November, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***54***, *3379—3386 (1981)* 3379

# Kinetics of the Oxidation of *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetate Complex of Di-*μ*-oxo-bis[oxomolybdenum(V)] with Hexachloroiridate(IV) and *μ*-Hyperoxo-bis[pentaamminecobalt(III)] Ions in Aqueous Media

Yoichi Sasaki* and Reiko Kawamura
*Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980*

(Received March 5, 1981)

Kinctics of outer-sphere oxidations of $[\mathrm{Mo}^{V}_{2}\mathrm{O}_4(\mathrm{hedta})(\mathrm{H_2O})]^-$ (**1**) ($\mathrm{H_3hedta}$=*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetic acid) with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ ($[\mathrm{H^+}]=10^{-5.8}$—0.10 M (1 M=1 mol dm$^{-3}$); ionic strength, $I$=0.1 M (adjusted with $\mathrm{LiClO_4}$); 25—45 °C) and with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ ($[\mathrm{H^+}]$=0.01—0.30 M; $I$=0.1 and 2.0 M; 10—30 °C), were studied under pseudo-first-order conditions (the reductant in large excess). The following reaction scheme is consistent with the observed rate laws:

$$\begin{aligned}
&\mathbf{1} \xrightleftharpoons{K_\mathrm{a}} [\mathrm{Mo}^{V}_{2}\mathrm{O}_4(\mathrm{hedta})(\mathrm{OH})]^{2-}\ (\mathbf{2}) + \mathrm{H^+}\\
&\mathbf{1} + [\mathrm{Ir^{IV}Cl_6}]^{2-} \xrightarrow{k_{(\mathrm{a})}} (\mathrm{Mo^{V}Mo^{VI}}) + [\mathrm{Ir^{III}Cl_6}]^{3-}\\
&\mathbf{2} + [\mathrm{Ir^{IV}Cl_6}]^{2-} \xrightarrow{k_{(\mathrm{b})}} (\mathrm{Mo^{V}Mo^{VI}}) + [\mathrm{Ir^{III}Cl_6}]^{3-}\\
&\mathbf{1} + [\mu\text{-}\mathrm{O}_2^{(-)}]^{5+} \xrightleftharpoons{K_{\mathrm{IP(a)}}} \mathrm{IP(a)}\ \text{(ion-pair)}\\
&\mathbf{2} + [\mu\text{-}\mathrm{O}_2^{(-)}]^{5+} \xrightleftharpoons{K_{\mathrm{IP(b)}}} \mathrm{IP(b)}\ \text{(ion-pair)}\\
&\mathrm{IP(b)} \xrightarrow{k_{\mathrm{e(b)}}} (\mathrm{Mo^{V}Mo^{VI}}) + [\mu\text{-}\mathrm{O}_2^{(2-)}]^{4+}\\
&(\mathrm{Mo^{V}Mo^{VI}}) + \text{oxidant} \xrightarrow{\text{fast}} 2(\mathrm{Mo(VI)}).
\end{aligned}$$

At 25 °C and $I$=0.1 M, $K_\mathrm{a}$, $k_{(\mathrm{a})}$, $k_{(\mathrm{b})}$, $K_{\mathrm{IP(a)}}$, $K_{\mathrm{IP(b)}}$, and $k_{\mathrm{e(b)}}$ are $7.9\times10^{-4}$ M, 23 M$^{-1}$ s$^{-1}$, $1.11\times10^{4}$ M$^{-1}$ s$^{-1}$, 40.5 M$^{-1}$, 1046 M$^{-1}$, and 2.56 s$^{-1}$, respectively. Activation parameters for the $k_{(\mathrm{b})}$ path are $\Delta H^*=38\pm8$ kJ mol$^{-1}$ and $\Delta S^*=-25\pm29$ J K$^{-1}$ mol$^{-1}$. The product $k_{\mathrm{e(b)}}K_{\mathrm{IP(b)}}K_\mathrm{a}$ is $7.35\times10^{-2}$ s$^{-1}$ at 25 °C and $I$=2.0 M, and the corresponding activation parameters are $\Delta H^*=67\pm8$ kJ mol$^{-1}$ and $\Delta S^*=-34\pm29$ J K$^{-1}$ mol$^{-1}$. The oxidation of **2** is *ca.* $10^4$ times as fast as that of **1**. The results are compared with the oxidation reactions of other $\mathrm{Mo}^{V}_{2}\mathrm{O_4}^{2+}$-complexes.

Redox reactions of molybdenum(V) complexes are attracting interest not only of coordination chemists but also of biochemists because of their importance in biochemical studies and biomimetic approach to complex catalysis.[1] We reported the kinetics of oxidations of two molybdenum(V) complexes containing di-*μ*-oxo-bis[oxomolybdenum(V)] ($\mathrm{Mo}^{V}_{2}\mathrm{O_4}^{2+}$) core, $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{edta})]^{2-}$ ($\mathrm{H_4edta}$=ethylenediaminetetraacetic acid) and $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{H_2O})_n]^{2+}$, with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ in aqueous perchloric acid solution,[2] and of $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{pdta})]^{2-}$ ($\mathrm{H_4pdta}$=propylenediaminetetraacetic acid) with $[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-}\mathrm{NH_2},\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{en})_2]^{4+}$ (en=ethylenediamine) in aqueous solution at pH 4.6.[3] Sykes and his co-workers studied the oxidation of edta and aqua complexes of the molybdenum(V) dimer with $[\mathrm{Fe^{III}}(\mathrm{phen})_3]^{3+}$ (phen=1,10-phenanthroline) and with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ in aqueous perchloric acid solution.[4,5] All these reactions proceeded via the outer-sphere mechanism. The rate of oxidation of $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{edta})]^{2-}$ with these one-electron oxidants is of first-order with respect to the concentration of $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{edta})]^{2-}$ and of the oxidant at 1.0 and 2.0 M (1 M=1 mol dm$^{-3}$) of ionic strength $I$, and is independent of $[\mathrm{H^+}]$ (0.01—0.5 M).[2,4]

The rate of the predominant pathway for the oxidation of $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{H_2O})_n]^{2+}$ is, on the contrary, independent of the concentration of the oxidant and reciprocally dependent on $[\mathrm{H^+}]$.[2,5] The proposed mechanism involves a rate-determining cleavage of one of the oxo bridges in $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{OH})(\mathrm{H_2O})_{n-1}]^+$ to give a single-bridged molybdenum(V) dimer prior to electron-transfer.[2,5]

The ligand environment including the presence of aqua ligands should play an important role in determining the pattern of oxidation mechanism. In order to clarify the factors controlling the oxidation mechanism, we have extended our study to the oxidation of $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{hedta})(\mathrm{H_2O})]^-$ ($\mathrm{H_3hedta}$=*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetic acid),[6] which is structurally similar to $[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{edta})]^{2-}$ but has no coordinated water molecule. Kinetics of the oxidation of the hedta complex with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$, $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$, and $[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-}\mathrm{NH_2},\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{en})_2]^{4+}$ are discussed in this paper.

