

The different attachment mode of the BH_4 group in the two isomorphous copper and cobalt analogues is not surprising, since the isomorphism of these complexes is mainly due to the requirements of the triphos ligand. As a matter of fact, all the compounds of the series (triphos)M(L) are isomorphous in spite of the nature of the ancillary ligand ($\text{L} = \text{I},^{15} \text{CS}_2,^{16} \text{SO}_2,^6 \text{SO}_4,^{17} \text{SeO}_4,^{17} \text{and} \text{BH}_4^{6,18}$).

Registry No. (triphos)Cu(BH_4), 82678-89-5.

Supplementary Material Available: A listing of structure factor amplitudes and Table II giving anisotropic thermal parameters (13 pages). Ordering information is given on any current masthead page.

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Kinetics of the Permanganate Ion Oxidation of the Bis(μ -oxo)bis(oxomolybdate(V)) Ion

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Studies of the kinetics behavior of the permanganate ion with one-electron inorganic reductants in acidic media have shown the $\text{Mn(VII)} \rightarrow \text{Mn(VI)}$ step to be rate determining, although the MnO_4^- ion is a strong multiequivalent oxidant.^{2,3} Since the reductant ions have been limited to those that undergo a one-electron change, it would be of interest to investigate the kinetic behavior of MnO_4^- with a reductant system that provides the opportunity of a two-electron change. Such a reductant might represent conditions in which the MnO_4^- ion would react via a two-electron step ($\text{Mn(VII)} \rightarrow \text{Mn(V)}$). The reactions of $\text{Pt(II)} \rightarrow \text{Pt(IV)}^4$ and $\text{U(IV)} \rightarrow \text{U(VI)}^5$ with MnO_4^- have been characterized, by means of ^{18}O -exchange experiments, as occurring via oxygen atom transfer.

The bis(μ -oxo)bis(oxomolybdate(V)) ion, $\text{Mo}_2\text{O}_4^{2+}$, was chosen because of its dimeric nature,⁶⁻⁸ its ability to be quantitatively oxidized to Mo(VI) by MnO_4^- , and the possible detection of a mixed-valence ($\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$) intermediate.¹⁰ There also exists the possibility of estimating the electrode potential for the $\text{Mo}^{\text{V}}_2 \rightarrow \text{Mo}^{\text{V}}\text{Mo}^{\text{VI}} + \text{e}^-$ reaction.¹¹ Murmann has shown the rate of oxygen exchange between $\text{Mo}_2\text{O}_4^{2+}$ and solvent and the rate of the opening of the bridging ring to be slow.¹² Redox experiments by Sykes have led to the characterization of the aquo dimer as an outer-sphere reactant.¹³

Experimental Section

The bis(μ -oxo)bis(oxomolybdate(V)) complex was prepared by three different methods. (a) Reduction of Na_2MoO_4 (8.0 g) in 250 mL of 3 M HCl was accomplished at 80 °C by slow addition with stirring of $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ (6 g).^{9,13} The brown Mo^{V}_2 solution was heated for 2-3 h to remove excess hydrazine and reduce the volume. This method

Table I. Rate Constants, k_{obsd} , for the $\text{MnO}_4^-/\text{Mo}_2\text{O}_4^{2+}$ Reaction ($T = 25.0$ °C, $[\text{H}^+] = 0.50$ M, $\mu = 1.00$ (LiClO_4))

$10^3 \times$ [$\text{Mo}_2\text{O}_4^{2+}$] ₀ , M	$10^5 \times$ [MnO_4^-] ₀ , M	k_{obsd} , s^{-1}	$10^3 \times$ [$\text{Mo}_2\text{O}_4^{2+}$] ₀ , M	$10^5 \times$ [MnO_4^-] ₀ , M	k_{obsd} , s^{-1}
0.90	4.68	5.35	1.47	7.72	8.00
2.29	4.68	12.9	2.29	9.37	12.0
3.37	7.72	19.2	5.38	7.72	31.0
4.40	11.3	23.2	6.60	15.1	36.6 ^a
4.87	4.91	27.0	6.60	15.1	36.5 ^b
5.28	2.85	29.5 ^c			

