Inorganica Chimica Acta, *130* (1987) 85–91

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

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(Received November 13, 1986)

Abstract

The reaction between VO_2^+ and two dimeric Mo(V) complexes, bis(μ-oxo)bis(oxomolybdenum(V)), $Mo_2O_4^{2+}$, and $Mo_2O_4(edta)^{2-}$ was studied in HCl and $HClO_4$ media via stopped-flow techniques. The overall reaction stoichiometry, in which an intermediate is formed, corresponds to the equation

$$[\mathrm{Mo(V)}]_2 + 2\mathrm{VO_2}^+ \xrightarrow{\mathrm{H}^+} 2\mathrm{Mo(VI)} + 2\mathrm{VO}^{2+}.$$

The rate law observed for decay of this intermediate, when $[Mo_2O_4^{2+}] > [VO_2^+]$, is $-d[\mathrm{Complex}]/dt = k_{obs}[\mathrm{Complex}]$, where

$$k_{obs} = \frac{(k_1[\mathrm{H}^+] + k_2K_h)}{([\mathrm{H}^+] + K_h)}$$

The rate constants, k_1 and k_2, and the hydrolysis constant, K_h, are 5.30 s^{-1}, 28.2 s^{-1} and 0.081 M respectively (25.0 °C, $\mu = 1.0$ M HCl). The value for k_{obs} is unaffected by the products but is retarded by ClO_4^-. An intermediate composed of $[Mo(V)]_2$ and V(V) is postulated.

Introduction

Much of the recent interest in the chemistry and reactivity of molybdenum and vanadium compounds is due to their presence and catalytic activity in a number of biological systems. Molybdenum is an essential part of enzymes which catalyze the uptake of inorganic nitrogen while vanadium has been shown to have an essential role in biological systems via its complexation and oxidation–reduction chemistry [1].

The reaction of VO_2^+ with $Mo_2O_4^{2+}$ was shown by Telep and Boltz [2] to be useful as a titrimetric reagent in the analysis of Mo(V) in solutions of high $[H^+]$. The dioxovanadium(1+) ion, like Ce(IV), is a one electron oxidant and again provides the opportunity to examine the oxidative kinetics of the aquo-$Mo_2O_4^{2+}$ ion with strong oxidants. In 1 M $HClO_4$, the reduction potential of the V(V)/V(IV) couple is 1.00 V against 1.76 V for the Ce(IV)/Ce(III) couple [3]. There is also the possible detection of the mixed valence (Mo(V)/Mo(VI)) intermediate [4].

The oxidation of $Mo_2O_4^{2+}$ has been investigated with a variety of oxidizing agents [4, 5a, b]. The results of the reaction of $Mo_2O_4^{2+}$ with Ce(IV) [6] and MnO_4^- [7], two oxidizing agents relevant to this study, have shown two interesting features: (1) the MnO_4^- ion reaction proceeded without the aid of a proton and via an outer sphere mechanism; (2) the Ce(IV) ion was found to form a complex with $Mo_2O_4^{2+}$ and the reaction to proceed with an inverse $[H^+]$ dependence. The rate constant with Ce(IV) as the oxidant is greater than that of MnO_4^-. It is of interest to know if $Mo_2O_4^{2+}$ is an outer- or an inner-sphere complex.

A variety of studies have suggested VO_2^+ reacts via an inner sphere mechanism. Kustin, Toppen and coworkers have shown the presence of complexation in the oxidation of a several organic compounds by VO_2^+ [8–10]. Cooper *et al.* [11] have shown that the oxidation of H_2PO_3 by VO_2^+ involves complexation at the initial stages of the reaction and Rosseinsky has presented the idea that VO_2^+ is an inner sphere reagent in his review of VO^{2+} reactions [12]. Results from our study of the VO_2^+ oxidation of $Mo(CN)_8^{4-}$ support that conclusion [13]. We report here an investigation of the oxidation of the outer-sphere aquo-molybdenum(V) dimer with VO_2^+.

Experimental

Stock solutions of $Mo_2O_4^{2+}$ were prepared by mercury reduction of 0.08 M solutions of Na_2MoO_4 dissolved in 3 M HCl. The reduced solutions were filtered free of Hg and Hg_2Cl_2 and stored over fresh Hg [7a, b].

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*Based in part on F. A. Issa, *M. Sc. Thesis*, Eastern Michigan University, 1983.