## Experimental

*Materials.* Sodium aqua-*μ*(*N*,*N′*)-*N*-(2-hydroxyethyl)-ethylenediamine-*N*,*N′*,*N′*-triacetato-di-*μ*-oxo-bis[oxomolybdate(V)] dihydrate, $\mathrm{Na}[\mathrm{Mo}^{V}_{2}\mathrm{O_4}(\mathrm{hedta})(\mathrm{H_2O})]\cdot2\mathrm{H_2O}$,[6] *μ*-hyperoxo-bis[pentaamminecobalt(III)] perchlorate dihydrate, $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5](\mathrm{ClO_4})_5\cdot2\mathrm{H_2O}$,[2] and *μ*-amido-*μ*-hyperoxo-bis[bis(ethylenediamine)cobalt(III)] chloride trihydrate, $[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-}\mathrm{NH_2},\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{en})_2]\mathrm{Cl_4}\cdot3\mathrm{H_2O}$,[7] were prepared by the known methods. Sodium hexachloroiridate(IV) hexahydrate, $\mathrm{Na_2[Ir^{IV}Cl_6]}\cdot6\mathrm{H_2O}$ (Johnson Matthey Chemical Limited), was used without further purification. Aqueous solution of lithium perchlorate was prepared as described previously.[2]

*Kinetic Runs.* All the kinetic runs were carried out under pseudo-first-order condition with the molybdenum(V) complex in at least ten fold excess to the oxidant. The oxidation with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ was studied by the stopped-flow method. The decrease in the concentration of $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ was followed by using its absorption peak at 487 nm ($\varepsilon$= 4070 $\mathrm{M^{-1}\,cm^{-1}}$).[4] The rate of oxidation with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ was markedly affected by the ionic strength of aqueous solution. The conventional spectrophotometry and the stopped-flow method were used for reactions at $I$=2.0 and 0.1 M, respectively. The decrease in the concentration of $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ was followed by using its absorption peak at 670 nm ($\varepsilon$= 832 $\mathrm{M^{-1}\,cm^{-1}}$).[8] The rate of oxidation with $[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-}\mathrm{NH_2,O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{en})_2]^{4+}$ was followed by the stopped-flow method by using its absorption peak at 690 nm ($\varepsilon$= 485 $\mathrm{M^{-1}\,cm^{-1}}$).[7] Errors for the activation parameters were determined by the least squares treatment with a confidence level 0.95.

*Measurements.* A Hitachi 124 spectrophotometer with a Hitachi recorder QPD-34 and a Union-Giken RA-401 stopped-flow spectrophotometer were used for kinetic measurement. The acid dissociation constant of $[\mathrm{Mo_2^VO_4(hedta)(H_2O)}]^-$ was determined by the pH titration with a Model E300B pH meter of Metrohm Herisau, which was standardized against perchloric acid solutions in 2.0 and 0.1 M $\mathrm{LiClO_4}$ to find the concentration rather than the activity of hydrogen ions.

## Results

*Preliminary Studies.* The binuclear complex anion $[\mathrm{Mo_2^VO_4(hedta)(H_2O)}]^-$ undergoes acid hydrolysis in aqueous perchloric acid solution ($[\mathrm{H^+}]>0.5$ M).[6] The complex is oxidized with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$, $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$, and $[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-}\mathrm{NH_2,O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{en})_2]^{4+}$ in aqueous solution. The $\mu$-hyperoxo complex $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ decomposes slowly in aqueous solutions containing less than 0.01 M $\mathrm{H^+}$.[2] The other two oxidants are stable over the pH range 1—5.8. Stoichiometries of the oxidation with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ and with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ were determined in 0.01 M perchloric acid solution at 25 °C. Solutions were prepared to contain 2 to 10 fold excess (in molar ratio of the complex ions) of the oxidant to the molybdenum complex (*ca.* $5\times10^{-4}$ M). The amount of unreacted oxidant was estimated as soon as the redox reaction was completed, so that the error caused by the slow decomposition of the oxidant was minimized. Two moles of both oxidants are consumed per one mole of the molybdenum complex. The overall reaction can be written similarly to that of the oxidation of $[\mathrm{Mo_2^VO_4(edta)}]^{2-}$ with these oxidants.[2,4]

$$[\mathrm{Mo_2^VO_4(hedta)(H_2O)}]^- + 2[\mathrm{Ir^{IV}Cl_6}]^{2-} \longrightarrow 2\text{“Mo(VI)”} + \text{“HEDTA”} + 2[\mathrm{Ir^{III}Cl_6}]^{3-} \qquad (1)$$

$$[\mathrm{Mo_2^VO_4(hedta)(H_2O)}]^- + 2[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+} \longrightarrow 2\text{“Mo(VI)”} + \text{“HEDTA”} + 4\text{“Co(II)”} + 2\,\mathrm{O_2} + 20\mathrm{NH_4^+}. \qquad (2)$$

Here, “Mo(VI)” and “Co(II)” represent Mo(VI) and Co(II) species, respectively, present in the solution, whose structures are not specified. “HEDTA” represents variously protonated forms of the ligand which would possibly coordinate to Mo(VI) and/or Co(II) under the given conditions.

*Kinetics of the Oxidation with* $[\mathrm{Ir^{IV}Cl_6}]^{2-}$. This was studied at $I$=0.1 M for most runs and at 25—45 °C. First-order plots $\log(\mathrm{OD}_t—\mathrm{OD}_\infty)$ *vs.* $t$ gave excellent straight lines up to almost completion of the reaction, where $\mathrm{OD}_t$ stands for the absorbance at 487 nm at time $t$. The first-order rate constant, $k_{\mathrm{obsd}}$, was not affected by the concentration of $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ (hereafter $[\mathrm{Ir^{IV}}]$) ($1.89\times10^{-5}$—$9.90\times10^{-5}$ M) at $[\mathrm{H^+}]$=0.1 and $10^{-5.1}$ M. Values of $k_{\mathrm{obsd}}$ at a given $[\mathrm{H^+}]$ are proportional to the concentration of $[\mathrm{Mo_2^VO_4(hedta)(H_2O)}]^-$ (hereafter $[\mathrm{Mo_2}]$) ($5.22\times10^{-4}$—$4.28\times10^{-3}$ M), and expressed by Eq. 3. The

$$-\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{Ir^{IV}}] = k_1[\mathrm{Mo_2}][\mathrm{Ir^{IV}}] \qquad (3)$$

dependence of $k_1$ on $[\mathrm{H^+}]^{-1}$ ($[\mathrm{H^+}]$=0.01—0.10 M) is given in Fig. 1. The plot gives a straight line with a small intercept (Fig. 1(a)), as formulated by Eq. 4.

$$k_1 = k_2 + k_3[\mathrm{H^+}]^{-1}. \qquad (4)$$

Values of $k_2$ and $k_3$ are 45±17 $\mathrm{M^{-1}\,s^{-1}}$ and 16.5±0.4 $\mathrm{s^{-1}}$ at 25 °C, and 58±32 $\mathrm{M^{-1}\,s^{-1}}$ and 27.7±0.7 $\mathrm{s^{-1}}$ at 35 °C, respectively.

