Reactions of molybdenum(VI) with metal ion reductants†‡

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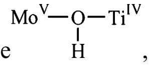
The reactions of aqueous H_2MoO_4 at low pH with titanium(II), titanium(III), europium(II), vanadium(II), and germanium(II), as monitored at 430 nm, give biphasic profiles featuring a sharp rise in absorbance followed by a marked decrease (Fig. 1). The final product is the dimeric Mo(V) cation, $[Mo_2O_4]^{2+}$, and the strongly absorbing intermediate is taken as a monomeric Mo(V) species. The molar absorbances of the transients from different reductants are not the same, nor are the rate laws governing the fadings. None of the decay curves exhibits evidence of a second order dependence on the transient. The kinetic behaviors of these systems are consistent with the intervention of successor complexes of the type  $\mathrm{Mo^{V}{-}\underset{\displaystyle H}{\underset{|}{O}}{-}Ti^{IV}}$, (formed by inner sphere reductions of Mo(VI)), which decompose, *via* first-order processes, to a monomeric Mo(V) species. The latter then experiences rapid dimerization, which is kinetically silent. The possibility that Ge(II) bypasses the unstable tripositive state by reducing Mo(VI) to Mo(IV) (which then undergoes rapid Mo(VI)–Mo(IV) comproportionation) is considered.

Introduction

Although the diverse role of molybdenum derivatives in redox catalysis is extensively recognized, past interest has been centered mainly around oxygen atom transfers from peroxy and oxo compounds to alkenes, sulfides, and amines, as promoted by molybdate centers. Such reactions are generally considered to involve complexes of Mo(VI) and the oxidant.[2] Catalysis of electron transfer between metal centers in aqueous media is less usual.

It has recently been noted that reductions of 1,4-quinones, vanadium(IV) and triiodide, by both di- and tripositive titanium are catalyzed by Mo(VI), and evidence has been offered implicating the pentapositive state, Mo(V), in such reactions. However, the dimeric cation, $[Mo_2O_4]^{2+}$, a persistent form of Mo(V) in the range 0.01–2.0 M H^+,[3] has been shown to be devoid of catalytic activity in such systems.

The present study deals with the generation of the catalytically active Mo(V) species and its conversion to the inactive dimeric form.

Experimental

Materials

All solutions were prepared using Millipore-Q system deionized water that had been boiled for 2 h and then purged with argon for a further 2 h to remove dissolved oxygen. Titanium metal wire, titanium(III) chloride, sodium molybdate, and trifluoromethanesulfonic acid (triflic acid) (all Aldrich reagents) were used as received. Preparations of V(II),[4] and Ti(II)[5] (used as triflate salts) and Eu(II)[6] and Ge(II)[7] (used as chlorides) were as described elsewhere.

Stoichiometric studies

The biphasic nature of the reactions studied made stoichiometric determinations unfeasible at or near 430 nm, the region of principal interest. However, information concerning the overall conversions could be obtained at 710 nm in 11.0 M HCl, where Mo(V) has been shown to be converted to the stable green complex, $[MoOCl_5]^{2-}$.[8] Measured, deficient quantities of Na_2MoO_4 were added to a known excess of the reductant. Increases in absorbance were compared with those from addition of excess Mo(VI). The results are summarized in Table 1.

Kinetic studies

Reactions were performed under argon, using freshly prepared solutions of the reductants. Rates were evaluated from changes in absorbance at 430 nm, using a Durrum–Gibson stopped flow spectrophotometer in conjunction with an OLIS computer system. Temperatures were kept at 22.0 ± 0.5 °C. The ionic strength was maintained with NaCl/LiCl/HCl or CF_3SO_3Na/CF_3SO_3H. All runs were carried out with the reducing agent in four- to tenfold excess.

In each case, a marked increase in absorbance, followed by a sharp decrease, was observed (for example, Fig. 1). Peak absorbance generally occurred within the first second after mixing, but with Eu(II) the very rapid initial rise was barely discernable. With the other reactants in excess, profiles were analyzed by treating the transformations as consecutive pseudo-first order processes (1),

$$\mathrm{Mo(VI)} + \mathrm{Red} \xrightarrow{k_1} \text{intermediate} \xrightarrow{k_2} \text{products} \qquad (1)$$

then, using the procedure of Bose[9] to disentangle the contributing rate constants (k_1 and k_2), and to estimate the extinction coefficient of the intermediate. For the Mo(VI)–Eu(II) reaction, k_1 could not be obtained.

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† Electron transfer. Part 163[1].

‡ Electronic supplementary information (ESI) available. Tables S-1 to S-6: detailed kinetic data for redox reactions.

