

Kinetics of Redox Reactions between Complexes of Molybdenum and Iron: The Oxidation of Iron(II) by Molybdenum(VI) and of $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ by $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

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In 8 mol dm⁻³ hydrochloric acid Mo^{VI} is reduced to Mo^V by Fe^{II}. Under these conditions, Mo^{VI} exists predominantly as MoO₂Cl₂ and Mo^V as MoOCl₅²⁻. Spectrophotometric studies indicate that the stoichiometry of the reaction is exactly 1 : 1 and that the equilibrium is far to the side of the products. Studies of the kinetics of this redox process by stopped-flow techniques revealed that the rate of reaction is first-order in each reactant and that the second-order rate constant is $k = (3.6 \pm 0.1) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (20 °C, 8 mol dm⁻³ HCl). The mechanism of the reaction is not known, but a chloride-bridged inner-sphere process appears plausible. Equilibrium studies of the oxidation of $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ by Fe³⁺ in 1 mol dm⁻³ *p*-toluenesulphonic acid (Hpts) indicate that a dimeric Mo^V species, Mo₂O₄²⁺, is the first stable product. With an excess of Fe³⁺, this species is oxidized to Mo^{VI}. In kinetic studies with Fe³⁺ in excess, three processes could be observed: (a) the disappearance of Mo³⁺, (b) the formation of Mo₂O₄²⁺, and (c) the disappearance of Mo₂O₄²⁺. Process (a) occurs in the ms range. It is described by the equation $-\text{d}[\text{Mo}^{3+}]/\text{d}t = k_1[\text{Mo}^{3+}][\text{Fe}^{3+}]$, with $k_1 = (1.30 \pm 0.05) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (25 °C, 1 mol dm⁻³ Hpts), and obviously proceeds by an outer-sphere mechanism. Steps (b) and (c) overlap strongly (seconds to minutes). The measured reaction curves for (b) and (c) can be satisfactorily described by two superimposed exponentials of rather similar time constants. The formation of Mo₂O₄²⁺ from the products of the fast step is discussed in terms of a mechanism which is in approximate though not complete agreement with the experimental data. The second-order rate constant for the oxidation of the intermediate Mo₂O₄²⁺ by Fe^{III} which has been evaluated from the reaction curves agrees well with that of a previous study in which Mo₂O₄²⁺ was oxidized directly.

Electron-transfer processes between molybdenum and iron centres are supposed to occur in a series of molybdenum enzymes, for instance in nitrate reductase, sulphite oxidase, xanthine oxidase, and nitrogenase.^{1,2} It is of interest, therefore, to gain insight into the kinetics and mechanisms of redox reactions between compounds of these two metals, including complexes of simple structures which are not closely related to the biological systems. In a previous paper³ we have reported on the kinetics of oxidation of Mo₂O₄²⁺ by Fe³⁺, and of Mo₂O₄²⁺, Mo₂O₂S₂²⁺, and Mo₃O₄⁴⁺ by $[\text{Fe}(\text{phen})_3]^{3+}$ (phen = 1,10-phenanthroline). In the present study we report on the kinetics of the reduction of Mo^{VI} by Fe^{II} in strong hydrochloric acid solution, and of the oxidation of $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ by $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Experimental

Materials.—Solutions of $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ were prepared by extended hydrolysis of MoCl₅²⁻ in aqueous *p*-toluenesulphonic acid (Hpts) solution as described in the literature.^{5,6} The product was purified *via* an ion exchange solution filled with Dowex 50W-X12 resin from which it was eluted, after washing, with 2 mol dm⁻³ Hpts. The Mo³⁺ solutions were stored at 0 °C under an inert gas atmosphere. The concentration of Mo³⁺ was determined by oxidation to Mo^{VI} with excess Fe³⁺ and back titration of the Fe²⁺ so formed with cerium(IV) sulphate, using ferroin as indicator. The pentachloro complex of Mo^{III} used for this preparation was obtained by electrolytic reduction (Hg cathode) of a solution of molybdate(VI) in 6 mol dm⁻³ HCl.⁷ Addition of NH₄Cl and volume reduction leads to the precipitation of $[\text{NH}_4]_2[\text{MoCl}_5] \cdot \text{H}_2\text{O}$.⁷

