REDOX REACTIONS BETWEEN COMPLEXES OF MOLYBDENUM AND IRON

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Abstract—Several redox reactions between complexes of molybdenum (oxidation states III– VI) and iron in aqueous solution have been investigated with respect to their stoichiometry, kinetics and mechanism. The reactions include the oxidation of Mo^{3^+} and $Mo_2O_4^{2^+}$, $Mo_2O_2S_2^{2^+}$ and $Mo_3O_4^{4^+}$ by Fe(phen)₃³⁺ (phen = 1,10-phenanthroline). The reduction of Mo(VI) by Fe(II) in 8 M HCl and of Mo(CN)₈³⁻ by Fe²⁺ have also been investigated. Three separate reaction steps were detected in the oxidation of Mo^{3^+} to Mo(VI) and in the reduction of Mo(CN)₈³⁻ by Fe²⁺. In the oxidation of $Mo_2O_4^{2^+}$ by Fe³⁺, and of $Mo_2O_4^{2^+}$ and $Mo_3O_4^{4^+}$ by Fe(phen)₃³⁺, however, only one reaction effect was observed. The rate equations reveal that, in these reactions, the transfer of the first electron represents the rate-determining step. The rate constants of individual electron-transfer steps are discussed in terms of mechanisms, thermodynamic effects and the nature of the coordinating ligands.

All of the Mo enzymes also contain Fe, and it has been suggested that direct electron transfer occurs between the Mo and Fe centers in some of these enzymes during the catalytic action.¹ In order to learn more about the general features of redox processes between Mo and Fe compounds, we have studied the kinetics of a series of redox reactions between simple complexes of these two metal ions. The reactions include the oxidation of Mo³⁺ and $Mo_2O_4^{2+}$ by Fe³⁺, of $Mo_2O_4^{2+}$, $Mo_2O_2S_2^{2+}$ and $Mo_3O_4^{4+}$ by Fe(phen)₃³⁺ (phen = 1,10-phenanthroline), and the reduction of Mo(VI) by Fe(II) and of Mo(CN)₈³⁻ by Fe²⁺.

EXPERIMENTAL

Solutions of the metal complexes used have been prepared and standardized according to procedures described in the literature.² All solutions were kept and handled under an atmosphere of N_2 . Absorption measurements were carried out by means of a Cary 118C spectrophotometer. The kinetics of the redox processes were followed spectrophotometrically

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using a Cary 118C spectrophotometer, a stoppedflow apparatus or a temperature-jump apparatus. The latter two instruments had been built at our institute. The reaction signals of the stopped-flow and relaxation measurements were stored in a transient recorder (Datalab DL 905 or DL 920) and evaluated either by means of an electronic simulator (developed by Dr C. R. Rabl) or by computer fitting procedures. At least three individual measurements were made with each solution studied.

RESULTS

Mo(VI) + Fe(II)

In accordance with reported redox potentials³ Mo(VI) is reduced to Mo(V) by Fe(II) in strong HCl solution, e.g. 8 M HCl. Under these conditions Mo(VI) is present in the form of $MoO_2Cl_2^4$ and Mo(V) as $MoOCl_5^{-}$ (or H_2MoOCl_5).⁵ The Mo(V) complex is of a green colour and its solution shows absorption maxima near 450 and 710 nm. Spectrophotometric titrations of Mo(VI) with Fe(II) in 8 M HCl confirmed the 1:1 stoichiometry and revealed that the equilibrium is far to the side of the products.

The kinetics of the fast redox reaction were studied

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by means of the stopped-flow technique with a large excess of Fe(II) (0.01–0.1 M) over Mo(VI) (0.001–0.005 M). The reaction was monitored at 710 nm, following the formation of Mo(V). In all experiments a single exponential reaction curve was observed (half-lifes 2.5–18 ms). The dependence of the apparent first-order rate constant on the concentration of Fe(II) is shown in Fig. 1. The straight line passes through the origin (i.e. the back reaction is negligible) and yields a second-order rate constant :

$$k = 3.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$
 (20°C, 8 M HCl).

