Kinetics of the Oxidation of Ethylenediaminetetraacetato and Aqua Complex of Dimeric Molybdenum(V) by the μ-Hyperoxo-bis[pentaamminecobalt(III)] Ion in Aqueous Perchloric Acid Solution

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Kinetics of the oxidation of double-bridged Mo(V) complexes, $[Mo_2O_4(edta)]^{2-}$ (H_4edta=ethylenediaminetetraacetic acid) and $[Mo_2O_4(aq)]^{2+}$ with $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$ has been studied in aqueous perchloric acid solution at 25—50 °C. The oxidation of $[Mo_2O_4(edta)]^{2-}$ is characterized by the electron transfer within the ion-pair formed between the two reactants. The first order rate constants for the electron transfer process (k_e) are independent of $[H^+]$ ($[H^+]=0.05$—0.1 M; $I=0.1$—2.0 M) (M=mol dm^{-3}). At 40 °C and $I=0.1$ M, k_e is equal to $(1.34\pm0.08)\times10^{-3}$ s^{-1} and the corresponding activation parameters are $\Delta H^{\neq}=28\pm4$ kcal mol^{-1} and $\Delta S^{\neq}=18\pm11$ cal K^{-1} mol^{-1}. The rate of oxidation of $[Mo_2O_4(aq)]^{2+}$ is independent of the oxidant concentration and accelerated by halide ions and Mo(VI). The rate-determining step is the formation of a single-bridged Mo(V) dimer (A) prior to electron transfer. The first order rate constants for the formation of A (k_1) are reciprocally dependent on $[H^+]$ ($[H^+]=0.5$—2.0 M; $I=2.0$ M). k_1 is $(4.3\pm0.3)\times10^{-6}$ s^{-1} at 25 °C and for $[H^+]=1.0$ M. The difference in the oxidation mechanism of the two complexes has been discussed in terms of the charge of the complex, stabilization of the Mo_2O_4-unit by the ligands, and the role of coordinated water.

The redox and substitution properties of molybdenum ions in various oxidation states are of current interest[1,2] in view of the involvement of molybdenum ions in biological systems.[3] The redox properties of simple molybdenum(V) complexes have been studied by many workers.[1,4–11]

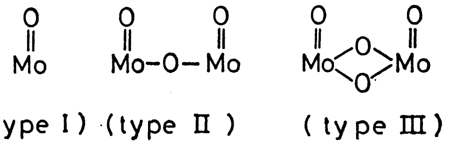

Fig. 1. Basic units of three types of structure of molybdenum(V) complexes.

Most of the molybdenum(V) complexes can be classified into three types (Fig. 1). Recent studies on the oxidation of some type I complexes by nitrate[6,10,11] and nitrite[7] ions revealed that they are much more readily oxidized than dimeric complexes. The oxidation of dimeric Mo(V) complex (structure not clearly described) by nitrate ions is considered to involve a small amount of monomeric Mo(V) which is in equilibrium with the Mo(V) dimer.[12] For the oxidation of the Mo(V) dimer with I_3^- and O_2, Mo(IV) was proposed as a redox active intermediate.[13] On the other hand, for the oxidation of $[Mo_2O_4(edta)]^{2-}$ with $[IrCl_6]^{2-}$ or $[Fe(phen)_3]^{3+}$ (phen=1,10-phenanthroline), it is not necessary to consider an intermediate formation prior to the electron transfer process.[8]

The purpose of this work is to get further information on the oxidation mechanism of the molybdenum(V) complexes of type III, by comparing the behavior of two complexes, $[Mo_2O_4(edta)]^{2-}$ [14] and $[Mo_2O_4(aq)]^{2+}$.[15,16] Coordinated water molecules in the latter are labile to substitution,[17] whereas $[Mo_2O_4(edta)]^{2-}$ is inert unless acid concentration is sufficiently high ($[H^+]>0.5$ M; M=mol dm^{-3}).[14] The μ-hyperoxo dicobalt(III) ion, $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$ was used as an oxidizing reagent which is known to be reduced through an outer-sphere mechanism to the corresponding μ-peroxo ion by one electron transfer process.[18,19]

Experimental

Materials. *Disodium* μ*(N,N′)-Ethylenediaminetetraacetato-di-*μ*-oxo-bis[oxomolybdate(V)] Dihydrate,* $Na_2[Mo_2O_4(edta)]\cdot 2H_2O$: The complex was prepared by a method similar to that described previously;[14] dipyridinium pentachlorooxomolybdate(V) ($(pyH)_2[MoOCl_5]$)[20] was used instead of the corresponding ammonium salt.