Sodium molybdate(VI) (Merck, p.A.), iron(II) perchlorate (Ventron), iron(III) perchlorate (Ventron), *p*-toluenesulphonic acid (Merck, p.A.) and all other chemicals were of the best grade commercially available and were used without further treat-

ment. The iron(II) perchlorate solutions were standardized by titrations with cerium(IV) sulphate (using ferroin as indicator), in the case of Fe^{III} after reduction by Sn^{II}.⁸

Methods.—Solutions of Mo³⁺ and Fe²⁺ were kept and handled under nitrogen. Since Mo³⁺ is slowly oxidized by water,⁹ fresh solutions of this metal ion were always used. Spectra were recorded by means of a Cary 118 spectrophotometer. The kinetics of the reactions, too, were monitored spectrophotometrically, using a stopped-flow apparatus which was described by Dr. C. R. Rable and built at our institute. The pneumatic driving unit of this apparatus was obtained from Durrum Instrument Corporation. The reaction signals were stored in a transient recorder (Datalab DL 905 or Biomation 1010) before evaluation by an electronic simulator or by a computer-programmed fitting procedure. At least four individual measurements were carried out with each pair of reactant solutions.

Results and Discussion

Molybdenum(VI) + Iron(II).—Molybdenum(VI) is not reduced by Fe^{II} in weakly acidic solutions. This is consistent with the redox potentials which have been reported for Mo^{VI/V} and Fe^{III/II} under similar conditions.¹⁰ In more concentrated hydrochloric acid solutions the redox potentials of the two couples change in such a way¹⁰ that reaction to give Mo^V + Fe^{III} will occur. In 8 mol dm⁻³ HCl the reaction proceeds practically to completion. At this HCl concentration the Mo compounds exist mainly as monomeric species, the reactant Mo^{VI} as MoO₂Cl₂ or MoO₂Cl₂(H₂O)₂,¹¹ and the product Mo^V as MoOCl₅²⁻ or H₂MoOCl₅.^{12,13} The Mo^V species appears green in solution and exhibits a characteristic absorption spectrum with maxima near 450 and 710 nm.¹² The

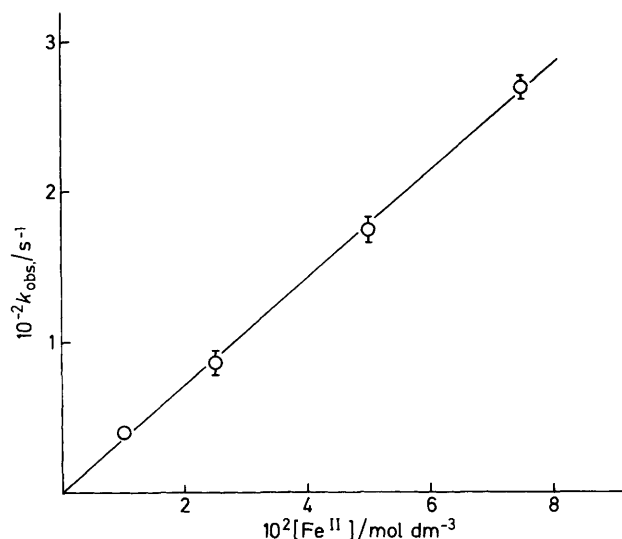
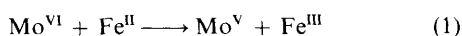


Figure 1. Reduction of Mo^{VI} by Fe^{II} . Dependence of the pseudo-first-order rate constant k_{obs} on the concentration of Fe^{II} (20 °C, 8 mol dm^{-3} HCl)

stability constants for the (weak) binding of Cl^- to Fe^{2+} are not known with certainty. From indirect evidence, differing values for the stability of the 1 : 1 complex have been reported;¹⁴ it may be expected that FeCl^+ is the predominant Fe^{II} species under our conditions.

The stoichiometry of the reduction of Mo^{VI} by Fe^{II} in 8 mol dm^{-3} HCl was determined by spectrophotometric measurements of 0.028 mol dm^{-3} Mo^{VI} solutions to which increasing amounts of Fe^{II} had been added. The resulting solutions exhibit the 710 nm absorption band of MoOCl_5^{2-} . A plot of the absorbance at 710 nm *vs.* $[\text{Fe}^{\text{II}}]_0/[\text{Mo}^{\text{VI}}]_0$ (where the subscript zero denotes initial concentrations) shows a break at a molar ratio of 1.0, indicating that the stoichiometry is given by equation (1) and



that the equilibrium lies far on the side of the products.