The $k_1$ value increases further in lower $[\mathrm{H^+}]$ regions to reach a limiting value ($k_4$) at about $[\mathrm{H^+}]=10^{-4.5}$ M (Fig. 1(b)). Values of $k_4$ at $[\mathrm{H^+}]=10^{-5.1}$ M are $2.22\times10^4$, $2.95\times10^4$, $4.08\times10^4$, $4.83\times10^4$, and $6.86\times10^4$ $\mathrm{M^{-1}\,s^{-1}}$ at 25, 30, 35, 40, and 45 °C, respectively. Activation parameters are $\Delta H^{*}$=38±8 kJ $\mathrm{mol^{-1}}$ and $\Delta S^{*}$=−29±29 J $\mathrm{K^{-1}\,mol^{-1}}$. The effect of ionic strength was briefly investigated; $k_4$ values at $I$=0.5 and 1.0 M at $[\mathrm{H^+}]=10^{-5.1}$ M are $3.42\times10^4$ and $4.23\times10^4$ $\mathrm{M^{-1}\,s^{-1}}$, respectively, at 25 °C.

*Kinetics of the Oxidation with* $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ *at Ionic Strength 2.0 M.* This was studied at 10—30 °C and $[\mathrm{H^+}]$=0.01—0.30 M. First-order plots, $\log(\mathrm{OD}_t')$ *vs.* $t$, were linear to more than 90% of the course of reaction for most runs, where

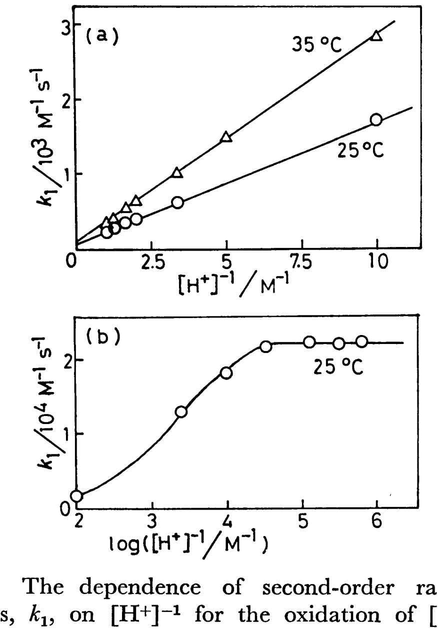

Fig. 1. The dependence of second-order rate constants, $k_1$, on $[\mathrm{H^+}]^{-1}$ for the oxidation of $[\mathrm{Mo_2^VO_4(hedta)(H_2O)}]^-$ with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ at $I$=0.1 M ($\mathrm{LiClO_4}$), (a) in aqueous perchloric acid solutions and (b) in acetate buffer solutions.

$OD_t'$ stands for the absorbance at 670 nm at time $t$. The first-order rate constant, $k_{obsd}$, was not affected by the concentration of $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$ (hereafter $[\mu\text{-}O_2^{(-)}]$) ($(2.96-8.05)\times10^{-4}$ M). First-order plot at $[H^+]=0.3$ M was not linear, probably due to acid hydrolysis of the oxidant,[6] and $k_{obsd}$ was obtained from the initial part of the plot.

The $k_{obsd}$ value depends linearly on $[Mo_2]$ at a given $[H^+]$ (Fig. 2), and is reciprocally dependent on $[H^+]$ at given concentrations of the reactants (Fig. 3). The rate law is expressed by Eq. 5. Values of

$$-d[\mu\text{-}O_2^{(-)}]/dt = k_{obsd}[\mu\text{-}O_2^{(-)}] = k_5[H^+]^{-1}[Mo_2][\mu\text{-}O_2^{(-)}] \tag{5}$$

$k_5$ are $3.17\times10^{-2}$, $6.39\times10^{-2}$, 0.100, 0.147, and 0.222 $s^{-1}$ at 10.5, 16.0, 22.0, 25.5, and 30.0 °C, respectively. Activation parameters are $\Delta H^*=67\pm8$ kJ mol$^{-1}$ and $\Delta S^*=-38\pm29$ J K$^{-1}$ mol$^{-1}$.

*Kinetics of the Oxidation with* $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$ *at Ionic Strength 0.1 M.* This was studied at 25 and 30.6 °C and $[H^+]=0.02$—0.10 M. First-order plots deviated from straight lines for the initial part of the reaction for *ca.* 1 s regardless of reactant concentrations and of $[H^+]$. The first-order rate constant ($k_{obsd}$) was obtained from the linear part of the plot. The dependence of $k_{obsd}$ on $[Mo_2]$ at a given $[H^+]$ was not linear (Fig. 4), but plot of $k_{obsd}^{-1}$ *vs.* $[Mo_2]^{-1}$ gave a straight line with a positive intercept at each $[H^+]$. Therefore, $k_{obsd}$ can be expressed by Eq. 6 at a given $[H^+]$. Values of $x$ and

$$k_{obsd}^{-1} = x + y[Mo_2]^{-1} \tag{6}$$

$y$ were obtained from 52 kinetic runs and their dependences on $[H^+]$ are shown in Figs. 5 and 6.

*Kinetics of the Oxidation with* $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{(-)})Co^{III}(en)_2]^{4+}$. This was studied briefly at $[H^+]=10^{-5.1}$ and $10^{-5.8}$ M, $I=0.1$ M and at 25 °C. First-order plots gave good straight lines up to almost completion of the reaction. The $k_{obsd}$ values for $[Mo_2]=1.04\times10^{-3}$ M at $[H^+]=10^{-5.1}$ and $10^{-5.8}$ M are 11.1 and 11.6 $s^{-1}$, respectively, suggesting that the dependence on $[H^+]$ is negligible in this $[H^+]$ range. The dependence of $k_{obsd}$ on $[Mo_2]$ ($[Mo_2]=5.19\times10^{-4}$—$3.11\times10^{-3}$ M; [oxidant]$=9.24\times10^{-5}$ M) con-

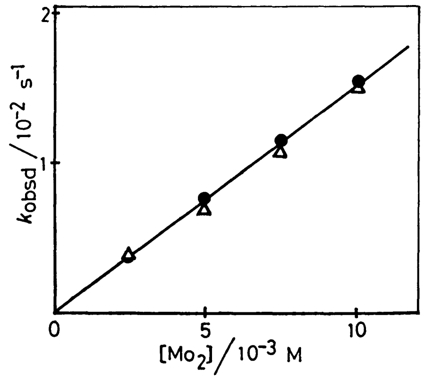

Fig. 2. The dependence of $k_{obsd}$ on $[Mo^V_2O_4(hedta)(H_2O)^-]$ for the oxidation of $[Mo^V_2O_4(hedta)(H_2O)]^-$ with $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$ in 0.1 M $HClO_4$ solution at 25 °C and $I=2.0$ M. $[\mu\text{-}O_2^{(-)}]=5.21\times10^{-4}$ (●) and $2.96\times10^{-4}$ M (△).

