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Kinetic Investigation of the Cerium(IV) Oxidation of the Bis(μ -oxo)bis(oxomolybdenum(V)) Ion

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The reaction between bis(μ -oxo)bis(oxomolybdenum(V)), $\text{Mo}_2\text{O}_4^{2+}$, and Ce(IV) has been studied in acidic perchlorate media via stopped-flow techniques. The reaction is rapid and quantitative, and the stoichiometry corresponds to $\text{Mo}_2\text{O}_4^{2+} + 2\text{Ce(IV)} \xrightarrow{\text{H}^+} \text{Mo}^{\text{VI}}_2 + \text{Ce(III)}$. The observed rate law for the reaction for $[\text{Mo}_2\text{O}_4^{2+}] > [\text{Ce(IV)}]$ is $-d[\text{Ce(IV)}]/2dt = k_2[\text{Mo}_2\text{O}_4^{2+}][\text{Ce(IV)}]$, where $k_2 = k_{2h}K_h/([H^+] + K_h)$. The rate constant, k_{2h} , was found to be $2.73 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $K_h = 0.46 \text{ M}$ ($\mu = 2.0 \text{ M}$, $T = 25.0 \text{ }^\circ\text{C}$). The observed rate constant was unaffected by added products or Cl^- ($< 5 \times 10^{-3}$) but increased slightly with ionic strength. Evidence for an ion pair formed between the aquomolybdenum(V) dimer and Ce(IV) is presented.

Introduction

In the investigation of the aquomolybdenum(V) dimer, $(\text{H}_2\text{O})_6\text{Mo}_2\text{O}_4^{2+}$, oxidation by several strong oxidizing agents¹ (Fe(phen)_3^{3+} (1.06 V), IrCl_6^{2-} (1.017 V), and $[(\text{NH}_3)_5\text{Co}(\text{O}_2)]^{5+}$ ($\mu\text{-O}_2^-$) (1.0 V),^{2,3} the reaction with Fe(phen)_3^{3+} and IrCl_6^{2-} was characterized by a rate law, rate = $k_1[\text{Mo}_2\text{O}_4^{2+}] + k_2[\text{Mo}_2\text{O}_4^{2+}][\text{Ox}]$, that showed a pathway independent of oxidant and another pathway that involved the oxidizing agent. The rate constants for the oxidant-independent steps were very slow (IrCl_6^{2-} , $1.48 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$; Fe(phen)_3^{3+} , $1.55 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$) while the oxidative pathways were more rapid (IrCl_6^{2-} , $0.140 \text{ M}^{-1} \text{ s}^{-1}$; Fe(phen)_3^{3+} , $34.0 \text{ M}^{-1} \text{ s}^{-1}$). The μ -superoxide complex, $[(\text{NH}_3)_5\text{Co}(\text{O}_2)]^{5+}$ ($\mu\text{-O}_2^-$), showed only the nonoxidative step ($4.3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$). Ce(IV), a strong oxidant (1.73 V),^{4a,b} is capable of quantitatively oxidizing the aquomolybdenum(V) dimer to Mo(VI) in 2 M HClO_4 .⁵ It is of some interest to determine whether a rate expression similar to those of Fe(phen)_3^{3+} and IrCl_6^{2-} or for MnO_4^- redox oxidation of the aquomolybdenum(V) dimer⁶ is present with the use of the stronger oxidant. The presence of a partially dissociated dimer species was inferred from the nonoxidative pathway of the Ir(IV) and Fe(III) work but was not observed in the more rapidly reacting Mn(VII).

Experimental Section

Stock solutions of the bis(μ -oxo)bis(oxomolybdenum(V)) complex were prepared by (1) reduction of a $\text{Na}_2\text{MoO}_4/3 \text{ M HCl}$ solution by shaking with metallic mercury^{6,7} (the solutions were filtered free of Hg and Hg_2Cl_2 and stored at $5 \text{ }^\circ\text{C}$ over fresh Hg) and (2) dissolving $(\text{NH}_4)_2\text{MoO}_4$ (gift from Climax Molybdenum Co.) in 1 M HCl. The dimer/HCl solutions were diluted with distilled water to $[\text{H}^+] < 0.1 \text{ M}$, deoxygenated with N_2 , and allowed to aquate in the dark overnight. The aquation time did not appear to influence the results.