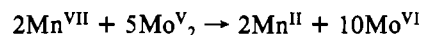
^a $[\text{Mo(VI)}]_0 = 4.2 \times 10^{-3}$ M. ^b $[\text{Mo(VI)}]_0 = 2.1 \times 10^{-3}$ M.
^c $\text{HClO}_4/\text{HTFMS}$ mixture.

was discontinued as it gave low stoichiometric values and erratic rate constants. The results were presumably due to the presence of N_2H_5^+ . (b) Reduction of the $\text{Na}_2\text{MoO}_4/3\text{M HCl}$ solution was accomplished by shaking with metallic mercury.¹⁴ The Hg and Hg_2Cl_2 were filtered, and the solution was stored at 5 °C over fresh Hg. (c) Dimerization of monomeric Mo(V) was accomplished by dissolving weighed samples of $(\text{NH}_4)_2(\text{MoOCl}_5)$ (gift from Climax Molybdenum) in 2 M HCl, followed by aqution for several hours.¹⁵

Chloride-free solutions were obtained by diluting an aliquot of the dimer/HCl solution with distilled water such that $[\text{H}^+] < 0.1$ M and collecting the dimer on a Dowex 50-X8 (50-100 mesh) or Amberlite IR-120 ion-exchange column (acid form). The column was washed free of Cl^- with deoxygenated distilled water and the $\text{Mo}_2\text{O}_4^{2+}$ ion eluted with deoxygenated HClO_4 or trifluoromethanesulfonic acid (HTFMS) of the desired molarity and ionic strength ($\mu = 1.0$, LiClO_4). While the decomposition of the dimer is slower in HTFMS than in HClO_4 , identical kinetic results were obtained. The $[\text{Mo}_2\text{O}_4^{2+}]$ was determined spectrophotometrically at $\lambda = 384$ nm ($\epsilon = 103 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁶ Total Mo analysis was accomplished by H_2O_2 oxidation.¹⁷ LiClO_4 (G. F. Smith) was recrystallized twice from distilled water, and stock solutions were standardized by ion-exchange methods. The permanganate stock solution was standardized against As_2O_3 . Reaction MnO_4^- solutions were prepared by diluting aliquots of the standardized stock with distilled water or $\text{H}^+/\text{LiClO}_4$ solutions of known molarity and ionic strength. Solutions of HTFMS are slowly oxidized by MnO_4^- .

Results

The reaction stoichiometry in 0.4-1.0 M HClO_4 ($\mu = 1.0$) was shown by visual and spectrophotometric titrations at 384 and 524 nm ($\lambda_{\text{max}}(\text{MnO}_4^-)$) to correspond to the ratio of 2.51 ± 0.30 (mol of $\text{Mo}_2\text{O}_4^{2+}$ consumed/mol of MnO_4^- added). The overall reaction can be represented by the equation



With use of pseudo-first-order conditions ($[\text{Mo}_2\text{O}_4^{2+}]_0 \geq$

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Table II. Dependence of k_2 on Hydrogen Ion Concentration ($\mu = 1.0$ (LiClO₄), $T = 25.0$ °C)

[H ⁺], M	$10^{-3}k_2$, M ⁻¹ s ⁻¹	[H ⁺], M	$10^{-3}k_2$, M ⁻¹ s ⁻¹
0.06	5.68 ^a	0.65	5.61 ^a
0.12	5.43 ^a	0.70	5.55 ^a
0.18	5.30 ^a	0.70	5.78 ^a
0.30	5.60	0.75	5.70 ^a
0.30	5.43 ± 0.39	1.00	5.77 ^a
0.40	5.51	1.00	5.82
0.50	5.59 ± 0.18	1.00	5.61
0.50	5.45	1.20	5.75 ^{a,b}
0.50	5.48 ^a	1.20	5.73 ^b
0.60	5.55	1.50	5.80 ^b
0.60	5.65	1.50	5.95 ^{a,b}

^a HClO₄/HTFMS mixture. ^b $\mu = [\text{H}^+]$.

Table III. Dependence of k_2 on Temperature ($[\text{H}^+] = 0.50$ M, $\mu = 1.0$ (LiClO₄))

T , °C	$10^{-3}k_2$, M ⁻¹ s ⁻¹	T , °C	$10^{-3}k_2$, M ⁻¹ s ⁻¹	T , °C	$10^{-3}k_2$, M ⁻¹ s ⁻¹
12.0	2.38	17.8	3.67	25.0	5.63
14.5	2.60	21.5	4.42	25.0	5.55 ^a
15.0	2.77	23.7	5.10	26.5	6.00

^a HClO₄/HTFMS mixture.