Table 1 Generation of molybdenum(V) from H_2MoO_4. Stoichiometric studies[a]

Reductant	[Red.]/mM	$[H_2MoO_4]$/mM	[Mo(V)]/mM	[Mo(V)]/[Red.]
Ti(II)	2.5	10.0	5.0	2.0
	5.0	15.0	10.0	2.0
Ti(III)	5.3	10.0	5.3	1.00
	6.0	10.0	6.2	1.03
Eu(II)	4.0	9.0	4.1	1.02
	6.6	11.0	6.6	1.00
V(II)	3.0	11.0	6.2	2.1
Ge(II)	4.5	11.0	9.2	2.0

[a] Reactions carried out in 11 M HCl: $\lambda = 710$ nm. (The product is $[MoOCl_5]^{2-}$.)

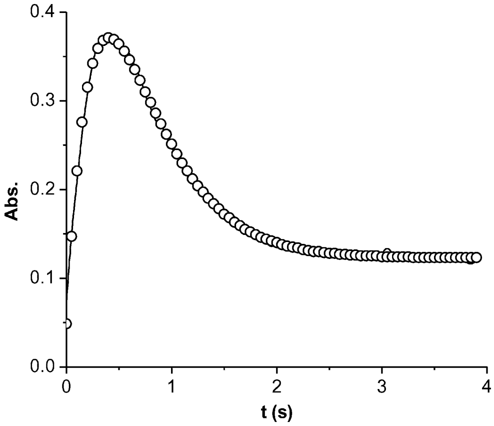


Fig. 1 Kinetic profile for the reaction of H_2MoO_4 (0.30 mM) with V(II) (12 mM), $[H^+] = 0.25$ M; $\mu = 0.50$ M, (CF_3SO_3H–CF_3SO_3Na); $\lambda = 430$ nm; $T = 22$ °C. The solid line represents the experimental curve; the circles were calculated by non-linear least squares refinement utilizing the relationship of Bose (ref. 9*a* in text), kinetic parameters in Tables 2 and 3, and $\varepsilon_{\mathrm{interm}}$ in Table 4.

Results

In the spectral region of interest (*ca.* 430 nm), neither H_2MoO_4 nor the predominant Mo(V) product, $Mo_2O_4^{2+}$(aq) ($\lambda_{\max} = 295$ nm), absorbs appreciably, but measurements at 710 nm in 11 M HCl (Table 1), where Mo(V) is converted to the green complex $MoOCl_5^{2-}$,[8] confirm the quantitative formation of pentavalent molybdenum.

$$2\ \mathrm{Mo(VI)} + \mathrm{Ti(II))} \rightarrow 2\ \mathrm{Mo(V)} + \mathrm{Ti(IV)} \tag{2}$$

$$\mathrm{Mo(VI)} + \mathrm{Ti(III)} \rightarrow \mathrm{Mo(V)} + \mathrm{Ti(IV)} \tag{3}$$

$$\mathrm{Mo(VI)} + \mathrm{Eu(II)} \rightarrow \mathrm{Mo(V)} + \mathrm{Eu(III)} \tag{4}$$

$$2\ \mathrm{Mo(VI)} + \mathrm{V(II)} \rightarrow 2\ \mathrm{Mo(V)} + \mathrm{V(IV)} \tag{5}$$

$$2\ \mathrm{Mo(VI)} + \mathrm{Ge(II)} \rightarrow 2\ \mathrm{Mo(V)} + \mathrm{Ge(IV)} \tag{6}$$

Note, however, that under the conditions used in the kinetic runs (reductant in excess), both Ti(II) and V(II) would be expected to yield the respective tripositive states.

Generation of the Mo(V) intermediate

Kinetic curves (*e.g.*, Fig. 1) are analyzed as a superposition of two consecutive pseudo-first order processes.[10] One of these components arises from the growth of an intermediate species, the other from its disappearance. The usual ambiguity associated with the assignment of rate constants from such components[10] does not apply here, since one of the rate constants in each system is proportional to the concentration of the reductant, whereas the other, in all cases except Ti(III), is independent of the reductant concentration.