The dimer was collected on a Dowex 50-X8 (50-100 mesh) column in the H^+ form and washed free of Cl^- with deoxygenated distilled water. The $\text{Mo}_2\text{O}_4^{2+}$ ion was eluted with either 1.0 or 2.0 M HClO_4 ($\mu = 2.0 \text{ M}$ (NaClO_4)) and diluted to the proper reaction conditions with deoxygenated $\text{HClO}_4/\text{NaClO}_4$ solutions of known concentrations. Deoxygenation retarded the decomposition of the dimer solutions. The dimer concentration was determined at $\lambda = 384 \text{ nm}$ ($\epsilon = 103 \text{ M}^{-1} \text{ cm}^{-1}$).¹ Total Mo was determined by the H_2O_2 method.⁸

Cerium(IV) perchlorate stock solutions were prepared by diluting an aliquot of $\text{H}_2\text{Ce}(\text{ClO}_4)_6/6 \text{ M HClO}_4$ (G. F. Smith Chemical Co.) with distilled water or standardized $\text{HClO}_4/\text{NaClO}_4$ solutions to obtain the proper $[\text{H}^+]$, ionic strength, and $[\text{Ce(IV)}]$. The stock Ce(IV) solution was standardized against As_2O_3 .

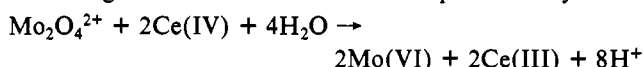
Several experiments were attempted by using trifluoromethanesulfonic acid. This acid was eliminated as it was slowly oxidized by Ce(IV).

Stock solutions of Ce(III) and Mo(VI) were prepared by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (G. F. Smith Chemical Co.) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Baker analyzed reagent) in 2 M HClO_4 .

The reaction was followed by measuring the decrease in absorbance of the reaction mixture with time at 384 nm on an Aminco-Morrow stopped-flow apparatus interfaced to a computer.⁹ The choice of $\lambda = 384 \text{ nm}$ and excess dimer was necessary as the initial and final absorbance values at $\lambda = 290$ and 384 nm, for reaction conditions where $[\text{Ce(IV)}] \gg [\text{dimer}]$, were both high and provided only a small absorbance change. The ϵ values for reactants and products at 384 nm are as follows ($\text{M}^{-1} \text{ cm}^{-1}$): $\text{Mo}_2\text{O}_4^{2+}$, 103 ± 5 ; Ce(IV), 225 ± 8 ;^{10b} Mo(VI), 1.5; Ce(III), ~ 0 . The observed absorbance change was due primarily to the decrease in $[\text{Ce(IV)}]$.

Results

The stoichiometry of the reaction was determined via spectrophotometric titrations at 384 nm by reacting a constant known concentration of $\text{Mo}_2\text{O}_4^{2+}$ with varying known concentrations of Ce(IV). The $[\text{HClO}_4]$ was varied from 1.0 to 3.0 M in these experiments. The ratio of mol of Ce(IV) consumed/mol of $\text{Mo}_2\text{O}_4^{2+}$ initially present was determined by observing the decrease in absorbance of the dimer at 384 nm. Plots of absorbance vs. $[\text{Ce(IV)}]$ data yielded a value of 1.97 ± 0.05 for the stoichiometric ratio $[\text{Ce(IV)}]/[\text{Mo}_2\text{O}_4^{2+}]_0$, indicating the overall reaction can be represented by



The dependence of the reaction rate on initial concentrations of $\text{Mo}_2\text{O}_4^{2+}$ and Ce(IV) was determined by observing the rate of disappearance of absorbance at 384 nm while varying Ce(IV) concentration. The reaction was conducted under pseudo-first-order conditions keeping the dimer in excess (Mo(V) concentration 10 times that of the Ce(IV) used). The rate constants obtained at various reactant concentrations ($[\text{H}^+] = \mu = 2.0 \text{ M}$ (HClO_4), $T = 25.0 \text{ }^\circ\text{C}$) under pseudo-first-order conditions are summarized in Table I.