The rate of this redox process is too fast to be measured by conventional techniques. Therefore the stopped-flow method was applied in the studies of the kinetics. The measurements were carried out at 20 °C in 8 mol dm^{-3} HCl with a large excess of Fe^{II} (0.01–0.08 mol dm^{-3}) over Mo^{VI} (0.001–0.005 mol dm^{-3}). The reaction was monitored using the characteristic absorption of the Mo^{V} product at 710 nm. In all experiments a single exponential reaction curve was observed (half-life 2.6–18 ms), equation (2). The apparent first-order rate constant k_{obs} ,

$$[\text{Mo}^{\text{V}}] = [\text{Mo}^{\text{V}}]_{\infty} (1 - e^{-k_{\text{obs}} t}) \quad (2)$$

increases linearly with the concentration of Fe^{II} as demonstrated in Figure 1. The near-zero intercept of the straight line of Figure 1 confirms that the back reaction is negligible. Thus the rate law may be written in the form of equation (3) with $k = 3.6$

$$d[\text{Mo}^{\text{V}}]/dt = k[\text{Fe}^{\text{II}}][\text{Mo}^{\text{VI}}] \quad (3)$$

(± 0.01) $\times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (20 °C, 8 mol dm^{-3} HCl). This value is considered to be an apparent rate constant, due to the presence of presumably several quickly equilibrating Fe^{II} species in these solutions (see above).

The overall process can be represented by the reactions in Scheme 1, where the two intermediates may be outer-sphere or

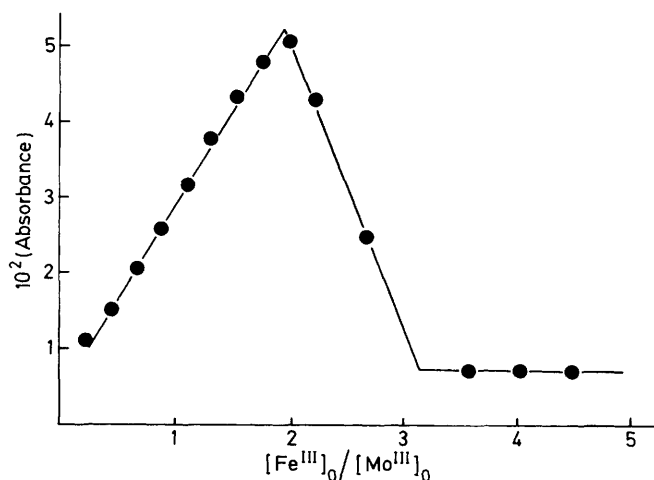
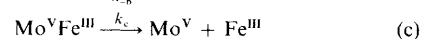
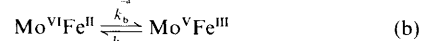
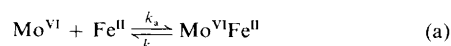


Figure 2. A spectrophotometric titration of $2.3 \times 10^{-3} \text{ mol dm}^{-3}$ Mo^{3+} with 0.62 mol dm^{-3} Fe^{3+} (25 °C, 1 mol dm^{-3} Hpts, ionic strength 1 mol dm^{-3} , $\lambda = 450 \text{ nm}$)



Scheme 1.

inner-sphere (*e.g.* Cl^- -bridged) complexes. The observation of just one reaction effect and the form of the rate law [equation (3)] suggest that the intermediates appear only as steady-state concentrations. With the steady-state approximations equation (4) is obtained.