**Project SEED Student, 1984.

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A Dowex 50-X8 (50–100 mesh) column in the H^+ form was used to concentrate the dimer from solutions of stock dimer that had been diluted such that $[H^+] \leqslant 0.1$ M. The $Mo_2O_4^{2+}$ was washed with deoxygenated H_2O and was eluted with acids (HCl, $HClO_4$, trifluoromethanesulfonic acid (HTFMS)) of known molarity and ionic strength. Further adjustments in concentration, acidity and ionic strength were made with the appropriate standard acid or Cl^- solution. Dimer concentration was determined at $\lambda = 384$ nm ($\epsilon = 103$ M^{-1} cm^{-1}). The sodium bis(μ-oxo)-(ethylenediaminetetraacetato)bis[oxo-molybdate(V)] trihydrate complex, $Na_2[Mo_2O_4(EDTA)] \cdot 3H_2O$, was prepared according to the method of Pecsok and Sawyer [14].

Stock VO_2^+ solutions were prepared by heating a weighed amount of V_2O_5 in 1.00 M HCl. Total vanadium was determined by the H_2O_2 method [15]. Solutions of VO^{2+} were prepared as previously described [16].

The kinetic studies were carried out at 365, 384 and 750 nm using an Aminco-Morrow stopped-flow apparatus interfaced to a computer. The choice of 365 nm allowed a larger absorbance change to be observed than at 384 nm due to the smaller contribution made by the excess dimer to the overall absorbance. 365 nm represents a minimum in the visible spectrum of the dimer. The kinetic results obtained at 365 and 384 nm were identical. The rate of formation of VO^{2+} was followed at 750 nm. The ϵ values at 365, 384 and 750 nm are (M^{-1} cm^{-1}): $Mo_2O_4^{2+}$; (87 ± 6, 103 ± 5, 0); VO_2^+, (65 ± 3, 17 ± 3, 0); Mo(VI), (12, 1.5, 0); VO^{2+}, (0, 0, 17 ± 1).

Results

Kinetic Studies

The reaction stoichiometry was verified using spectrophotometric titration methods and absorbance values from stopped-flow experiments. The stoichiometric value of 2.03 ± 0.05 for the ratio $[VO_2^+]_0/[Mo_2O_4^{2+}]_0$ indicates that the equation

$$12H^+ + 2VO_2^+ + Mo_2O_4^{2+} \longrightarrow 2VO^{2+} + 2Mo(VI) + 6H_2O$$

can be used to represent the overall reaction. A plot of A_∞ values (A_∞ = absorbance at infinite time) obtained from stopped-flow experiments, ($\lambda = 750$ nm) *versus* $[VO_2^+]_\infty$ gave $\epsilon(VO^{2+}) = 17.1 \pm 0.8$ M^{-1} cm^{-1}. This indicated all the VO_2^+ was converted to VO^{2+}.

When the reactants, $[Mo_2O_4^{2+}] > [VO_2^+]_0$, were mixed in the stopped-flow apparatus, the absorbance of the resulting solution increased rapidly from its initial A_0 value, indicating the formation of an absorbing intermediate, went through a maximum A_{max}, and decreased to an A_∞ value characteristic of the reacted solutions (Fig. 1). This behavior was observed from 340 to 750 nm. Experimental A_0 values were found to be greater than absorbances calculated using initial concentrations of reactants and their respective molar absorption coefficients. Normally, the observed A_0 value is lower than predicted for a given set of concentrations due to the consumption of the initial reactants while being mixed and transported to the observation cell. For a wide range of reactant concentrations, ($[Mo_2O_4^{2+}](8 - 3 \times 10^{-3}$ M) and $[VO_2^+](2.0 - 0.6 \times 10^{-3}$ M)) the absorbance was found to reach a maximum at 0.026 ± 0.002 s, after which it decayed to products via a first order process.

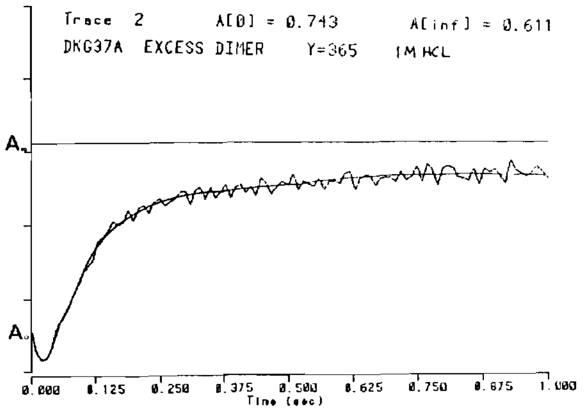

Fig. 1. Stopped-flow kinetic trace. $[Dimer]_0 = 8.17 \times 10^{-3}$ M, $[VO_2^+]_0 = 0.80 \times 10^{-3}$ M ($[H^+] = \mu = 1.0$ M (HCl), T = 25.0 °C).