25[MnO₄⁻]₀), the decay of the MnO₄⁻ absorbance at 524 nm was followed via stopped-flow instrumentation. The rate expression $-d[\text{MnO}_4^-]/dt = 2k_{\text{obsd}}[\text{MnO}_4^-]$ was found to be valid for more than 4 half-lives. The rate constant, k_{obsd} , was obtained by a computer fit of the expression $\ln(A_t - A_\infty)$ vs. time. A_t and A_∞ represent the absorbances at time t and infinite time, respectively. A plot of k_{obsd} vs. $[\text{Mo}_2\text{O}_4^{2+}]_0$ (Table I, Figure 1) was linear with a zero intercept and showed no trend as $[\text{MnO}_4^-]_0$ was increased (Figure 1). This indicated the expression rate = $k_2[\text{MnO}_4^-][\text{Mo}_2\text{O}_4^{2+}]$ was adequate to account for the behavior of the reaction. Plots from several experiments in which the buildup of products was appreciable (stoichiometric ratio <15) showed no significant deviation from linear first-order behavior.

Experiments performed between 350 and 475 nm showed no evidence of an absorbing intermediate. The absorbance values at $t = 0$, A_0 , agreed with values calculated with use of the appropriate molar absorption coefficients and initial reactant concentrations.

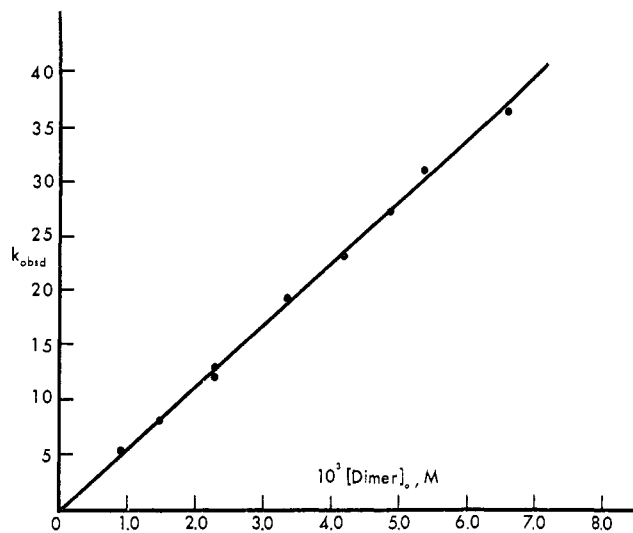
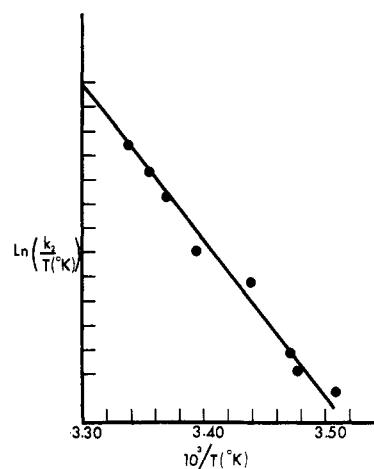
A plot of k_2 vs. $[\text{H}^+]$ was linear (Table II) with a nonzero intercept, and the expression $k_2 = k_0 + k_{2\text{H}}[\text{H}^+]$ was used to describe the dependence of the reaction between Mn(VII) and the Mo(V) dimer on hydrogen ion concentration. The values for the acid-independent, k_0 , and -dependent, $k_{2\text{H}}$, pathways are $(5.42 \pm 0.42) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $(2.44 \pm 0.21) \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$, respectively. Alteration of the ionic strength from $\mu = 0.5$ to $\mu = 1.03$ ($[\text{H}^+] = 0.50$ M, $T = 27.0$ °C) and from $\mu = 0.7$ to $\mu = 1.50$ ($[\text{H}^+] = 0.70$ M, $T = 25.0$ °C) showed no variation in k_2 .