$$k = k_a k_b k_c / (k_{-a} k_{-b} + k_{-a} k_c + k_b k_c) \quad (4)$$

It can safely be excluded that the first step of Scheme 1 is rate determining (*i.e.* $k_b k_c \gg k_{-a} k_{-b}$, $k_{-a} k_c$, and therefore $k = k_a$), since both the diffusion-controlled encounter of the reactants and substitution at the Fe^{II} centre are rapid processes, and k_a must be higher than the observed second-order rate constant k by several orders of magnitude. Thus either the electron-transfer process [Scheme 1(b)] must be rate determining with $k = K_a k_b$ (where $K_a = k_a/k_{-a}$), or possibly the third step (c) in the case of an inner-sphere mechanism, with $k = K_a K_b k_c$. A distinction between these two cases cannot be made. Also, the type of mechanism cannot be elucidated. Since chloride ions are known to be good bridging ligands, an inner-sphere mechanism appears quite plausible. Finally, it should be pointed out that Scheme 1 is a simplified description of the overall process since it does not include the ligand exchange at the Mo centre which takes place during the reaction, $\text{MoO}_2\text{Cl}_2 \longrightarrow \text{MoOCl}_5^{2-}$.

$[\text{Mo}(\text{H}_2\text{O})_6]^{3+} + [\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.—The hexa-aqua ion $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ is stable only in strongly acidic solutions of non-complexing and non-oxidizing acids.¹⁵ The absorption spectrum of Mo^{3+} in 1 or 2 mol dm^{-3} Hpts (yellowish solution) which was measured during this study (providing for strict exclusion of oxygen) agrees with literature reports: absorption maxima at 308 ($\epsilon = 28.5$) and 380 nm ($\epsilon = 16.1 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).^{5,15} Even very slight oxidation (<1%) is detected easily by an $\epsilon_{308}/\epsilon_{380}$ ratio appreciably higher than 1.8 (formation of dimeric Mo^{V}).

The stoichiometry of the redox reactions under consideration was investigated spectrophotometrically by titrating a $2.3 \times 10^{-3} \text{ mol dm}^{-3}$ solution of Mo^{3+} with 0.62 mol dm^{-3} Fe^{3+} . Experimental data for 450 nm are shown in Figure 2. At

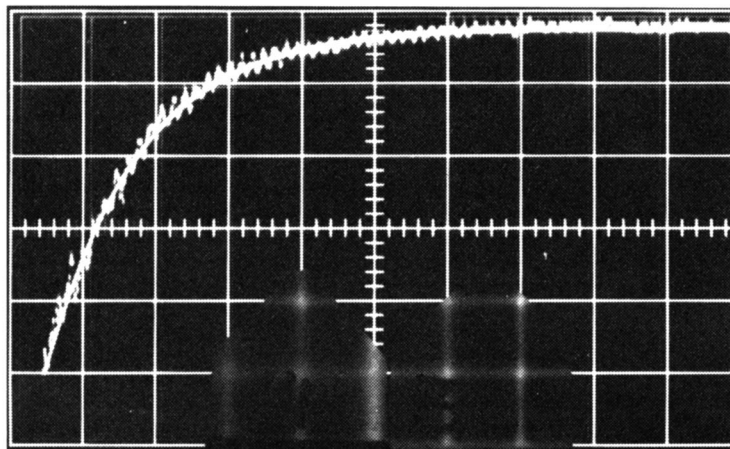
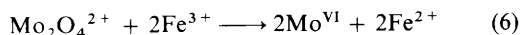


Figure 3. Oxidation of Mo^{3+} by Fe^{3+} ; fast reaction effect ($[\text{Mo}^{3+}] = 9.6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Fe}^{3+}] = 0.012 \text{ mol dm}^{-3}$, 1 mol dm^{-3} Hpts, ionic strength 1 mol dm^{-3} , $\lambda = 450 \text{ nm}$, sweep 50 ms cm^{-1} , sensitivity 5 mV cm^{-1})

this wavelength the contributions of Fe^{3+} and Fe^{2+} to the total absorbance are very small. A plot of the absorbance *vs.* the ratio $[\text{Fe}^{\text{III}}]_0/[\text{Mo}^{\text{III}}]_0$ (initial concentrations) reveals breaks at the molar ratios 2.0 and near 3 (Figure 2). The data indicate that the first stable oxidized state is Mo^{V} . Indeed, the spectrum of the solution at $[\text{Fe}^{\text{III}}]_0/[\text{Mo}^{\text{III}}]_0 = 2.0$ is identical with that of the well known Mo^{V} dimer, $\text{Mo}_2\text{O}_4^{2+}$.¹⁶ Build-up of Mo^{IV} is not observed, presumably because of the high reactivity and instability of monomeric oxo- or aqua-molybdenum(IV) species.¹⁷ The initial reaction, up to $[\text{Fe}^{\text{III}}]_0/[\text{Mo}^{\text{III}}]_0 = 2.0$, is therefore described by equation (5) (water and protons neglected).



