Bull. Chem. Soc. Jpn., 57, 194—197 (1984) [Vol. 57, No. 1

# Mechanism of the Reactions of Oxomolybdenum(V) Tetraphenylporphyrin Complex with Alcohols in the Presence of Superoxide

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(Received June 6, 1983)

The successive addition of ROH (R=$CH_3$ and $C_2H_5$) to the dichloromethane solution of $Mo^VO(tpp)Br$ (tpp=*meso*-tetraphenylporphinato) causes two-step reactions at 25 °C. The products of the first and the second step of the reactions are alcohol complex, $[Mo^VO(tpp)(ROH)]Br$, and alkoxo complex, $Mo^VO(tpp)OR$, respectively. In the presence of superoxide ion, $O_2^-$, in the dichloromethane solution of $Mo^VO(tpp)X$ (X=Br and NCS) containing alcohol, $Mo^VO(tpp)OR$ is formed through competitive two reaction paths where $O_2^-$ acts as a proton acceptor and a reducing agent. The reaction steps of the two paths were confirmed by optical and ESR studies.

Much attention has been given to the studies of the reactions of metal complexes with superoxide to elucidate the mechanisms of the formation reaction and the electronic structure of dioxygen complex and of disproportionation reactions of superoxide by superoxide dismutases.[1,2] Superoxide possesses versatile reactivities as a ligand, a reductant, an oxidant, and a base depending on the reaction conditions such as solvents and temperature.[2,3]

Recently, the authors reported that $Mo^VO(tpp)Br$ was reduced to $Mo^{IV}O(tpp)$ by superoxide ion in aprotic solvents *via* an intermediate which was suggested to be a dioxygen complex.[4] When the reaction system contained a small amount of alcohol, alkoxo complex, $Mo^VO(tpp)OR$, was finally formed.[5,6] The present paper reports the mechanism of the reaction of $Mo^VO(tpp)X$ with alcohols ($CH_3OH$ and $C_2H_5OH$) in the presence of superoxide ion. In this reaction system, superoxide ion acts as a base to remove a proton from alcohol and a reducing agent for $Mo^VO(tpp)X$.

## Experimental

The syntheses of the complexes, $Mo^VO(tpp)X$,[5] $Mo^VO(tpp)OC_2H_5$,[5] $Mo^VO(tpp)OCH_3$,[7] and $Mo^{IV}O(tpp)$,[4] were reported previously. Dichloromethane was distilled, passed through a column of basic alumina to remove stabilizer,[8] and again distilled immediately before use. Methanol and ethanol were purified by the usual methods.[9] Dimethyl sulfoxide was kept with calcium hydride for several days, distilled at 37 °C under reduced pressure, and stored under Ar atmosphere. Potassium superoxide (ICN Pharmaceuticals) and 18-crown-6 (Nippon Soda) were used without further purification. The solution of superoxide was prepared from potassium superoxide solubilized by 18-crown-6 in dimethyl sulfoxide under Ar atmosphere.[10] The concentration of superoxide in dimethyl sulfoxide was determined by photometric titration with iodine.[6]

Visible absorption spectra were measured at 25.0±0.1 °C with a Hitachi 808 spectrophotometer. ESR spectra were recorded with a JEOL JES-FE1X spectrometer at 25 °C.

## Results and Discussion

*Reactions of $Mo^VO(tpp)X$ with Alcohols.* The successive addition of methanol to the dichloromethane solution of $Mo^VO(tpp)Br$ at 25 °C causes two-step reactions. In the first step, the absorbance of the Soret band of $Mo^VO(tpp)Br$ at 508 nm is decreased with increasing absorbance of a new Soret band at 478 nm (spectra 1—4 in Fig. 1). This spectral change has isosbestic points. Asmus plot[11] for this spectral change indicates that the reaction is the type of $A+B \rightleftarrows C$, where A and B denote the reactants (Fig. 2). By the further addition of a large excess of methanol, the Soret band at 478 nm diminishes with appearance of a new absorption band at 454 nm (spectrum 5 in Fig. 1). The absorption spectrum of the final product agrees with that of the complex, $Mo^VO(tpp)OCH_3$, synthesized and isolated independently.[7] The product of the first step of the reaction is assigned to the alcohol complex, $[Mo^VO(tpp)(CH_3OH)]Br$, which is namely formed by the substitution of $Br^-$ in $Mo^VO(tpp)Br$ with methanol.[12] The spectral change shown in Fig. 1 suggests that the second step reaction is the deprotonation