The activation parameters, $\Delta H^\ddagger = 10.8 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -5.1 \pm 1$ eu, were obtained from a least-squares fit of

Table IV. Data Summary for Several Mo₂O₄²⁺ and VO²⁺ Oxidation Reactions

reactants	k''_{H} , M ⁻¹ s ⁻¹	k_0 , M ⁻¹ s ⁻¹	k'_{H} , ^a M ⁻¹ s ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol K)	ref
Mo ₂ O ₄ ²⁺ + Fe(phen) ₃ ³⁺	6.0	31		10.9, 8.9	-18.4, -21.7	13
+ IrCl ₆ ²⁻	0.052	0.114				13
+ [(Co(NH ₃) ₅) ₂ O ₂] ⁵⁺		4.3×10^{-6}		18.5	-21	13
+ MnO ₄ ⁻		5.42×10^3	97.0×10^3	10.8	-5.1	this work
VO ²⁺ + MnO ₄ ⁻		72.9	9.63×10^3	10.8	-13	2
+ IrCl ₆ ²⁻	97×10^3	0.027				24
+ Mn ³⁺	0.38×10^3	88.7		9.6, 11.1	-14, -11.5	25 ^b

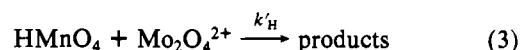
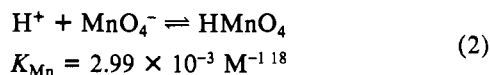
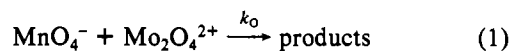
^a The rate constants refer to the expression where $k_2 = k''_{\text{H}}K[\text{H}^+]^{-1} + k_0 + k'_{\text{H}}K[\text{H}^+]$. ^b $\mu = 3.0$ M (NaClO₄).

Figure 1. Plot of k_{obsd} vs. $[\text{Mo}_2\text{O}_4^{2+}]_0$.Figure 2. Plot of $\ln(k_2/T)$ vs. $1/[T (\text{K})]$.

$\ln(k_2/T)$ vs. $1/[T (\text{K})]$ (Table III and Figure 2).

Discussion

The presence of a proton-independent and proton-dependent pathway has come to be a recognized feature for reactions of MnO₄⁻ with inorganic ions. The observed rate equation and hydrogen ion dependence can be accommodated by the mechanism given by eq 1-3. In these reactions, the proton-



dependent pathways remain the more rapid step due to the large thermodynamic driving force of the redox reaction derived from the couple $\text{HMnO}_4/\text{HMnO}_4^-$ ($E^\circ \approx 1.11 \text{ V}$).^{2b}

Although the form of the rate law provides no detailed information concerning an inner- or outer-sphere mechanism, the aquomolybdenum(V) dimer has been compared in recent studies to aquovanadium(IV).^{19,20} Both ions are d^1 systems and are similar in their overall structure as both contain terminal oxo groups. Solid-state structural data show a lengthening of the bond to the trans ligand for various compounds of both ions, and it is thought that the terminal oxo group weakens the bond trans to it.²¹ This weakened bond is felt to be responsible for the rapid exchange of the trans ligand with solvent in $\text{Mo}_2\text{O}_4(\text{NCS})_6^{4-}$.²² A comparison of the rate constants from the expression $k_2 = k_O + k'_H K_{\text{Mn}}[\text{H}^+]$ for the reaction of MnO_4^- with the aquo dimer and VO^{2+} shows the dimer is more rapidly oxidized. The sizes of the ratios $k_O(\text{dimer})/k_O(\text{VO}^{2+}) \approx 74$ and $k'_H(\text{dimer})/k'_H(\text{VO}^{2+}) \approx 10$ appear to suggest a similar mechanism for these ions with MnO_4^- .^{23,24}