The pseudo-first order rate constants (k_{obs}) for the disappearance of the intermediate are presented in Table I. The reaction traces were linear for at least 3 half-lives when analyzed via a first order computer fit and gave reproducible rate constants. Values of k_{obs} were found to be independent of the initial concentrations of dimer, and VO_2^+ and the presence of Mo(VI) and VO^{2+} in the initial reaction mixture produced no significant variation in k_{obs}. Lower values of k_{obs} were obtained when 1.0 M $HClO_4$ was substituted for HCl but the observed kinetic wave form was unchanged. These results are summarized in Table I. The data yielded a rate law of the form RATE = k_{obs}[Complex]. The term [Complex] is used to indicate the absorbing intermediate.

Hydrogen ion dependence

The hydrogen ion dependence was studied over the temperature range 15 to 30 °C, while μ was maintained at 1.0 with NaCl. The observed rate constant (Table II) showed an inverse hydrogen ion dependence and the data fit an equation of the form $k_{obs}(s^{-1}) = (k_1(H^+) + k_2K_h)/([H^+] + K_h)$. A plot of $k_{obs}([H^+] + K_h)$ *versus* $[H^+]$ (Fig. 2) yielded a straight line. Another function, k_{obs} *versus* $[H^+]^{-1}$, was tried with the data but did not give a straight

TABLE I. Rate Constants for the $Mo_2O_4^{2+}/VO_2^+$ Reaction ($[H^+] = \mu = 1.0$ M (HCl), $T = 25.0$ °C)

10^3 $[Mo_2O_4^{2+}]_0$ (M)	10^3 $[VO_2^+]_0$ (M)	10^3 [Mo(VI)]$_0$ (M)	10^3 $[VO^{2+}]_0$ (M)	k_{obs} (s^{-1})
8.17	0.80			6.25
	1.00			6.91
	1.30			6.80
	1.60			6.51
	2.00			6.87
8.21	1.00			6.83
6.53	1.20	0.00		6.59
		0.70		6.89
		1.00		6.47
6.50	0.80			7.08
	1.20			6.58
6.20	1.00		0.00	6.27
			0.70	6.87
			1.00	7.04
			2.00	7.14
6.02	0.60			4.30[a]
	0.80			4.70[a]
	1.00			5.10[a]
5.04	0.60			6.87
	0.80			6.90
	1.00			6.46
	1.20			6.46
3.62	0.70		0.00	6.67
			1.00	6.69
			2.00	6.69
3.50	0.60			6.67
	0.70			6.55
	0.90			6.71
			average k_{obs}	6.71 ± 0.24

[a] 1.0 M $HClO_4$ data.

TABLE II. Hydrogen Ion/Temperature Dependence of k_{obs} ($\mu = 1.0$ (HCl/NaCl))

$[H^+]$ (M)	k_{obs} (s^{-1})			
	$T = 15$ °C	$T = 20$ °C	$T = 25$ °C	$T = 30$ °C
1.00	3.16	5.18	6.36	9.87
0.80	3.04	5.16	7.13	12.2
0.70	3.16	5.29	8.25	11.1
0.60	3.60	5.68	8.42	10.6
0.40	3.29	5.75	8.56	13.2
0.30	3.36	6.17	10.2	13.9
0.23	3.72	8.12	12.5	14.7

line. Plots of the ln values for the appropriate hydrolysis and rate constants (K_h, k_1, k_2) *versus* $1/T$ (K) were linear. The kinetic and thermodynamic values obtained for k_1, k_2 and K_h are presented in Table III. Values of k_{obs} from the ionic strength dependence studies ($[H^+] = 0.26$ M, $T = 25.0$ °C) gave a straight line with a positive slope for a plot of log k_{obs} *versus* $[\mu/(1 + \mu)]$.

