thickness (n) give increases of 3.904 and 3.936 Å for each NbO$_6$ octahedron added to the layer for the hydrated and anhydrous materials, respectively. The values are consistent with preservation of the connectivity of the perovskite layers, and the small differences observed in the slopes probably reflect differences in the relative tilting of NbO$_6$ octahedra. The intercept, 2.58 Å, obtained by extrapolating the data for the anhydrous phases to $n = 0$ is consistent with a structural model in which the proton is bonded to a terminal layer oxygen atom to form an –OH that is hydrogen bonded to a terminal oxygen atom from an adjacent layer. On hydration the lattices expand by 1.7–1.9 Å.

The proton-exchanged forms of these perovskite-layered compounds are solid acids and react with organic bases. For example, reaction of the solid phases with excess n-octylamine in heptane at 95 °C leads to the formation of the octylammonium compounds n-C$_8$H$_{17}$NH$_3$[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$].[12] This acid–base reaction produces large increases in the layer separations as shown by the X-ray data summarized in Figure 2 and Table III. The results for the compounds with n = 4–7 give a linear increase in c-axis spacing with increase in the layer thickness (3.964 Å/NbO$_6$ octahedron); the data point for $n = 3$ is 1.1 Å too short relative to the other members of the series, which may indicate a slightly different orientation of the hydrocarbon chain in the interlayer. In all cases, the spacings are too large to be accounted for by a single layer of organoammonium cations and indicate a bilayer arrangement with inclined hydrocarbon chains.[13]

In summary, the perovskite-related layer structures KCa$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$ ($3 \leq n \leq 7$) have been synthesized and shown to have interlayer reactivity under mild conditions both in ion-exchange reactions and in intercalation of large organic bases. The chemical reactivity is largely independent of the layer thickness even when the oxide layers are very thick (27.2 Å for $n = 7$). Further studies of the reaction chemistry and properties of these new phases are in progress.

---

(12) The stoichiometry of the reaction was determined by thermogravimetric oxidation in air up to 1000 °C. Observed and calculated weight changes for n-C$_8$H$_{17}$NH$_3$[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$]: $n = 3$, 21.9% obsd, 21.3% calcd; $n = 4$, 17.9% obsd, 17.0% calcd; $n = 5$, 14.2% obsd, 14.2% calcd.; $n = 6$, 11.4% obsd, 12.1% calcd; $n = 7$, 8.7% obsd, 10.6% calcd. The weight losses observed indicate nearly stoichiometric reaction except for the case of the $n = 7$ compound, where the analysis indicates intercalation of 0.8 mol of octylamine/mol of solid.

(13) From the unit cell dimensions the calculated area for each alkylammonium cation is 15 Å^2, assuming a single-layer arrangement. This area is too small to accommodate alkyl chains close-packed at van der Waals contacts, and consequently a bilayer structure is observed.

Corporate Research-Science Laboratories
Exxon Research and Engineering Company
Annandale, New Jersey 08801

A. J. Jacobson*
Jack W. Johnson
J. T. Lewandowski

Received July 12, 1985

Articles

Contribution from the Max-Planck-Institut für Biophysikalische Chemie,
34 Göttingen-Nikolausberg, West Germany

Kinetics of Oxidation of Simple Complexes of Molybdenum(IV) and -(V) by Iron(III)

C. MILLAN[1] and H. DIEBLER*

Received May 22, 1985

The kinetics of the oxidation of the dimer Mo(V) cation Mo$_2$O$_4^{2+}$ by Fe(H$_2$O)$_6^{3+}$ and Fe(phen)$_3^{3+}$ in aqueous solution have been studied at 25 °C, ionic strength I = 2.0 M (NaClO$_4$), by conventional spectrophotometry. In both systems the rate of reaction is first order in reductant and oxidant and thus indicates that the first electron-transfer step is rate determining for the overall process. With the Fe(III) aquo complex as oxidant, the predominant pathway involves a hydroxo species, probably Fe(OH)$^{2+}$, which reacts with a second-order rate constant $k_{\mathrm{FeOH}} = 1.3 \times 10^3$ M^{-1} s^{-1}, presumably by an inner-sphere mechanism. Oxidation by Fe(H$_2$O)$_6^{3+}$ is much slower, $k_{\mathrm{Fe}} \leq 0.2$ M^{-1} s^{-1}. The reaction of Fe(phen)$_3^{3+}$ with Mo$_2$O$_4^{2+}$ is expected to proceed by an outer-sphere path; the rate constant of this process is k_{FePh} = 13 M^{-1} s^{-1}. The mechanism of the (outer-sphere) oxidation of the (μ-S)$_2$Mo$^{\mathrm{V}}$ complex Mo$_2$O$_2$S$_2^{2+}$ by Fe(phen)$_3^{3+}$ is more complicated, involving either a change in the rate-determining step or the appearance of a non-steady-state intermediate. The initial slopes of the reaction curves yield for the rate of the first electron-transfer step k = 0.4 or 0.8 M^{-1} s^{-1}, respectively, depending on the interpretation (25 °C, 1 M HClO$_4$, I = 1.0 M). The results reveal that Mo$_2$O$_2$S$_2^{2+}$ is a less efficient reducing agent than Mo$_2$O$_4^{2+}$. The oxidation of the trimeric Mo(IV) species Mo$_3$O$_4^{4+}$ by Fe(phen)$_3^{3+}$ is characterized by a rate-determining first electron-transfer step (outer sphere) with k = 51 M^{-1} s^{-1} in 1 M HCl, I = 2.0 M (NaCl). Due to coordination of Cl$^-$ to the Mo(IV) cation, the rate in the chloride solution is much higher than that in a noncomplexing medium.