Two of the rate laws for formation of the intermediate are straightforward monomial expressions:

$$\mathrm{rate} = k\ [\mathrm{Mo(VI)}][\mathrm{Red.}]\ \begin{array}{l} k_{\mathrm{V(II)}}(2.3 \pm 0.1) \times 10^2\,\mathrm{M^{-1}s^{-1}} \\ k_{\mathrm{Ge(II)}}(9.4 \pm 0.8) \times 10^2\,\mathrm{M^{-1}s^{-1}} \end{array} \tag{7}$$

In contrast, reductions by Ti(II) (Table S-1‡) and Ti(III) (Table S-2‡) are appreciably inhibited by H^+, and that by Ti(III) is also retarded slightly by chloride. Data for intermediate formation by Ti(II) conform to eqn (8) and that by Ti(III) to eqn (9).

$$(\mathrm{rate})_{\mathrm{Mo,Ti(II)}} = \frac{[\mathrm{Mo(VI)}][\mathrm{Ti(II)}]k\,K_{\mathrm{A}}}{K_{\mathrm{A}} + [\mathrm{H^+}]} \tag{8}$$

$$(\mathrm{rate})_{\mathrm{Mo,Ti(III)}} = \frac{[\mathrm{Mo(VI)}][\mathrm{Ti(III)}]k\,K_{\mathrm{A}}[\mathrm{H^+}]}{(1 + K_{\mathrm{A}}[\mathrm{Ti(III)}](1 + K_{\mathrm{A}}[\mathrm{H^+}] + K_{\mathrm{Cl}}[\mathrm{Cl^-}])} \tag{9}$$

Refinement of data for the formation of the intermediate by Ti(II) and Ti(III) yields the kinetic parameters listed in Table 2. Calculated and observed rate constants (in parentheses) are compared in Tables S-1 and S-2‡.

The generation of the intermediate formed by the action of Eu(II) was too rapid to measure.

Decay of the Mo(V) intermediate

With one exception, rate laws for the decomposition of the intermediate do not include concentrations of the redox partners. The transient formed in the Mo(V)–Ge(II) reaction is consumed exponentially ($k = 0.40 \pm 0.03$) s^{-1}. Decays of those formed from the Mo(VI)–Ti(II) and the Mo(VI)–V(II) systems (Tables S3 and S4‡) are retarded at higher acidities, with both decompositions proceeding in accordance with rate law (eqn (10)),

$$-\mathrm{d[Int]}/\mathrm{d}t = \frac{kK_{\mathrm{A}}[\mathrm{Int}]}{K_{\mathrm{A}} + [\mathrm{H^+}]} \tag{10}$$

with the k value for V(II) almost three times as great as that pertaining to Ti(II) (Table 3).

Table 2 Generation of Mo(V) intermediate. Rate laws and kinetic parameters[a]

Red.	Medium	Rate laws	Parameters
V(II)	CF_3SO_3H/CF_3SO_3Na	$k[\text{Mo(VI)}][\text{V(II)}]$	$k = (2.3 \pm 0.1) \times 10^2\ M^{-1}s^{-1}$
Ge(II)	HCl/LiCl	$k[\text{Mo(VI)}][\text{Ge(II)}]$	$k = (9.4 \pm 0.8) \times 10^2\ M^{-1}s^{-1}$
Ti(II)	CF_3SO_3H/CF_3SO_3Na	$\dfrac{[\text{Mo(VI)}][\text{Ti(II)}]kK_A}{K_A + [H^+]}$	$k = (6.2 \pm 0.3) \times 10^3\ M^{-1}s^{-1}$ $K_A = (0.23 \pm 0.02)$ M
Ti(III)	HCl/LiCl	$\dfrac{[\text{Mo(VI)}][\text{Ti(III)}]kK_A[H^+]}{(1 + K_A[\text{Ti(III)}])(1 + K_A[H^+] + K_{Cl}[Cl^-])}$	$k = (150 \pm 20)\ M^{-1}s^{-1}$ $K_A = (0.44 \pm 0.02)$ M $K_{Cl} = (0.7 \pm 0.3)\ M^{-1}$
Eu(II)	HCl/LiCl		$k > 1 \times 10^4\ M^{-1}s^{-1}$[b]

[a] Reactions at 22.0 ± 0.5 °C, $\mu = 0.50$ M, $\lambda = 430$ nm. [b] Lower limit, assuming rate = k [Mo(VI)][Eu(II)].

Table 3 Decomposition of Mo(V) intermediate. Rate laws and kinetic parameters[a]