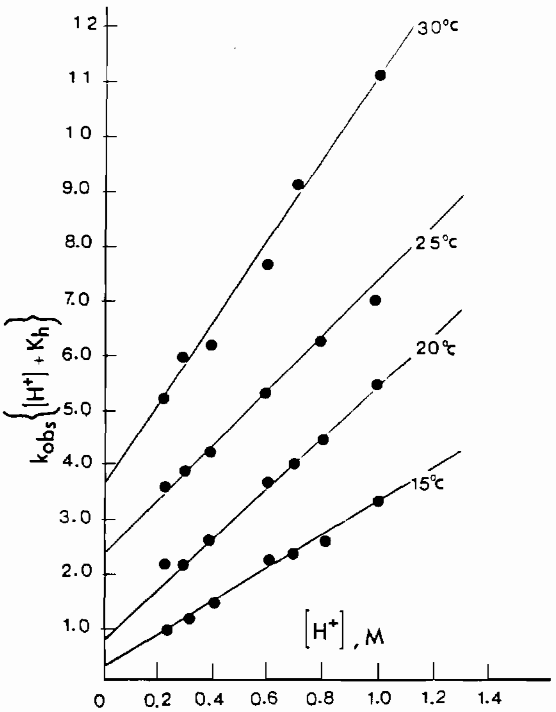

Fig. 2. $[H^+]$ dependence. Plot of k_{obs} ($[H^+] + K_h$) *vs.* $[H^+]$ ($\mu = 1.0$ M (HCl/NaCl), $T = 25.0$ °C).

TABLE III. Temperature Dependence of K_h, k_1, and k_2

T (°C)	K_h[a] (M)	k_1[b] (s^{-1})	k_2[c] (s^{-1})
15	0.03	3.03	10.0
20	0.05	4.50	15.0
25	0.08	5.30	28.2
30	0.12	6.80	30.1

[a] K_h: $\Delta H° = 15.5 \pm 0.4$ kcal M^{-1}. $\Delta S° = 11.6$ cal M^{-1} K^{-1}. [b] k_1: $\Delta H^‡ = 8.42 \pm 1.1$ kcal M^{-1}, $\Delta S^‡ = -2.70 \pm 0.9$ cal M^{-1} K^{-1}. [c] k_2: $\Delta H^‡ = 13.1 \pm 2.6$ kcal M^{-1}, $\Delta S^‡ = -8.3 \pm 1.2$ cal M^{-1} K^{-1}.

Investigation of the Reaction Intermediate

To determine the spectrum of the intermediate, a 0.40×10^{-3} M VO_2^+ solution in 1.0 M HCl was mixed in the stopped-flow apparatus with a 4.09×10^{-3} M $Mo_2O_4^{2+}$ solution in 1.0 M HCl. Kinetic traces were obtained at 20 nm intervals. Three plots were constructed representing (1) A_0 (the absorbance at $t = 0$) *versus* wavelength; (2) A_{max} (the maximum absorbance) *versus* λ; and (3) A_∞ (the absorbance at

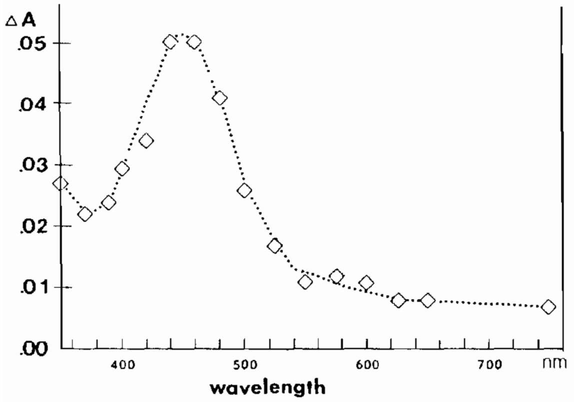

Fig. 3. ΔA *vs.* wavelength ($\Delta A = A_{max} - A_0$). Difference spectra obtained at $t = 0.026$ s ($[H^+] = \mu = 1.0$ M (HCl), $T = 25.0$ °C).