Introduction

The chemistry of molybdenum has found much interest in recent years. New compounds have been prepared and characterized,[2] and mechanistic aspects of reactions involving molybdenum compounds are also studied to an increasing extent.[3]

The interest in molybdenum chemistry arises to a good deal from the occurrence of this element in biological systems. Molybdenum is an essential component of a series of enzymes that catalyze biological redox processes.[4] All of these enzymes contain also iron, and it is believed that at least in some of them direct electron transfer occurs between the Mo and Fe centers during the catalytic action.[4,5]

It is desirable, therefore, to learn more about the kinetics and mechanisms of redox reactions between Mo and Fe compounds, including simple complexes of these metal ions which cannot be considered as models of the biological systems. Until recently, very little has been done in this area. In this paper we report on the reactions Mo$_2$O$_4^{2+}$ + Fe(H$_2$O)$_6^{3+}$, Mo$_2$O$_4^{2+}$ + Fe(phen)$_3^{3+}$, Mo$_2$O$_2$S$_2^{2+}$ + Fe(phen)$_3^{3+}$, and Mo$_3$O$_4^{4+}$ + Fe(phen)$_3^{3+}$ in

---

(1) Permanent address: Instituto Central de Quimica, Universidad de Concepcion, Concepcion, Chile.

(2) See, e.g.: *J. Less-Common Met.* **1977**, *54*.

(3) Sykes, A. G. *J. Less-Common Met.* **1977**, *54*, 401.

(4) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

(5) Olson, J. S.; Ballou, D. P.; Palmer, G.; Massey, V. *J. Biol. Chem.* **1974**, *249*, 4363.

aqueous solutions (phen = 1,10-phenanthroline).

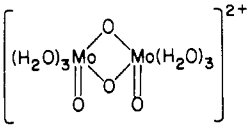
Experimental Section

Materials. Solutions of $Mo_2O_4^{2+}$ in $HClO_4$ were prepared and standardized as described.[6,7] Solutions of the $(\mu\text{-}S)_2Mo^V$ cation $Mo_2O_2S_2^{2+}$ in $HClO_4$ were prepared according to Sykes at al.[8] via the cysteine complex $K_2Mo_2O_2S_2(cys)_2$. This complex was made by adding KOH, KCl, and L-cysteine to a hot solution of $(NH_4)_2MoO_2S_2$.[9] The ammonium salt of dithiomolybdate was obtained by following known procedures.[10] Stock solutions of $Mo_3O_4^{4+}$, the aquo–oxo complex of Mo(IV), were prepared according to Ardon and Pernick[11] by the reaction of equimolar amounts of Mo(V) (as $Mo_2O_4^{2+}$) and Mo(III) (as $MoCl_5^{2-}$). $MoCl_5^{2-}$ was obtained by electrolytic reduction of Mo(VI) in 6 M HCl.[12] Solutions of $Fe(H_2O)_6^{3+}$ were prepared from $Fe(ClO_4)_3\cdot 6H_2O$ (Ventron). They were standardized by reduction to Fe(II) with Sn(II) and back-titration with Ce(IV) sulfate (ferroin). Solutions of tris(1,10-phenanthroline)iron(3+) in $HClO_4$ were prepared and standardized as described by Ford-Smith and Sutin.[13] All other chemicals used were of the best grade commercially available.

Methods. Solutions of Mo(IV) and Mo(V) were always kept and handled under an inert atmosphere of N_2 (Messer-Griesheim, 99.996%). Absorption spectra were recorded by means of a Cary 118C Spectrophotometer. The same instrument was used to follow the kinetics of the redox processes. Usually three runs were made with each solution and the results averaged. All measurements were carried out at 25.0 (±0.1) °C and at ionic strength I = 1.0 or 2.0 M, adjusted with $NaClO_4$ or NaCl.

Results and Discussion

$Mo_2O_4^{2+}$ + $Fe(H_2O)_6^{3+}$. In 1973 is was finally established[14] that in diluted perchloric acid Mo(V) exists in the form of a dimeric aquo–oxo cation



usually abbreviated as $Mo_2O_4^{2+}$. Initially this species was reported[7] to be stable in the $[H^+]$ range 0.5–5 M; later[15] it was shown to be stable down to $[H^+] \approx 0.01$ M. The absorption spectrum obtained during the present study agrees with literature reports.[7,14]

The stoichiometry of the oxidation of $Mo_2O_4^{2+}$ by Fe^{3+} was evaluated from spectrophotometric titrations. The data obtained indicate a 1:2 stoichiometry and reveal that the equilibrium lies far on the side of the products:

$$Mo_2O_4^{2+} + 2Fe^{3+} \rightleftharpoons 2Mo(VI) + 2Fe^{2+} \qquad (1)$$

The kinetics of this reaction have been studied with a large excess of Fe^{3+} (0.01–0.04 M) over $Mo_2O_4^{2+}$ (0.001 M) and at H^+ concentrations 0.4–1.5 M ($HClO_4$). The reaction was monitored at 450 nm, observing the decrease in the concentration of $Mo_2O_4^{2+}$. Fe^{3+} does not contribute appreciably to the total absorbance A at this wavelength. Only one reaction effect was observed under the given conditions, half-lives of 8–90 s. Plots of log $(A_t - A_\infty)$ against time t were linear for more than 90% of the reaction, and the corresponding slopes increase linearly with $[Fe^{3+}]$ at a given H^+ concentration (see Figure 1). Therefore