A Solution of the Aqua Complex of Di-μ*-oxo-bis[oxomolybdenum(V)],* $[Mo_2O_4(aq)]^{2+}$: Ten grams of $(pyH)_2[MoOCl_5]$ was dissolved in 500 cm^3 of 0.1 M perchloric acid ($HClO_4$). An orange solution was obtained, containing $[Mo_2O_4(aq)]^{2+}$ as the main species. In order to remove impurities, the solution was treated with an ion-exchange column, Dowex 50W-X8 resin (H^+-form). An orange band remained on the column. The column was washed with 100 cm^3 each of 0.1, 0.2, and 0.5 M $HClO_4$ and 50 cm^3 of 1 M $HClO_4$ successively. $[Mo_2O_4(aq)]^{2+}$ was eluted with 2 M $HClO_4$. About 0.05 M (as dimer) solution of $[Mo_2O_4(aq)]^{2+}$ was obtained (*ca.* 150 cm^3). All the preparative and the ion-exchange work was carried out under nitrogen atmosphere to avoid air oxidation of $[Mo_2O_4(aq)]^{2+}$.[14] This procedure is important since Mo(VI)[21]did not seem to have been completely removed by ion-exchange purification. The concentration of $[Mo_2O_4(aq)]^{2+}$ in the eluate was determined spectroscopically from the optical density at 384 nm ($\varepsilon=103$ per dimer[14]).

Other Materials: μ-Hyperoxo-bis[pentaamminecobalt(III)] perchlorate dihydrate, $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5](ClO_4)_5\cdot 2H_2O$, was prepared from the chloride salt[23] according to the method of Linhard and Weigel.[24] Sodium perchlorate (special grade) was used for the adjustment of ionic strength without further purification. Lithium perchlorate, used for the adjustment of ionic strength, was prepared from lithium carbonate and perchloric acid, and recrystallized twice. The concentration of the solution of lithium perchlorate (*ca.* 3 M) was determined by exchanging the lithium ion for proton with an ion-exchange regin of H^+-type (Amberlite IR-120), and titration with a standard sodium hydroxide solution.

Measurements. A Hitachi 124 spectrophotometer with a Hitachi recorder QPD-34 was used for the measurement of visible and ultraviolet absorption spectra and for kinetic studies.

Kinetic Runs. Solutions of $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5](ClO_4)_5\cdot 2H_2O$ and $Na_2[Mo_2O_4(edta)]\cdot 2H_2O$ were prepared every day, whereas that of $[Mo_2O_4(aq)]^{2+}$ was kept in a refrigerator for *ca.* a week under nitrogen atmosphere. Each solution was kept in a thermostat at the desired temperature for at least 30 min, and mixed to start kinetic runs. The rate of decrease in concentration of the μ-hyperoxo ion was followed at 670 nm, where it has a strong absorption peak (ε= 832 per dimer[25]), and no other compounds involved in the reaction have significant absorption. The reaction cell was shaken quickly at appropriate time intervals in order to remove the bubbles of oxygen gas on the cell walls formed during the course of reaction. For the reaction of $[Mo_2O_4(aq)]^{2+}$, all the procedures were carried out under nitrogen atmosphere with use of syringes, needles and rubber caps. Without such a precaution, it was difficult to get reproducible results. A strong catalytic effect of Mo(VI) on the rate of the reaction seems to be responsible. It was difficult to get the solution of $[Mo_2O_4(aq)]^{2+}$ free from pyridinium ion by the ion-exchange separation. $[Mo_2O_4(aq)]^{2+}$ seems to be eluted easily for dipositive ion. It was found that pyridinium ion does not affect the rate of the reaction up to the concentration 0.01 M.

Results

Kinetics of the Oxidation of $[Mo_2O_4(edta)]^{2-}$ *with* $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$. $[Mo_2O_4(edta)]^{2-}$ undergoes acid hydrolysis in aqueous perchloric acid solution ($[H^+]>0.5$ M).[14] In this work, $[H^+]$ was adjusted to 0.1 M or lower so that it was not necessary to consider the effect of acid hydrolysis. When an aqueous solution of $[Mo_2O_4(edta)]^{2-}$ was mixed with that of the μ-hyperoxo dicobalt(III) ion in 0.1 M $HClO_4$, the light absorption of these two ions in the visible region decreased slowly, no rapid change in absorption spectra preceding. No rapid reaction between these two ions other than weak interaction such as ion-pair formation is feasible.