This reaction lies far on the side of the products (sharp break in Figure 2). The same type of stoichiometry was observed also for the oxidation of Mo^{3+} by several other one-equivalent oxidants.¹⁸ Further addition of Fe^{3+} leads to a second reaction in which the $\text{Mo}_2\text{O}_4^{2+}$ is oxidized to Mo^{VI} , equation (6),



producing the decline in the absorbance between the molar ratios 2 and 3. Reaction (6) has been studied before separately and was found to be rather slow.³ This explains why it took a long time (*ca.* 1–1.5 h) to reach a final value of the absorbance for molar ratios of 2–3 at the low reactant concentrations used in the spectrophotometric titrations.

The kinetic studies in this system were carried out by means of the stopped-flow technique. Using an excess of Fe^{3+} over Mo^{3+} , three reaction effects were observed: a fast one in the ms range and two slow effects with half-lives of seconds ($\lambda = 450 \text{ nm}$, no noticeable absorption due to the Fe species). The fast effect is sufficiently separated from the slower ones, so that its time constant could be evaluated with good accuracy by the electronic curve-fitting procedure. Measurements were carried out with $[\text{Mo}^{3+}] = 9.6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Fe}^{3+}] = (0.2\text{--}1.2) \times 10^{-2} \text{ mol dm}^{-3}$ (25°C , 1 mol dm^{-3} Hpts, ionic strength $I = 1 \text{ mol dm}^{-3}$, $\lambda = 450 \text{ nm}$). Figure 3 shows an example of the fast effect; it corresponds to a decrease in absorbance.

The reaction curves are exponential functions which describe the disappearance of Mo^{3+} (and the formation of an intermediate), according to equation (7). The dependence of the

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

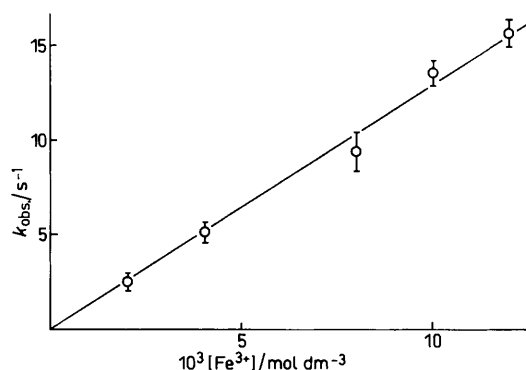


Figure 4. Oxidation of Mo^{3+} by Fe^{3+} ; fast reaction effect. Dependence of the pseudo-first-order rate constant (k_{obs}) on the concentration of Fe^{3+} (25°C , 1 mol dm^{-3} Hpts, ionic strength 1 mol dm^{-3})

pseudo-first-order rate constant k_{obs} on the concentration of Fe^{3+} is of the form in equation (8) as demonstrated by the data shown in Figure 4.

$$k_{\text{obs}} = k_1[\text{Fe}^{3+}] \quad (8)$$

Whatever the first real intermediate on the way to the Mo^{V} dimer may be (see below), the form of the rate law [equations (7) and (8)] establishes that the first electron-transfer step is rate determining in the formation of the intermediate, equation (9),



with $k_1 = (1.30 \pm 0.05) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (25°C , 1 mol dm^{-3} Hpts, ionic strength 1 mol dm^{-3}). Rate-determining formation of Mo^{IV} was also reported for the oxidation of monomeric Mo^{III} by several other one-equivalent oxidants.¹⁸ Based upon the Eigen–Fuoss equation,¹⁹ the stability constant of the encounter complex between Mo^{3+} and Fe^{3+} is estimated to be near $0.05 \text{ dm}^3 \text{ mol}^{-1}$ under our conditions. This value, together with literature data about the rates of substitution at Mo^{3+} ^{15,20} and Fe^{3+} ,²¹ leads to the conclusion that the observed second-order rate constant, $k_1 = 1.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, is by at least two orders of magnitude too high to be accounted for by an inner-sphere mechanism. The same applies if $\text{Fe}(\text{OH})^{2+}$ were the oxidant; substitution at $\text{Fe}(\text{OH})^{2+}$ is up to 10^3 -fold faster than at Fe^{3+} ,²¹ but the concentration of $\text{Fe}(\text{OH})^{2+}$ is about 10^3 -fold lower than that of Fe^{3+} in 1 mol dm^{-3} acid. Furthermore, substitution at $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ was found to be