 $Mo_2O_4^{2+} + Fe^{3+}$

In dilute HClO₄ Mo(V) exists in form of a dimer of structure $(H_2O)_3MoO(\mu-O)_2OMo(H_2O)_3^{2+}$,⁶ usually abbreviated by $Mo_2O_4^{2+}$. Spectrophotometric titrations of $Mo_2O_4^{2+}$ with Fe³⁺ at 384 nm (an absorption maximum of $Mo_2O_4^{2+}$) indicated a stoichiometry according to:

$$Mo_2O_4^{2+} + 2Fe^{3+} \rightleftharpoons 2Mo(VI) + 2Fe^{2+}, \quad (1)$$

with the equilibrium far to the side of the products [the predominant form of Mo(VI) under the conditions of this study is a monomeric cationic species,⁷ HMoO₃⁺].

The kinetics of this reaction have been investigated with a large excess of Fe³⁺ (0.01–0.04 M) over Mo₂O₄²⁺ (0.001 M) and at H⁺ concentrations of 0.4–1.5 M (HClO₄), and ionic strength (I) of 2.0 M (NaClO₄). The reaction was monitored at 450 nm, observing the decrease in $[Mo_2O_4^{2+}]$. Only one reaction effect was detected (half-lifes 8–90 s). Plots of log $(A_i - A_{\infty})$ vs t were linear for more than 90% of the reaction. The



Fig. 2. Oxidation of $Mo_2O_4^{2+}$ by Fe^{3+} . Dependence of the pseudo first-order rate constant on $[Fe^{3+}]$ and $[H^+]$ [25°C, I = 2.0 M (NaClO₄)].

dependence of the pseudo first-order rate constant on $[Fe^{3+}]$ is shown in Fig. 2 for various H⁺ concentrations. The apparent second-order constant (slopes of Fig. 2) depends on $[H^+]$ as shown in Fig. 3. The data reveal that the rate equation is of the form :

$$-d[Mo_2O_4^{2^+}]/dt = (k_a + k_b/[H^+]) \times [Mo_2O_4^{2^+}][Fe^{3^+}], \quad (2)$$

with $k_a \leq 0.2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = 1.27 \text{ s}^{-1}$ (25°C, I = 2.0 M).

The overall reaction [eqn (1)] is assumed to proceed by a step-wise transfer of two electrons from



Fig. 1. Reduction of Mo(VI) by Fe(II). Dependence of the apparent first-order rate constant on [Fe(II)] (20°C, 8 M HCl).



Fig. 3. Oxidation of $Mo_2O_4^{2+}$ by Fe^{3+} . Dependence of the apparent second-order rate constant on $[H^+]^{-1}$ [25°C, $I = 2.0 \text{ M} (\text{NaClO}_4)$].

the Mo(V) dimer to two Fe(III), with Mo(V)Mo(VI) as a steady-state intermediate. The form of eqn (2) clearly demonstrates that the first electron-transfer step is rate-determining in the overall reaction. Assuming that the term with $k_b/[H^+]$ [eqn (2)] indicates a reaction path in which Mo₂O₄²⁺ is oxidized by FeOH²⁺, this interpretation yields, with a $K_{\rm H}$ ([FeOH²⁺][H⁺]/[Fe³⁺]) of 1×10⁻³ M⁻¹ (25°C, I = 2 M),⁸ a second-order rate constant (k) of 1.3×10^3 M⁻¹ s⁻¹ for the oxidation by FeOH²⁺.

 $Mo_2O_4^{2+} + Fe(phen)_3^{3+}$

Measurements of the kinetics of the oxidation of $Mo_2O_4^{2+}$ by the phen complex of Fe(III) have been carried out either with the Mo(V) dimer in excess (1.1 $\times 10^{-4}$ -1.1 $\times 10^{-3}$ M) over Fe(III) (5.6 $\times 10^{-5}$ M) or with Fe(III) in excess (5 $\times 10^{-5}$ -2.6 $\times 10^{-4}$ M) over $Mo_2O_4^{2+}$ (5 $\times 10^{-6}$ -1 $\times 10^{-5}$ M): [H⁺] = 0.5-1.5 M (HClO₄), I = 2.0 M (NaClO₄). The strong absorption of the Fe(II) product at 510 nm was used in order to follow the reaction. Both series of measurements conform to the rate law:

$$d[Fe(II)]/dt = 2k_1[Fe(III)][Mo_2O_4^{2+}],$$
 (3)

with $k_1 = k_a + k_b / [H^+]$.