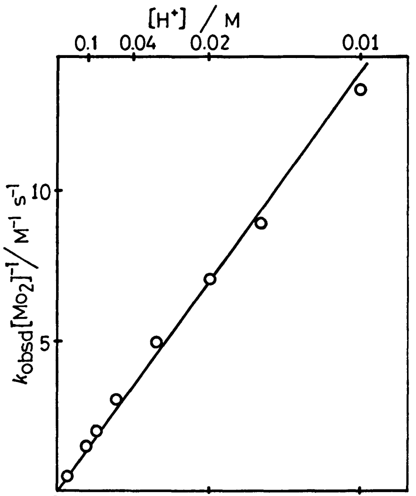

Fig. 3. The dependence of $k_{obsd}/[Mo_2]$ on $[H^+]^{-1}$ for the oxidation of $[Mo^V_2O_4(hedta)(H_2O)]^-$ with $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$ at 25 °C and $I=2.0$ M with $[Mo^V_2]$ in large excess.

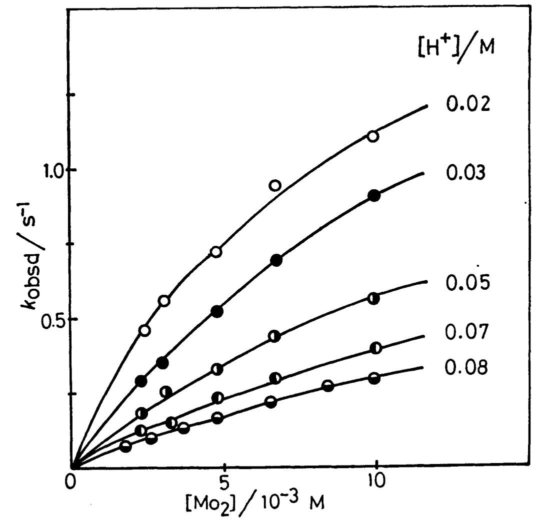

Fig. 4. The dependence of $k_{obsd}$ on $[Mo^V_2O_4(hedta)(H_2O)^-]$ for the oxidation of $[Mo^V_2O_4(hedta)(H_2O)]^-$ with $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$ at $I=0.1$ M in aqueous perchlorate media ($HClO_4$–$LiClO_4$) at 25 °C and $[\mu\text{-}O_2^{(-)}]=3.0\times10^{-4}$ M.

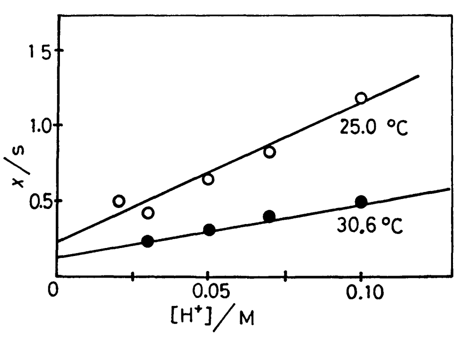

Fig. 5. The dependence of $x$ on $[H^+]$ for the oxidation of $[Mo^V_2O_4(hedta)(H_2O)]^-$ with $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$ at $I=0.1$ M.

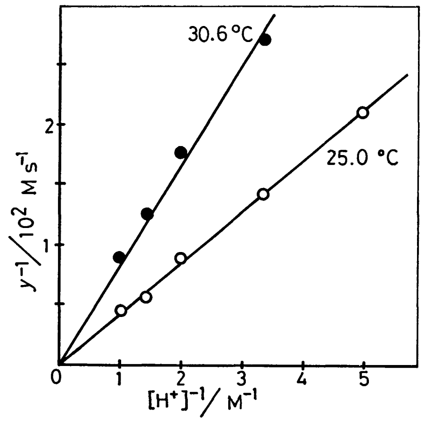

Fig. 6. The dependence of $y^{-1}$ on $[\mathrm{H^+}]^{-1}$ for the oxidation of $[\mathrm{Mo_2^{V}O_4(hedta)(H_2O)}]^-$ with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ at $I=0.1$ M.

formed to the rate law (6). Values of $x$ and $y$ at $[\mathrm{H^+}]=10^{-5.1}$ M are $(1.7\pm0.6)\times10^{-2}$ s and $(7.9\pm0.6)\times10^{-5}\ \mathrm{M^{-1}}$ s, respectively.

*Effect of Added Halide Ions.* The effect of added chloride and bromide ions was studied with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ as oxidant at given concentrations of the reactants (Table 1). The pseudo-first-order rate constant becomes smaller on addition of halide ions. Various conditions shown in the footnote of Table 1 do not seem to change the degree of influence by the halide ions.

*The* $\mathrm{p}K_\mathrm{a}$ *Value of* $[\mathrm{Mo_2^{V}O_4(hedta)(H_2O)}]^-$. Values of $\mathrm{p}K_\mathrm{a}$ of this complex are 3.10 and 3.25 at 25 °C and $I=0.1$ and 2.0 M, respectively. The latter value was carefully determined, since it is clearly different from our previously determined value (3.02);[6] the value should therefore be revised to 3.25. At 35 °C $\mathrm{p}K_\mathrm{a}$ is 3.18 ($I=0.1$ M).

TABLE 1. THE EFFECT OF HALIDE IONS ON THE RATE OF OXIDATION OF $[\mathrm{Mo_2^{V}O_4(hedta)(H_2O)}]^-$ WITH $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2^{(-)}})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ AT 25 °C[a)]

| Halide ion ($\mathrm{X^-}$) | $[\mathrm{X^-}]$/M | $k_\mathrm{obsd}/10^3\ \mathrm{s^{-1}}$ |
|---|---|---|
| $\mathrm{Cl^-}$ | 0 | 6.70[b)] |
| | 0.1 | 6.35[b)] |
| | 0.5 | 4.37[b)] |
| | 0.5 | 4.00[c)] |
| | 0.5 | 4.02[d)] |
| | 0.5 | 4.02[e)] |
| $\mathrm{Br^-}$ | 0.5 | 4.46[b)] |

a) $I=2.0$ M ($\mathrm{LiClO_4}$), $[\mathrm{H^+}]=0.10$ M ($\mathrm{HClO_4}$), $[\mathrm{Mo_2}]=5\times10^{-3}$ M, $[\mu\text{-}\mathrm{O_2^{(-)}}]=5\times10^{-4}$ M. b) The $\mu$-hyperoxo complex solution containing lithium halide was mixed with the molybdenum solution to cause the electron transfer to start. c—e) The $\mu$-hyperoxo complex solution was mixed with the molybdenum complex solution containing lithium chloride to cause the electron transfer reaction to start. Lithium chloride was added to the molybdenum complex solution c) 40 m, d) 220 m, and e) 345 m before the redox reagents were mixed.

