between two species in solution.

It is interesting to note that oxidation of Mo^{IV} to Mo^{V} (peak II) gives rise to substantially larger currents at fast scan rates than at slow scan rates. This is evident from an examination of peak II from Figures 4 and 5. At slow scan rates a reformation of the covalent six-coordinate complex can occur after initial reduction, but at fast-scan rates mainly the five-coordinate or the six-coordinate, partially ionic species will exist as the reduction product.

On the basis of the scan-rate dependence of the current–voltage curve, the mechanism shown in Scheme I is postulated for the first reduction and first reoxidation of (TPP)Mo(O)(OCH_3) in CH_2Cl_2.

The initial Mo^V complex containing covalently bound OCH_3^- is reduced to the negatively charged Mo^{IV} form of the same complex which can be further reduced after a partial dissociation of OCH_3^- to yield an ionic species (peak IV, Figures 1 and 4) or can completely dissociate to yield the neutral (TPP)Mo(O). Evidence for this as the ultimate product comes from bulk and thin-layer spectra which show this to be the sole end product of bulk electrolysis.[16] (TPP)Mo(O) can then be reoxidized, in the presence of OCH_3^- (generated from the starting complex) to give an anionic form of Mo^V, $[(TPP)Mo(O)]^+OCH_3^-$. Peak II is only observed after the first scan, indicating that the ionic form of the complex is not present in the bulk of solution but is generated at the electrode surface after reduction of the covalently bound starting species. The fact that some peak IIa is observed on subsequent reduction sweeps indicates that an equilibrium must be present between the electrochemically generated ionic $[(TPP)Me(O)]^+OCH_3^-$ and the covalent complex (TPP)Me(O)(OCH_3). This process, however, is slow since both peaks II and IIa are observed. These results are consistent with those obtained by polarography and coulometry and thus lead to the overall scheme shown in Figure 6 for the three-electron reduction of (TPP)Mo(O)(OCH_3) to yield $[(TPP)Mo(O)]^{2-}$ in CH_2Cl_2.

(TPP)Mo(O)(OCH_3) may be reduced in a one-electron-transfer step directly to the six-coordinate covalent complex $[(TPP)Mo(O)(OCH_3)]^-$ or may form a new partially ionic complex, $[(TPP)Mo(O)]^+OCH_3^-$, which is reduced at $E_{p,c}$ = –0.68 V to yield (TPP)Mo(O) (peak IIa). Alternatively, an exchange of ClO_4^- with OCH_3^- may occur to yield $[(TPP)Mo(O)]^+ClO_4^-$, which is reduced at 0.02 V. This is the same potential observed for reaction 1 when the starting material is (TPP)Mo(O). In addition, the covalent complex $[(TPP)Mo(O)(OCH_3)]^-$ may form a partially ionic species before reduction.

It is interesting to note the apparent presence of the six-coordinate negatively charged $[(TPP)Mo(O)(OCH_3)]^-$. This covalently bound OCH_3^- species may be quasi-reversibly reduced at $E_{1/2} \simeq -1.26$ V to yield a dinegatively charged species which rapidly dissociates to give $[(TPP)Mo(O)]^-$ (this peak also indicates a coupled chemical reaction). Alternatively, $[(TPP)Mo(O)(OCH_3)]^-$ may completely dissociate to yield (TPP)Mo(O) before electron transfer and then be reversibly reduced at –1.15 V (peak III). The difference of 180 mV between the five- and six-coordinate Mo^{IV} reduction potentials (peaks III and IV) are consistent with the added negative charge on the former complex. The fact that both are in equilibrium is strongly suggested by the shift of peaks III and IV with additions of ClO_4^- (which displaces OCH_3^-) and the overall coulometric value of 2.0 faradays/mol of (TPP)Mo(O)(OCH_3) obtained upon controlled reduction between peaks IV and V.

The identification of peaks I and V is simplified by comparing the cyclic voltammetry peak potentials to those for (TPP)Mo(O) under similar experimental conditions (Table II and Figure 3). This complex exhibits two reversible reductions that can be assigned to porphyrin ring reductions and an oxidation which corresponds to the reaction Mo^{IV}/Mo^{V}. Table II shows that the two ring reductions of (TPP)Mo(O) are at identical potentials as those for peaks III and V of (TPP)Mo(O)(OCH_3).

The coulometric data suggests that the species responsible for peaks III and IV are also in equilibrium. Increasing the potential scan rate does not change the peak current ratios for peaks III and IV, indicating that, on the cyclic voltammetry time scale, equilibrium between the two species is attained very quickly. Addition of excess ClO_4^- in the form of TBAP forces the equilibrium away from methoxy coordination for both Mo^V and Mo^{IV}, thus decreasing the currents for peaks II and IV as the supporting electrolyte concentration is decreased. This is shown in Figure 4a–c.

At fast scan rates under the original experimental conditions (0.05 M TBAP), continuous-potential scanning reveals a new cathodic wave (peak IIa) approximately 200 mV positive of peak II and an anodic peak coupled to either or both of the cathodic peaks. The potential of the new peak would suggest that it is associated with OCH_3^- coordination, although the nature of the bond would be different from that in the bulk of solution. If one notes that the potential difference between the OCH_3^- and ClO_4^- axial species is over 700 mV, then one may be able to tentatively assign peak IIa as a mainly ionic methoxy species where charge delocalization has not yet occurred.