infinite time) *versus* λ. All plots appeared to follow the general composite spectral curve of the reactants and showed no new features. Since $[Mo_2O_4^{2+}]_0 \gg [VO_2^+]_0$ and the absorbance of $[Mo_2O_4]^{2+}$ dominates, a plot of wavelength *versus* ($A_{max} - A_0$) was constructed (Fig. 3). This difference plot revealed a peak at $\lambda = 440$ nm, indicating the intermediate has a spectrum that differs significantly from that of the dimer at 440 nm. The spectra may have additional peaks but the large absorbance due to the dimer and a low ϵ value of the peak could prevent detection of other peaks. Pulse radiolysis of $Mo_2O_4(oxalate)_2^{2-}$ showed that the $Mo_2(IV, V)$ mixed valence complex absorbs weakly in the visible range (~300–500 M^{-1} cm^{-1}) [17] and complexes of V(V) with a variety of reactants have spectra with λ_{max} in the 350–450 nm range. The spectrum did not resemble that of 'Mo-Blue' which is known to form in the reaction between Mo(V) and Mo(VI) or air oxidation of $Mo_2O_4^{2+}$ in solutions of low $[H^+]$ [18]. The additional absorbance observed at $t = 0$ was shown, by using stopped-flow mixing experiments which involved mixing various combinations of reactants and products, to be due to interaction between $Mo_2O_4^{2+}$ and Mo(VI). However, this interaction did not produce an additional absorbance peak at $\lambda = 440$.

Beer's law plots obtained under reaction conditions ($\lambda = 384$ nm) from stopped-flow experiments showed an increase in the molar absorption coefficient of VO_2^+ ($\epsilon = 65.2$ M^{-1} cm^{-1}) over that obtained from batch mixing experiments ($\epsilon VO^{2+} = 1.5$ M^{-1} cm^{-1}) or mixing solutions of VO_2^+ with 1.0 M HCl in the stopped-flow experiments. The molar absorption coefficient of the dimer remained the same. Similar behavior was observed in the Ce(VI)/dimer reaction [6]. Figure 4 is a plot of A_0 *versus* $[VO_2^+]_0$. Each line represents a constant $[Mo_2O_4^{2+}]_0$ concentration. The intercepts of the lines represent the absorbance due only to dimer concentration (A_0^D). The slopes of the lines represent the combined molar absorption coefficient of VO_2^+ and the absorbing species. The values of A_0^D are plotted *versus* the initial dimer concentration ($[Mo_2O_4^{2+}]$) (Fig. 5). The open circles reported in the Figure represent results from an experiment in which only dimer and 1.0 M HCl were mixed. The triangular points represent results from a previous work [5] where dimer was mixed with 2 M $HClO_4$.

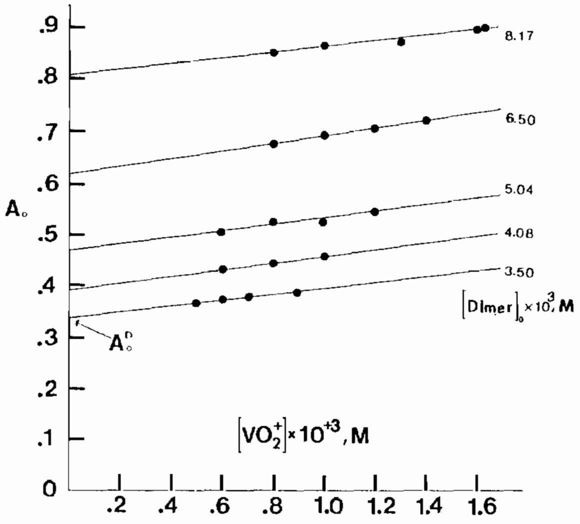

Fig. 4. A_0 *vs.* $[VO_2^+]_0$ for five dimer solutions. The intercepts of each line corresponds to A_0^D; the absorbance at $t = 0$ corresponds to that due only to dimer.

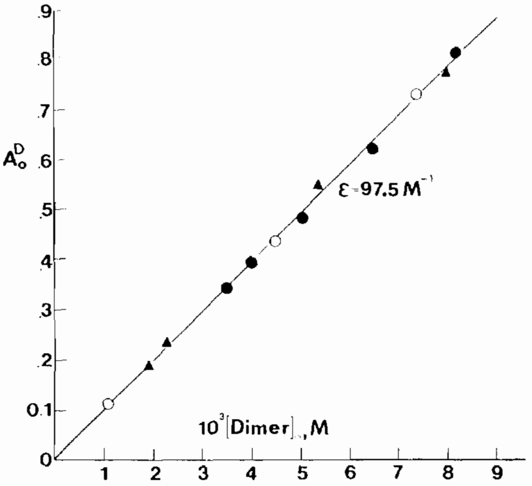

Fig. 5. Plot of A_0^D *vs.* $[Mo_2O_4^{2+}]_0$. The slope of the line represents ϵ_{dimer}.