TABLE 1. ABSORPTION PEAKS IN UV AND VISIBLE REGIONS

| Complex | $\lambda_{max}$/nm ($\varepsilon/10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | In $CH_2Cl_2$ at 25 °C | | | | | |
| $Mo^VO(tpp)Br$[a)] | 350 (6.40) | 375, 390 (sh) | 421 (2.63) | 508 (3.45) | 638 (0.71) | 686 (0.86) |
| $Mo^VO(tpp)NCS$[a)] | 333 (5.42) | 370 (sh) | 410 (sh) | 493 (4.55) | 622 (0.91) | 667 (0.93) |
| $[Mo^VO(tpp)(dmso)]Br$[b)] | 330 (4.6) | 375 (sh) | 405 (sh) | 477 (6.0) | 604 (1.0) | 648 (0.9) |
| $[Mo^VO(tpp)(CH_3OH)]Br$ | 340 (5.1) | 375 (sh) | 407 (sh) | 478 (5.4) | 600 (1.0) | 645 (0.8) |
| $Mo^{IV}O(tpp)$[c)] | 320 (0.9) | | | 428 (29.0) | 554 (1.59) | 589 (0.31) |
| $Mo^VO(tpp)OC_2H_5$[a)] | 320 (3.42) | 385 (sh) | | 454 (15.8) | 582 (1.51) | 622 (1.04) |
| $Mo^VO(tpp)OCH_3$[d)] | | | | 454 (17.0) | 581 (1.57) | 621 (1.08) |

a) Ref. 5 b) Ref. 12 c) Ref. 4 d) Ref. 19

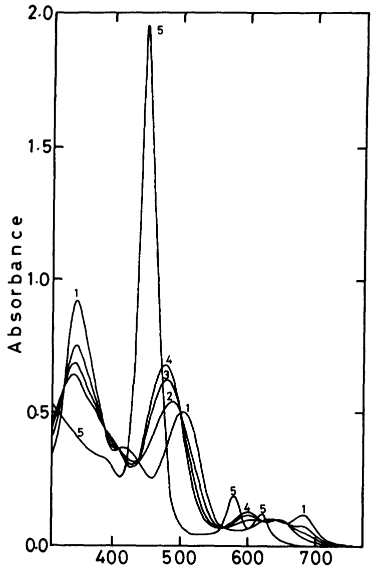


Fig. 1. The spectral change in the reaction of Mo$^{V}$(tpp)Br with methanol in dichloromethane at 25 °C. The initial concentrations are $[Mo^{V}O(tpp)Br]_0=1.44\times10^{-5}$ mol dm$^{-3}$ and $[CH_3OH]_0=0$ (0) (1); 0.2 (0.049) (2); 0.5 (0.12) (3); 0.9 (0.22) (4); 5.0%(v/v) (1.24 mol dm$^{-3}$) (5).

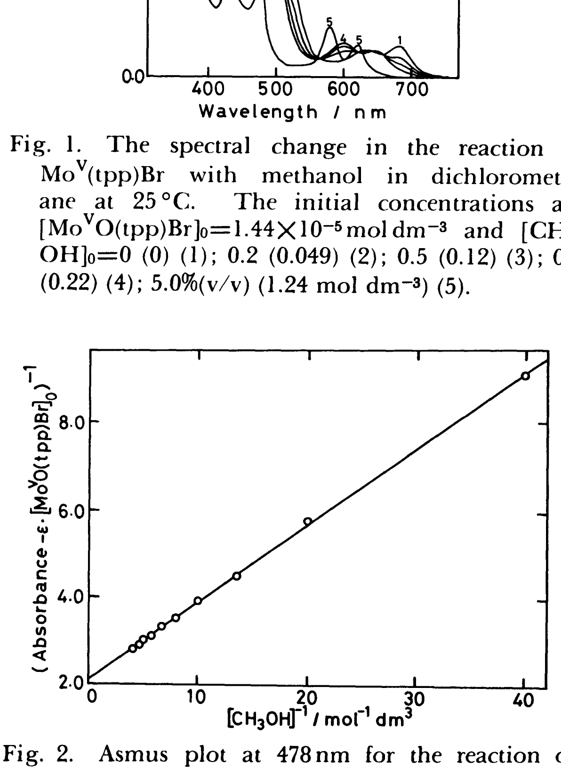


Fig. 2. Asmus plot at 478 nm for the reaction of Mo$^{V}$O(tpp)Br with methanol at 25 °C.

reaction of [Mo$^{V}$O(tpp)($CH_3OH$)]Br enhanced by the presence of a large amount of alcohol in the reaction system. This deprotonation reaction could be resulted from the change in the dielectric constant of the solution or the role of alcohol as a base.