$$-d[Mo_2O_4^{2+}]/dt = k[Mo_2O_4^{2+}][Fe^{3+}] \qquad (2)$$

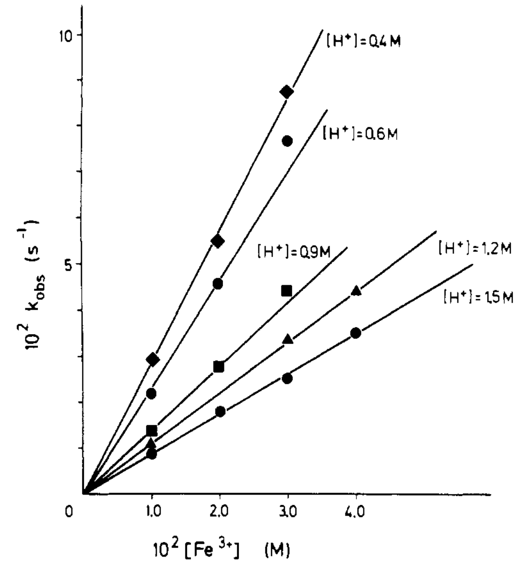


Figure 1. Oxidation of $Mo_2O_4^{2+}$ by Fe^{3+}: dependence of k_{obsd} on $[Fe^{3+}]$ and $[H^+]$ (25 °C, I = 2.0 M ($NaClO_4$), 450 nm).

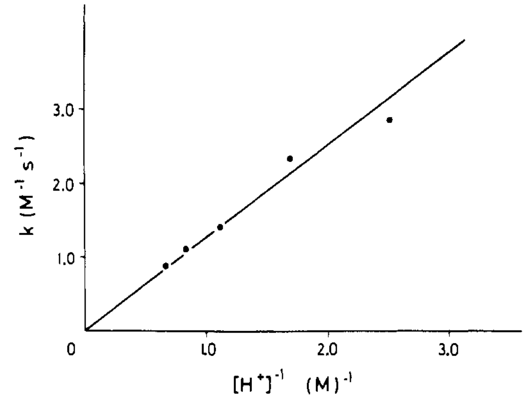


Figure 2. Oxidation of $Mo_2O_4^{2+}$ by Fe^{3+}: dependence of the second-order rate constant on $1/[H^+]$.

Within the experimental accuracy k was found to vary with $[H^+]$ according to eq 3 (see Figure 2), with k_b = 1.27 (±0.06) s^{-1}.

$$k = k_b/[H^+] \qquad (3)$$

During the oxidation of $Mo_2O_4^{2+}$ by an excess of Fe^{3+} two electrons are withdrawn from each Mo(V) dimer, e.g.

$$Mo_2O_4^{2+} + Fe^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo^VMo^{VI} + Fe^{2+} \qquad (4a)$$

$$Mo^VMo^{VI} + Fe^{3+} \xrightarrow{k_2} 2Mo^{VI}\ (\text{or}\ Mo^{VI}{}_2) + Fe^{2+} \qquad (4b)$$

Dinuclear compounds of the type Mo^VMo^{VI} are known.[16] Under the conditions of this study a cationic monomeric species, $HMoO_3^+$, is the predominant form of Mo(VI), besides smaller amounts of cationic dimeric species.[17]

Since only one reaction effect is observed, it has to be concluded that the product of the first step, Mo^VMo^{VI}, appears only as a steady-state intermediate. Introducing the steady-state approximation leads to the expression (5) for the rate law. Equation

$$-\frac{d[Mo_2O_4^{2+}]}{dt} = \frac{k_1k_2[Fe^{3+}]^2[Mo_2O_4^{2+}]}{k_{-1}[Fe^{2+}] + k_2[Fe^{3+}]} \qquad (5)$$

5 is consistent with the empirical rate law (eq 2) only if $k_2[Fe^{3+}] >> k_{-1}[Fe^{2+}]$. This condition is indeed fulfilled, as was demonstrated by the deliberate addition of 4×10^{-2} M Fe^{2+} to the

---

(6) Sasaki, Y.; Taylor, R. S.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, *396*.

(7) Sasaki, Y.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 1468.

(8) Armstrong, F. A.; Shibahara, T.; Sykes, A. G. *Inorg. Chem.* **1978**, *17*, 189.

(9) König, N. Diplom-Thesis, Anorg.-Chem. Inst., Universität Göttingen, 1978.

(10) Krüss, G. *Justus Liebigs Ann. Chem.* **1884**, *225*, 1.

(11) Ardon, M.; Pernick, A. *J. Am. Chem. Soc.* **1973**, *95*, 6871. Müller, A.; Ruck, A.; Dartmann, M.; Reinsch-Vogell, U. *Angew. Chem.* **1981**, *93*, 493.

(12) Lohmann, K. H.; Young, R. C. Inorg. *Synth.* **1953**, *4*, 97.

(13) Ford-Smith, M. H.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 1830.

(14) Ardon, M.; Pernick, A. *Inorg. Chem.* **1973**, *12*, 2484.

(15) Cayley, G. R.; Taylor, R. S.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1977**, *16*, 1377.

(16) Chaudhuri, M. *J. Chem. Soc., Dalton Trans.* **1983**, 857.

(17) Cruywagen, J. J.; Heyns, J. B. B.; Rohwer, E. F. C. H. *J. Inorg. Nucl. Chem.* **1978**, *40*, 53. Ojo, J. F.; Taylor, R. S.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 500.

reactant solutions; no effect on the rate was observed. The results reveal that under our conditions the first step (eq 4a) is rate determining, i.e. $k = k_1 = k_b/[H^+]$. The $[H^+]$ dependence of k_1 indicates that a deprotonated reactant, either $Fe(OH)^{2+}$ or $Mo_2O_4(H_2O)_5OH^+$, is involved in the first redox step. The hydrolysis constant of the Mo species is not known; only an upper limit of 10^{-2} was reported[15] for the acid dissociation constant of $Mo_2O_4(H_2O)_6^{2+}$. Three possible mechanisms may be considered:

(i) $Fe(OH)^{2+}$ is the deprotonated reactant. With $K_H = [Fe(OH)^{2+}][H^+]/[Fe^{3+}] = 1 \times 10^{-3}$ M at 25 °C, $I = 2$ M,[18] this interpretation leads to a second-order rate constant of $k_b' = k_b/K_H = 1.3 \times 10^3$ M^{-1} s^{-1} for the oxidation of $Mo_2O_4^{2+}$ by $Fe(OH)^{2+}$, a value which is at least by a factor $\sim 10^4$ higher than that for oxidation by Fe^{3+} ($k_a \leq 0.2$ M^{-1} s^{-1}, from the near-zero intercept of the plot shown in Figure 2). This difference in reactivity of the two Fe(III) species can be accounted for by assuming an outer-sphere mechanism with Fe^{3+} and an inner-sphere mechanism in the case of $Fe(OH)^{2+}$, with OH^- as the bridging ligand.[19] The exchange of water at $Mo_2O_4(H_2O)_6^{2+}$ is fast enough for such a mechanism; a rate constant of 2.9×10^4 M^{-1} s^{-1} was reported[6] for the binding of NCS^- to $Mo_2O_4^{2+}$. If charge effects are taken into account, substitution at $Mo_2O_4(H_2O)_6^{2+}$ by $Fe(OH)^{2+}$ via a dissociative mechanism[6] is expected to occur with a second-order rate constant near 2×10^3 M^{-1} s^{-1}. A comparison with the experimental value (1.3×10^3) suggests that substitution at $Mo_2O_4(H_2O)_6^{2+}$ may well be the rate-determining step in the inner-sphere oxidation by $Fe(OH)^{2+}$.

(ii) If $Mo_2O_4(H_2O)_5OH^+$ were the deprotonated reactant, then $k_b' > 1.3 \times 10^2$ M^{-1} s^{-1} and for the first-order substitution rate at $Fe(H_2O)_6^{3+}$ one would have to assume $k_s = k_b'/K_{os} > 1.3 \times 10^3$ s^{-1} (K_{os} = outer-sphere complex stability constant),a value that is appreciably higher than the water-exchange rate of $Fe(H_2O)_6^{3+}$, $k_{ex} = 1.6 \times 10^2$ s^{-1}.[20] Because of the associative nature of substitution processes at $Fe(H_2O)_6^{3+}$ a ratio $k_s/k_{ex} > 1$ cannot be excluded; however, the inner-sphere substitution rate k_s required for $Mo_2O_4(H_2O)_5(OH)^+$ as incoming ligand would be larger than those for other ligands of comparable basicity (calculated from the data in Table III of ref 20), and therefore this interpretation is considered to be less likely.

(iii) Finally, the reaction could in principle proceed also via inner-sphere structures which result from rate-determining substitution of a terminal oxygen of $Mo_2O_4^{2+}$ (Mo=O) at $Fe(H_2O)_5(OH)^{2+}$ and $Fe(H_2O)_6^{3+}$, respectively. However, the ratio $k_b'/k_a \geq 10^4$ appears to be too high for this interpretation; other ligands studied show substitution rate ratios 50–10^3.[20,21] According to Grant and Jordan[20] the absolute value of k_b' (1.3×10^3) would also be unusually high if compared (after correction for the charge type) to a series of other substitution processes at $Fe(OH)^{2+}$. The first mechanism mentioned above (i) is therefore considered to be the most likely.

$Mo_2O_4^{2+}$ + $Fe(phen)_3^{3+}$. The standard oxidation potential of $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ is appreciably higher than that of the Fe–aquo complexes, and the redox equilibrium corresponding to eq 1 lies very far on the side of the products. The kinetic studies have been carried out at $[H^+] = 0.5$–1.5 M ($HClO_4$), $I = 2.0$ M ($NaClO_4$), under pseudo-first-order conditions, either with $Mo_2O_4^{2+}$ in excess ($[Mo_2O_4^{2+}] = 1.1 \times 10^{-4}$–$1.1 \times 10^{-3}$ M, $[Fe(phen)_3^{3+}] = 5.6 \times 10^{-5}$ M) or with $Fe(phen)_3^{3+}$ in excess ($[Fe(phen)_3^{3+}] = (0.5$–$2.6) \times 10^{-4}$ M, $[Mo_2O_4^{2+}] = (0.5$–$1.0) \times 10^{-5}$ M). In the latter case the concentrations of $Mo_2O_4^{2+}$ were necessarily very low, because of the limited solubility of $Fe(phen)_3(ClO_4)_3$ in perchlorate solutions. The progress of the reaction was followed by monitoring the strong absorption of the $Fe(phen)_3^{2+}$ product at 510 nm. In all experiments a single exponential reaction effect was observed (half-lives 10–740 s), with $k_{obsd} = k'[Fe(III)]$ or $k''[Mo_2O_4^{2+}]$, respectively, depending which reactant is in excess (Fe(II) and Fe(III) denote the phen complexes). Assuming a two-step mechanism as outlined above (eq 4), one has to conclude again that the half-oxidized Mo(V) dimer represents a steady-state intermediate and that the first step is rate determining. Then

$$\frac{d[Fe(II)]}{dt} = 2k_1[Fe(III)][Mo_2O_4^{2+}] \qquad (6)$$

If Fe(III) is in excess, mass conservation conditions and the stoichiometry lead to $k' = k_{obsd}/[Fe(III)] = k_1$. With $Mo_2O_4^{2+}$ in excess is obtained $k'' = k_{obsd}/[Mo_2O_4^{2+}] = 2k_1$. In the latter case the dependence of the second-order rate constant on $[H^+]$ is given by $k_1 = k_a + k_b/[H^+]$, with $k_a = 13.5$ M^{-1} s^{-1} and $k_b = 9$ s^{-1}. The experiments with an excess of $Fe(phen)_3^{3+}$ yielded $k_a = 11.5$ M^{-1} s^{-1} and $k_b = 4$ s^{-1}. While the values of k_a of the two sets are in fair agreement, those of k_b are not. The experimental uncertainties are larger for the runs with an excess of Fe(III) since the slowness of the redox process (low reactant concentrations, half-lives 170–740 s) leads to some decomposition of the Fe(phen) complexes during the time of the reaction.[22] Therefore, the higher value of k_b is probably more reliable. Similar rates were reported by Sykes et al.[15] for this reaction under somewhat different conditions (ionic strength 1.0 M, adjusted with $LiClO_4$): $k_a = 31$ M^{-1} s^{-1}, $k_b = 6.0$ s^{-1}.