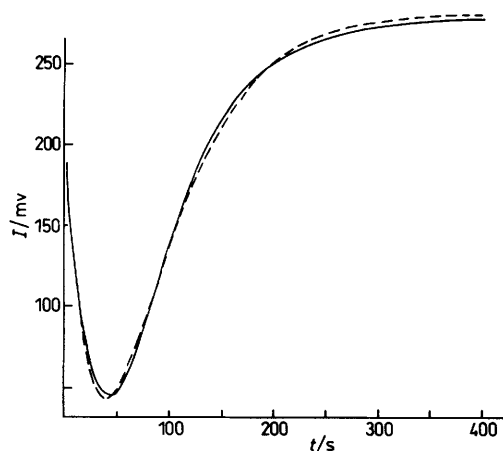
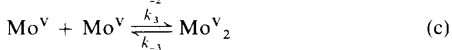
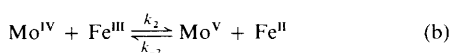
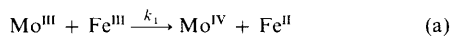


Figure 5. Oxidation of Mo^{3+} by Fe^{3+} ; slow reaction effects. (—) Experimental curve with $[\text{Mo}^{3+}]_0 = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Fe}^{3+}]_0 = 0.012 \text{ mol dm}^{-3}$ (25 °C, 1 mol dm^{-3} Hpts, ionic strength 1 mol dm^{-3} , $\lambda = 450 \text{ nm}$). (---) Best fit by equation (12)

slow and independent of $[\text{H}^+]$ in the range $[\text{H}^+] = 0.17\text{--}1.0 \text{ mol dm}^{-3}$.¹⁵ It is to be concluded, therefore, that the first electron-transfer step [equation (9)] proceeds by an outer-sphere mechanism.

The two slower effects have been studied under similar conditions, $[\text{Mo}^{3+}] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Fe}^{3+}] = (1.8\text{--}4.5) \times 10^{-2} \text{ mol dm}^{-3}$ (25 °C, 1 mol dm^{-3} Hpts, ionic strength 1.0 mol dm^{-3} , $\lambda = 450 \text{ nm}$). A reaction curve is shown in Figure 5. The initial decrease in signal intensity corresponds to an increase in absorption. The strongly absorbing species which is formed and then disappears again is the Mo^{V} dimer cation, $\text{Mo}_2\text{O}_4^{2+}$, as mentioned already in connection with Figure 2. For the reaction sequence in the presence of excess Fe^{3+} a mechanism of the type in Scheme 2 may be considered. Step (a)



Scheme 2.

is the rate-determining process for the observed fast reaction effect. As has been reported before,³ step (d) is rate determining in the oxidation of Mo_2^{V} to 2Mo^{VI} by Fe^{III} . The mechanism which leads to the formation of Mo_2^{V} , giving rise to the decrease in the reaction signal (Figure 5), is uncertain. The following two cases will be considered.

(I) The first real intermediate formed during the fast process is monomeric Mo^{IV} . Formation of Mo_2^{V} is then due to steps (b) and (c), with the concentration of monomeric Mo^{V} assumed to remain at a steady-state level.

(II) Monomeric Mo^{IV} appears only as a steady-state concentration, and monomeric Mo^{V} is the first true intermediate. In this case the formation of Mo_2^{V} is given solely by step (c).