The stoichiometry of the reaction corresponding to the slow change was determined as follows. 0.1 M perchloric acid solutions containing the μ-hyperoxo ions more than twice $[Mo_2O_4(edta)]^{2-}$ in molar concentration were kept at 40 °C for a day, and the amount of remaining μ-hyperoxo ions was estimated from the intensity of the absorption peak at 670 nm. Two moles of the μ-hyperoxo ions were consumed per one mol of $[Mo_2O_4(edta)]^{2-}$. Thus each molybdenum(V) ion in the complex was oxidized to Mo(VI) by one μ-hyperoxo ion. The μ-peroxo ion, $[(NH_3)_5CoO_2{}^{(2-)}Co(NH_3)_5]^{4+}$, the initial product of the electron transfer reaction should have decomposed rapidly in acid solutions to give Co(II), O_2, and ammonium ions.[26] Mo(VI) is in dimer-monomer equilibrium.[22] The coordination of the edta-ligand is unlikely under the given acid concentration.[27] The entire reaction can be written as follows.

$$
\begin{aligned}
&[Mo_2O_4(edta)]^{2-} + 2[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+} \\
&\quad + (20+n)H^+ \longrightarrow 2Mo(VI) + H_nedta^{(4-n)-} \\
&\qquad + 4Co(II) + 2O_2 + 20NH_4{}^+ \qquad (1)
\end{aligned}
$$

Kinetics of the reaction was studied at 35—50 °C and ionic strength 0.1—2.0 M (adjusted with $NaClO_4$). The molybdenum(V) complex was used in at least 10 fold excess to the μ-hyperoxo ion. The first-order plots log (OD_t) against time t are linear to over 90% of the course of reaction (OD_∞ was approximated to zero), where OD_t stands for the absorbance at 670 nm at time t. The first-order rate constant k_{obsd} is independent of $[H^+]$ in the range 0.05—0.1 M. The dependence of k_{obsd} on the concentration of $[Mo_2O_4(edta)]^{2-}$ at various ionic strengths is shown in Fig. 2. The rate constant increases with decrease in the ionic strength, tending to be saturated at higher concentrations of $[Mo_2O_4(edta)]^{2-}$. The plots $k_{obsd}{}^{-1}$ against $[Mo_2O_4(edta)^{2-}]^{-1}$ are linear (Fig. 3). Intercepts of the straight

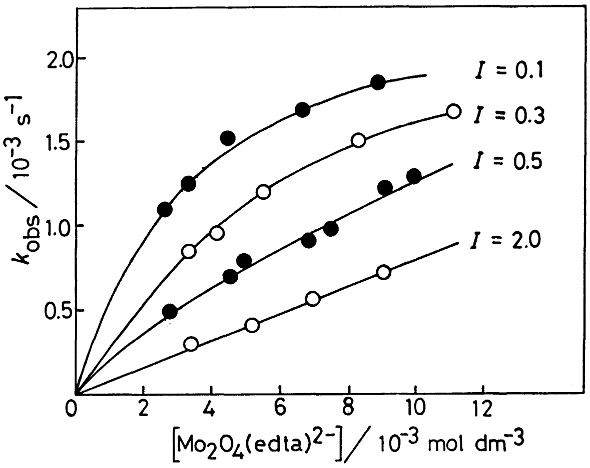

Fig. 2. The dependence of k_{obsd} on $[Mo_2O_4(edta)^{2-}]$ for the oxidation of $[Mo_2O_4(edta)]^{2-}$ with $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$ in 0.1 M perchloric acid, with $[Mo_2O_4(edta)]^{2-}$ in large excess at various ionic strengths (adjusted with $NaClO_4$), at 40 °C and $[\mu\text{-}O_2{}^{(-)}] = (2—5) \times 10^{-4}$ mol dm^{-3}.