The reaction traces showed first-order behavior for 3-4 half-lives and showed no deviation when Ce(III) or Mo(VI)

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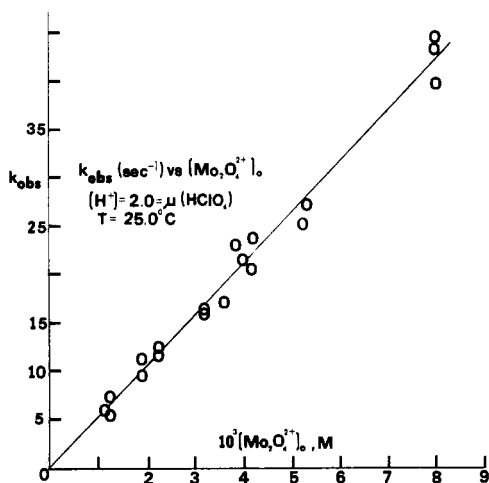
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[†] Based in part on: Chappelle, G. A., M.S. Thesis, Eastern Michigan University, 1982.

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Table I. Rate Constants for the $\text{Mo}_2\text{O}_4^{2+}/\text{Ce(IV)}$ Reaction ($[\text{H}^+] = \mu = 2.0 \text{ M (HClO}_4\text{)}, T = 25.0 \text{ }^\circ\text{C}$)

$10^3 \times [\text{Mo}_2\text{O}_4^{2+}]_0$, M	$10^4 \times [\text{Ce(IV)}]_0$, M	$10^3 \times [\text{Mo(VI)}]_0$, M	$10^3 \times [\text{Ce(III)}]_0$, M	$k_{\text{obsd}}, \text{ s}^{-1}$
1.12	2.20			5.99 ± 0.04^a
1.23	1.49			7.32 ± 0.06
1.15	1.49			5.45 ± 0.04
1.90	2.96	0.00		11.2 ± 0.42
	2.96	1.74		11.4 ± 0.42
	2.96	8.00		9.5 ± 0.10
2.31	2.20			12.4 ± 0.16
2.37	4.37			11.5 ± 0.34
3.25	2.20			15.9 ± 0.44
	3.75			16.4 ± 0.86
	7.80			14.6 ± 0.63
3.42	5.22	0.00		16.2 ± 0.50
		2.25		15.5 ± 0.44
		4.10		15.6 ± 0.63
3.50	6.90		0.00	18.6 ± 0.78
	6.90		0.376	18.8 ± 0.62
	6.90		0.940	17.0 ± 0.28
	6.90		1.30	17.1 ± 0.36
3.60	5.00			17.0 ± 0.70
3.85	4.30	0.00		22.9 ± 0.84
	4.30	8.00		18.0 ± 0.55
	4.30	24.00		16.6 ± 0.73
4.00	8.40	0.00		21.4 ± 0.26
		4.90		18.4 ± 0.24
		9.90		17.0 ± 0.22
		14.80		15.9 ± 0.36
4.20	8.10	0.00		23.5 ± 0.30
		2.50		23.7 ± 0.24
		5.00		23.2 ± 0.72
		7.50		20.4 ± 0.54
5.25	3.9			25.2 ± 0.44
5.34	6.8			27.1 ± 0.60
8.00	4.04	0.00		44.3 ± 0.75
		6.87		43.1 ± 0.87
		10.10		39.7 ± 0.62

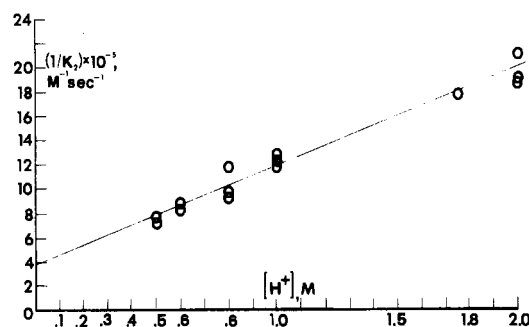
^a $[\text{Cl}^-]_0 = 0, 7.7 \times 10^{-3}, 15.4 \times 10^{-3} \text{ M}$.**Figure 1.** k_{obsd} vs. $[\text{Mo}_2\text{O}_4^{2+}]_0$ ($\lambda = 384 \text{ nm}$, $[\text{H}^+] = \mu = 2 \text{ M (HClO}_4\text{)}, T = 25.0 \text{ }^\circ\text{C}$).