The presence of the absorbing complex observed can be accounted for by the following formulation:

$$A_0 = \epsilon_D[D]_0 + \epsilon_{ox}[Ox]_0 + \epsilon_x[X]_0 \qquad (1)$$

where A_0 = initial absorbance value and ϵ_D, ϵ_{ox} and ϵ_x are the molar absorption coefficients of the dimer, oxidant (VO_2^+) and the absorbing intermediate, respectively. $[D]_0$, $[Ox]_0$, and $[X]_0$ are the molar

TABLE IV. Results of A_0 *versus* Concentration Plots

$10^3\,[Mo_2O_4{}^{2+}]_0$ (M)	Intercept ($A_0{}^D$)	Slope[a] (M^{-1})
8.17	0.807	62.5 (5)
6.50	0.635	63.6 (4)
5.04	0.450	68.8 (4)
4.08	0.394	66.7 (3)
3.50	0.340	64.2 (4)
	$\epsilon_D = 97.5 \pm 1.8\ M^{-1}\ cm^{-1}$	Average = 65.2 ± 2.6 slope

[a] Number of experimental points used to determine line.

concentrations of dimer oxidant and absorbing intermediate at initial time. Under pseudo-first order conditions, with the assumption that a 1:1 complex is formed

$$D + Ox \underset{K_{eq}}{\rightleftharpoons} X \tag{2}$$

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

if $[D]_0 \gg [Ox]_0$, then $([D]_0 - [X]) \sim [D]_0$ and

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

Substitution of eqn. (4) into eqn. (1) gives eqn. (5)

$$A_0 = \epsilon_D[D]_0 + \left[\epsilon_{ox} + \frac{\epsilon_x(K_{eq}[D]_0)}{(1 + K_{eq}[D]_0)}[Ox]_0\right] \tag{5}$$

The third term of eqn. (5) is of the form derived in the Benesi–Hildebrand equation [19]. Least-squares plots of A_0 *versus* $[VO_2{}^+]$ for five dimer solutions gave intercept $(\epsilon_D[D]_0)$ and slope values listed in Table IV. A plot of intercept values, $A_0{}^D$, (absorbance due only to dimer) *versus* $[Dimer]_0$ was linear (Fig. 4) and gave 97.5 M^{-1} cm^{-1} for ϵ_D. The plot of slope values derived from Fig. 3 against $[D]_0$ was horizontal suggesting $K_{eq}[D]_0 \gg 1$ and that eqn. (5) can be rewritten as $A_0 = \epsilon_D[D]_0 + (\epsilon_{ox} + \epsilon_x)[Ox]_0$. This equation predicts the slope values derived from plots of A_0 *versus* $[V(V)]_0$ (Table IV) should be independent of initial reactants and represent the expression $(\epsilon_{ox} + \epsilon_x)$. Since $(\epsilon_{ox} + \epsilon_x) = 65.2 \pm 2.6$ M^{-1} cm^{-1} and ϵ_{ox} (17 M^{-1} cm^{-1}) can be determined independently, $\epsilon_x = 48$ M^{-1} cm^{-1}.

The results obtained from Job's experiment [20] conducted on the stopped-flow apparatus to determine the composition of the absorbing species were inconclusive due to the small changes in A_{max} between solutions.

Comparison between the reactions of $[Mo_2O_4(H_2O)_6]^{2+}$ and $Mo_2O_4(edta)^{2-}$ with $VO_2{}^+$ at 750 nm and 384 nm

An attempt was made to compare the kinetic behaviour of the Mo(V)–aquodimer with that of the sterically hindered $[Mo(V)]_2$–edta complex [21, 22], when oxidized with $VO_2{}^+$. The kinetic traces taken on the stopped-flow at λ = 750 nm represent the production of the uncomplexed VO^{2+} product. A series of experiments in 1.0 M HCl showed complex formation to be present at 384 and 750 nm for both dimer complexes. The kinetic traces for the production of VO^{2+} showed the formation of an absorbing intermediate, which decayed to an absorbance indicative of the $[VO^{2+}]$ expected. The formation of the absorbing species at both wavelengths could be prevented only by reacting $VO_2{}^+$ with $Mo_2O_4(edta)^{2-}$ in 1.0 M $HClO_4$, in the absence of chloride ion. The reaction traces, for this system, showed only the disappearance of the intermediate (λ = 384 nm) or the formation of $VO_2{}^+$ (λ = 750 nm).