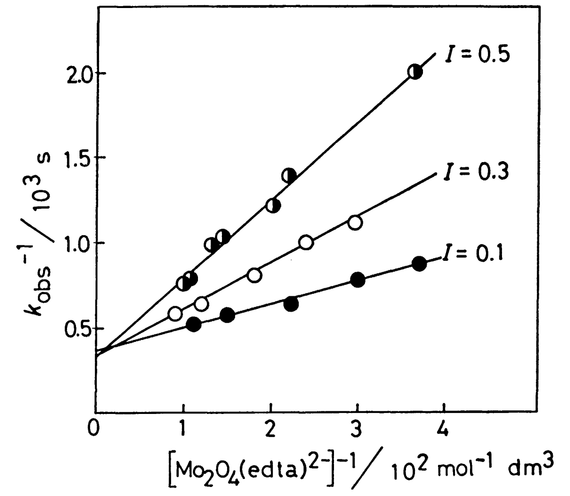

Fig. 3. The dependence of $k_{obsid}{}^{-1}$ on $[Mo_2O_4(edta)^{2-}]^{-1}$ for the oxidation of $[Mo_2O_4(edta)]^{2-}$ with $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$ in 0.1 M perchloric acid, with $[Mo_2O_4(edta)]^{2-}$ in large excess at various ionic strength (adjusted with $NaClO_4$), at 40 °C and $[\mu\text{-}O_2{}^{(-)}] = (2—5) \times 10^{-4}$ mol dm^{-3}.

lines at three different ionic strengths coincide with each other within experimental error. The rate of Reaction 1 does not change in the presence of Cl^- up to 0.1 M.

Kinetics of the Oxidation of $[Mo_2O_4(aq)]^{2+}$ *with* $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$. Similar to the case of the oxidation of $[Mo_2O_4(edta)]^{2-}$, the reaction of $[Mo_2O_4(aq)]^{2+}$ with the μ-hyperoxo ion is expressed as follows from the change of absorption spectra and stoichiometric studies in 2 M $HClO_4$:

$$[Mo_2O_4(aq)]^{2+} + 2[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+} + 20H^+ \longrightarrow 2Mo(VI) + 4Co(II) + 2O_2 + 20NH_4{}^+. \quad (2)$$

Kinetics of the reaction was studied at 25—40 °C for $[H^+]=0.5$—2.0 M. It was difficult at lower $[H^+]$ to get the concentration of $[Mo_2O_4(aq)]^{2+}$ high enough for the kinetic studies. $[Mo_2O_4(aq)]^{2+}$ undergoes structural change for $[H^+]<0.1$ M.[14,17] The molybdenum complex was used in large excess as compared to the μ-hyperoxo ion. The concentration ranges of the reactants are $(8—35)\times10^{-3}$ M for $[Mo_2O_4(aq)]^{2+}$ and $(2.5—5)\times10^{-4}$ M for the μ-hyperoxo ion.

The decrease of absorbance (OD) at 670 nm did not obey the first order rate law. The OD decreased linearly with time at the initial stage of the reaction (until the concentration of the μ-hyperoxo ion reached *ca.* 1.5×10^{-4} M), and subsequently more slowly. The slope of the plots, OD_t against t, did not change when the concentration of the μ-hyperoxo ion changed from 3×10^{-4} to 5×10^{-4} M at a constant concentration of $[Mo_2O_4(aq)]^{2+}$.

The OD change per second was converted into the molar consumption of the μ-hyperoxo ion per second (denoted by k_i) by using the ε value (832)[25] at 670 nm. The dependence of k_i on the concentration of $[Mo_2O_4(aq)]^{2+}$ at $[H^+]=2.0$ M (Fig. 4) suggests that k_i is of first-order with respect to $[Mo_2O_4(aq)^{2+}]$.

The effect of $[H^+]$ on k_i was studied with a fixed concentration of the reactants and at $I=2.0$ M ($LiClO_4$). The k_i values seem to be inversely proportional to $[H^+]$.

The effect of anions added was studied for Cl^- and Br^-. Significant acceleration of the rate by both ions was observed. The rate of disappearance of the μ-hyperoxo ion turned out to be of first-order. Under the conditions $[H^+]=2.0$ M, $[Mo_2O_4(aq)^{2+}]=8.55\times10^{-3}$ M, $[\mu\text{-}O_2{}^{(-)}]=3.50\times10^{-4}$ M, and $[Cl^-]=0.12$ M and at 35 °C, $\tau_{1/2}$ is about 4 min, whereas under similar conditions in the absence of Cl^-, it took more than 8 h for the reaction to complete. The effect of Br^- is of similar magnitude to that of Cl^-. Mo(VI) also accelerates the rate. The rate of disappearance of the μ-hyperoxo ion remained in zero-order for a much longer part of the reaction. Under the conditions $[H^+]=2.0$ M, $[Mo_2O_4(aq)^{2+}]=8.55\times10^{-3}$ M, $[\mu\text{-}O_2{}^{(-)}]=3.50\times10^{-4}$ M and [Mo(VI)] (as sodium molybdate) $=0.015$ M, the rate was *ca.* 4 times greater than that without Mo(VI). The extent of enhancement depends approximately linearly on the concentration of the Mo(VI) ($[Mo(VI)]=(0.5—3)\times10^{-2}$ M). The effect was more remarkable at lower acid concentrations. Apparently the effect depends on the time after mixing of $[Mo_2O_4(aq)]^{2+}$ and Mo(VI).