were initially present. The plot of $k_{\text{obsd}} (\text{s}^{-1})$ vs. $[\text{Mo}_2\text{O}_4^{2+}]_0$ was linear with a zero intercept (Figure 1; Table I) and yielded a rate law of the form $-\text{d}[\text{Ce(IV)}]/2\text{d}t = k_{\text{obsd}}[\text{Ce(IV)}]$, where $k_{\text{obsd}} = k_2[\text{Mo}_2\text{O}_4^{2+}]$. The second-order rate constant was found to equal $5.25 \pm 0.42 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

The dependence of the rate constant, k_{obsd} , on $[\text{Mo(VI)}]$ and $[\text{Ce(III)}]$ was determined by reacting various amounts of Mo(VI) or Ce(IV) while holding $[\text{dimer}]_0$ and $[\text{Ce(IV)}]_0$ constant. This was accomplished by adding the desired concentrations of Na_2MoO_4 or $\text{Ce(NO}_3)_3$ solutions in 2 M HClO_4 to the Ce(IV) flask. It was observed that the rate did not

Table II. Hydrogen Ion Dependence ($T = 25.0 \text{ }^\circ\text{C}$, $\mu = 2.0 \text{ M (NaClO}_4\text{)}$)

$[\text{H}^+], \text{ M}$	$10^{-3}k_2, \text{ M}^{-1} \text{ s}^{-1}$	$[\text{H}^+], \text{ M}$	$10^{-3}k_2, \text{ M}^{-1} \text{ s}^{-1}$
0.50	13.7	1.0	8.47
	13.0		8.33
			7.99
			7.80
0.60	12.4	1.75	5.62
	12.4		
	11.4		
0.80	10.8	2.00	5.35
	10.1		5.23
			4.80

**Figure 2.** $1/k_2$ vs. $[\text{H}^+]$ ($\mu = 2.0 \text{ M (NaClO}_4\text{)/HClO}_4$), $T = 25.0 \text{ }^\circ\text{C}$).

depend upon $[\text{Mo(VI)}]_0$ up to approximately $5 \times 10^{-3} \text{ M}$. However, as the amount of Mo(VI) introduced was increased beyond $5 \times 10^{-3} \text{ M}$, the rate showed a definite decrease. The first-order rate constant, k_{obsd} , did not appear to be affected by the presence of Ce(III) or Cl^- .

Hydrogen Ion Dependence. The effect of the hydrogen ion concentration on the rate was determined by varying the acidity while maintaining a constant ionic strength, $\mu = 2.0 \text{ M (HClO}_4\text{)/NaClO}_4$ (Table II). A plot of $1/k_2$ (k_2 = the second-order rate constant) vs. $[\text{H}^+]$ was linear with a nonzero intercept (Figure 2). This indicated the hydrogen ion dependence data were of the form $k_2 = (k_{20}[\text{H}^+] + k_{2h}K_h)/([\text{H}^+] + K_h)$. Here K_h is the hydrolysis constant for the reaction $\text{Ce}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{CeOH}^{3+} + \text{H}^+$. If $k_{20}[\text{H}^+] \ll k_{2h}K_h$, the equation reduces to the form $k_2 = k_{2h}K_h/([\text{H}^+] + K_h)$, which can be plotted as $1/k_2 = 1/k_{2h} + [\text{H}^+]/k_{2h}K_h$. Here the (intercept) $^{-1} = k_{2h} = 2.73 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and (slope) $^{-1} = k_{2h}K_h = 1.25 \times 10^4 \text{ s}^{-1}$. This provides a calculated value of 0.46 M for K_h . Literature values for K_h range from 0.2 to 12 M.^{4a,b,10} A plot of k_2 vs. $[\text{H}^+]^{-1}$ showed curvature at low $[\text{H}^+]$.

Ionic strength studies $[\text{H}^+] = 0.60 \text{ M}$, $\mu = 0.6\text{--}1.16$; $[\text{H}^+] = 0.80 \text{ M}$, $\mu = 1.0\text{--}2.0$) showed a slight increase in k_2 with increasing μ . An increase in k_2 is expected for a reaction system in which the charge product is of the $Z_a^+Z_b^+$ type.