The formation constant, $K_s$, of the first step of the reaction,

$$\underset{\lambda_{Soret}=508\text{ nm}}{Mo^{V}O(tpp)Br + CH_3OH} \overset{K_s}{\rightleftharpoons} \underset{\lambda_{Soret}=478\text{ nm}}{[Mo^{V}O(tpp)(CH_3OH)]Br}$$

$$\xrightleftharpoons{+CH_3OH} \underset{\lambda_{Soret}=454\text{ nm}}{Mo^{V}O(tpp)OCH_3 + HBr} \qquad (1)$$

and the molar absorption coefficient at 478 nm of [Mo$^{V}$O(tpp)($CH_3OH$)]Br were determined to be $K_s=$ 12.5 mol$^{-1}$ dm$^3$ and $\varepsilon_{478\,nm}=5.4\times10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$ from Asmus plot at 25 °C.

By the reaction of Mo$^{V}$O(tpp)Br with ethanol, Mo$^{V}$O(tpp)$OC_2H_5$ is also formed *via* the formation of [Mo$^{V}$O(tpp)($C_2H_5OH$)]Br. The formation constant of the [Mo$^{V}$O(tpp)($C_2H_5OH$)]Br is $K_s=2.8\pm0.2$ mol$^{-1}$ dm$^3$ at 25 °C. The spectral change of the reaction does not show any isosbestic points since the first step of the reaction is not discriminated from the second step owing to the small value of the formation constant, $K_s$.

The solution of the complex, [MoO(tpp)($CH_3OH$)]Br, resulted from the reaction of Mo$^{V}$O(tpp)Br with methanol shows ESR signals due to molybdenum which indicates that the oxidation state of the central molybdenum atom of the complex is 5+ as that of the complexes, MoO(tpp)Br and MoO(tpp)OR.[13)]

The successive addition of methanol to the dichloromethane solution of Mo$^{V}$O(tpp)NCS causes the shift of absorption peak from 493 to 480 nm followed by the appearance of a new band at 454 nm. The bands at 480 and 454 nm are ascribed to [Mo$^{V}$O(tpp)($CH_3OH$)]NCS and Mo$^{V}$O(tpp)$OCH_3$, respectively. The amount of the alcohol complex, [Mo$^{V}$O(tpp)($CH_3OH$)]NCS, formed in the course of the reaction is relatively small compared to that of the reaction system of Mo$^{V}$O(tpp)Br, which is due to the small value of the formation constant, $K_s<1.0$ at 25 °C. The order of the magnitude of the formation constant of the dimethyl sulfoxide complexes, [Mo$^{V}$O(tpp)(dmso)]-X, was also found to be $K^{DMSO}_{X=NCS} \ll K^{DMSO}_{X=Br}$.[12)]

*Mechanisms of the Reactions between Mo$^{V}$O(tpp)X, Alcohols, and Superoxide.* The complex, Mo$^{V}$O(tpp)X, is present as the reaction species, Mo$^{V}$O(tpp)X, [Mo$^{V}$O(tpp)(ROH)]X, and Mo$^{V}$O(tpp)OR, in dichloromethane solutions containing $10^{-3}$—2% (v/v) alcohol at 25 °C. By the addition of dimethyl sulfoxide solution of superoxide to the solution, the absorption peak of the alkoxo complex, Mo$^{V}$O(tpp)OR, is rapidly increased (Fig. 3).[5,6)] The formation reaction of Mo$^{V}$O(tpp)OR proceeds through competitive two