Experiments involving the oxidation of $Mo_2O_4(edta)^{2-}$ and $Mo_2O_4(hedta)^-$ by Ce(IV) show a marked decrease in their reactivity as Cl^- is added. The oxidation reaction can be prevented when $[Cl^-] > 0.25$ M. Solutions in which Ce(IV) was complexed by $edta^{4-}$ to prevent formation of Ce(IV)–Cl^- complexes showed no tendency towards reaction [23]. Although Ce(IV) can oxidize $edta^{4-}$ and $hedta^{3-}$, the reaction occurs at a much slower rate than that observed in these experiments and does not compete with the redox step [24]. Under the experimental conditions of this study Ce(IV) is never in excess to react with the free ligand. The $Mo_2O_4(edta)^{2-}$ and $Mo_2O_4(hedta)^-$ complexes were equilibrated in acid free media (μ = 1.0 M) to avoid decomposition.

Discussion

In the reaction of $Mo_2O_4{}^{2+}$ with $VO_2{}^+$, as in the Ce(IV) oxidation of $Mo_2O_4{}^{2+}$, the $[Mo(V)]_2$ undergoes complexation to form an intermediate complex ($X(H_2O)$) in which the redox process occurs. However, with VO_2^+, the disappearance of ($X(H_2O)$) is unaffected by reactants and products and is accelerated in acidic Cl^- media over that of non-complexing ClO_4^-. The ionic strength study suggests the complex is composed of $Mo_2O_4^{2+}$ and VO_2^+, as a hydrolyzed species of $VO_2^+(VO_2\text{–}OH)$ would have caused a different behavior of k_{obs} with μ. $Mo_2O_4^{2+}$ does not hydrolyze in strong acid and apparently is not extensively complexed in 1 M HCl media.

The acceleration of oxidation reactions involving $Mo_2O_4^{2+}$ by Cl^- was interpreted by Sykes [4, 5] to indicate the presence of a dimeric Mo(V) in which one of the oxo bridges of the dimer is broken. This pathway was proposed in the oxidative studies of $Mo_2O_4^{2+}$ by $Fe(phen)^{3+}$, $IrCl_6^{2-}$, and (μ-O_2^-). The Cl^- was felt to facilitate bridge cleavage by substituting for a coordinated H_2O and providing an acceleration of the redox process. Given the results from the investigation of Ce(IV) and VO_2^+ with dimer–edta complexes in Cl^- and ClO_4^- media, the chloride ion is seen to play a major role in the formation of the intermediate, although VO_2^+ is an effective complexer. Complexation by VO_2^+ would serve to remove coordinated H_2O molecules and would be effective in causing the oxo bridge to open. The Cl^- is perhaps serving as a bridging ligand. Hence, k_{obs} for VO_2^+ as the oxidant is larger than that for the corresponding term from the other oxidative studies in which this process is postulated. Acceleration by Cl^- was not observed in the reaction of $Mo_2O_4(edta)^{2-}$ and $Mo_2O_4(hedta)^-$ by $Fe(phen)_3^{3+}$, $IrCl_6^{2-}$ and (μ-O_2^-) [25].

The observed formation of an intermediate and the presence of the inverse hydrogen ion dependence expression can be accommodated by the mechanism:

$$Mo_2O_4^{2+} + VO_2^+ \underset{K_{eq}}{\rightleftharpoons} (Mo^{5+/5+}\text{- - -}V^{5+})$$

$$\text{Complex} \equiv [X(H_2O)]$$

$$\begin{tikzcd}
{[X(H_2O)]} \arrow[r, shift left] \arrow[d, "k_1"] & X\text{–}OH^- + H^+ \arrow[l, shift left, "K_h"] \arrow[d, "k_2"] \\
Mo^{(V)}\text{–}Mo^{(VI)} + V^{(VI)} \arrow[d] & Mo^{(V)}\text{–}Mo^{(VI)} + V^{(IV)} \arrow[d] \\
\text{PRODUCTS} & \text{PRODUCTS}
\end{tikzcd}$$

The mixed valence $Mo_2(V/VI)$ species rapidly decomposes to monomeric Mo(V) and Mo(VI). Monomeric Mo(V) is oxidized rapidly by another mole of VO_2^+ to Mo(VI). Further reactions involving conversion of monomeric Mo(VI) to the dimeric form present in high $[H^+]$ are assumed to be rapid [26].