It appears likely that the back reactions of steps (b) and (c) are negligible. Then, in case (I), step (b) is rate determining in the formation of Mo_2^{V} . In other words, the differential equation

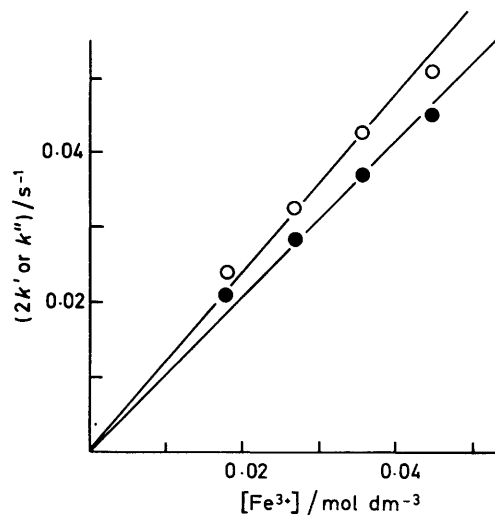


Figure 6. Oxidation of Mo^{3+} by Fe^{3+} ; slow reaction effects. Dependence of the pseudo-first-order rate constants $2k'$ (○) and k'' (●) on the concentration of Fe^{3+} (25 °C, 1 mol dm^{-3} Hpts, ionic strength 1 mol dm^{-3})

which describes the formation and disappearance of Mo_2^{V} is composed of two pseudo-first-order terms, equation (10), where

$$\frac{d[\text{Mo}_2\text{O}_4^{2+}]}{dt} = \frac{k_2}{2} [\text{Fe}^{3+}][\text{Mo}^{\text{IV}}] - k_4 [\text{Fe}^{3+}][\text{Mo}_2\text{O}_4^{2+}] = k'[\text{Mo}^{\text{IV}}] - k''[\text{Mo}_2\text{O}_4^{2+}] \quad (10)$$

$k' = k_2[\text{Fe}^{3+}]/2$ and $k'' = k_4[\text{Fe}^{3+}]$. With $d[\text{Mo}^{\text{IV}}]/dt = -2k'[\text{Mo}^{\text{IV}}]$, an integrated form of equation (10) can be derived²² [equation (11)]. The observed reaction curves (which

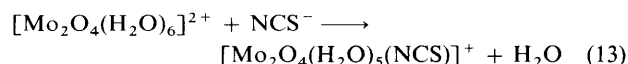
$$[\text{Mo}_2\text{O}_4^{2+}] = [\text{Mo}]_0 \left(\frac{k'}{k'' - 2k'} \right) (e^{-2k't} - e^{-k''t}) \quad (11)$$

describe the change in light intensity I) should then be of the form in equation (12).

$$I = A + B(e^{-2k't}) - C(e^{-k''t}) \quad (12)$$

The experimental curves were stored in a Biomation 1010 transient recorder, transferred to a computer system (PDP 11/60 and Univac 1108) and attempted to be fitted by equation (12), using a suitable program.²³ Figure 5 shows a measured reaction curve and a best fit. The agreement between both curves is not perfect but satisfactory. The computer best-fit values of $2k'$ and k'' increase approximately linearly with the concentration of Fe^{3+} , as expected [equation (10)], see Figure 6.

The slopes of the straight lines of Figure 6 yield $k_2 = 1.21 (\pm 0.1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_4 = 1.06 (\pm 0.1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Clearly, the similarity of the values of k_2 and k_4 (or $2k'$ and k'') inhibits the accuracy of the evaluation. Mechanism (I) requires that the rate constant k_3 is appreciably higher ($\approx 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) than k_2 and k_4 . This condition may well be fulfilled, since it has been demonstrated that substitution at the aqua-oxo complex of dimeric Mo^{V} is fast [equation (13), $k = 3 \times 10^4$



$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$].²⁴ A similar lability towards substitution may be

expected for the monomeric Mo^{V} species, thus enabling a fast dimerisation process.

In the case of mechanism (II) the rate of formation and disappearance of $\text{Mo}_2\text{O}_4^{2+}$ is given by equation (14).

$$\frac{d[\text{Mo}_2\text{O}_4^{2+}]}{dt} = k_3[\text{Mo}^{\text{V}}]^2 - k_4[\text{Fe}^{3+}][\text{Mo}_2\text{O}_4^{2+}] \quad (14)$$