The form of the rate law demonstrates that the first electron-transfer step (rate constant k_1) is again the rate-determining process. The studies with excess of $Mo_2O_4^{2+}$ yielded $k_a = 13.5 M^{-1} s^{-1}$, and $k_b = 9 s^{-1}$, and those with excess of Fe(phen)³⁺₃ gave $k_a = 11.5$ $M^{-1}s^{-1}$, and $k_b = 4s^{-1}$. The two values of k_a are in fair agreement but those of k_b differ appreciably. In case of excess of Fe(III) the low reactant concentrations slow down the redox process (halflifes 170-740 s) and some spontaneous decomposition of the Fe(phen) complexes occurs during the time of the reaction.⁹ Therefore, the results of this series may be considered as less reliable. The moderate variation of the rate with $[H^+]$ can be assigned to a contribution of the reaction path $Mo_2O_4(H_2O)_5OH^+ + Fe(phen)_3^{3+}$. Similar results had been reported by Cayley et al.¹⁰ for this system under conditions somewhat different from ours: $k_a = 31 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}, k_b = 6.0 \,\mathrm{s}^{-1} \,[I = 1.0 \,\mathrm{M}$ $(LiClO_4)$].

 $Mo_2O_2S_2^{2+} + Fe(phen)_3^{3+}$

The structure of this Mo(V) species is analogous to that of the oxo complex, $(H_2O)_3MoO(\mu-S)_2OMo(H_2O)_3^{2+.11}$ The rate of its oxidation by Fe(phen)_3^{3+} is rather low and some spontaneous decomposition of the Fe(phen) complexes occurs during the time of the reaction. High concentrations of $Mo_2O_2S_2^{2+}$ were used $(1.8 \times 10^{-3}-8.1 \times 10^{-3} M)$ in order to enhance the rate of reaction. A reaction curve (510 nm) is shown in Fig. 4. The final value of the absorbance corresponds to practically complete reduction of the Fe(III) complex. Contrary to all other systems described so far, the reaction curves are not exponential. This behaviour can be accounted for either by a change in the ratedetermining step during the reaction or by the formation of a non-steady-state intermediate. Important information can be evaluated very conveniently from the initial rate of reaction. The initial slopes of the reaction curves are given by:

$$(\mathrm{d}A/\mathrm{d}t)_o = k[\mathrm{Mo}_2\mathrm{O}_2\mathrm{S}_2^{2^+}] \times [\mathrm{Fe}(\mathrm{III})]_o \varepsilon_{\mathrm{Fe}(\mathrm{II})}.$$
(4)

The dependence of $(dA/dt)_o$ on $[Mo_2O_2S_2^{2+}]$ yields $k = 0.8 \text{ M}^{-1} \text{ s}^{-1} (25^{\circ}\text{C}, 1 \text{ M} \text{ HClO}_4)$. If k_1 denotes the rate constant of the first electron-transfer step, then $k = k_1$ in the non-steady-state model (formation of a true intermediate) and $k = 2k_1$ if steady-state conditions are maintained and a change in the rate-determining step occurs.

 $Mo_3O_4^{4+} + Fe(phen)_3^{3+}$

In aqueous solution Mo(IV) exists in the form of trimeric species characterized by a $Mo_3O_4^{4+}$ core.¹² Spectrophotometric measurements of $Mo_3O_4^{4+}$ -Fe(phen)₃³⁺ mixtures (510 nm, 1 M HCl indicated a stoichiometry of the redox reaction according to:

$$6Fe(phen)_{3}^{3^{+}} + Mo_{3}O_{4}^{4^{+}}$$

 $\approx 6Fe(phen)_{3}^{2^{+}} + 3Mo(VI).$ (5)

The reaction curves observed in the kinetic studies $\{[Mo_3O_4^{4+}] = 4 \times 10^{-5} - 2.2 \times 10^{-4} \text{ M}, [Fe(phen)_3^{3+}] = 4 \times 10^{-5} \text{ M}, 25^{\circ}\text{C}, 1.0 \text{ M} \text{ HCl}, I = 2.0 \text{ M} (NaCl), 510 \text{ nm} \}$ were always single



