Volume 23
Number 3
February 1, 1984

Inorganic Chemistry

Communications

Reduction of *cis*-Dioxo(tetraphenylporphinato)molybdenum(VI): One- or Two-Electron-Transfer Pathway

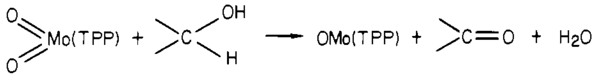
Sir:

High-valent oxo–iron porphyrin complexes have been proposed as the active intermediates of dioxygen activation by cytochrome P_{450} dependent monooxygenases, which are able to selectively hydroxylate aliphatic or aromatic hydrocarbons and epoxidize olefins using molecular oxygen.[1-5] Because of this, attempts to design simple biomimetic models for these enzymes have led to the blooming of much high-valent iron porphyrin chemistry in the last few years. Several species exhibiting cytochrome P_{450} like reactivity have been prepared by oxidation of iron(III) porphyrin complexes with use of either iodosylarenes,[6-11] peracids,[10] or amine oxides[11,12] and have been tentatively described as ferryl complexes, $OFe^{V}(P)^{+}$. However, the actual nature of these intermediates is poorly understood.[10,13]

Recently, we reported that tertiary phosphines could be oxidized by *cis*-dioxomolybdenum(VI) tetra-*p*-tolylporphyrin,[14] a complex whose structure has been determined by X-ray crystallographic analysis.[15] We now wish to report other chemical oxidations using *cis*-dioxomolybdenum(VI) tetraphenylporphyrin, $O_2Mo(TPP)$ (**1**) as well as to compare the chemical and electrochemical reductions of this complex.

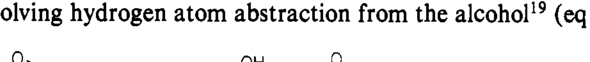
A 15-mg amount of **1** and 13 mg of 2-propanol (10-fold molar excess) were dissolved in 5 mL of thiophene-free anhydrous benzene in a glass Carius tube. After three freeze–pump–thaw cycles, the tube was sealed and kept at 60 °C in the dark for 4 days. After this time the electronic absorption spectrum of the reaction mixture was identical with that of oxoisopropoxomolybdenum(V) tetraphenylporphyrin, OMo(TPP)O-*i*-Pr.[16] The presence of molybdenum(V) was also indicated by ESR spectroscopy. Acetone (46% yield relative to Mo) was detected by gas chromatography. When the same reaction was carried out for 3 days in the presence of air, the yield of acetone increased to 300%. At the same time the absorption spectrum of the reaction mixture exhibited a new broad peak near 480 nm due to the presence of hydrogen peroxide[17] as demonstrated by the formation of the bis(peroxo) complex $(O_2)_2Mo(TPP)$[18] upon addition of a small amount of water. Similar results were obtained for reaction with 1-phenylethanol, from which acetophenone was produced in 42% yield under strictly anaerobic conditions or in 95% yield in the presence of air. Finally, 3-cholestanone was obtained in 45% yield by oxidation of 3-cholestanol after 2 weeks at 70 °C.

In oxygen-free conditions, the stoichiometry of the reaction that is observed is 2 mol of **1** consumed/mol of ketone formed. Therefore, the two-electron oxidation process by direct oxygen transfer of **1** as shown in eq 1 can be ruled out since it would

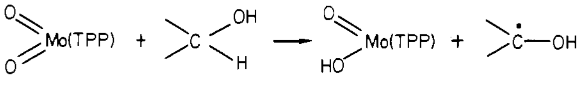


(1)

give a 1:1 stoichiometry. Moreover, OMo(TPP) was not detected in the reaction mixture by UV–visible spectroscopy although it does not react either with **1**[14] or with alcohols under oxygen-free conditions. Thus, the most reasonable pathway for these reactions is by two one-electron processes, first involving hydrogen atom abstraction from the alcohol[19] (eq 2),



(2)



(3)

---

(1) Groves, J. T. In "Catalysis of Organic Reactions"; Moser, W. R., Ed.; Marcel Dekker: New York, 1981; pp 131–138.