Detection of an Intermediate. Although the observed kinetic traces obtained from a stopped-flow spectrophotometric scan taken between 285 and 500 nm gave no direct evidence of the formation of an intermediate, a series of experiments was conducted to investigate its possible existence. Ce(IV) is known to complex with a variety of reactants.^{11,12} This effort was also prompted by the observation that calculations of the absorbance expected upon mixing, A_0^c , were consistently lower than A_0 values observed in the kinetic traces. Normally, the observed A_0 value for a given set of reactant concentrations is lower than that predicted. This absorbance difference is due to reaction of the initial substances while being mixed and

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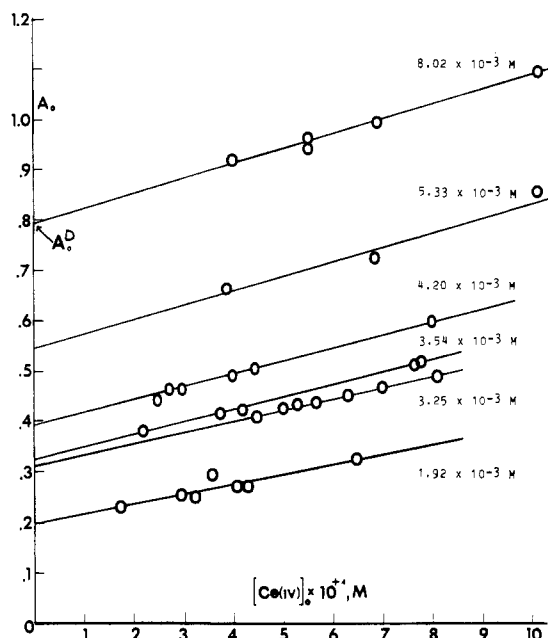


Figure 3. A_0 vs. $[\text{Ce(IV)}]_0$ for six dimer solutions. The intercept of each line corresponds to A_0^D ; the absorbance at $t = 0$ corresponds to that due only to dimer.

transported to the observation cell. The molar absorption coefficients of both reactants and products used were determined with the stopped-flow instrument at $\lambda = 384$ nm. These values correlated well with corresponding molar absorption values obtained with the recording spectrophotometer.

Plots of A_0 vs. $[\text{Ce(IV)}]_0$ (Figure 3), taken under a variety of reaction conditions ($[\text{H}^+]$, molarity of reactants and products, and temperature), were linear with increasing $[\text{Ce(IV)}]_0$. A_0 represents absorbance at $t = 0$. However, the slopes of the lines were consistently higher than the value of $\epsilon_{\text{Ce}^{4+}}$ determined experimentally. The plots of A_0 vs. $[\text{Ce(III)}]_0$ or $[\text{Mo(VI)}]_0$ (at constant initial dimer and Ce(IV) concentrations) gave slopes for $\epsilon_{\text{Ce}^{3+}} \approx 0 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{\text{Mo}^{6+}} = 18.6 \pm 4 \text{ M}^{-1} \text{ cm}^{-1}$.

Plots of A_∞ vs. added $[\text{Mo(VI)}]_0$ for the same group of reactants gave $\epsilon_{\text{Mo}^{6+}} = 4.3 \pm 1.5 \text{ M}^{-1} \text{ cm}^{-1}$. Absorbance data taken at A_∞ represent the reacted solutions at infinite time. This value for $\epsilon_{\text{Mo}^{6+}}$ is comparable to that obtained under nonreaction conditions ($1.5 \text{ M}^{-1} \text{ cm}^{-1}$). Experiments in which solutions of Ce(IV) and Mo(VI) were mixed in both the stopped-flow and DK-2A apparatus showed an increase in absorbance over that expected if the absorbance of the individual solutions were additive.