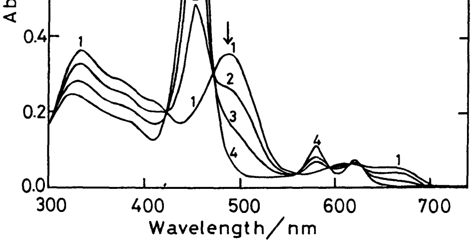


Fig. 3. The spectral change in the reaction between Mo$^{V}$O(tpp)NCS, methanol, and superoxide in dichloromethane at 25 °C. The initial concentrations are $[Mo^{V}O(tpp)NCS]_0=7.54\times10^{-6}$ mol dm$^{-3}$, $[CH_3OH]_0=2\%$(v/v) (0.49 mol dm$^{-3}$), $[DMSO]_0=1\%$ (v/v) (0.14 mol dm$^{-3}$), and $[O_2^-]_0=0$ (1); $3.05\times10^{-6}$ (2); $5.59\times10^{-6}$ (3); $1.12\times10^{-5}$ mol dm$^{-3}$ (4).

reaction paths, A and B.

Reaction path A

$$\mathrm{ROH + O_2^- \rightleftarrows RO^- + HO_2} \tag{2}$$

$$\mathrm{Mo^{V}O(tpp)X + DMSO \rightleftarrows [Mo^{V}O(tpp)(dmso)]X} \tag{3}$$

$$\mathrm{Mo^{V}O(tpp)X + ROH \rightleftarrows [Mo^{V}O(tpp)(ROH)]X} \tag{4}$$

$$\mathrm{[Mo^{V}O(tpp)(ROH)]X \rightleftarrows Mo^{V}O(tpp)OR + HX} \tag{5}$$

$$\mathrm{Mo^{V}O(tpp)X + RO^- \rightleftarrows Mo^{V}O(tpp)OR + X^-} \tag{6}$$

$$\mathrm{[Mo^{V}O(tpp)(dmso)]X + RO^- \rightleftarrows Mo^{V}O(tpp)OR + X^- + DMSO} \tag{7}$$

$$\mathrm{[Mo^{V}O(tpp)(ROH)]X + RO^- \rightleftarrows Mo^{V}O(tpp)OR + X^- + ROH} \tag{8}$$

$$\mathrm{[Mo^{V}O(tpp)(ROH)]X + O_2^- \rightleftarrows Mo^{V}O(tpp)OR + X^- + HO_2} \tag{9}$$

Reaction path B

$$\mathrm{Mo^{V}O(tpp)X + O_2^- \rightleftarrows Mo^{IV}O(tpp) + O_2 + X^-} \tag{10}$$

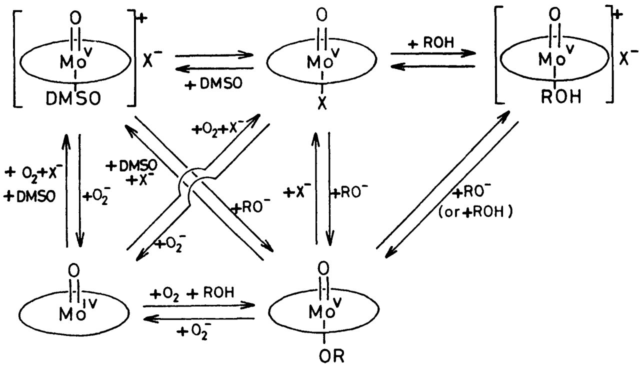
$$\mathrm{[Mo^{V}O(tpp)(dmso)]X + O_2^- \rightleftarrows Mo^{IV}O(tpp) + O_2 + X^- + DMSO} \tag{11}$$

$$\mathrm{Mo^{IV}O(tpp) + O_2 + ROH \rightleftarrows Mo^{V}O(tpp)OR + HO_2} \tag{12}$$

The reaction path A starts with the formation of alkoxide ion, $RO^-$. The $RO^-$ is first formed by the reaction of alcohol with superoxide (Eq. 2).[14,15] The formation of the dimethyl sulfoxide complex, $[Mo^{V}O(tpp)(dmso)]X$, is confirmed by adding dimethyl sulfoxide to the dichloromethane solution of $Mo^{V}O(tpp)X$ (Eq. 3).[12] The spectral change of the reaction of the complex, $Mo^{V}O(tpp)X$ or $[Mo^{V}O(tpp)(dmso)]X$, with $C_2H_5O^-$ derived from $C_2H_5ONa$ solubilized by 18-crown-6 to dichloromethane reveals the occurrence of the reactions 6 and 7.[13] Reaction 8 was also confirmed by the spectral change in the reaction of $[Mo^{V}O(tpp)(CH_3OH)]Br$ with $C_2H_5O^-$ ion. The reaction of alcohol with superoxide (Eq. 2) suggests the presence of the reaction 9 in which superoxide directly reacts with the coordinated alcohol in $[Mo^{V}O(tpp)(ROH)]X$ to form $Mo^{V}O(tpp)OR$.