Fig. 4. Oxidation of $Mo_2O_2S_2^{2+}$ by Fe(phen)³⁺. Reaction curve with $[Mo_2O_2S_2^{2+}] = 8.1 \times 10^{-3}$ M and $[Fe(phen)_3^{3+}] = 1.8 \times 10^{-4}$ M (25°C, 1.0 M HClO₄, I = 1.0 M, $\lambda = 510$ nm).

exponentials and the apparent first-order rate constant depends on $[Mo_3O_4^{4+}]$ as shown in Fig. 5. The results reveal a rate law of the form:

$$d[Fe(II)]/dt = 6k_1[Mo_3O_4^{4+}][Fe(III)], \quad (6)$$

which indicates that the first electron-transfer process is rate-determining. For this step a rate constant (k_1) of 51 M⁻¹ s⁻¹ [25°C, 1 M HCl, I = 2.0 M (NaCl)] is obtained.

$M_0(H_2O)_6^{3+} + Fe(H_2O)_6^{3+}$

The monomeric aquo ion $Mo(H_2O)_6^{3+}$ is stable only in strongly acidic non-complexing solutions.¹³ The results of a spectrophotometric titration of Mo^{3+} with Fe³⁺ in 1 M *p*-toluenesulfonic acid (HPTS) at 450 nm (at this wavelength the absorption of the Fe species is very small) is shown in Fig. 6. Obviously the Mo(III) is first oxidized to Mo(V) and then to Mo(VI). The spectrum at the position of the first break is that of the Mo(V) dimer, $Mo_2O_4^{2+}$.

In the kinetic studies of the oxidation of Mo^{3+} by Fe^{3+} (stopped-flow techniques, $\lambda = 450$ nm), three reaction effects were observed with Fe^{3+} in excess : a fast one in the millisecond range, and two slower ones with half-lifes of seconds. The fast effect describes the disappearance of Mo^{3+} . The rate law of this process was found to be :

$$-d[Mo^{3+}]/dt = k_{f}[Mo^{3+}][Fe^{3+}], \quad (7)$$

with $k_f = 1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (25°C, 1 M HPTS).

The nature of the first true intermediate (between Mo^{3+} and $Mo_2O_4^{2+}$) is unknown. Equation (7) demonstrates, however, that the rate-determining step on the way to this intermediate is given by:

$$Mo^{3+} + Fe^{3+} \xrightarrow{\kappa_f} Mo(IV) + Fe^{2+}.$$
 (8)



Fig. 5. Oxidation of $Mo_3O_4^{4+}$ by Fe(phen) $_3^{3+}$. Dependence of the apparent first-order rate constant on $[Mo_3O_4^{4+}]$ $[25^{\circ}C, 1.0 \text{ M HCl}, I = 2.0 \text{ M (NaCl)}].$



Fig. 6. Spectrophotometric titration of 2.3×10^{-3} M Mo³⁺ with 0.6 M Fe³⁺ (25°C, 1.0 M HPTS, I = 1.0 M, $\lambda = 450$ nm).

An experimental curve of the two slower processes is shown in Fig. 7. The decrease in and recovery of the signal intensity reflect the formation and disappearance of $Mo_2O_4^{2+}$. The final part of the curve is described by a single exponential function and a rate constant (k) of $0.5 \text{ M}^{-1} \text{ s}^{-1}$ (1 M HPTS, I = 1.0 M) has been evaluated for the oxidation of the intermediate $Mo_2O_4^{2+}$ by Fe³⁺ in these experiments. This value is consistent with the one which was determined directly [see above, $k = 1.27 \text{ M}^{-1} \text{ s}^{-1}$ (1 M HClO₄, I = 2.0 M)], since like-charged reactants are expected to react with a higher rate at the higher ionic strength.