The term $k_b/[H^+]$ may be assigned to a contribution of the reaction path $Fe(phen)_3^{3+} + Mo_2O_4(H_2O)_5OH^+$. It can also not be excluded that the observed modest variation of k_1 with $[H^+]$ is in part an effect of the changes of medium (0.5 M $HClO_4$ + 1.5 M $NaClO_4$ to 1.5 M $HClO_4$ + 0.5 M $NaClO_4$) on the rate between $Fe(phen)_3^{3+}$ and $Mo_2O_4^{2+}$. A slight decrease in rate with increasing H^+ concentration was observed also for the oxidation of Fe^{2+} by $Fe(phen)_3^{3+}$ and was discussed in terms of a less reactive protonated complex species, $HFe(phen)_3^{4+}$.[23] The contribution of the reaction path with $Mo_2O_4(H_2O)_5OH^+$ is therefore difficult to assess quantitatively.

Since $Fe(phen)_3^{3+}$ is inert toward substitution and phen ligands are unable to act as bridging ligands, electron transfer between $Fe(phen)_3^{3+}$ and the Mo(V) dimer must proceed by an outer-sphere mechanism. This outer-sphere path (k_a) is about 100 times less efficient than the inner-sphere mechanism in the case of $Fe(OH)^{2+}$ (see above). On the other hand, outer-sphere oxidation of $Mo_2O_4^{2+}$ by $Fe(phen)_3^{3+}$ ($k = 13$ M^{-1} s^{-1}) is appreciably faster than oxidation by Fe^{3+} ($k \leq 0.2$ M^{-1} s^{-1}), which probably proceeds also by an outer-sphere mechanism. The higher rate of oxidation by $Fe(phen)_3^{3+}$ as compared to that by Fe^{3+} can readily be rationalized in terms of Marcus' theory by the larger $\Delta G°$ and the much higher self-exchange rate of the Fe(II,III) species.[24]

$Mo_2O_2S_2^{2+}$ + $Fe(phen)_3^{3+}$. The structure of the $(\mu\text{-}S)_2Mo^V{}_2$ complex is analogous to that of the oxo complex given above, $(H_2O)_3MoO(\mu\text{-}S)_2MoO(H_2O)_3^{2+}$. It shows a remarkable stability toward strong acids; even in 10 M HCl no decomposition is observed.[25] Our measurements of the absorption spectrum agree well with literature data.[8,25] The stoichiometry of the reaction with $Fe(phen)_3^{3+}$ could not be established since at comparable low concentrations of Mo(V) and Fe(III) the redox reaction is very slow and the gradual spontaneous decomposition of the Fe(phen) complexes overlaps with the redox process.

Kinetic investigations were carried out with $[Mo_2O_2S_2^{2+}] = 2.5 \times 10^{-3}$–$8.1 \times 10^{-3}$ M and $[Fe(phen)_3^{3+}] = 1.8 \times 10^{-4}$ M in 1 M $HClO_4$. At these concentration conditions the rate of reaction is fast enough in order to keep the extent of the spontaneous decomposition of the Fe–phen complexes at a moderate level (ca. 6% in 30 min). The reaction was monitored at 510 mn, the absorption maximum of the Fe(II) product. The absorbance approaches a value that corresponds to practically complete re-

---

(18) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; p 230.

(19) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225.

(20) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.

(21) Perlmutter-Hayman, B.; Tapuhi, E. *J. Coord. Chem.* **1976**, *6*, 31.

(22) Dickens, J. E.; Basolo, F.; Neumann, N. M. *J. Am. Chem. Soc.* **1957**, *79*, 1286. Lee, T. S.; Kolthoff, I. M.; Leussing, D. L. *J. Am. Chem. Soc.* **1948**, *70*, 3596.

(23) Sutin, N.; Gordon, B. M. *J. Am. Chem. Soc.* **1961**, *83*, 70.

(24) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(25) Spivack, B.; Dori, Z. *J. Chem. Soc., Chem. Commun.* **1973**, 909.

duction of the Fe(III) complex. Despite the large excess of $Mo_2S_2S_2^{2+}$, the time dependence of the change in adsorption can not be described by a single-exponential function. This behavior may be accounted for by the following considerations: We assume again a two-step mechanism to apply, with Mo^VMo^{VI} as a steady-state intermediate, and obtain the rate law

$$\frac{d[Fe(II)]}{dt} = \frac{2k_1k_2[Mo_2O_2S_2^{2+}][Fe(III)]^2}{k_{-1}[Fe(II)] + k_2[Fe(III)]} \qquad (7)$$

Now, however, $k_{-1}[Fe(II)]$ is not always small compared to $k_2[Fe(III)]$ during the redox reaction; i.e., the first step (k_1) is rate determining only during the early stages of the reaction. After the substitution $[Fe(II)] = [Fe(III)]_0 - [Fe(III)]$, where $[Fe(III)]_0$ denotes the initial concentration of $Fe(phen)_3^{3+}$, eq 7 can be integrated and gives

$$\frac{[Fe(III)]_0}{[Fe(III)]} + \frac{k_{-1} - k_2}{k_{-1}} \ln \frac{[Fe(III)]}{[Fe(III)]_0} = \frac{2k_1k_2}{k_{-1}}[Mo_2O_2S_2^{2+}]t + 1 \qquad (8)$$

Since $[Fe(III)]_0/[Fe(III)] = (A_\infty - A_0)/(A_\infty - A_t)$, corresponding values of t and $[Fe(III)]_0/[Fe(III)]$ can be read from the experimental curves and introduced into eq 8 for a fitting of $(k_{-1} - k_2)/k_{-1}$ and k_1k_2/k_{-1}. This procedure allows the determination of k_1 and k_2/k_{-1}. The fit is not perfect, and k_2/k_{-1} can be evaluated only approximately, $k_1 = 0.5\ (\pm 0.1)\ M^{-1}\ s^{-1}$, $k_2/k_{-1} = 0.85\ (\pm 0.4)$.