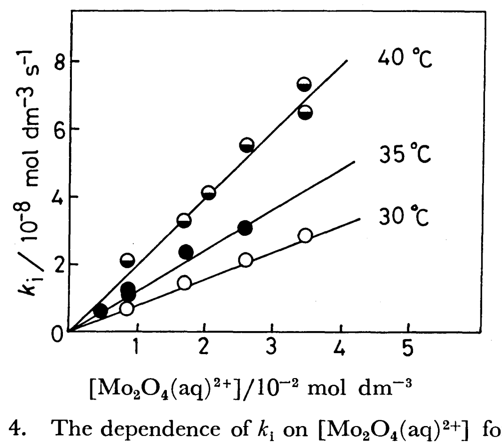

Fig. 4. The dependence of k_i on $[Mo_2O_4(aq)^{2+}]$ for the oxidation of $[Mo_2O_4(aq)]^{2+}$ with $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$ in 2 M perchloric acid, with $[Mo_2O_4(aq)]^{2+}$ in large excess, at various temperatures and $[\mu\text{-}O_2{}^{(-)}]=(2.5—5)\times10^{-4}$ mol dm^{-3}.

It must be considered whether the Mo(VI) which is built up during the kinetic runs is catalytic to Reaction 2. The Mo(VI) concentrations are equal to the initial concentrations of the μ-hyperoxo ion at the end of the runs: $(2.5—5)\times10^{-4}$ M. It is therefore concluded that the Mo(VI) produced does not have a significant effect upon the rate of the reaction, at least at the initial part of the reaction which is important in this study.

Discussion

Mechanism of the Oxidation of $[Mo_2O_4(edta)]^{2-}$ *by* $[(NH_3)_5CoO_2{}^{(-)}Co(NH_3)_5]^{5+}$. The results shown in Figs. 1 and 2 can be interpreted in terms of an ion-pair formation between the two reactants, the formation constant being expected to be large since they have high opposite charges (+5 and −2).

Since the μ-hyperoxo ion is one electron oxidizing reagent, oxidation of dimeric $[Mo_2O_4(edta)]^{2-}$ should proceed in two steps, and an immediate product of the first electron transfer process should be a mixed valence dimer, "Mo^VMo^{VI}," the structure of which is not known. Wharton *et al.*[8] studied the oxidation of $[Mo_2O_4(edta)]^{2-}$ with $[IrCl_6]^{2-}$ and $[Fe(phen)_3]^{3+}$, and found that the following reactions are reversible:

$$[Mo_2O_4(edta)]^{2-} + \underset{([Fe(phen)_3]^{3+})}{[IrCl_6]^{2-}} \rightleftarrows \text{“}Mo^VMo^{VI}\text{”} + \underset{([Fe(phen)_3]^{2+})}{[IrCl_6]^{3-}}. \quad (3)$$

They suggested that the mixed valence dimer most likely decomposes into two monomers Mo(V) and Mo(VI), the former being rapidly oxidized by the oxidant. In the present case, the process corresponding to Reaction 3 is not reversible since the reduced form of the oxidant decomposes rapidly under the experimental conditions.[26] The oxidation of "Mo^VMo^{VI}" by the second μ-hyperoxo ion should be rapid possibly through the decomposition into the monomers. There was no intermediate (corresponding to "Mo^VMo^{VI}") detectable from the change of absorption spectra during the course of reaction and from the kinetic treatment.

The following mechanism (4—7) is proposed for

Reaction 1, where $\mu\text{-}O_2^{(-)}$ and $\mu\text{-}O_2^{(2-)}$ stand for $[(NH_3)_5CoO_2^{(-)}Co(NH_3)_5]^{5+}$ and $[(NH_3)_5CoO_2^{(2-)}Co(NH_3)_5]^{4+}$, respectively:

$$[Mo_2O_4(edta)]^{2-} + \mu\text{-}O_2^{(-)} \overset{K_{IP}}{\rightleftharpoons} \text{ion-pair}, \qquad (4)$$

$$\text{ion-pair} \xrightarrow{k_e} \text{“Mo}^{V}\text{Mo}^{VI}\text{”} + \mu\text{-}O_2^{(2-)}, \qquad (5)$$

$$\text{“Mo}^{V}\text{Mo}^{VI}\text{”} + \mu\text{-}O_2^{(-)} \xrightarrow{\text{fast}} 2\text{Mo(VI)} + \mu\text{-}O_2^{(2-)}, \qquad (6)$$

$$\mu\text{-}O_2^{(2-)} \xrightarrow[H^+]{\text{fast}} 2\text{Co(II)} + O_2 + 10NH_4^+. \qquad (7)$$