In an attempt to determine the composition of these absorbing species, two Job's plot experiments was conducted: (1) on the stopped-flow apparatus using $\text{Mo}_2\text{O}_4^{2+}$ and Ce(IV) as the reactants; (2) on the DK apparatus using Mo(VI) and Ce(IV). Both experiments showed a break at $\chi_{\text{Ce}} = 0.8$ and correspond to the ratio of 4 Ce(IV)/Mo species. Spectral scans of the Mo(VI)/Ce(IV) mixtures did not show a spectral envelope different from that of Ce(IV), nor was "molybdenum blue"¹³ observed in any of these experiments. Efforts to detect an absorbing species in the near-IR region (650–900nm) using the stopped-flow technique were negative. Thus, the interaction of Ce(IV) with either Mo^{V}_2 or Mo^{VI} (Mo(VI) is a dimer at the acidities used¹⁴) gives rise to a complex of similar composition. Ce(IV) has been shown not to polymerize at the concentrations used in this kinetic study¹⁰ but might well form

Table III. Results of A_0 vs. Concentration Plots

10^3 [dimer], M	intercept	slope, ^a M^{-1}	cc ^b
8.0	0.766	337 (3)	0.999
8.05	0.794	312 (5)	0.994
7.04	0.708	...	
5.33	0.545	283 (3)	0.986
4.74	0.443	...	
4.20	0.384	264 (5)	0.994
3.54	0.368	244 (4)	0.974
3.25	0.323	249 (3)	0.999
3.25	0.315	218 (9)	0.971
2.31	0.233	295 (2)	1.00
1.92	0.196	194 (3)	0.998
	0.005	$\epsilon_D = 98.7$ (11)	0.997

^a Number of experimental points used to determine line in parentheses. ^b cc = correlation coefficient.

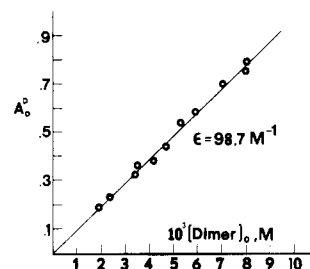


Figure 4. A_0^D vs. $[\text{Mo}_2\text{O}_4^{2+}]_0$. The slope of the line represents ϵ_{dimer} .

dimers at the concentrations used in the Job's plot studies.^{10a} Thus, the apparent indication of a 4:1 complex. We have also observed that VO_2^+ interacts with both Mo^{V}_2 and Mo(VI) to give a nonadditive increase in the absorbance of the resulting mixture.¹⁵

These observations suggested the formulation

$$A_0 = \epsilon_D[D]_0 + \epsilon_{\text{Ox}}[\text{Ox}]_0 + \epsilon_X[X]_0 \quad (1)$$

to account for the presence of another absorbing substance. Here, A_0 = initial absorbance value, and ϵ_D , ϵ_{Ox} , and ϵ_X = molar absorption coefficients of the dimer, oxidant (Ce(IV)), and absorbing intermediate. $[D]_0$, $[\text{Ox}]_0$, and $[X]_0$ = molar concentrations of the dimer, oxidant, and absorbing intermediate present at $t = 0$.

Assuming the 1:1 complex dominates under the pseudo-first-order conditions used



where

$$K_{\text{eq}} = \frac{[X]}{([D]_0 - [X])([\text{Ox}]_0 - [X])} \quad (3)$$

If $[D]_0 \gg [\text{Ox}]_0$, then $([D]_0 - [X]) \approx [D]_0$ and

$$[X] = \frac{K_{\text{eq}}[D]_0[\text{Ox}]_0}{1 + K_{\text{eq}}[D]_0} \quad (4)$$

Substitution of eq 4 into eq 1 leads to eq 5. The third term of eq 5 is of the form derived in the Benesi-Hilderbrand equation.¹⁶

$$A_0 = \epsilon_D[D]_0 + \left[\epsilon_{\text{Ox}} + \frac{\epsilon_X(K_{\text{eq}}[D]_0)}{1 + K_{\text{eq}}[D]_0} \right] [\text{Ox}]_0 \quad (5)$$

Least-squares plots of A_0 vs. $[\text{Ce(IV)}]_0$ for nine dimer solutions (Figure 3) gave intercept ($\epsilon_D[D]_0$) and slope values

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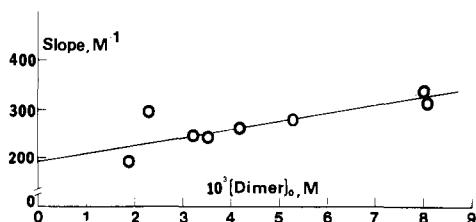


Figure 5. Slope values from eq 5 vs. $[\text{Mo}_2\text{O}_4^{2+}]_0$.