(2) Dolphin, D., McKenna, C., Murakami, Y., Tabushi, I., Eds. "Biomimetic Chemistry"; American Chemical Society: Washington, DC, 1980; Adv. Chem. Ser. No. 191.

(3) Spiro, T. G., Ed. "Metal Ion Activation of Dioxygen"; Wiley-Interscience: New York, 1980.

(4) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315–356.

(5) Ullrich, V. *Top. Curr. Chem.* **1979**, *83*, 67–104.

(6) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3413–3415.

(7) Chang, C. K.; Ebina, F. *J. Chem. Soc., Chem. Commun.* **1981**, 778–779.

(8) Groves, J. T.; Nemo, T. E.; Meyers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–1033.

(9) Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169–177.

(10) Groves, J. T.; Haushalter, R. C.; Nekamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886.

(11) Shannon, P.; Bruice, T. C. *J. Am. Chem. Soc.* **1981**, *103*, 4580–4582.

(12) Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123–6125.

(13) Gold, A.; Ivey, W.; Bowen, M. *J. Chem. Soc., Chem. Commun.* **1981**, 293–294.

(14) Ledon, H.; Bonnet, M. *J. Mol. Catal.* **1980**, *7*, 309–313.

(15) Mentzen, B. F.; Bonnet, M. C.; Ledon, H. J. *Inorg. Chem.* **1980**, *19*, 2061–2066.

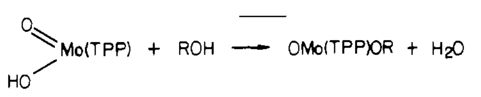
(16) Ledon, H. J.; Bonnet, M. C.; Brigandat, Y.; Varescon, F. *Inorg. Chem.* **1980**, *19*, 3488–3491.

(17) Treatment of OMo(TPP)OMe with an excess of anhydrous hydrogen peroxide solution in dioxane gave a spectrum with λ_{max} ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1}) at 653 (8.2), 609 (10.5), 484 (54), and 342 nm (37.3). This is very similar to that obtained for OMo(TPP)OO-*t*-Bu: Ledon, H. J.; Durbutt, P.; Varescon, F. "Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1982; pp 319–322.

(18) Chevrier, B.; Diebold, Th.; Weiss, R. *Inorg. Chim. Acta* **1976**, *19*, L57–L58.

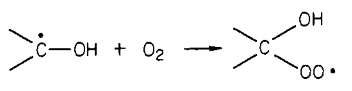
0020-1669/84/1323-0261$01.50/0

then oxidation of the ketyl radical by another molecule of **1** (eq 3), and finally reaction of the hydroxymolybdenum(V) porphyrin complex with the alcohol (eq 4).

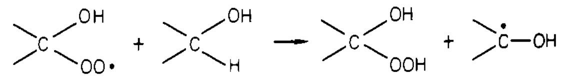


$$\mathrm{O(HO)Mo(TPP)} + \mathrm{ROH} \longrightarrow \mathrm{OMo(TPP)OR} + \mathrm{H_2O} \qquad (4)$$

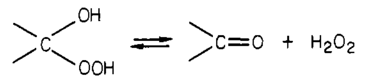
In the presence of oxygen the intermediate radical would be trapped and would induce an autoxidation chain affording both the ketone and H_2O_2 (eq 5–7).