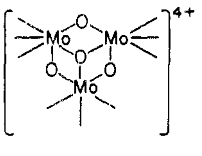
The assumption that the intermediate Mo^VMo^{VI} appears only as a steady state was introduced by analogy with the situation for the oxidation of $Mo_2O_4^{2+}$ but is without further support. If this assumption is abandoned, the kinetics are described by a system of two nonlinear differential equations for which there is no simple solution. Therefore, only the initial slopes of the reaction curves were evaluated. The initial slopes are defined by

$$(dA/dt)_0 = k[Mo_2O_2S_2^{2+}][Fe(III)]_0\epsilon_{Fe(II)} \qquad (9)$$

and can be measured with sufficient accuracy. At constant $[Fe(III)]_0$ a plot of $(dA/dt)_0$ vs. $[Mo_2O_2S_2^{2+}]$ yields a straight line, the slope of which gives $k = 0.8\ (\pm 0.1)\ M^{-1}\ s^{-1}$. If a true intermediate (Mo^VMo^{VI}) is formed, then $k = k_1$, where k_1 denotes the rate constant of the first electron-transfer step. On the other hand, if a steady-state mechanism operates, then $k = 2k_1$ (see eq 7) and $k_1 = 0.4\ M^{-1}\ s^{-1}$, a value that is in good agreement with the one evaluated via eq 8 (see above).

The first step of the overall reaction is a one-electron transfer (outer sphere) from $Mo_2O_2S_2^{2+}$ to $Fe(phen)_3^{3+}$, which occurs with a second-order rate constant of 0.8 or 0.4 $M^{-1}\ s^{-1}$ (depending on the mechanistic model) in 1 M $HClO_4$. This rate is lower by more than 1 order of magnitude than that in the system $Mo_2O_4^{2+}$ + $Fe(phen)_3^{3+}$. Consistent with the low reductive power of $Mo_2O_2S_2^{2+}$ are the observations that this complex is not noticeably oxidized by air and that after the addition of Fe^{3+} no oxidation was found to occur within 24 h. Apparently μ-thio ligands stabilize the Mo(V) state relative to Mo(VI) more than μ-oxo ligands.

$Mo_3O_4^{4+}$ + $Fe(phen)_3^{3+}$. Since its first synthesis in 1966, the structure of Mo(IV) in aqueous solution has been discussed in several publications. Only in 1978 was it finally established that it is a trimeric species, characterized by a $Mo_3O_4^{4+}$ core:[26]



In weakly complexing aqueous solutions three water molecules are coordinated to each of the Mo(IV) ions.[27] It had been reported that perchlorate is reduced to Cl^- by $Mo_3O_4^{4+}$.[28] Therefore, the present studies on the oxidation by $Fe(phen)_3^{3+}$ have been carried out in aqueous HCl in which the Mo(IV) complex is stable.[27] The stoichiometry of the oxidation of $Mo_3O_4^{4+}$ by $Fe(phen)_3^{3+}$ was established from spectrophotometric measurements (510 nm, absorption maximum of the Fe(II) product) and conforms to the reaction

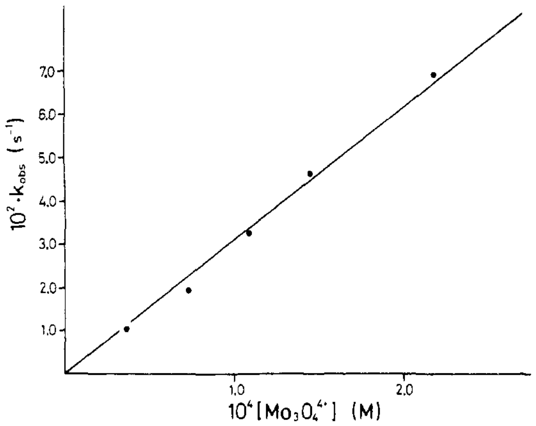


Figure 3. Oxidation of $Mo_3O_4^{4+}$ by $Fe(phen)_3^{3+}$: dependence of k_{obsd} on $[Mo_3O_4^{4+}]$ (25 °C, 1.0 M HCl, I = 2.0 M (NaCl), 510 nm).

$$6Fe(phen)_3^{3+} + Mo_3O_4^{4+} \rightleftharpoons 6Fe(phen)_3^{2+} + 3Mo(VI) \qquad (10)$$