Attempts were made to fit the total experimental curve (Fig. 7) with the help of a computer program based on a four-step mechanism of the type Mo(III) \rightarrow Mo(IV) \rightarrow Mo(V) \rightarrow Mo(V)₂ \rightarrow Mo(V)Mo(VI)



Fig. 7. Oxidation of Mo³⁺ by Fe³⁺. Reaction curve with $[Mo^{3+}] = 1.2 \times 10^{-3} \text{ M} \text{ and } [Fe^{3+}] = 0.045 \text{ M} (25^{\circ}\text{C}, 1.0 \text{ M} \text{ HPTS}, I = 1.0 \text{ M}, \lambda = 450 \text{ nm}).$

and assuming that: (a) either monomeric Mo(IV), or (b) monomeric Mo(V) is the first true intermediate. Neither assumption gave a very good fit [although (a) was better than (b)], deviations occurring in particular near the intensity minimum. Possibly the neglect of all back reactions is not justified, or the assumed mechanism is incorrect.

 $Mo(CN)_{8}^{3-} + Fe^{2+}$

The product of the reduction of $Mo(CN)_8^{3-}$ by Fe^{2+} was identified by its spectrum to be $Mo(CN)_8^{4-}$. A spectrophotometric titration in 0.1 M HClO₄ confirmed the expected 1:1 stoichiometry. Thus:

$$\operatorname{Fe}^{2^{+}} + \operatorname{Mo}(\operatorname{CN})_{8}^{3^{-}} \stackrel{K_{r}}{\rightleftharpoons} \operatorname{Fe}^{3^{+}} + \operatorname{Mo}(\operatorname{CN})_{8}^{4^{-}}.$$
 (9)

A quantitative evaluation of the spectrophotometric data yielded a value for K_r of 11.7 [25°C, 0.1 M HClO₄, I = 1.0 M (NaClO₄), 387 nm].

In studies of the kinetics of reaction (9) by stoppedflow techniques ([Mo(CN)₈³⁻] = 2×10^{-5} M, $[Fe^{2+}] = 1 \times 10^{-4} - 6 \times 10^{-4}$ M), one reaction effect in the millisecond range was detected. The absorbance at the starting point of this reaction $(\lambda = 387 \text{ nm})$ is not that calculated from the initial concentration of $Mo(CN)_8^{3-}$ and it is concluded that other reaction steps precede the one observed by the stopped-flow method. This was confirmed by studies with the temperature-jump relaxation technique which showed that there are two more reaction effects, one in the microsecond range ($\tau = 100-400$ μ s) and one with a time constant <0.2 μ s (cable Tjump). The results demonstrate that the reaction does not proceed by an outer-sphere path, and the following three-step inner-sphere mechanism is considered:

(a)
$$Mo(V) + Fe(II) \xrightarrow{k_1}_{k_{-1}} Mo(V)Fe(II),$$

(b)
$$Mo(V)Fe(II) \xrightarrow{k_2}{k_{-2}} Mo(IV)Fe(III),$$
 (10)

(c)
$$Mo(IV)Fe(III) \xrightarrow{k_3} Mo(IV) + Fe(III).$$

Steps (a) and (c) involve inner-sphere substitution processes, the time constants of which should be measurable by the techniques used. Therefore, the extremely rapid process was assigned to step (b), yielding $1/\tau_b = k_2 + k_{-2} > 5 \times 10^6$ s⁻¹. This very fast effect is not observed in the absence of Fe(II) and Fe(III), i.e. it is not due to a protonation reaction of the Mo(CN)₈ species.

The relaxation time of the microsecond effect depends on the concentration of Fe(II) but is independent of [Fe(III)]. This effect is assigned to step (a), to which the rapid equilibrium (b) is coupled. Then, with $[Fe(II)] \gg [Mo(V)]$:

$$1/\tau_a = k_{-1}/(1+K_2) + k_1$$
[Fe(II)], (11)

where $K_2 = k_2/k_{-2}$. A plot of $1/\tau_a$ vs [Fe(II)] gave $k_1 = 1.15 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} [3.0^{\circ}\text{C}, 0.1 \text{ M} \text{ HClO}_4, I = 1 \text{ M}$ (NaClO₄)]. (In order to reduce cavitation effects, the T-jump experiments were carried out at low temperature.)