Finally, we are faced with relating our work to that of Matsuda et. al.[11] These workers have recently reported cyclic voltmmetry, controlled-potential electrolysis, and spectrophotometric studies of several oxomolybdenum(V) complexes including Mo(O)(TPP)(X), where X = OCH_3^-, OAc^-, and Cl^- in 0.05 M TBAP–CH_2Cl_2. Results obtained for X = OAc^- and Cl^- are not generally comparable with data in our study because of the presence of added 1 M AcOH and 9 × 10^{-3} M TEAC, which the authors maintained was necessary to obtain reversibility. It should be noted, however, that both of these complexes gave reductions at –1.11 and –1.50 V which correspond to our peaks III and V.

Of the compounds studied by Matsuda et al.,[11] a direct comparison is only possible for (TPP)Mo(O)(OCH_3). Their published cyclic voltammogram of 0.5 mM (TPP)Mo(O)(OCH_3) in dichloromethane containing 0.05 M TBAP at a scan rate 100 mV s^{-1} was obtained under exactly the same exper-

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[16] Kadish, K. M.; Malinski, T.; Ledon, H., manuscript in preparation.

imental conditions as our Figure 4a and showed four redox couples in the potential range from +0.3 to −1.8 V vs. SCE. It was reported that every observed peak was due to a fully reversible one-electron transfer. Their first couple at $E_{1/2}$ = 0.02 V is about eight times smaller than that observed for the last three waves ($E_{1/2}$ = −0.74 V, $E_{1/2}$ = −1.14, and $E_{1/2}$ = −1.49 V), which are approximately equal. The couple at −0.74 V has been assigned as due to the reaction $\mathrm{Mo^{V}/Mo^{IV}}$ while that at more negative potentials as due to reduction at the porphyrin ring. The first reduction at ~0.02 V was assigned as due to reaction of $\mathrm{(TPP)Mo(O)(ClO_4)}$ which is formed from a substitution of $\mathrm{OCH_3^-}$ by $\mathrm{ClO_4^-}$, which is present as supporting electrolyte. Substitution of the methoxo group in $\mathrm{(TPP)Mo(O)(OCH_3)}$ by acetate or chloride ion also resulted in this same effect,[11] i.e., an anodic shift (about 0.7 V) from that of the original peak at −0.71 V. However, these results with $\mathrm{OAc^-}$ or $\mathrm{Cl^-}$ are suspect due to the large concentration of common ion added to solution.

When the reported potentials for $\mathrm{(TPP)Mo(O)(OCH_3)}$ reduction are considered, the results of Matsuda et al.[11] are, in part, consistent with our results. However, two fundamental differences are found in the actual cyclic voltammetric data. The first is that we observed, not four, but five redox couples in the potential range +0.3 to −1.8 V vs. SCE (Figure 4a). The second difference is that their couple at −0.76 V appears to be reversible while ours at −0.86 V is partially irreversible. No explanation is available as to the difference between the two studies, and, despite repeated attempts, we were unable to reproduce their data under the same experimental conditions. However, at low concentrations of supporting electrolyte (≤0.03 M), peaks III and IV are overlapped, yielding only a single process.

In summary, it is interesting to note that six-coordinate anionic forms of $\mathrm{Mo^{IV}}$ are formed in solution. Similar negatively charged ligated species have recently been reported in the form of $\mathrm{[(TPP)Fe^{II}]^-}$[17] and $\mathrm{[(TPP)Mn^{II}X]^-}$.[18] Of most interest is the nature of the ligand–metal bond in $\mathrm{(TPP)Mo(O)(OCH_3)}$ and $\mathrm{[(TPP)Mo(O)OCH_3]^-}$. From the existing data it appears that an equilibrium may exist between an ionic and a covalent form of the complex for both $\mathrm{Mo^{V}}$ and $\mathrm{Mo^{IV}}$. Finally, these investigations have provided a necessary baseline for electrochemical studies which can be performed after dioxygen is reacted homogeneously with complexes of either $\mathrm{(TPP)Mo(O)}$ or $\mathrm{(TPP)Mo(O)(OCH_3)}$. This will be the basis of a later publication.

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Electrochemical Characterization of a Novel Rhodium(II) Dimer, $\mathrm{Rh_2(ONHCCF_3)_4}$

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The electrochemical reactivity of a novel rhodium(II) dimer, $\mathrm{Rh_2(ONHCCF_3)_4}$, was investigated in nonaqueous media. In all solvents investigated a one-electron oxidation was observed at potentials between +0.91 and +1.08 V vs. SCE. In seven solvents investigated this oxidation was reversible, but in pyridine or acetonitrile/pyridine mixtures a rapid chemical reaction followed the reversible oxidation. In THF an ill-defined irreversible reduction was also observed at −1.8 V vs. SCE. No other reduction or oxidation peak was observed in any of the solvents between +1.5 and −1.6 V. Measurements of pyridine binding were made by using both spectrophotometric and electrochemical techniques. In acetonitrile only a single pyridine ligand was observed to add to the complex. The stability constant for this ligand addition was 250. Finally, correlations were made between the electrochemical reactivity of the investigated complex and the nature of the solvent as well as comparisons to reactions of the similar rhodium(II) carboxylates, $\mathrm{Rh_2(O_2CCR)_4}$.

Introduction

During recent years the electrochemistry and chemical reactivity of dinuclear rhodium(II) complexes have received considerable attention in the literature.[1–13] Investigations have included studies of both the kinetics and the thermodynamics of axial and equatorial ligand addition as well as studies of redox reactions to yield stable dimeric complexes of unusual oxidation states. Our own interest has been in the properties of rhodium(II) carboxylate dimers of the type $\mathrm{Rh_2(O_2CR)_4}$ (shown in Figure 1a), where R varied from an electron-donating to an electron-withdrawing substituent.[14–18]

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