## Discussion

*Interpretation of Kinetic Data.* None of the three oxidants is likely to be protonated or deprotonated in the pH range employed. Therefore, the pH dependence of the oxidation rate should be interpreted by considering the protonation-deprotonation equilibrium of the reductant. A consideration similar to those for the oxidation[2,4] of $[\mathrm{Mo_2^{V}O_4(edta)}]^{2-}$ suggests that the oxidation of the first molybdenum(V) ion in the dimer is the rate-determining step, which is followed by a rapid oxidation of the second molybdenum(V) ion.

*The Oxidation with* $[\mathrm{Ir^{IV}Cl_6}]^{2-}$: Kinetic data were most reasonably interpreted in terms of the following mechanism.

$$\begin{tikzcd}
{[\mathrm{Mo_2^{V}O_4(hedta)(H_2O)}]^- + [\mathrm{Ir^{IV}Cl_6}]^{2-}} \arrow[r, "k_{(\mathrm{a})}"] \arrow[d, shift left, "K_\mathrm{a}"'] & \text{“}\mathrm{Mo^{V}Mo^{VI}}\text{”} + [\mathrm{Ir^{III}Cl_6}]^{3-} \\
{[\mathrm{Mo_2^{V}O_4(hedta)(OH)}]^{2-} + [\mathrm{Ir^{IV}Cl_6}]^{2-}} \arrow[r, "k_{(\mathrm{b})}"] \arrow[u, shift left] & \text{“}\mathrm{Mo^{V}Mo^{VI}}\text{”} + [\mathrm{Ir^{III}Cl_6}]^{3-}
\end{tikzcd}$$

Rate law (7) is obtained for this mechanism. A

$$\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = \{2(k_{(\mathrm{a})}[\mathrm{H^+}]+K_\mathrm{a}k_{(\mathrm{b})})[\mathrm{Mo_2}][\mathrm{Ir^{IV}}]\}/(K_\mathrm{a}+[\mathrm{H^+}]) \quad (7)$$

comparison with the experimental rate law (4) indicates that $k_{(\mathrm{a})}$ and $K_\mathrm{a}k_{(\mathrm{b})}$ correspond to $k_2/2$ and $k_3/2$, respectively, under the condition $K_{(\mathrm{a})}\ll[\mathrm{H^+}]$. The term $k_{(\mathrm{b})}$ should correspond to $k_4/2$, since $k_{(\mathrm{a})}[\mathrm{H^+}]$ is negligible as compared with $K_\mathrm{a}k_{(\mathrm{b})}$ at $[\mathrm{H^+}]\ll K_\mathrm{a}$. The $K_\mathrm{a}$ values determined by the pH titration and the observed $k_3$ values give $k_{(\mathrm{b})}$ as $1.04\times10^4$ and $2.09\times10^4\ \mathrm{M^{-1}\,s^{-1}}$ at 25 and 35 °C, respectively. These values are in excellent agreement with the experimentally obtained $k_4/2$ values at given temperatures. Also the $\mathrm{p}K_\mathrm{a}$ values (3.13 and 3.17 at 25 and 35 °C, respectively) calculated from the observed values of $k_3$ and $k_4$ are in good agreement with those determined by the pH titration. These facts support the proposed mechanism. Activation parameters for $k_4/2$ must correspond to those for $k_{(\mathrm{b})}$ ($\Delta H^*=38\pm8$ kJ $\mathrm{mol^{-1}}$, $\Delta S^*=-42\pm29\ \mathrm{J\ K^{-1}\,mol^{-1}}$). Those for $k_{(\mathrm{a})}$ were not obtained because of big uncertainty in $k_2$ values.

*The Oxidation with* $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$: The marked influence of ionic strength upon the rate suggests the importance of electrostatic interaction of the charged redox couple. The kinetics can be more precisely discussed at lower ionic strengths where such an interaction is expected to be stronger.

The observed rate law at $I=0.1$ M (Eq. 6) is consistent with a mechanism involving an ion-pair formation prior to electron transfer. Thus, the following mechanism is considered.[10] The terms $K_{\mathrm{IP(a)}}$ and $K_{\mathrm{IP(b)}}$ stand for the ion-pair formation constants for the original complex and its conjugate base, respec-

$$\begin{tikzcd}
{[\mathrm{Mo_2^{V}O_4L(H_2O)}]^- + [\mu\text{-}\mathrm{O_2^{(-)}}]^{5+}} \arrow[r, shift left, "K_{\mathrm{IP(a)}}"] \arrow[d, shift right, "K_{\mathrm{a}}"'] & {\begin{array}{c}[\mathrm{Mo_2O_4L(H_2O)}\cdots\mu\text{-}\mathrm{O_2^{(-)}}]^{4+} \\ \mathrm{(IP(a))}\end{array}} \arrow[l, shift left] \arrow[r, "k_{\mathrm{e(a)}}"] \arrow[d, shift right, "K_{\mathrm{a}}'"'] & {} \\
{[\mathrm{Mo_2^{V}O_4L(OH)}]^{2-} + [\mu\text{-}\mathrm{O_2^{(-)}}]^{5+}} \arrow[r, shift left, "K_{\mathrm{IP(b)}}"] \arrow[u, shift right] & {\begin{array}{c}[\mathrm{Mo_2O_4L(OH)}\cdots\mu\text{-}\mathrm{O_2^{(-)}}]^{3+} \\ \mathrm{(IP(b))}\end{array}} \arrow[l, shift left] \arrow[r, "k_{\mathrm{e(b)}}"] \arrow[u, shift right] & {}
\end{tikzcd}$$

tively, $L^{3-}$ is hedta$^{3-}$, and $k_{e(a)}$ and $k_{e(b)}$ are the rate constants for the electron transfer within the ion-pairs, IP(a) and IP(b), respectively. The following rate law is derived for this mechanism. Thus, $k_{obsd}$ is expressed by Eq. 9. The terms $x$ and $y$ in Eq. 6

$$-\frac{d[\mu\text{-}O_2^{(-)}]}{dt}$$

$$= \frac{2\{k_{e(a)}K_{IP(a)}[H^+]+k_{e(b)}K_{IP(b)}K_a\}[Mo_2][\mu\text{-}O_2^{(-)}]}{K_a+[H^+]+\{K_{IP(a)}[H^+]+K_{IP(b)}K_a\}[Mo_2]} \quad (8)$$

$$k_{obsd} = \frac{2\{k_{e(a)}K_{IP(a)}[H^+]+k_{e(b)}K_{IP(b)}K_a\}[Mo_2]}{K_a+[H^+]+\{K_{IP(a)}[H^+]+K_{IP(b)}K_a\}[Mo_2]} \quad (9)$$

are expressed by Eqs. 10 and 11, respectively. Since $K_a \ll [H^+]$, Eq. 11 is rearranged to Eq. 12. A plot

$$x = \{K_{IP(a)}[H^+]+K_{IP(b)}K_a\}/2\{k_{e(a)}K_{IP(a)}[H^+] + k_{e(b)}K_{IP(b)}K_a\} \quad (10)$$