The slow effect is assigned to step (c) with (a) and (b) as preequilibria. It is evaluated more conveniently from the stopped-flow rather than from the T-jump measurements. The apparent first-order rate constant is given by:

$$\frac{1}{k_{\rm obs}} = \frac{1 + K_2}{k_3 K_2} + \frac{1}{k_3 K_1 K_2 [\text{Fe(II)}]}.$$
 (12)

A plot of $1/k_{obs}$ vs 1/[Fe(II)] yielded $k_3K_1K_2 = 3.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. K_1K_2 was determined from K, and K_3 ([Mo(IV)Fe(III)]/[Mo(IV)][Fe(III)]) = 172 M^{-1} (obtained during this study by spectrophotometric measurements), leading finally to $k_3 = 160 \text{ s}^{-1}$, and $k_{-3} = 2.75 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

DISCUSSION

The rates of individual reaction steps which have been determined during this study are summarized in Table 1. The mechanism of the reduction of Mo(IV) by Fe(II) in 8 M HCl is uncertain, but Cl⁻ is known to be a good bridging ligand and an innersphere mechanism may tentatively be assumed. It can safely be excluded that the formation of the precursor complex (inner- or outer-sphere) is ratelimiting, since both the diffusion-controlled encounter of the reactants and substitution at an Fe(II) center are very rapid processes. Thus, either the electron-transfer step or (in the case of an innersphere mechanism) the dissociation of the successor complex must be rate-limiting. An additional complication arises from the fact that the overall reaction includes ligand exchange processes $(MoO_2Cl_2 \rightarrow MoOCl_5^{2-}).$

The interesting point in the oxidation of $Mo_2O_4^{2+}$ by Fe³⁺ is the origin of the term showing a 1/[H⁺] dependence. Three possible mechanisms may be considered: (a) FeOH²⁺ reacts with the Mo(V) dimer via an efficient inner-sphere path with OH⁻ bridging;¹⁴ (b) Mo₂O₄(H₂O)₅OH⁺ reacts with Fe(H₂O)₆³⁺ by an OH⁻-bridged inner-sphere path; and (c) reaction via inner-sphere structures which result from rate-determining substitution of a terminal oxygen of Mo₂O₄²⁺ at Fe(H₂O)₅OH⁺ and Fe(H₂O)₆³⁺, respectively. A comparison with other Fe³⁺ and FeOH²⁺ reactions¹⁵ disfavours (b) and (c).

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Reaction	Rate constant (M ⁻¹ s ⁻¹)	Conditions
$MoO_{2}Cl_{2} + Fe(II) \rightarrow MoOCl_{5}^{2-} + Fe(III)$	3.6 × 10 ³	20°C, 8 M HCl
$Mo_2O_4^{2^+} + Fe^{3^+} \rightarrow Mo(V)Mo(VI) + Fe^{2^+}$	≤ 0.2	$25^{\circ}C, I = 2 M (NaClO_4)$
$Mo_2O_4^{2+} + FeOH^{2+} \rightarrow Mo(V)Mo(VI) + Fe^{2+}$	1.3×10^{3}	$25^{\circ}C, I = 2 M (NaClO_4)$
$Mo_2O_4^{2+} + Fe(phen)_3^{3+} \rightarrow Mo(V)Mo(VI) + Fe(phen)_3^{2+}$	13	$25^{\circ}C, I = 2 M (NaClO_4)$
$Mo_2O_2S_2^{2^+} + Fe(phen)_3^{3^+} \rightarrow Mo(V)Mo(VI) + Fe(phen)_3^{2^+}$	0.8 or 0.4	25°C, 1 M HClO₄
$Mo_3O_4^{4+} + Fe(phen)_3^{3+} \rightarrow Mo(IV)_2Mo(V) + Fe(phen)_3^{2+}$	51	25° C, 1 M HCl, $I = 2$ M (NaCl)
$Mo^{3+} + Fe^{3+} \rightarrow Mo(IV) + Fe^{2+}$	1.3×10^{3}	25°C, 1 M HPTS
$Mo(CN)_8^{3-} + Fe^{2+} \rightarrow [(CN)_7 Mo(V)CNFe(II)]^{-}$	1.1×10^{6}	$3^{\circ}C, 0.1 \text{ M HClO}_4, I = 1 \text{ M}(\text{NaClO}_4)$
$[(CN)_7 Mo(V)CNFe(II)]^{-\frac{k_2}{k-2}} [(CN)_7 Mo(IV)CNFe(III)]^{-1}$	$k_2 + k_{-2} > 5 \times 10^6 \mathrm{s}^{-1}$	1
		$3^{\circ}C, 0.1 \text{ M HClO}_4, I = 1 \text{ M}(\text{NaClO}_4)$
$[(CN)_7 Mo(IV)CNFe(III)]^{-\frac{k_3}{k_{-3}}} Mo(CN)_8^{4-} + Fe^{3+}$	$k_3 = 160 \text{ s}^{-1}$	25° C, 0.1 M HClO ₄ , $I = 1$ M (NaClO ₄)
	$k_{-3} = 2.7 \times 10^4$	25° C, 0.1 M HClO ₄ , $I = 1$ M (NaClO ₄)