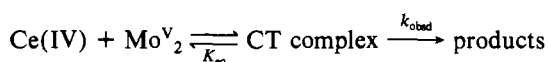
listed in Table III. The intercept values, A_0^D , represent the absorbance present at $t = 0$ due only to dimer. A plot of these intercept values vs. $[\text{dimer}]_0$ (Figure 4) gave $98.7 \text{ M}^{-1} \text{ cm}^{-1}$ for ϵ_D and agreed with literature value ($103 \text{ M}^{-1} \text{ cm}^{-1}$)¹ when corrected for the path length of the stopped-flow reaction cell. A plot of slope values, $\epsilon_{\text{Ox}} + [\epsilon_X K_{\text{eq}} [\text{D}]_0 / (1 + K_{\text{eq}} [\text{D}]_0)]$, vs. $[\text{dimer}]_0$ was linear (Figure 5) and not curved as predicted by eq 5. This suggested that $K_{\text{eq}} [\text{D}]_0 \ll 1$, such that slope $\approx \epsilon_{\text{Ox}} + \epsilon_X K_{\text{eq}} [\text{D}]_0$. A similar relationship was shown by Kochi in the study of alkylmetal-iodine charge-transfer complexes.¹⁷ Such linearity would be obtained for weak complexes at low donor concentrations. The value for ϵ_{Ox} ($196 \text{ M}^{-1} \text{ cm}^{-1}$) is in reasonable agreement with that obtained under nonreaction conditions. Little can be said about the composit term $\epsilon_X K_{\text{eq}}$ ($15.8 \times 10^3 \text{ M}^{-2} \text{ cm}^{-1}$), as the Bensi-Hilderbrand treatment does not provide a means of determining either term separately. However, if it is assumed that $K_{\text{eq}} \approx 0.1\text{--}1 \text{ M}^{-1}$, the $\epsilon_X \approx (1.6\text{--}16) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, not unreasonable values for such an interaction.

Discussion

The results from the study of the oxidation of $\text{Mo}_2\text{O}_4^{2+}$ by Ce(IV) appear best viewed in terms of a rapid ion pair (charge-transfer) formation between the aquomolybdenum(V) dimer and Ce(IV), followed by a one-electron-redox step to produce a mixed-valence dimer, $\text{Mo}^V\text{--Mo}^{\text{VI}}$. While the structure of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ ($\text{Mo}^V\text{--Mo}^V$) is known,¹⁸ that of the mixed-valence $\text{Mo}^V\text{--Mo}^{\text{VI}}$ species is not. However, the results of this study do provide an indication of the type of species involved along the reaction pathways.

The absence of a term in the observed rate expression that is independent of oxidant concentration and the observation that chloride ion did not effect the reaction rate points to the retention of the two oxo bridges during the oxidation process. In the other oxidative studies of the aquomolybdenum(V) dimer with $\text{Fe}(\text{phen})_3^{3+}$, IrCl_6^{2-} , and $[(\text{NH}_3)_5\text{Co}(\mu\text{-O}_2)\text{Co}(\text{NH}_3)_5]^{3+}$, the oxidant-independent term in the general rate expression, $\text{rate} = k_d[\text{Mo}_2\text{O}_4^{2+}] + k_{\text{Ox}}[\text{Mo}_2\text{O}_4^{2+}][\text{Ox}]$ ($\text{rate} = k_d[\text{Mo}_2\text{O}_4^{2+}]$ for $\mu\text{-O}_2^-$),² was interpreted to indicate the presence of a dimeric Mo(V) species in which one of the oxo bridges was broken. The Cl^- was felt to facilitate bridge cleavage by substituting for coordinated H_2O , thus providing an acceleration of the electron-transfer process. These reactions were also accelerated by Mo(VI).

The inverse $[\text{H}^+]$ independence is due to Ce(IV) hydrolysis, with $\text{CeOH}(\text{H}_2\text{O})_5^{3+}$ being much more reactive than $\text{Ce}(\text{H}_2\text{O})_6^{4+}$. The range of values obtained by various investigators suggest that in 2 M HClO_4 CeOH^{3+} predominates. From the $\text{p}K_a$ value for $[\text{Mo}_2\text{O}_4(\text{hedta})(\text{H}_2\text{O})]^-$ of 3.25 ($\text{H}_3\text{hedta} = N\text{-(2-hydroxyethyl)ethylenediamine-}N,N',N'$ -triacetic acid),¹⁹ the Mo(V) dimer is present in the acid form, $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$, under the conditions of this study. A general equation for the reaction can be written as



and a more detailed description can be written (Scheme I).