$$y = (K_a+[H^+])/2\{k_{e(a)}K_{IP(a)}[H^+]+k_{e(b)}K_{IP(b)}K_a\} \quad (11)$$

$$y^{-1} = 2\{k_{e(a)}K_{IP(a)}+k_{e(b)}K_{IP(b)}K_a[H^+]^{-1}\} \quad (12)$$

of experimental $y^{-1}$ against $[H^+]^{-1}$ gives a straight line without intercept (Fig. 6). This fact suggests that $k_{e(a)}K_{IP(a)}$ is negligible as compared with $k_{e(b)} \times K_{IP(b)}K_a[H^+]^{-1}$ and $x$ is rewritten to Eq. 13. A plot

$$x = \{K_{IP(a)}[H^+]/2k_{e(b)}K_{IP(b)}K_a\} + 1/(2k_{e(b)}) \quad (13)$$

of $x$ against $[H^+]$ gives a straight line (Fig. 5). All the parameters are obtained as follows by use of the $K_a$ value ($7.9\times10^{-4}$ M) at $I$=0.1 M and 25 °C: $K_{IP(a)}$= 40.5 M$^{-1}$, $K_{IP(b)}$=1046 M$^{-1}$, $k_{e(a)}$ not observed, and $k_{e(b)}$=2.56 s$^{-1}$ at 25 °C; $K_{IP(a)}$=30 M$^{-1}$, $K_{IP(b)}$=1100 M$^{-1}$, $k_{e(a)}$ not observed, and $k_{e(b)}$=4.3 s$^{-1}$ at 35 °C. These values are subject to nearly 50% uncertainty because of such a complicated analysis. No further trials for obtaining their temperature dependence were made. Nevertheless, the results provide additional example of first-order rate constant for the electron transfer within an ion-pair.[2,3,11,12]

For the reaction at $I$=2.0 M, the following assumptions are required to obtain a rate law which is of a form similar to the experimentally obtained rate law, Eq. 5: (i) the third term in the denominator of Eq. 9 is negligible (reasonable since the ion-pair formation at higher ionic strengths is expected to be less significant); (ii) $k_{e(a)}K_{IP(a)}$ is negligible as compared with $k_{e(b)}K_{IP(b)}K_a[H^+]^{-1}$ (this relation is experimentally derived at $I$=0.1 M (*vide supra*)); (iii) $K_a$ is negligible as compared with $[H^+]$ (experimental condition). Under these assumptions Eq. 9 is simplified to Eq. 14.

$$k_{obsd} = 2k_{e(b)}K_{IP(b)}K_a[H^+]^{-1}[Mo_2] \quad (14)$$

The product $k_{e(b)}K_{IP(b)}K_a$ is $7.35\times10^{-2}$ s$^{-1}$ at 25.5 °C, thus $k_{e(b)}K_{IP(b)}$ is estimated to be $2.97\times10^4$ M$^{-1}$ s$^{-1}$ by use of the p$K_a$ value (3.25).

*The Oxidation with* $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{(-)})Co^{III}(en)_2]^{4+}$: The molybdenum(V) dimer is present almost entirely in the conjugate base form, $[Mo_2^VO_4(hedta)(OH)]^{2-}$, at $[H^+]=10^{-5.1}$ and $10^{-5.8}$ M. The following scheme is consistent with the kinetic behavior of the system (Eq. 6). The following rate law 15

$$[Mo_2^VO_4(hedta)(OH)]^{2-} + [\mu\text{-}NH_2,O_2^{(-)}]^{4+} \underset{}{\overset{K_{IP(c)}}{\rightleftharpoons}} IP(c) \xrightarrow{k_{e(c)}} \text{products}$$

is derived for this mechanism. A comparison of Eq. 15 with Eq. 6 leads to the values $K_{IP(c)}=210\pm90$

$$k_{obsd} = 2k_{e(c)}K_{IP(c)}[Mo_2]/\{1+K_{IP(c)}[Mo_2]\} \quad (15)$$

M$^{-1}$ and $k_{e(c)}=30\pm10$ s$^{-1}$ at $I$=0.1 M and at 25 °C.

*Ion-pair Formation Constants.* The ion-pair formation constant between $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH)_3)_5]^{5+}$ and $[Mo_2^VO_4(hedta)(OH)]^{2-}$ at $I$=0.1 M (1046 M$^{-1}$ at 25 °C) is *ca.* 4 times bigger than that between the $\mu$-$O_2^{(-)}$ complex and $[Mo_2^VO_4(edta)]^{2-}$ (270 M$^{-1}$ at 40 °C).[2] The electronic charge may be more localized in $[Mo_2^VO_4(hedta)(OH)]^{2-}$ than in the more symmetrical edta complex. Such a locarization would produce a more negatively charged site within the complex anion, at which the ion-pair formation would be more extensive.

*Reaction Mechanism.* Present reactions must proceed *via* the outer-sphere mechanism for the following reasons. The oxidation of $[Mo_2^VO_4(edta)]^{2-}$ with $[Ir^{IV}Cl_6]^{2-}$ and with $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$ are believed to occur by the outer-sphere mechanism, since these oxidants are unable to coordinate to the molybdenum(V) unless the edta ligand is partially displaced.[2,4,13] The present hedta complex has a coordinated water, for which the oxidant can substitute. The remarkable increase in the rate of oxidation on changing from $[Mo_2^VO_4(hedta)(H_2O)]^-$ to its conjugate base, $[Mo_2^VO_4(hedta)(OH)]^{2-}$, does not support the inner-sphere mechanism, however, since the $OH^-$ ligand is more strongly coordinated than $H_2O$ and should be less easily dissociated from the metal ion.[14] There seems to be no example that $\mu$-hyperoxo-dicobalt(III) complexes behave as inner-sphere oxidants.[3,16]

The Marcus theory predicts that when a series of oxidants are reduced by two different reductants *via* the outer-sphere process, ratio of the two rate constants should be similar for all members of the series.[17,18] Such ratios are often used as a diagnostic criterion for assigning redox reactions involving chromium(II), vanadium(II), *etc.* as proceeding by an outer-sphere mechanism.[19] Ratios of the oxidation rate of $[Mo_2^VO_4(hedta)(OH)]^{2-}$ to that of $[Mo_2^VO_4(edta)]^{2-}$ ($k_{hedta(OH)}/k_{edta}$) are listed in Table 2. Ratios for the two oppositely charged oxidants are within one order of magnitude, and can be taken as an evidence for the outer-sphere mechanism for the present reactions.