Table 1.

Thus interpretation (a) is considered to be the most likely. The results of Sasaki *et al.*¹⁶ on substitution at $Mo_2O_4(H_2O)_6^{2+}$ indicate that the replacement of water at the Mo(V) dimer may well be the rate-determining step in mechanism (a).

The oxidation processes involving $Fe(phen)_3^{3+}$ must proceed, of course, by outer-sphere pathways. The higher rate of the oxidation of $Mo_2O_4^{2+}$ by $Fe(phen)_3^{3+}$ (13 M^{-1} s⁻¹), compared to the oxidation by $Fe(H_2O)_6^{3+}$ ($\leq 0.2 M^{-1} s^{-1}$, probably also outer-sphere), is easily rationalized in terms of Marcus' theory: $Fe(phen)_3^{3+}$ is the stronger oxidizing agent (higher ΔG^o), and the Fe-phen complexes have a much higher self-exchange rate than the Fe-aquo complexes.¹⁷

The rate of oxidation of $Mo_2O_2S_2^{2+}$ by $Fe(phen)_3^{3+}$ is more than one order of magnitude lower than that of $Mo_2O_2^{2+}$. The low reductive power of $Mo_2O_2S_2^{2+}$ is observed also in other cases : $Mo_2O_2S_2^{2+}$ is not noticeably oxidized by air, and, after the addition of Fe^{3+} , no oxidation was found to occur within 24 h. Obviously the μ -thio ligands stabilize the Mo(V) state relative to Mo(VI) more than the μ -oxo ligands.

The rate of the first electron-transfer step in the oxidation of $Mo_3O_4^{4+}$ by $Fe(phen)_3^{3+}$ was found to be 51 M⁻¹s⁻¹ in 2 M chloride solution. While these studies were in progress, a paper by Harmer *et al.* appeared¹⁸ which reported on the kinetics of this reaction in perchlorate solution (they had managed to keep $Mo_3O_4^{4+}$ stable in the presence of ClO_4^{-}) and gave a rate constant of only 0.47 M⁻¹ s⁻¹. Since spectrophotometric studies had provided evidence for the coordination of Cl^- to the trimeric Mo(IV)

ion¹⁹ in chloride solution

 $[Mo_3O_4(H_2O)_{9-n}Cl_n^{+(4-n)}],$

it is probably the strong reduction of the electrostatic repulsion which provides most of the rate enhancement in the chloride medium.

The reaction between Mo³⁺ and Fe³⁺ in noncomplexing media is also strongly retarded by electrostatic repulsion. Using an (educated) estimate of 4×10^{-2} M⁻¹ for the outer-sphere association constant under our conditions, the first-order rate constant of the outer-sphere precursor complex $[k_1 (k/K_0)]$ is $\approx 1.3 \times 10^3/0.04 = 3 \times 10^4$ s⁻¹. This value is by orders of magnitude too high for substitution at Fe³⁺¹⁵ or Mo^{3+.13} It has to be concluded, therefore, that this redox reaction proceeds by an outer-sphere path.