(5)

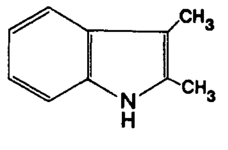


(6)

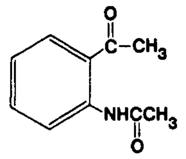


(7)

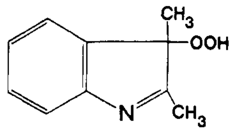
Induction of free radical chain oxidation by **1** was observed in the case of 2,3-dimethylindole (**2**). *o*-Acetamidoacetophenone (**3**) was obtained in 10% yield when **1** was heated for 3 days at 60 °C in benzene open to the atmosphere. When the same reaction was carried out in strictly oxygen-free conditions, reduction of **1** to a molybdenum(V) species was observed but, in this case, no *o*-acetamidoacetophenone was obtained. This is in agreement with the involvement of 2,3-dimethyl-3-(hydroperoxy)indolenine (**4**) formation[20,21] analogous to that shown in eq 2, 5, and 6. No reaction was observed with xanthine, but several other reductions of **1** to molybdenum(V) complexes were observed with anthracene, phenanthrene, dimethylaniline, and *N*-methylimidazole, which required a 10^3–10^4-fold excess of substrate to observe the disappearance of the UV–visible spectrum of **1** over a period of weeks. This precluded any identification of the oxidation products.



2



3



4

In order to determine the number of electrons transferred in the absence of chemical reducing agents, an electrochemical reduction of **1** was carried out at a Pt electrode by cyclic voltammetry and the products were investigated by spectroelectrochemistry. As shown in Figure 1, the electrochemical reduction of **1** proceeds in three steps. The first wave has a cathodic peak potential at $E_{pc} = -0.96$ V and is totally irreversible. Additional reductions occur at $E_{1/2} = -1.10$ and -1.50 V and are diffusion controlled. These last values are at potentials characteristic of OMo(TPP) reduction to form the anion radical and dianion.[22] It is interesting to note that, in contrast to the chemical reductions described above, the first electrochemical reduction involves an overall two-electron-transfer process as determined by coulometric measurements. The spectrum of the first electrogenerated species (Figure 2) is characterized by a strong Soret peak at 430 nm. This peak, as well as peaks at 514, 554, and 592 nm, are identical with those reported for OMo(TPP).[23] Thus, on the basis of the voltammetric, coulometric, and spectroelectrochemical data, the mechanism of the first reduction can be described as shown by eq 8–10. In this ECE mechanism,[24] a protonation (arising

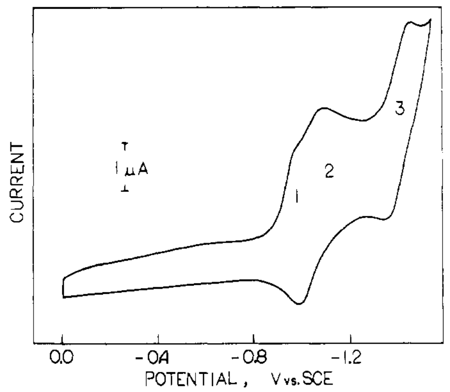


Figure 1. Cyclic voltammogram of $O_2Mo(TPP)$ in 1,2-dichloroethane containing 0.1 M tetrabutylammonium perchlorate. Scan rate = 0.1 V/s.

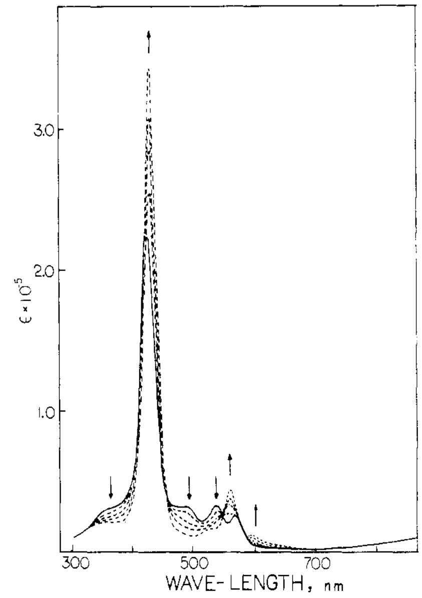
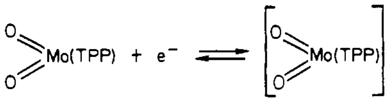
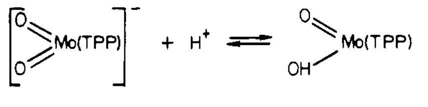