TABLE 2. RATIOS OF THE RATE CONSTANT FOR THE OXIDATION OF $[\mathrm{Mo^V_2O_4(hedta)(OH)}]^{2-}$ ($k_{\mathrm{hedta(OH)}}$) TO THAT OF $[\mathrm{Mo^V_2O_4(edta)}]^{2-}$ ($k_{\mathrm{edta}}$) WITH THE GIVEN OXIDANT AT 25 °C

| Oxidant | $I$/M | Order of the rate constant | $k_{\mathrm{hedta(OH)}}/k_{\mathrm{edta}}$ |
|---|---|---|---|
| $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ | 1.0 | second-order[b)] | $3.9\times10^3$ |
| $[\mu\text{-}\mathrm{O_2^{(-)}}]^{5+}$ [a)] | 0.1 | first-order ($k_e$)[c)] | $9.8\times10^3$ |
| | 2.0 | second-order ($k_eK_{\mathrm{IP}}$)[c)] | $29.7\times10^3$ |

a) $[\mu\text{-}\mathrm{O_2^{(-)}}]^{5+}=[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2^{(-)}})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$. b) The $k_{\mathrm{hedta(OH)}}$ value at $I=0.1$ M was estimated from those at $I=0.1$ and 2.0 M, to be $3.9\times10^4\ \mathrm{M^{-1}\,s^{-1}}$. c) The $k_{\mathrm{edta}}$ values at 25 °C were calculated from the activation parameters in Ref. 2, to be $2.60\times10^{-4}\ \mathrm{s^{-1}}$ and $8.81\times10^{-3}\ \mathrm{M^{-1}\,s^{-1}}$ at $I=0.1$ and 2.0 M, respectively.

Ratio of the first-order rate constants $k_e$ for the oxidation with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ at $I=0.1$ M is *ca.* 3 times smaller than that of $k_eK_{\mathrm{IP}}$ at $I=2.0$ M, where $k_e$ and $K_{\mathrm{IP}}$ values cannot be obtained separately. The difference in $K_{\mathrm{IP}}$ values should be responsible for such a difference in the ratios. This fact indicates that electrostatic interactions should significantly affect the ratio of the redox rates which are usually obtained as a product of $k_e$ and $K_{\mathrm{IP}}$.

*Comparison with Other Reactions.* *Rate of the Reaction*: The second-order rate constants of the oxidations of $\mathrm{Mo^V_2O_4}^{2+}$-complexes with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$, $[\mathrm{Fe^{III}(phen)_3}]^{3+}$, $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$, and $[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-}\mathrm{NH_2,O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{en})_2]^{4+}$ are summarized in Table 3. The following sequence is given for the decrease in oxidation rate. This sequence suggests

$$[\mathrm{Mo^V_2O_4(hedta)(OH)}]^{2-} > [\mathrm{Mo^V_2O_4(hedta)(H_2O)}]^{-}$$
$$> [\mathrm{Mo^V_2O_4(edta)}]^{2-} > [\mathrm{Mo^V_2O_4(H_2O)}_n]^{2+}$$
$$([\mathrm{Mo^V_2O_4(OH)(H_2O)}_{n-1}]^{+}\text{ must be more reactive than }[\mathrm{Mo^V_2O_4(hedta)(H_2O)}]^{-})$$

that the total charge of the complex is not important in determining the rate. The two hydroxo complexes are significantly more reactive than thier conjugate acids. A possible interpretation may be that the stronger Lewis base, the hydroxide, makes the metal ion more negative and more electron donating. Outer-sphere oxidations of $[\mathrm{V^{III}(H_2O)_6}]^{3+}$,[20)] $[\mathrm{V^{IV}O(H_2O)}_n]^{2+}$,[21)] $[\mathrm{V^{IV}O(pmida)(H_2O)}]$ ($\mathrm{H_2pmida}$=*N*-(2-pyridylmethyl)-iminodiacetic acid),[22)] $[\mathrm{V^{IV}O(nta)(H_2O)}]^{-}$ ($\mathrm{H_3nta}$ =nitrilotriacetic acid),[22)] and $[\mathrm{Ti^{III}(H_2O)_6}]^{3+}$ [23,24)] with various oxidants exhibit predominant rate-terms proportional to $[\mathrm{H^+}]^{-1}$. The products in all of these reactions are mono- or dioxo metal ions; the number of oxo ligands increases and protons are reliesed on the oxidation. Such a structural requirement was claimed to be responsible for the higher reactivity of conjugate bases of these complexes.[24)] A similar interpretation may be applied to the oxidation of $\mathrm{Mo^V_2O_4}^{2+}$-complexes, although the rate-determining electron-transfer gives a mixed valence (V, VI) dimer as an immediate product, the structure of which is not known.

*Activation Parameters*: Table 4 shows that $\Delta H^*$ for $[\mathrm{Mo^V_2O_4(hedta)(OH)}]^{2-}$ is significantly smaller than that for $[\mathrm{Mo^V_2O_4(edta)}]^{2-}$ whenever a common oxidant is used. The big difference in oxidation rate between these two complexes seems to be due to the difference in $\Delta H^*$ rather than $\Delta S^*$.

The activation entropy for a given molybdenum(V) complex is more positive and the activation enthalpy is bigger for the oxidation with $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2}^{(-)})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$ than those for the oxidation with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$. Such differences can be explained in terms of the change in solvation accompanied by the encounter complex formation from the separated reactants. Negative $\Delta S^*$ for redox reactions between reactants with charges of the same sign were claimed to be largely the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated water molecules.[25)] On the other hand, the positive entropy brought about on the encounter complex (ion-pair) formation between oppositely charged reactants,[2,11)] may be attributed to the weakening of solute-solvent interaction by the partial compensation of charges in the ion-pair. The change in $\Delta H^*$ with the charge of oxidant is more difficult to explain. The contributions of $\Delta H^*$ and $\Delta S^*$ to the rate constant seem

TABLE 3. A COMPARISON OF SECOND-ORDER RATE CONSTANTS/$\mathrm{M^{-1}\,s^{-1}}$ AT 25 °C FOR THE OXIDATIONS OF SOME $\mathrm{Mo^V_2O_4}^{2+}$-COMPLEXES WITH FOUR OXIDANTS

| $\mathrm{Mo^V_2O_4}^{2+}$-complexes | Oxidants | | | | Ref. |
|---|---|---|---|---|---|
| | $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ | $[\mathrm{Fe^{III}(phen)_3}]^{3+}$ | $[\mu\text{-}\mathrm{O_2^{(-)}}]^{5+}$ [a)] | $[\mu\text{-}\mathrm{NH_2,O_2^{(-)}}]^{4+}$ [b)] | |
| $[\mathrm{Mo^V_2O_4(edta)}]^{2-}$ | 6.6[c)] | $1.9\times10^3$ [c)] | $8.8\times10^{-3}$ [d,e)] | | 2, 4 |
| $[\mathrm{Mo^V_2O_4(pdta)}]^{2-}$ | | | | $1.87\times10^{-1}$ [f)] | 3 |
| $[\mathrm{Mo^V_2O_4(hedta)(OH)}]^{2-}$ | $1.1\times10^4$ [g)] | | $2.62\times10^2$ [e)] | $6.30\times10^3$ [g)] | This work |
| $[\mathrm{Mo^V_2O_4(hedta)(H_2O)}]^{-}$ | $2.3\times10^1$ [f)] | | $5\times10^{-2}$ [e)] | | This work |
| $[\mathrm{Mo^V_2O_4(OH)(H_2O)}_{n-1}]^{+}$ | 26< [c,h,i)] | 3000< [c,h,i)] | (Not observed)[j)] | | 2, 5 |
| $[\mathrm{Mo^V_2O_4(H_2O)}_n]^{2+}$ | $5.7\times10^{-2}$ [c)] | $1.6\times10^1$ [c)] | (Not observed)[j)] | | 2, 5 |