The reaction path B is started by the direct reduction of the complex, $Mo^{V}O(tpp)X$ and $[Mo^{V}O(tpp)(dmso)]X$, by an excess of superoxide to $Mo^{IV}O(tpp)$ (Eqs. 10 and 11); the reaction was confirmed by spectral and ESR measurements.[4] The ESR spectrum of the dichloromethane solution of $Mo^{V}O(tpp)X$ consists of a strong central line ($\bar{g}=1.967$) due to $^{94,96,98,100}Mo$ nuclei ($I=0$)(natural abundance *ca.* 75%) which is split to nine lines by coordinated four nitrogens of the ligand.[13] By the addition of an excess of superoxide to the solution of $Mo^{V}O(tpp)X$, ESR signal due to $Mo^{V}(d^1)$ diminished, owing to the formation of $Mo^{IV}O(tpp)$ which is ESR silent. Equation 12[16] was also confirmed by adding alcohol to the dichloromethane solution of $Mo^{IV}O(tpp)$ synthesized and isolated independently.[4]

The reaction ratio of the paths A to B to form $Mo^{V}O(tpp)OR$ largely depends on the concentrations of alcohol and superoxide ion. The reaction path through A is of greater advantage than that through B and completes within 1 min under the conditions of high alcohol concentration, *e.g.* 2%(v/v) methanol (0.49 mol dm$^{-3}$).



Scheme 1.

The stoichiometry of the $Mo^{V}O(tpp)OCH_3$ formation reaction in 2%(v/v) methanol–dichloromethane was determined to be $Mo^{V}O(tpp)NCS : O_2^- = 1:1$ by the molar ratio method.[6] Equations 10 and 11 which reveal respectively the reduction reactions of $Mo^{V}O(tpp)X$ and $[Mo^{V}O(tpp)(dmso)]X$ with superoxide lie on the left. More than tenfold excess of superoxide over the complex is required to complete the reduction. It takes more than 20 min at 25 °C to complete the reactions 10 and 11 with the initial concentrations of $[O_2^-]_0=2.2\times10^{-4}$ and $[Mo^{V}O(tpp)Br]_0=7.9\times10^{-6}$ mol dm$^{-3}$.[4] Thus, under the conditions of 2%(v/v) methanol and $[CH_3OH]_0 \gg [O_2^-]_0$, the formation reaction of $Mo^{V}O(tpp)OCH_3$ proceeds almost (>90%) through the reaction path A. The lower the concentration of methanol becomes, the more the reaction through the path B increases. The complex, $Mo^{V}O(tpp)OR$, formed finally is relatively stable in the solution but is reduced by a very large excess, *e.g.* $10^{-1}$—$10^{-2}$ mol dm$^{-3}$, of superoxide over the initial concentrations of $[Mo^{V}O(tpp)X]_0$ and $[ROH]_0$ (Eq. 13).

$$\mathrm{Mo^{V}O(tpp)OR + O_2^- \rightleftarrows Mo^{IV}O(tpp) + RO^- + O_2} \tag{13}$$

Under the experimental conditions such as in Fig. 3, this equilibrium lies far on the left, which is supported by the large differences of the oxidation-reduction potentials between the $O_2/O_2^-$ couple (−0.5—−0.65 V *vs.* NHE in aprotic solvents)[17] and $Mo^{V}O(tpp)OCH_3/Mo^{IV}O(tpp)$ couple (−0.74—−0.89 V *vs.* SCE in dichloromethane).[18] All reactions among $Mo^{V}O(tpp)X$, ROH, and superoxide and the absorption spectral data are shown in Scheme 1 and Table 1, respectively.