From this, we obtain

$$-\frac{d[\mu\text{-}O_2^{(-)}]}{dt} = \frac{2k_eK_{IP}[Mo_2O_4(edta)^{2-}][\mu\text{-}O_2^{(-)}]}{1+K_{IP}[Mo_2O_4(edta)^{2-}]}, \qquad (8)$$

which is in line with the experimental results. k_{obsd} can be expressed by

$$k_{obsd} = \frac{2k_eK_{IP}[Mo_2O_4(edta)^{2-}]}{1+K_{IP}[Mo_2O_4(edta)^{2-}]}, \qquad (9)$$

which can be rearranged to

$$\frac{1}{k_{obsd}} = \frac{1}{2k_eK_{IP}[Mo_2O_4(edta)^{2-}]} + \frac{1}{2k_e}. \qquad (10)$$

For I=2.0, where the ion-pair formation is less favorable due to the presence of higher concentration of the electrolyte, $NaClO_4$, the assumption $1 \gg K_{IP}[Mo_2O_4(edta)^{2-}]$ would be useful for interpretation of the experimental results. The values of k_e, K_{IP}, and k_eK_{IP} are calculated from the data for various ionic strengths (Table 1). The k_e values are almost constant regardless of ionic strength, suggesting that the rate of electron transfer process within the ion-pair is not affected by ionic strength. The results provide an excellent example of electron transfer within an ion-pair.

TABLE 1. RATE CONSTANTS AND ION-PAIR FORMATION CONSTANTS FOR THE OXIDATION OF $[Mo_2O_4(edta)]^{2-}$ WITH $[(NH_3)_5CoO_2^{(-)}Co(NH_3)_5]^{5+}$ IN 0.1 M PERCHLORIC ACID[a)]
(Ionic strengths were adjusted with $NaClO_4$)

Ionic strength (I)	Temperature (°C)	$\frac{k_e}{(10^{-3}\,s^{-1})}$	$\frac{K_{IP}}{(mol\,dm^{-3})}$	$\frac{k_eK_{IP}}{(10^{-1}\,s^{-1}\,mol\,dm^{-3})}$
0.1	35.4	0.64±0.01	320±10	2.02±0.05
0.1	40.0	1.34±0.08	270±40	3.62±0.05
0.1	45.0	2.5 ±0.2	350±70	8.9 ±1.3
0.3	40.0	1.5 ±0.1	120±20	1.8 ±0.1
0.5	40.0	1.5 ±0.2	70±20	1.07±0.05
2.0	40.0			0.40±0.02
2.0	45.0			0.78±0.04
2.0	51.2			1.8 ±0.2

a) Errors were determined by the least-square treatment with no weighing (confidence level, 0.7).

The activation parameters were compared with those of oxidation of $[Mo_2O_4(edta)]^{2-}$ with other oxidants (Table 2). The parameters vary remarkably with the charge of the oxidant. This suggests the important role of electrostatic interactions on the reaction mechanism.

TABLE 2. COMPARISON OF THE ACTIVATION PARAMETERS FOR THE OXIDATION OF $[Mo_2O_4(edta)]^{2-}$ WITH VARIOUS OXIDANTS

Oxidant	Term	I (M)	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})
$[(NH_3)_5CoO_2^{(-)}\text{-}Co(NH_3)_5]^{5+}$	k_e	0.1	28 ±4	18 ±11
$[(NH_3)_5CoO_2^{(-)}\text{-}Co(NH_3)_5]^{5+}$	k_eK_{IP}	2.0	26.5±0.8	21 ± 3
$[Fe(phen)_3]^{3+}$ a)	k_eK_{IP} b)	1.0	16.6±0.4	12.3±1.3
$[IrCl_6]^{2-}$ a)	k_e b)	1.0	13.3±0.3	−10.0±1.0

a) From Ref. 8. b) The term was assumed from the charge of the reactants.