a) $[(\mathrm{NH_3})_5\mathrm{Co^{III}}(\mu\text{-}\mathrm{O_2^{(-)}})\mathrm{Co^{III}}(\mathrm{NH_3})_5]^{5+}$. b) $[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-}\mathrm{NH_2,O_2^{(-)}})\mathrm{Co^{III}}(\mathrm{en})_2]^{4+}$. c) $I=1.0$ M. d) Calculated from the activation parameters in Ref. 2. e) $I=2.0$ M. f) $I=0.2$ M. g) $I=0.1$ M. h) Estimated on the reasonable assumption that the acid-dissociation constant of $[\mathrm{Mo^V_2O_4(H_2O)}_n]^{2+}$ is less than $10^{-3}$ M. i) For these reactions, significant part of the redox reaction proceeds *via* a pathway independent of the oxidant concentration.[5)] j) The oxidation rate is independent of the concentration of the $\mu$-hyperoxo complex.[2)]

TABLE 4. ACTIVATION PARAMETERS FOR THE OXIDATION OF THE COMPLEXES WITH $Mo^{V}_{2}O_4{}^{2+}$-CORE

| Oxidant | | $I$/M | $\Delta H^{*}$/kJ mol$^{-1}$ | $\Delta S^{*}$/J K$^{-1}$ mol$^{-1}$ | Ref. |
|---|---|---|---|---|---|
| $[Ir^{IV}Cl_6]^{2-}$ | $[Mo^{V}_{2}O_4(edta)]^{2-}$ | 1.0 | 56± 1 | −42± 4 | 4 |
| | $[Mo^{V}_{2}O_4(hedta)(OH)]^{2-}$ | 0.1 | 38± 8 | −29±29 | This work |
| $[\mu\text{-}O_2^{(-)}]^{5+}$ a) | $[Mo^{V}_{2}O_4(edta)]^{2-}$ | 0.1 b) | 118±17 | 76±46 | 2 |
| | $[Mo^{V}_{2}O_4(edta)]^{2-}$ | 2.0 | 111± 3 | 88±13 | 2 |
| | $[Mo^{V}_{2}O_4(hedta)(OH)]^{2-}$ | 2.0 | 80±13 | 55±42 | This work |

a) $[(NH_3)_5Co^{III}(\mu\text{-}O_2^{(-)})Co^{III}(NH_3)_5]^{5+}$. b) For the first-order rate constant of the electron-transfer within the ion-pair. c) In evaluating $\Delta H^{*}$ and $\Delta S^{*}$, it is assumed that $\Delta H^{\circ}$ and $\Delta S^{\circ}$ for $K_a$ are −8 — −15 kJ mol$^{-1}$ and −80 — −100 J K$^{-1}$ mol$^{-1}$, respectively, which were estimated from the $K_a$ data at 25 and 35 °C as given in the text.

to compensate each other. Such a relationship is more clearly observed for the oxidations of $[V^{IV}O(pmida)(OH)]^-$ and $[V^{IV}O(nta)(OH)]^{2-}$ with $[Ir^{IV}Cl_6]^{2-}$ and $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2{}^{(-)})Co^{III}(en)_2]^{4+}$ (isokinetic relationship is observed).[22] This fact suggests that the factors controlling $\Delta H^{*}$ must be closely related to those controlling $\Delta S^{*}$. Therefore, the solvation state of the encounter complex would be important in determining $\Delta H^{*}$. Activation enthalpy is smaller for redox reactions involving more solvated encounter complexes, and is larger for reactions between oppositely charged reactants which form less solvated encounter complexes.[22]

*Reaction Pattern*: Existence of a rate-term independent of the oxidant concentration is the characteristic feature of the oxidation of $[Mo^{V}_{2}O_4(OH)(H_2O)_{n-1}]^+$ with the three oxidants in Table 3.[2,5] The cleavage of one of the two oxo-bridges to give a single-bridged species was claimed to be the rate-determining step, the $OH^-$ ligand being responsible for the bridge cleavage.[2] Chloride ions were found to catalyze markedly the oxidation of $[Mo^{V}_{2}O_4(H_2O)_n]^{2+}$ with $[(NH_3)_5Co^{III}(\mu\text{-}O_2{}^{(-)})Co^{III}(NH_3)_5]^{5+}$. The chloride ion was reckoned to substitute for the coordinated water and facilitate the bridge cleavage.[2] Such a mechanism is not plausible for the present reaction, since the rate formulae misses the term independent of the oxidant concentration and the positive catalytic effect by the halide ion was not observed. $[Mo^{V}_{2}O_4(H_2O)_n]^{2+}$ and $[Mo^{V}_{2}O_4(hedta)(H_2O)]^-$ are oxidized mainly *via* their conjugate bases, but mechanism is different. The present work stresses that the rate and mechanism of oxidations of the complexes with $Mo^{V}_{2}O_4{}^{2+}$-core depend significantly on the ligand environment.

This work is a part of the project supported by a Grant-in-Aid (511301) which is given to Professor Kazuo Saito from the Ministry of Education, Science and Culture. We are grateful to Professor K. Saito for his constant encouragement and valuable discussions throughout this work. We thank Mr. Susumu Kondo for the preparation of $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{(-)})Co^{III}(en)_2]Cl_4\cdot 3H_2O$.

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9) Transient absorption spectra during the course of the redox reaction measured by a rapid-scanning technique, did not show any evidence for intermediate formation. Since the deviation from the straight line for the first-order plot was small, we did not attempt to find the reason for the behavior further.

10) An alternative mechanism consistent with the rate law 6 is that the $\mu$-hyperoxo complex formed an active intermediate which oxidized the molybdenum(V) dimer (a steady-state treatment for the active intermediate leads to the expected rate law). Although the kinetics of the oxidation with the $\mu$-hyperoxo complexes were studied for various reductants, none of these reactions proceeded through such an active intermediate. Since the mechanism proposed in the text is reasonable, we exclude this alternative mechanism for the present reaction.

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14) Partial dissociation of the hedta ligand, if occured, can be faster in the conjugate base complex, $[Mo^{V}_{2}O_4(hedta)(OH)]^{2-}$, than in $[Mo^{V}_{2}O_4(hedta)(H_2O)]^-$. We do not consider that the electron transfer mechanism involving an inner-sphere precursor formed by the rate-determining partial dissociation of the hedta ligand in $[Mo^{V}_{2}O_4(hedta)(OH)]^{2-}$, is likely, since the activation enthalpies for ligand substitution reactions *via* the conjugate base are usually bigger than 80 kJ mol$^{-1}$,[15] while those for the present reactions are much smaller.

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