Addition of an excess of superoxide to the dichloromethane solution of $Mo^{V}O(tpp)X$ containing a trace amount of water gives the hydroxo complex, $Mo^{V}O(tpp)OH$, which has the Soret peak at 464 nm.[19] The equilibrium of the reaction 15 also depends on the concentration of superoxide.

$$\mathrm{Mo^{V}O(tpp)X + H_2O + O_2^- \rightleftarrows Mo^{V}O(tpp)OH + X^- + HO_2} \tag{14}$$

$$\mathrm{Mo^{V}O(tpp)OH + O_2^- \rightleftarrows Mo^{IV}O(tpp) + OH^- + O_2} \tag{15}$$

The hydroxo complex, $Mo^{V}O(tpp)OH$, should be formed through the same competitive two reaction paths of A and B as in the formation reaction of the alkoxo complex, $Mo^{V}O(tpp)OR$. The slow reaction of superoxide ion with dichloromethane[20] does not affect the mechanism of the reaction between $Mo^{V}O(tpp)X$, alcohol, and superoxide.

## References

1) "Superoxide and Superoxide Dismutases," ed by A. M. Michelson, J. M. McCord, and I. Fridovich, Academic Press, New York, N. Y. (1977).

2) D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, **14**, 393 (1981).

3) J. S. Valentine, "Biochemical and Clinical Aspects of Oxygen," ed by W. S. Caughey, Academic Press, New York, N. Y. (1979), pp. 659—677.

4) T. Imamura, K. Hasegawa, and M. Fujimoto, *Chem. Lett.*, **1983**, 705.

5) T. Imamura, T. Numatatsu, M. Terui, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **54**, 170 (1981).

6) K. Kitamura, K. Hasegawa, K. Mochizuki, T. Imamura, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **54**, 1400 (1981).

7) $Mo^VO(tpp)OCH_3$ was synthesized according to the modified method of the synthesis of $Mo^VO(tpp)OC_2H_5$.[5]

8) G. Wohlleben, *Angew. Chem.*, **68**, 752 (1956).

9) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York, N. Y. (1970).

10) J. S. Valentine and A. B. Curtis, *J. Am. Chem. Soc.*, **97**, 224 (1975).

11) E. Asmus, *Fresenius' Z. Anal. Chem.*, **178**, 104 (1960).

12) The dimethyl sulfoxide complex, $[Mo^VO(tpp)(dmso)]X$, is also formed by the reaction of $Mo^VO(tpp)X$ with dimethyl sulfoxide in dichloromethane. The order of the magnitude of the formation constant of $[Mo^VO(tpp)(dmso)]X$ is

$$K^{\mathrm{DMSO}}_{\mathrm{X=F}} \ll K^{\mathrm{DMSO}}_{\mathrm{X=NCS}} \approx K^{\mathrm{DMSO}}_{\mathrm{X=Cl}} \ll K^{\mathrm{DMSO}}_{\mathrm{X=Br}}.$$

T. Imamura, T. Tanaka, and M. Fujimoto, unpublished data.

13) T. Imamura, M. Terui, Y. Takahashi, T. Numatatsu, and M. Fujimoto, *Chem. Lett.*, **1980**, 89.

14) A. Le Berre and Y. Berguer, *C. R. Acad. Sci., Paris*, **260**, 1995 (1965).

15) A. Le Berre and Y. Berguer, *Bull. Soc. Chim. Fr.*, **1966**, 2363.

16) H. J. Ledon, M. Bonnet, and D. Galland, *J. Am. Chem. Soc.*, **103**, 6209 (1981).

17) D. T. Sawyer and J. L. Roberts, Jr., *J. Electroanal. Chem.*, **12**, 90 (1966); M. E. Peover and B. S. White, *Electrochim. Acta*, **11**, 1061 (1966); D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965); E. L. Johnson, K. H. Pool, and R. E. Hamm, *ibid.*, **38**, 183 (1966).

18) These values are half-wave potentials obtained by cyclic voltammetry. K. M. Kadish, T. Malinski, and H. Ledon, *Inorg. Chem.*, **21**, 2982 (1982).

19) H. J. Ledon, M. C. Bonnet, Y. Brigandat, and F. Varescon, *Inorg. Chem.*, **19**, 3488 (1980).

20) J. L. Roberts, Jr., and D. T. Sawyer, *J. Am. Chem. Soc.*, **103**, 712 (1981).