Scheme I

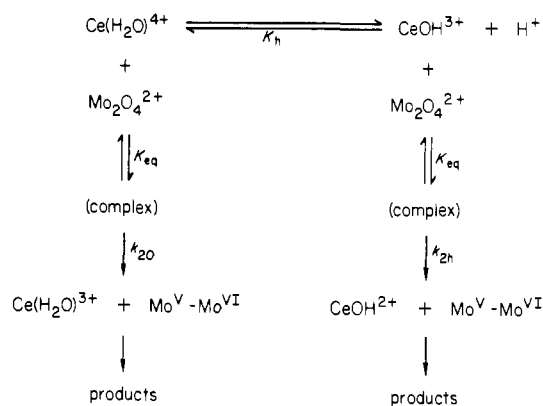


Table IV. Effect of $[\text{H}_2\text{SO}_4]$ on the Ce(IV) Oxidation of $\text{Mo}_2\text{O}_4^{2+}$

$[\text{H}^+], \text{M}$	0.45	0.37	0.30	0.22	0.15
$10^{-4}k_{\text{HSO}_4}, \text{M}^{-1} \text{ s}^{-1}$	5.17	4.50	3.27	2.41	1.62

The subsequent redox, $\text{Mo}^V\text{--Mo}^{\text{VI}} \rightarrow 2\text{Mo}(\text{VI})$, and dimerization steps to give the final products are presumed to be rapid and parallel previous $\text{Mo}_2\text{O}_4^{2+}$ redox systems.

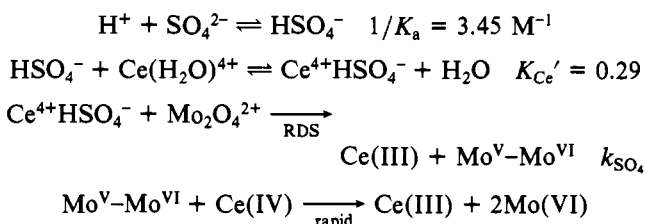
Experiments performed in H_2SO_4 media contrasted those done in HClO_4 , as they showed a linear increase in k_{obsd} with $[\text{H}^+]$, with a near-zero intercept (Table IV).

The observed rate expression was of the form

$$-d[\text{Ce(IV)}]/dt = 2k_{\text{HSO}_4}[\text{H}^+][\text{Mo}_2\text{O}_4^{2+}][\text{Ce(IV)}]$$

Since Ce(IV) is known to form complexes in acidic sulfate media,^{11b} the mechanism (Scheme II) can accommodate the observed behavior. $k_{\text{HSO}_4} = (K_{\text{Ce}'} / K_a)k_{\text{SO}_4} = 1.10 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$; $k_{\text{SO}_4} = 1.10 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

Scheme II



Comparison of the rate constants in HSO_4^- and ClO_4^- media shows the reaction of $\text{Mo}_2\text{O}_4^{2+}$ with CeHSO_4^{3+} is slightly less rapid than with CeOH^{3+} . Presumably the larger HSO_4^- prevents close approach to $\text{Mo}_2\text{O}_4^{2+}$. Both species, however, are more reactive than the pathways observed in the $\text{Mo}_2\text{O}_4^{2+}/\text{MnO}_4^-$ reaction and in reaction of the aquo dimer with $\text{Fe}(\text{phen})_3^{3+}$, IrCl_6^{2-} , and $\mu\text{-O}_2^-$. It appears that the Mo(V) dimer reacts rapidly via an inner-sphere mechanism with Ce(IV) or with other oxidants that have a preference for that pathway. The solvent molecules coordinated to $\text{Mo}_2\text{O}_4^{2+}$ are noted to exchange rapidly,²⁰ allowing a vacant site for complexation by the inner-sphere oxidant. The rate constants, $k_{2h} = 2.73 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{SO}_4} = 1.10 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, are very similar to that found in the study of complexation of the aquomolybdenum(V) dimer by SCN^- ($k = 2.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$),²¹ further suggesting that the removal of a water molecule from the cis position may be a controlling factor in these reactions.

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