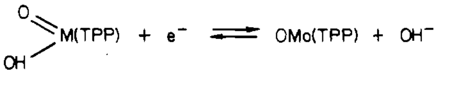
Figure 2. Electronic absorption spectra of $O_2Mo(TPP)$ obtained during the first reduction step in 1,2-dichloroethane containing 0.5 M tetrabutylammonium perchlorate.



$$\mathrm{O_2Mo(TPP)} + e^- \rightleftharpoons [\mathrm{O_2Mo(TPP)}]^- \qquad (8)$$



$$[\mathrm{O_2Mo(TPP)}]^- + H^+ \rightleftharpoons \mathrm{O(OH)Mo(TPP)} \qquad (9)$$



$$\mathrm{O(OH)M(TPP)} + e^- \rightleftharpoons \mathrm{OMo(TPP)} + \mathrm{OH^-} \qquad (10)$$

---

(19) This mechanism has been proposed for the oxidation of benzyl alcohol by OCr(TPP): Buchler, J. W.; Lay, K. L.; Castle, L.; Ullrich, V. *Inorg. Chem.* **1982**, *21*, 842–844.

(20) Dufour, M. N.; Crubmliss, A. L.; Johnston, G.; Gaudemer, A. *J. Mol. Catal.* **1980**, *7*, 277–287.

(21) Fraser, M. S.; Hamilton, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 4203–4212.

(22) Kadish, K. M.; Malinski, T.; Ledon, H. *Inorg. Chem.* **1982**, *21*, 2982–2987.

(23) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chm.* **1979**, *18*, 1193–1200.

either from the solvent or from minor traces of water) follows the first electron-transfer step and yields HO(O)Mo(TPP), which has a reduction potential at $E_{1/2} = -0.1$ V. Afterwards, a second one-electron-transfer reaction can take place at the potential of reaction 8, producing an overall apparent two-electron-transfer reduction.

A similar mechanism as shown in eq 8-10 was also observed at 223 K, and attempts to spectrally identify the site of the first reduction (i.e., metal, oxygen atom, or ring based) were unsuccessful due to the rapid protonation (eq 9) yielding (OH)OMo(TPP). Previous studies of the bis(peroxo)molybdenum(VI) complex $(O_2)_2$Mo(TmTP)[26] have shown that an initial one-electron reduction occurs at the metal center, yielding a Mo(V) species. This possibility cannot be ascertained or ruled out in the present case.

In summary, although the reactivity of **1** is much lower than that of higher valent iron porphyrin complexes, the dual behavior observed—oxygen ligand transfer, in the case of phosphine oxidation, or an initial one-electron reduction either by hydrogen abstraction or at an electrode—seems to be related to the commonly accepted mechanism for oxidation by cytochrome P_{450}.

Acknowledgment. The support of the Centre National de la Recherche Scientifique and of the National Science Foundation (Grant CHE 8215507) is gratefully acknowledged.

Registry No. 2, 91-55-4; O_2Mo(TPP), 78229-89-7; 2-propanol, 67-63-0.

Institut de Recherches sur la Catalyse
69626 Villeurbanne Cedex, France
H. Ledon*[27]
F. Varescon[28]

Department of Chemistry
University of Houston
Houston, Texas 77004
T. Malinski[29]
K. M. Kadish*

Received August 9, 1983

---

(24) Analysis of the peak potentials and current-voltage curves fit the case of an ECE mechanism (electrochemical step followed by the chemical conversion to another electroactive species) where both electron transfers are reversible and the second reduction occurs at an $E_{1/2}$ positive of the first reduction. This thus leads to currents suggesting an apparent overall two-electron-transfer reaction.[25]

(25) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178.

(26) Kadish, K. M.; Chang, D.; Malinski, T.; Ledon, H. *Inorg. Chem.* **1983**, *22*, 3490.

(27) Present address: l'Air liquide, CRCD, 78350 Jouy-en-Josas, France.