The kinetics of this redox reaction were investigated with $[Mo_3O_4^{4+}] = 3.7 \times 10^{-5}$–$2.2 \times 10^{-4}$ M, $[Fe(phen)_3^{3+}] = 4 \times 10^{-5}$ M (25 °C, 1.0 M HCl, I = 2.0 M (NaCl)). Under these conditions the equilibrium is completely on the side of the products and the back-reaction can be neglected. Plots of ln $(A_\infty - A_t)$ vs. time were linear for more than 90% of the reaction, with slopes that are proportional to $[Mo_3O_4]$, as shown in Figure 3. The rate law can therefore be written in the form

$$d[Fe(II)]/dt = k[Mo_3O_4^{4+}][Fe(III)] \qquad (11)$$

where $k = 306\ M^{-1}\ s^{-1}$ (25 °C 1 M HCl, I = 2.0 M (NaCl)). The first-order dependence of the rate on [Fe(III)] demonstrates that the first electron-transfer step (outer sphere) is rate determining for the overall process. Since six Fe(II) complexes are formed per $Mo_3O_4^{4+}$ disappearing, it follows that $k = 6k_1$, where $k_1 = 51\ M^{-1}\ s^{-1}$ is the second-order rate constant of the first step. The stoichiometry explains also why an exponential reaction curve was obtained even when the initial concentrations of the two reactants were about equal: only one-sixth of the $Mo_3O_4^{4+}$ is needed to reduce all of the Fe(III); i.e., $[Mo_3O_4^{4+}]$ is almost constant.

While this work was in progress, a study by Sykes et al.[29] on the oxidation of $Mo_3O_4^{4+}$ was published, including oxidation by $Fe(phen)_3^{3+}$ in perchlorate solution (actually, after a suitable treatment $Mo_3O_4^{4+}$ is stable in perchlorate solution for at least 1 day[29]). The basic features of the reaction in perchlorate solution are the same as reported here for chloride solutions (stoichiometry, pseudo-first-order kinetics, rate-determining step). However, the second-order rate constant of the rate-determining step in 1 M $HClO_4$, I = 2.0 M ($LiClO_4$), is only 0.47 $M^{-1}\ s^{-1}$, as compared to 51 $M^{-1}\ s^{-1}$ in 1 M HCl, I = 2.0 M (NaCl). There is strong evidence that in 2 M chloride solutions Cl^- is coordinated to the $Mo_3O_4(H_2O)_9^{4+}$ cation (replacing water ligands); for instance, the maximum of the absorption spectrum of $Mo_3O_4^{4+}$ is shifted from 505 to 515 nm on going from a noncomplexing medium to 2 M chloride solutions,[30] and ϵ_{max} increases from 180 to 218 $M^{-1}\ cm^{-1}$. Coordination of Cl^- to $Mo_3O_4^{4+}$ strongly reduces the unusually large electrostatic repulsion between the reactants (charge

---

(26) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252.
(27) Murmann, R. K.; Shelton, M. E. *J. Am. Chem. Soc.* **1980**, *102*, 3984.
(28) Ardon, M.; Bino, A.; Yahav, G. *J. Am. Chem. Soc.* **1976**, *98*, 2338.
(29) Harmer, M. A.; Richens, D. T.; Soares, A. B.; Thornton, A. T.; Sykes, A. G. *Inorg. Chem.* **1981**, *20*, 4155.
(30) Souchay, P.; Cadiot, M.; Viossat, B. *Bull. Soc. Chim. Fr.* **1970**, 892.

type +4, +3). It is certainly this electrostatic factor that contributes most to the observed difference in rate (100-fold) of this outer-sphere reaction in the two media.

Acknowledgment. We are grateful to the DAAD (Deutscher Adademischer Austauschdienst) for a fellowship to C.M. and to the Universidad de Concepcion for partial support to C.M.

Registry No. $Mo_2O_4^{2+}$, 40804-49-7; $Mo_2O_2S_2^{2+}$, 52700-51-3; $Fe(H_2O)_6^{3+}$, 15377-81-8; $Fe(phen)_3^{3+}$, 13479-49-7; $Mo_3O_4^{4+}$, 74353-85-8.

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332,
and Istituto di Teoria e Struttura Elettronica, Consiglio Nationale della Ricerche, 00016 Monterotondo Stazione, Roma, Italy

Spectroelectrochemistry of a μ-Nitrido-Bridged Iron Phthalocyanine Dimer

LAWRENCE A. BOTTOMLEY,[*†] JEAN-NOEL GORCE,[†] VIRGIL L. GOEDKEN,[‡] and CLAUDIO ERCOLANI[‡]

Received May 30, 1985

The synthesis of (μ-nitrido)bis[(phthalocyaninato)iron($\mathrm{III}^{1}/_{2}$)], $[(Pc)Fe]_2N$, has been achieved, and its physicochemical properties have been determined. The electrochemistry of $[(Pc)Fe]_2N$ was studied in neat pyridine at a Pt-button electrode. One single-electron-oxidation and three single-electron-reduction processes were observed for the dimer within the accessible potential window of the solvent-supporting electrolyte system. Variable potential sweep rate cyclic voltammetric experiments verified the chemical reversibility of the oxidation and reduction processes at short times. Coulometry confirmed that the first oxidation and first reduction steps each involved the passage of 1 equiv of charge/dimer. Spectra taken on the electrogenerated dimer cation and anion verified complete retention of the single-atom bridging moiety. The other electron transfers resulted in the decomposition of the dimer. An electron-transfer pathway based upon the combined voltammetric, spectroelectrochemical, and coulometric results is proposed and compared to that observed for the analogous porphyrin complex (μ-nitrido)bis[(tetraphenylporphinato)iron($\mathrm{III}^{1}/_{2}$)], $[(TPP)Fe]_2N$.