Finally, the rate constants for the formation of the inner-sphere complexes Mo(V)CNFe(II) from $Mo(CN)_8^{3-} + Fe^{2+}$ $(k_1 = 1.1 \times 10^6 M^{-1} s^{-1})$ and Mo(IV)CNFe(III) from Mo(CN) $_{8}^{4-}$ + Fe³⁺ (k_{-3} = 2.7×10^4 M⁻¹ s⁻¹) appear reasonable for substitution at $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, respectively, if the charge effects are taken into account. The electron transfer within the inner-sphere complex is fast, $k_2 + k_{-2} > 5 \times 10^6$ s⁻¹. This might have been expected, since cyano ligands are known to be very good electron-transferring groups. For instance, the outer-sphere reduction of $Mo(CN)_8^{3-}$ by $Fe(CN)_6^{4-}$ occurs with a second-order rate constant of 3×10^4 $M^{-1} s^{-1}$ and that of $Mo(CN)_8^{3-}$ by $W(CN)_8^{4-}$ with one of 5×10^6 M⁻¹ s⁻¹.²⁰ Considering the charge type of these reactions (-3 and -4), the first-order electron-transfer rates within the encounter complexes (i.e. through two layers of CN^- ligands) are estimated to be near 1×10^7 s⁻¹ and 1×10^9 s⁻¹, respectively.

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REFERENCES

- 1. E. I. Stiefel, Prog. Inorg. Chem. 1977, 22, 1.
- 2. References are given in the dissertation of C. Millan, Göttingen (1982).
- 3. G. Charlot, Oxidation-Reduction Potentials, Tables of Constants and Numerical Data, Vol. 8. Pergamon Press, Oxford (1958).
- (a) F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd Edn, p. 951. Wiley Interscience, New York (1972). (b) J. Aveston, E. W. Anacker and J. S. Johnson, Inorg. Chem. 1964, 3, 735.
- 5. (a) Ref. 4(a), p. 966; (b) S. Himeno, A. Saito and M. Hasegawa, *Inorg. Chim. Acta* 1984, **88**, 93.
- 6. M. Ardon and A. Pernick, Inorg. Chem. 1973, 12, 2484.
- J. J. Cruywagen, J. B. B. Heyns and E. F. C. H. Rohwer, J. Inorg. Nucl. Chem. 1978, 40, 53; J. F. Ojo, R. S. Taylor and A. G. Sykes, J. Chem. Soc., Dalton Trans. 1975, 500.

- 8. C. F. Baes and R. E. Mesmer, The Hydrolysis of Cations, p. 230. John Wiley, New York (1976).
- J. E. Dickens, F. Basolo and N. M. Neumann, J. Am. Chem. Soc. 1957, 79, 1286; T. S. Lee, I. M. Kolthoff and D. L. Leussing, J. Am. Chem. Soc. 1948, 70, 3596.
- G. R. Cayley, R. S. Taylor, R. K. Wharton and A. G. Sykes, *Inorg. Chem.* 1977, 16, 1377.
- 11. B. Spivack and Z. Dori, J. Chem. Soc., Chem. Commun. 1977, 909.
- A. Bino, F. A. Cotton and Z. Dori, J. Am. Chem. Soc. 1978, 100, 5252; R. K. Murman and M. E. Shelton, J. Am. Chem. Soc. 1980, 102, 3984.
- 13. Y. Sasaki and A. G. Sykes, J. Chem. Soc., Dalton Trans. 1975, 1048.
- 14. N. Sutin, Acc. Chem. Res. 1968, 1, 225.
- M. Grant and R. B. Jordan, *Inorg. Chem.* 1981, 20, 55;
 B. Perlmutter-Hayman and E. Tapuhi, *J. Coord. Chem.* 1976, 6, 31.
- Y. Sasaki, R. S. Taylor and A. G. Sykes, J. Chem. Soc., Dalton Trans. 1975, 396.
- B. S. Brunschwig, C. Creutz, D. H. Macartney, T.-K. Sham and N. Sutin, *Faraday Discuss. Chem. Soc.* 1982, 74, 113.
- M. A. Harmer, D. T. Richens, A. B. Soares, A. T. Thornton and A. G. Sykes, *Inorg. Chem.* 1981. 20, 4155.
- P. Souchay, M. Cadiot and B. Viossat, Bull. Soc. Chim. Fr. 1970, 892.
- R. J. Campion, N. Purdie and N. Sutin, *Inorg. Chem.* 1964, 3, 1091.