(28) Present address: E.I. du Pont de Nemours GMBH, Research Center, D-6700 New-Isenburg, Germany.

(29) Present address: Department of Chemistry, Oakland University, Rochester, MI 48063.

Articles

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65211

Studies on the Kinetics and Mechanism of Oxygen Exchange between Solvent Water and $[MoOCl_5]^{2-}$

CHANG-SU KIM and R. KENT MURMANN*

Received April 29, 1983

A study of the ^{18}O exchange between HCl solutions of K_2MoOCl_5 and water indicates that the major ionic species in >10 M HCl is $[MoOCl_5]^{2-}$ and that the half-time for exchange is highly dependent on acidity, $[Cl^-]$, and $[Mo]_t$. At constant $[Mo]_t$ and acidity the isotopic-oxygen-exchange rate follows first-order kinetics with a small, consistent, time-zero exchange. In aqueous solutions containing only HCl and K_2MoOCl_5, the rate constant shows a minimum at about 11 M HCl; $k_{obsd} = 0.91 \times 10^{-4}$ s^{-1} at $[Mo]_t = 3.23 \times 10^{-2}$ M and 0 °C. Over an acidity range of 2.6-12.1 M HCl the rate follows the law $k_{obsd} = k_1[Mo]_t/[Cl^-] + k_2[Mo]_t^2[HCl]$ where $k_1 = (1.49 \pm 0.15) \times 10^{-4}$ M s^{-1} and $k_2 = (1.73 \bullet 0.33) \times 10^{-4}$ M^{-2} s^{-1} at 0 °C and $I = 12.1-12.3$; $\Delta H^* = 64.2 \bullet 0.2$ kJ/mol, and $\Delta S^* = -78.1 \pm 0.2$ J/(mol K). The kinetic results are interpreted in terms of the reversible formation of $[Cl_5Mo-O-MoCl_5]^{2-}$ in the most acidic media and the internal electronic rearrangement of the hydrolysis product, $[MoO(OH_2)Cl_4]^-$, at lower $[Cl^-]$. It is concluded that even in 2 M HCl the major ion present is $[MoOCl_5]^{2-}$ provided the total $[Cl^-]$ is >12 M. $[MoOBr_5]^{2-}$ is somewhat faster exchanging and shows the same general features.

Introduction

For some years now there has been an interest in the mechanism of oxygen exchange between solvent water and oxo, hydroxo, and aquo metal ions, but little definitive progress has been made. The advent of methods for measuring very fast reaction rates, i.e. NMR, stopped-flow, temperature-jump, etc., has allowed water-exchange rates for many aquo metal ions to be quantitatively studied, but even here our mechanistic understanding and our predictive capability are incomplete. ^{18}O-exchange methods, though limited to relatively slowly reacting systems, often give highly precise and significant results. The method is especially applicable to the kinetically slower oxo and hydroxo metal ions. A recent review of the subject[1] shows that only one mono-yl ion is known to exist in aqueous media, VO^{2+}(aq), and its rate of oxygen exchange has been studied in detail.[2] Chloro-oxo complexes of the group 6 transtion-metal ions are known in the solid state and may also exist in solution, i.e. $[CrOCl_5]^{2-}$, $[MoOCl_5]^{2-}$, and $[WOCl_5]^{2-}$.[3-5] These ions, red, green, and green, respectively, form the basis of a mechanistically informative series. Our original intent was to carry out a comparative study with these

---

(1) Gamsjäger, H.; Murmann, R. K. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 317-380.

(2) Johnson, M. D.; Murmann, R. K. *Inorg. Chem.* **1983**, *22*, 1068.

(3) Brown, D. *J. Chem. Soc.* **1964**, 4944.

(4) Allen, E. A.; Brisdon, B. J.; Edwards, D. A.; Fowles, G. W. A.; Williams, R. G. *J. Chem. Soc.* **1963**, 4649.

(5) Jørgensen, C. K. *Acta Chem. Scand.* **1957**, *11*, 73.