Introduction

Until recently, the μ-nitrido dimer of iron tetraphenylporphyrin, $[(TPP)Fe]_2N$, represented the only well-characterized example of an N-bridged complex containing two first-row transition-metal atoms. The physicochemical properties of this complex have been the subject of considerable interest.[1-5] Its electronic structure has been examined, and an orbital diagram that accounts for the observed structural and magnetic properties has been constructed.[6]

The surprising stability of the μ-nitrido complex, $[(TPP)Fe]_2N$, suggested that, in general, μ-nitrido bridges might be more stable than previously thought. Accordingly, we have sought to synthesize and characterize related species in order to place the $[(TPP)Fe]_2N$ complex within a general framework of μ-bridged and μ-nitrido-bridged complexes.[7,8] The obvious similarities between porphyrins and phthalocyanines (dianionic charge, tetraaza donor atoms, aromatic planar ligand skeleton) suggested the μ-nitrido complex of (Pc)Fe as the most reasonable starting place to synthesize other nitrido dimers. The thermal decomposition of $(TPP)Fe(N_3)$ was the route used for the synthesis[1a] of $[(TPP)Fe]_2N$. As previously described[9], the thermal decomposition of NaN_3 in boiling α-chloronaphthalene in the presence of (Pc)Fe produced $[(Pc)Fe]_2N$. Although not isolated and definitely characterized, a similar $(Pc)Fe(N_3)^-$ derivative is very likely present as an unstable intermediate in the preparation of $[(Pc)Fe]_2N$.

Unlike $[(TPP)Fe]_2N$, $[(Pc)Fe]_2N$ is highly insoluble in nondonor solvents and only sparingly soluble in donor solvents such as nitrogenous bases. This property severely impedes studies of the physical properties of this complex. The aim of the present study was mainly devoted to the exploration of the physicochemical properties of $[(Pc)Fe]_2N$ in pyridine and to compare these properties with those determined for $[(TPP)Fe]_2N$ under identical conditions.

Experimental Section

Materials. $[(TPP)Fe]_2N$ was synthesized by the method of Summerville and Cohen.[1a] Solid samples of $[(TPP)Fe]_2N$ were slowly oxidized in air over the course of several weeks. Pure $[(TPP)Fe]_2N$ was obtained by the following chromatographic procedure. A saturated solution of the crude material in CH_2Cl_2 was prepared and applied to a column of freshly activated basic alumina. Elution with CH_2Cl_2 yielded a fast moving greenish red band, which was identified as the μ-oxo dimer by its characteristic visible spectrum. Gradient elution (from 0.0 to 100%) with freshly distilled tetrahydrofuran (THF) produced a dark red band. Spectral measurements identified this fraction as pure $[(TPP)Fe]_2N$. Elution with 1:9 methanol/THF yielded the dimeric cation, $([(TPP)Fe]_2N)^+$. This material was reduced to the neutral compound either by electrochemical means or by treatment with a deoxygenated aqueous solution of sodium dithionite.

(Pc)Fe was purchased from Eastman Kodak and purified by vacuum sublimation to remove insoluble oxide impurites. In a typical preparation of $[(Pc)Fe]_2N$, 1.0 g of (Pc)Fe was placed in 20 mL of α-chloronaphthalene and heated to the boiling point of 265 °C. A large excess, 1.0 g, of NaN_3 was added with constant stirring for 1 h. During this period, N_2 gas evolved and the color of the solution changed from the typical blue-green of (Pc)Fe to the pure dark blue-purple of the suspended product. Because the reaction is heterogeneous, it is difficult to determine visually when the reaction is complete. Reaction progress was monitored by taking small aliquots of the reaction mixture, filtering the sample, washing the filtrate with water and methanol, and then drying the sample. The IR spectrum measured for material treated in this fashion was then examined for the disappearance of the N_3^- absorption and the appearance of the antisymmetric Fe–N–Fe absorption, which is one of the most intense in the spectrum. After the reaction was completed, the reaction mixture was cooled and the product filtered, washed with chloroform (to remove α-chloronaphthalene), alcohol, and finally water (to remove any excess N_3^- and other water-soluble impurities), and then dried under vacuum; yield 90%. Anal. Calcd for $Fe_2C_{64}H_{32}N_{17}$: C, 66.80; H, 2.80; N, 20.69. Found: C, 66.68; H, 2.85; N, 20.51.

In a typical preparation of $[(py)(Pc)Fe]_2N)PF_6$, a suspension of $[(Pc)Fe]_2N$ in chloroform and a solution of 1.0 g of oxidant (e.g. ferro-

---

[†] Georgia Institute of Technology.

[‡] Consiglio Nationale della Ricerche.

(1) (a) Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 1747–1752. (b) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623–6628.

(2) (a) Schick, G. A.; Bocian, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 7982–7984. (b) *Ibid.* **1983**, *105*, 1830–1838. (c) Schick, G. A.; Findsen, E. W.; Bocian, D. F. *Inorg. Chem.* **1982**, *21*, 2885–2887.

(3) (a) Kadish, K. M.; Cheng, J. S.; Cohen, I. A.; Summerville, D. A. *ACS Symp. Ser.* **1977**, *No. 38*, Chapter 5. (b) Kadish, K. M.; Bottomley, L. A.; Brace, J. G.; Winograd, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4341–4344. (c) Kadish, K. M.; Rhodes, R. K.; Bottomley, L. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3195–3200.

(4) Bottomley, L. A.; Garrett, B. B. *Inorg. Chem.* **1982**, *21*, 1260.

(5) (a) English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1983**, *22*, 367–368. (b) Bocian, D. F.; Findsen, E. W.; Hofmann, J. A., Jr.; Schick, G. A.; English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1984**, *23*, 800–807. (c) English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1985**, *24*, 121–122.

(6) Tatsumi, K.; Hoffmann, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3328–3341.

(7) Ercolani, C.; Rossi, G.; Monacelli, F. *Inorg. Chim. Acta* **1980**, *44*, L215–L216.

(8) Ercolani, C.; Gardini, M.; Monacelli, F.; Pennesi, G.; Rossi, G. *Inorg. Chem.* **1983**, *22*, 2584–2589.

(9) Goedken, V. L.; Ercolani, C. *J. Chem. Soc., Chem. Commun.* **1984**, 378–379.

0020-1669/85/1324-3733$01.50/0