Sykes has called the $(\text{H}_2\text{O})_6\text{Mo}_2\text{O}_4^{2+}$ ion an outer-sphere reductant from comparison of rate and thermodynamic data from the reaction of $\text{Mo}_2\text{O}_4^{2+}$ and $\text{Mo}_2\text{O}_4(\text{EDTA})^{2-}$ with those for the reaction of IrCl_6^{2-} and $\text{Fe}(\text{phen})_3^{3+}$, both outer-sphere oxidants.¹³ Table IV presents data from the oxidation of $\text{Mo}_2\text{O}_4^{2+}$ and VO^{2+} by MnO_4^- and several other oxidants. It is interesting to note that, while the values of ΔH^\ddagger for the reactions of MnO_4^- with $\text{Mo}_2\text{O}_4^{2+}$ and VO^{2+} are similar and not unlike those of the $\text{Mo}_2\text{O}_4^{2+}/\text{Fe}(\text{phen})_3^{3+}$ reaction, the activation entropy, ΔS^\ddagger , values differ considerably. It has been shown^{2b,3} that ΔS^\ddagger values for a group of outer-sphere reactant/ MnO_4^- reactions tend to be much more positive (-5.6 to $+36.5 \text{ cal}/(\text{mol K})$) than ΔS^\ddagger for a set of inner-sphere reactants (-13 to $-30 \text{ cal}/(\text{mol K})$).²⁶ An isokinetic plot using ΔH^\ddagger and ΔS^\ddagger values from various reductant/ MnO_4^- reactions also shows the aquo dimer behaves as an outer-sphere reductant and not an inner-sphere reactant like VO^{2+} .

Since the aquo Mo(V) dimer can be considered a one-electron reductant with MnO_4^- , an E° value was estimated for the reaction $\text{MoV}_2 \rightarrow \text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}} + e^-$, from a plot of the rate constants for the unprotonated pathways, $\log k_O$, vs. $E^\circ(\text{reductant})$ for a series of $\text{MnO}_4^-/\text{inorganic ion}$ reactions.²⁷ The value, -0.53 V , is in reasonable agreement with the one-electron value of -0.52 to -0.56 V estimated by Pope from studies of Mo(V)-substituted "Keggin anions".¹¹

Results (ΔH^\ddagger , kcal/mol; ΔS^\ddagger , cal/(mol K)) from complexation studies of SCN^- with $(\text{H}_2\text{O})_6\text{MoV}_2$ (11.3, -0.3) and VO^{2+} (10.8, -3.7) have been interpreted as indicating substantial involvement of the equatorial position with the incoming ligand.¹⁹ It is likely that the interaction of the permanganate ion with these two ions is similar. We are presently examining this idea.

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Molecular Orbital Calculation of Migration Barriers in the LiAlF_4 and MgAlF_5 Complexes¹

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Numerous metal halide complexes of the type MAIX_n (M is a mono- or divalent metal; X is a halogen) have recently been studied in the vapor phase by various physicochemical techniques.² Experimental evidence has indicated that these complexes exist as edge-bridged structures in which the two metal atoms are bridged by two of the halogen atoms. There has also been some experimental work suggesting that these complexes have face-bridged structures (three halogens in the bridge) or C_s structures (a nonplanar edge-bridged ring). Questions as to the exact structure of these MAIX_n complexes and the mobility of the cation fragment (MX_{n-4}^+) in the complex, which could make structural determination difficult, have not yet been completely resolved.

In previous work we addressed the question of the relative stabilities of corner- (one fluorine in the bridge), edge-, and face-bridged structures of MAIX_n -type complexes by carrying out ab initio molecular orbital calculations on LiAlF_4 ,³ BeAlF_5 ,⁴ and MgAlF_5 .⁴ In all three cases the edge-bridged structure was most stable (by 5–25 kcal mol⁻¹) and could be described as an AlF_4^- anion interacting with an MF_{n-4}^+ cation (Li^+ , BeF^+ , or MgF^+). Others⁵ have similarly found the edge-bridged structure for the related LiBeF_3 complex to be most stable.

In the work presented here we have calculated energies of points on the pathway for migration of the cation between edge, face, and corner bridges in LiAlF_4 and MgAlF_5 . The motivation for these calculations was to shed light on the following unresolved questions concerning MAIX_n complexes:

(1) Are the less stable bridging structures (face and corner bridges) metastable enough to be observed; i.e., what are the barriers for transition from the less stable structures to the equilibrium structure? (2) Does the potential energy of this path allow for easy migration of the cation over the entire anion MX_4^- ? (3) Is the potential energy curve in the region of the edge-bridged structure shallow enough to explain the C_s structure observed in electron diffraction studies?

Computational Methods

Calculations were carried out by using standard LCAO-SCF methods⁶ with an extended-basis set. The 6-31G basis was used on

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