Kinetics of the Oxidation of $[Mo_2O_4(aq)]^{2+}$ *with* $[(NH_3)_5CoO_2^{(-)}Co(NH_3)_5]^{5+}$. The following mechanism is proposed to explain the experimental results: It involves the conversion of $[Mo_2O_4(aq)]^{2+}$ into an intermediate A which is then oxidized by the μ-hyperoxo ion;

$$[Mo_2O_4(aq)]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A, \qquad (11)$$

$$A + \mu\text{-}O_2^{(-)} \xrightarrow{k_2} \text{“Mo}^{V}\text{Mo}^{VI}\text{”} + \mu\text{-}O_2^{(2-)}. \qquad (12)$$

Reaction 12 is followed by similar steps to those of Reactions 6 and 7. By applying stationary state approximation to A, we obtain

$$-\frac{d[\mu\text{-}O_2^{(-)}]}{dt} = \frac{2k_1k_2[\mu\text{-}O_2^{(-)}][Mo_2O_4(aq)^{2+}]}{k_{-1}+k_2[\mu\text{-}O_2^{(-)}]}. \qquad (13)$$

If $k_{-1} \ll k_2[\mu\text{-}O_2^{(-)}]$, this can be simplified to

$$-\frac{d[\mu\text{-}O_2^{(-)}]}{dt} = 2k_1[Mo_2O_4(aq)^{2+}], \qquad (14)$$

which is consistent with the observed zero-order dependence of the rate on $[\mu\text{-}O_2^{(-)}]$ at the initial part of the reaction.

For most of the runs, only k_i (equal to $2k_1$) was estimated from the initial part of the absorbance change. No other rate constants were estimated since the reaction was too slow to be followed until completion. Attempts to work with a large excess of the μ-hyperoxo ion as compared to the molybdenum complex, which may be more useful for checking Eq. 13, were not successful. No appropriate wavelength was found at which absorbance change was sufficiently big.

The reciprocal dependence of k_i on $[H^+]$ can best be explained by assuming a conjugate base of the aqua ion, $[Mo_2O_4(OH)(aq)]^+$. As the $[H^+]$-independent path is negligible, intermediate A should be formed almost exclusively from this conjugate base. k_i is then expressed by

$$k_i = 2k_1 = 2k_{OH}K_a[H^+], \qquad (15)$$

where k_{OH} is the rate constant for the formation of A from $[Mo_2O_4(OH)(aq)]^+$. K_a is the acid dissociation constant of $[Mo_2O_4(aq)]^{2+}$. It is assumed to be negligibly small as compared with $[H^+]$. The K_a value was not obtained, and the only relevant datum is the pK_a value (3.02) of the aqua ligand of $[Mo_2O_4(hedta)(H_2O)]^-$ (H_3hedta=N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid).[28] At 25 °C, k_{OH} K_a=$(4.3\pm0.3)\times10^{-6}$

mol dm^{-3} s^{-1} and the corresponding activation parameters (25—40 °C) are $\Delta H^{*}=18.5\pm1.4$ kcal mol^{-1} and $\Delta S^{*}=-21\pm5$ cal K^{-1} mol^{-1}.

Structure of the Intermediate of the Oxidation of $[Mo_2O_4(aq)]^{2+}$. Intermediate A is considered to have a structure similar to that of the type II species (Fig. 1), a single bridged Mo(V) species.

The conversion of type III complexes into type II is known. The structure of Mo(V) was studied in hydrochloric and sulfuric acid solutions of various acid concentrations.[29] Equilibrium 17 exists in these acid solutions, and shifts in a rightward direction as the concentation of acid becomes higher.

$$\underset{\text{(type III)}}{Mo_2O_4^{2+}} \rightleftharpoons \underset{\text{(type II)}}{Mo_2O_3^{4+}} \rightleftharpoons \underset{\text{(type I)}}{2MoO^{3+}} \tag{16}$$

Our preliminary observation suggests that the rate of interconversion is very great, the interconversion finishing within several seconds at 25 °C in *ca.* 5 M HCl solution. Type II species is known to be predominant in 5 M HCl, and type III in 5 M $HClO_4$.[14] Thus the formation of type II (and possibly type I) complexes seems to be mainly due to the presence of Cl^- or HSO_4^- and not that of proton.

Also the color change of $[Mo_2O_4(\text{L-cys})_2]^{2-}$ (L-cys= L-cysteinate dianion) from orange to blue in basic solution (pH=*ca.* 10) was claimed to be due to slow formation of a single-bridged species.[30,31] Such a change was not observed in a solution of lower pH (<7). The resulting single-bridged species was far more easily oxidized by flavines[32] and cytochrome c[9] than was the parent complex.