The observed intermediate (precursor complex) is not viewed as a mixed $Mo_2(V/VI)$ species based on the report by Chaudhury [27] of the preparation of a dioxo-bridged Mo(V)–Mo(VI) glycinato compound. This mixed valence complex is characterized by absorption bands at 306 nm (4240 M^{-1} cm^{-1}) and 695 nm (36 M^{-1} cm^{-1}) that would be evident in plots of ΔA *versus* λ. Other Mo–amino acid complexes with similar bands have been reported [28–30].

Initial rate measurements at 385 and 750 nm for the production of the intermediate indicate the expression $RATE_i = k_{initial}[D]_0[V(V)]_0$ and $k_{initial} \simeq 2 \times 10^5$ M^{-1} s^{-1}. This value is close to the range of $(1\text{–}10) \times 10^4$ M^{-1} s^{-1} for the reaction of VO_2^+ with a variety of ligands and suggests that loss of coordinated aquo ligands are involved in the complexation process. The rate constant for H_2O removal from $Mo_2O_4^{2+}$ was determined to be 2.9×10^4 M^{-1} s^{-1} from the complexation of aquo-dimer by SCN^- [4a].

This study allows a contrast of the complexing behavior of $Mo_2O_4^{2+}$ with Ce(IV), VO_2^+, and outer sphere reagents. The permanganate ion was shown not to complex with $Mo_2O_4^{2+}$, while VO_2^+ and Ce(IV) interact with different complexation constants. The formation of a long lived kinetic intermediate by VO_2^+ has been observed for various substances and represents a primary mode of interaction with substrates. Our studies indicate $K_{eq}(Ce(IV)) \sim 0.1\text{–}1$ M^{-1} while $K_{eq}(VO_2^+) > 10^3$ M^{-1} in the interaction with $Mo_2O_4^{2+}$. $K_{eq}(VO_2^+/H_2Ascorbic)$ is 488 M^{-1} [9].

Examination of the activation parameters from reactions in which VO_2^+ is involved in complex formation (inner sphere mechanism) followed by substrate oxidation (Table V) show the entropy of activation values are small and negative. The negative $\Delta S^\ddagger$ is indicative of the transformation of VO_2^+ to VO^{2+}, an ion which can exert a greater influence on the solvent molecules than the activated complex. The reactions of $Mo_2O_4^{2+}$ with outer-sphere reactants exhibit values of $\Delta S^\ddagger$ that are more negative. Values of $\Delta S^\ddagger$ from the reactions of two other strong, positively charged oxidants, Ce(IV) [31] and Mn(III) [32], with several of the substrates are positive.

Acknowledgements

Our thanks to Ms. Janice Johnson for data manipulation. This research was supported in part by funds from NSF-URP Grant No. 20320 (S.T.P.) and funds from an Eastern Michigan University Graduate School Research Grant (1981–83). Support from ACS Project SEED for A.H. is greatfully acknowledged. F. Ali Issa was supported by an AFGRAD Fellowship.

TABLE V. Some Activation Parameters for the Reactions of Vanadium(V) and $Mo_2O_4^{2+}$

	Substrate		$\Delta H^{\ddagger}$ (kcal M^{-1})	$\Delta S^{\ddagger}$ (cal M^{-1} K^{-1})	Reference
$Mo_2O_4^{2+}$ +	$Fe(phen)_3^{3+}$	k_h	10.9	−18.4	5a
		k_0	8.9	−21.7	
	$(\mu\text{-}O_2^{-})^{5+}$		18.5	−21	5b
	MnO_4^{-}		10.2	−19	7a
	Ce(IV)		7.95	−15	6
	SCN^{-}		11.3	−0.3	4b
	VO_2^{+}	k_1	8.42	−2.7	this work
		k_2	13.1	−8.3	
VO_2^{+} +	$Fe(CN)_6^{4-}$[a]		14.1	−4.4	17
	H_3PO_2		18.8	−5.7	33
	hmpa[b]		18.7	−9.8	33

[a] Decay of intermediate formed from $V(V)\text{–}Fe(CN)_6^{4-}$ reaction. [b] hmpa = 2-hydroxy-2-methylpropanoic acid.

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