Red.	Medium	Rate laws[b]	Parameters
V(II)	CF_3SO_3H/CF_3SO_3Na	$\dfrac{kK_A[\text{Int}]}{K_A + [H^+]}$	$k = (5.7 \pm 0.9)\ s^{-1}$ $K_A = (0.15 \pm 0.04)$ M
Ti(II)	CF_3SO_3H/CF_3SO_3Na	$\dfrac{kK_A[\text{Int}]}{K_A + [H^+]}$	$k = (2.1 \pm 0.05)\ s^{-1}$ $K_A = (0.42 \pm 0.02)$ M
Ge(II)	HCl/LiCl	$k[\text{Int}]$	$k = (0.41 \pm 0.03)\ s^{-1}$
Ti(III)	HCl/LiCl	$\dfrac{k[\text{Ti(III)}][H^+][Cl^-][\text{Int}]}{1 + K_{Ti}[\text{Ti(III)}]}$	$k = (8.7 \pm 0.7) \times 10^3\ M^{-3}\ s^{-1}$ $K_{Ti} = (2.1 \pm 0.3) \times 10^2\ M^{-1}$
Eu(II)	HCl/LiCl	$\dfrac{(k + k'[Cl^-])[\text{Int}]}{(1 + [H^+]/K_{HA} + K_{Cl}[Cl^-])}$	$k = (21 \pm 1)\ s^{-1}$ $k' = (58 \pm 4)\ M^{-1}\ s^{-1}$ $K_{Cl} = (0.29 \pm 0.15)\ M^{-1}$ $K_{HA} = (0.22 \pm 0.04)$ M

[a] Reactions at 22.0 ± 0.5 °C; $\mu = 0.50$ M, $\lambda = 430$ nm. [b] Rates refer to decomposition of the intermediate, Int, $-\mathrm{d}[\text{Int}]/\mathrm{d}t$.

The intermediate from the Eu(II) reduction is consumed according to a two-component rate law (eqn (11)),

$$-\mathrm{d}[\text{Int}]/\mathrm{d}t = \frac{(k + k'[Cl^-])[\text{Int}]}{(1 + [H^+]/K_{HA} + K_{Cl}[Cl^-])} \qquad (11)$$

in which the denominator reflects partition of the intermediate into three species; protonated, deprotonated (inactive) and a Cl^- addition complex (active).

Among the systems examined, only the Mo(VI)–Ti(III) reaction involves a transient that decays with the participation of the parent reductant. The rate law (eqn (12))

$$-\mathrm{d}[\text{Int}]/\mathrm{d}t = \frac{k[\text{Ti(III)}][H^+][Cl^-][\text{Int}]}{1 + K_{Ti}[\text{Ti(III)}]} \qquad (12)$$

exhibits kinetic saturation, suggesting formation of a Ti(III)–intermediate adduct ($K_{\text{formation}} = 210\ M^{-1}$).

Note that none of the decay curves display evidence of a kinetic component that is second order in the disappearing intermediate.

Table 4 lists the molar absorptivity of the transient species, calculated from the disentangling of each of the reaction profiles.[9a] Extinction coefficients for intermediates in the reductions by Ti(III) and by V(II) are in fair agreement, but those obtained in the remaining systems are quite different, with the mismatch well outside the estimated uncertainty. The implication is that we are dealing with four different absorbing species.

Table 4 Extinction coefficients of Mo(V) intermediate (430 nm)[a]

Red.	$10^3\ \varepsilon_{\text{Int}}/M^{-1}\ cm^{-1}$
Ti(II)	1.12 ± 0.11
Ti(III)	1.54 ± 0.28
V(II)	1.50 ± 0.23
Ge(II)	0.84 ± 0.02
Eu(II)	0.33 ± 0.02

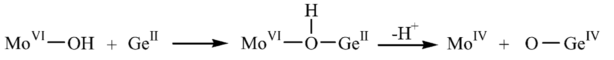
[a] ε Values obtained by disentangling the biphasic reaction curves using the method of Bose (ref. 9*a*).

Discussion

The array of biphasic reaction profiles observed in this study indicates that Mo(VI) reacts quickly in acid solutions with each of our metal-center reductants, yielding an intermediate of lower oxidation state which strongly absorbs near 430 nm and which decays ultimately to the familiar cation, $[Mo_2O_4]^{2+}$. The properties of the intermediate correspond to the metastable monomeric Mo(V) species proposed by Sykes[11] and generated electrolytically by Chalipoyil and Anson.[12] This monomer is converted to a more stable chloro complex in 10 M HCl[8] but decomposes quickly in 2 M CF_3SO_3H,[13] and appears to be involved also in the

Mo(VI)-catalyzed reductions of benzoquinone, vanadium(IV), and tri-iodide by hypovalent titanium.[1]

The generation of Mo(V) by both V(II) and Ge(II) proceeds according to straightforward monomial rate laws (Table 2), but both conversions pose mechanistic questions. The Mo(VI)–Ge(II) reaction may avoid the unstable state Ge(III) by preliminary formation of Mo(IV), probably *via* oxo transfer (13), followed by rapid Mo((IV),(VI)) comproportionation (14).