Guymon and Spence studied the oxidation of dimeric Mo(V) with NO_3^-,[12] I_3^-,[13] and O_2[13] in tartrate and phosphate buffer solutions, but did not discuss the detailed structure of the Mo(V) dimer they were dealing with. It is now possible to assume reasonably that the complex had type III structure with some buffer anions coordinated.[1] From the EPR measurement and half-order dependence of the rate on the Mo(V) dimer concentration, they proposed monomeric Mo(V) species as an intermediate of the reaction with NO_3^-. For the reaction with I_3^- and O_2, they observed zero-order dependence of the rate on the dimer concentration, and proposed Mo(IV)[33] as a redox active intermediate, assuming the disproportionation of Mo(V) dimer to Mo(IV) and Mo(VI). Reports have recently been given on the disproportionation of some dimeric Mo(V) complexes,[34,35] but they are of only type II complexes with sulfur-donor ligands. No disproportionation of type III complex is yet known. Both Mo(IV) and monomeric Mo(V) species would be regarded as secondary products of type III complexes through type II species. The results of Guymon and Spence on the reactions with I_3^- and O_2 might be explained also in terms of a single-bridged intermediate.

It should be noted that we cannot deny the existence of Mo(IV) and monomeric Mo(V) as a real reacting species for our reaction, if the postulated single-bridged species formed Mo(IV) or monomeric Mo(V) very rapidly (*viz.*, the rate-determining step is still the formation of the single-bridged species). However, the positive catalytic effect of Mo(VI) would not support the involvement of Mo(IV), since the addition of Mo(VI) would be expected to suppress the disproportionation of Mo(V) dimer.[34]

We thus concluded that A is a single-bridged Mo(V) dimer rather than the Mo(V) monomer or the Mo(IV) species.

Influence of Halide Ions and Mo(VI) on the Oxidation of $[Mo_2O_4(aq)]^{2+}$. The presence of Cl^- and HSO_4^- makes a single-bridged Mo(V) dimer predominant over a double-bridged dimer in aqueous acid solutions. The positive catalytic effect of Cl^- and Br^- on Reaction 2 can be explained by this fact. Since the aqua ligands in $[Mo_2O_4(aq)]^{2+}$ are labile,[17] Cl^- and Br^- would readily substitute for the water and might facilitate bridge cleavage. The halide ions and OH^- in $[Mo_2O_4(OH)(aq)]^+$ may exert a similar electronic effect on the bridge cleavage.

We have no explanation for the catalytic effect of Mo(VI) on the rate of Reaction 2. It is possible that a similar interaction to that in molybdenum blue would reduce the stability of Mo_2O_4-moiety, increasing the sensitivity to oxidative attack. The effect depends on the time after mixing Mo(VI) with $[Mo_2O_4(aq)]^{2+}$.

Comparison of the Oxidation Mechanism of the Two Mo(V) Complexes. The most interesting feature of the present results is the difference in the kinetic behavior of the two complexes $[Mo_2O_4(edta)]^{2-}$ and $[Mo_2O_4(aq)]^{2+}$ towards their oxidation by $[(NH_3)_5CoO_2^{(-)}Co(NH_3)_5]^{5+}$. The ion-pair formation was important for the oxidation of $[Mo_2O_4(edta)]^{2-}$ but not favorable for that of positively charged $[Mo_2O_4(aq)]^{2+}$, which gave the zero-order dependence on $[\mu\text{-}O_2^{(-)}]$. In the latter case, formation of a more easily oxidizable intermediate was proposed.

Recently Cayley *et al.*[36] examined the oxidation of $[Mo_2O_4(aq)]^{2+}$ by $[Fe(phen)_3]^{3+}$ or $[IrCl_6]^{2-}$ and found two term rate laws, one term independent of the oxidant concentration and the other linearly dependent on it. Their oxidants (E_0=1.06 V and 1.017 V respectively)[37] are marginally better than the μ-hyperoxo ion (E_0=*ca.* 1.0 V)[38] in terms of redox potentials, and the 5+ charge and inaccessibility of the μ-hyperoxo group are presumably responsible for exclusion of the direct bimolecular route.

Oxidation of $[Mo_2O_4(edta)]^{2-}$ by these three oxidants gave no oxidant independent path. Multidentate edta-ligand would stabilize the Mo_2O_4-moiety through firm coordination, making the cleavage of the oxo bridge more difficult. Also the lack of coordinated water may be an important factor to determine the reaction pattern, since the water ligands of $[Mo_2O_4(aq)]^{2+}$ play important roles for the formation of intermediate. The absence of the effect of Cl^- and the independence of $[H^+]$ for the rate of the reaction of $[Mo_2O_4(edta)]^{2-}$ are explained also by the lack of water ligand.

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