$$\mathrm{Mo^{VI}{-}OH + Ge^{II} \longrightarrow Mo^{VI}{-}\overset{H}{O}{-}Ge^{II} \xrightarrow{-H^+} Mo^{IV} + O{-}Ge^{IV}} \quad (13)$$

$$\mathrm{Mo(VI) + Mo(IV) \longrightarrow 2\,Mo(V)\quad (rapid)} \quad (14)$$

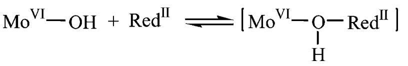
The rate constant for the Mo(VI)–V(II) reaction, $2.30 \times 10^2\ \mathrm{M^{-1}s^{-1}}$, exceeds the $1 \times 10^2\ \mathrm{M^{-1}s^{-1}}$ upper limit imposed by slow substitution at the V(II) center,[4,14] thus indicating either a predominant outer-sphere path or an inner-sphere path involving substitution at the Mo(V) center for this transfer.

The Mo(VI)–Ti(II) rate law (eqn (8)) mirrors partition of the reductant into two protonation levels, of which only the deprotonated form is active, and brings to mind the reduction of chlorinated quinine, chloranilic acid,[15] by Ti(II). In contrast, the denominator of the rate law for the Mo(VI)–Ti(III) reaction, (eqn (9)), indicates partition of Ti(III) into *three* species: deprotonated and protonated forms and a chloro-complex. Of the three, only $[\mathrm{Ti(OH)}]^{2+}$ is significantly active, a feature common of many reductions by this center.[16]

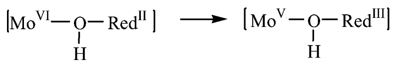
The second phase of our profiles, a sharp absorbance decrease in all cases (Table 3), is taken here to reflect the transformations of the monomeric Mo(V) transient to the inactive dimer, $[\mathrm{Mo_2O_4}]^{2+}$. Two features of these curves are quite unexpected: (A) The decay portions exhibit no sign of second order character, which one would expect for a monomer-to-dimer conversion; and (B) The calculated molar absorbances of transients generated from the several reductants do not match (Table 4).

We therefore conclude that the losses of the transients are first order processes preceding a rapid, kinetically silent, dimerization, and that these transients, although related, are not the same species. Moreover, the rate laws and kinetic parameters associated with the decays are not the same (Table 3).

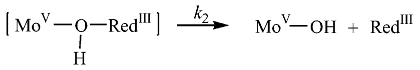
The kinetic behavior of these intermediates is consistent with the intervention, in at least some cases, of binuclear successor complexes that are formed in the initial electron transfer (15) and which subsequently dissociate into a monomeric Mo(V) species (17) before rapid conversion to the dimeric product (18):[17]



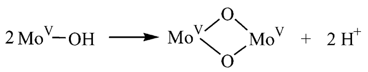
$$\mathrm{Mo^{VI}{-}OH + Red^{II} \rightleftharpoons [Mo^{VI}{-}\underset{H}{O}{-}Red^{II}]} \quad (15)$$



$$\mathrm{[Mo^{VI}{-}\underset{H}{O}{-}Red^{II}] \longrightarrow [Mo^{V}{-}\underset{H}{O}{-}Red^{III}]} \quad (16)$$



$$\mathrm{[Mo^{V}{-}\underset{H}{O}{-}Red^{III}] \xrightarrow{k_2} Mo^{V}{-}OH + Red^{III}} \quad (17)$$



(18)

The various rate laws for decomposition of the Mo(V) transients (Table 3) provide information concerning the speciation of the successor complexes. With both the V(II) → V(III) and Ti(II) → Ti(III) systems, dissociation (17) requires deprotonation, (as indicated by $[\mathrm{H^+}]$ in the denominators), whereas the Eu(III) intermediate exists in both protonated (reactive) and nonprotonated (inactive) forms, and a modestly stable chloro-complex ($K_{\mathrm{Cl}} = 0.3\ \mathrm{M^{-1}}$) as well.

The Ti(III) → Ti(IV) intermediate, alone among the successors listed, requires action of additional reductant for dissociation, as well as both protonation and $\mathrm{Cl^-}$ attachment. The kinetic saturation with respect to Ti(III) noted here allows us to estimate a stability constant near 200 $\mathrm{M^{-1}}$ for coordination of the additional reductant. The possibility of interaction between Ti(III) and Ti(IV) centers calls to mind the formation of a Ti(III)–Ti(IV) complex in aqueous sulfate solution as reported by Fraser and coworkers.[18]

Acknowledgements

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$$\mathrm{Mo(VI) + V(II){-}OH_2 \rightarrow Mo(VI){-}OH{-}V(II) + H^+.} \quad (19)$$

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