If all molybdenum is present as Mo^{V} after the fast reaction effect, one obtains from $d[\text{Mo}^{\text{V}}]/dt = -2k_3[\text{Mo}^{\text{V}}]^2$ by integration $[\text{Mo}^{\text{V}}] = [\text{Mo}]_0/(1 + 2[\text{Mo}]_0 k_3 t)$. Therefore, this gives equation (15), with $k_4' = k_4[\text{Fe}^{3+}]$. Equation (15) contains only $[\text{Mo}_2\text{O}_4^{2+}]$ and t as variables but nevertheless cannot be integrated readily. Therefore, equation (15) itself was used for

$$\frac{d[\text{Mo}_2\text{O}_4^{2+}]}{dt} = k_3 \left(\frac{[\text{Mo}]_0}{1 + 2[\text{Mo}]_0 k_3 t} \right)^2 - k_4' [\text{Mo}_2\text{O}_4^{2+}] \quad (15)$$

the evaluation, applying a computer-programed numerical procedure based on the insertion of the experimental data for $[\text{Mo}_2\text{O}_4^{2+}]$, $[\text{Mo}]_0$, and t into equation (15). The concentration of $\text{Mo}_2\text{O}_4^{2+}$ was expressed in terms of the measured light intensity (in mV, photo voltage), and the relationship (16) was

$$[\text{Mo}_2\text{O}_4^{2+}] = \frac{(I_0 - I_t) + 2[\text{Mo}]_0 k_3 (I_\infty - I_t)t}{2.3I_a \varepsilon (1 + 2[\text{Mo}]_0 k_3 t)} \quad (16)$$

derived for this purpose. Here, I_0 , I_∞ , and I_t are the intensities at times zero, infinity, and t ; I_a is the full (uncompensated) incoming light intensity (5 000 mV), and ε is the absorption coefficient of $\text{Mo}_2\text{O}_4^{2+}$ at 450 nm. By varying k_3 and k_4 , equation (15) was fitted to the experimental data. The best fits were clearly less satisfactory than those obtained assuming mechanism (I).

There are some more pieces of experimental evidence which speak in favour of mechanism (I). It was observed that $t_{\min}[\text{Fe}^{3+}]$ (where t_{\min} is the time at which the light intensity shows its minimum, see Figure 5) is constant, $0.83 (\pm 0.03)$ mol dm^{-3} s. This is as expected for mechanism (I) {setting the first derivative of equation (11) [or (12)] equal to zero} but not for mechanism (II), at least not in general (only under special conditions could this product show near-constancy).

A further criterion is given by the initial slopes of the curves of the type shown in Figure 5. According to equations (10) and (12) the initial slope should increase linearly with the concentration of Fe^{3+} for mechanism (I), whereas in the case of mechanism (II) it should be constant for constant $[\text{Mo}]_0$ [equation (15)]. Experimentally, the initial slopes, $(dI/dt)_{t=0}$, were evaluated from plots with a strongly expanded time-scale and found to depend on $[\text{Fe}^{3+}]$. However, the variation of the initial slope (-15.4 to -25.6 mV s^{-1}) was less than that of $[\text{Fe}^{3+}]$ (0.018 – 0.045 mol dm^{-3}).

Thus all experimental evidence indicates that mechanism (I) is an approximate but not a truly correct description of the redox process. It may be, for instance, that neglecting the back reaction of step (b) of Scheme 2 is justified, or that the concentration of monomeric Mo^{V} is not confined to a steady-state level. It is also conceivable that reaction steps not considered in Scheme 2 may play a role, e.g. dimerization of Mo^{IV} , or disproportionation of Mo^{IV} . Under these circumstances, the rate constant $k_2 = 1.2$ dm³ mol⁻¹ s⁻¹ which has been evaluated as described (see above) cannot be assigned just to step (b) of Scheme 2. On the other hand, the rate constant $k_4 = 1.06$ dm³ mol⁻¹ s⁻¹ (in 1 mol dm⁻³ Hpts, ionic strength 1.0

mol dm⁻³) which has been obtained by the same procedure and which accounts for the disappearance of $\text{Mo}_2\text{O}_4^{2+}$ through oxidation by Fe^{III} , agrees very well with the value which has been determined previously³ by the direct oxidation of $\text{Mo}_2\text{O}_4^{2+}$ with Fe^{III} , $k = 1.27$ dm³ mol⁻¹ s⁻¹ in 1 mol dm⁻³ HClO_4 , ionic strength 2.0 mol dm⁻³. The slight difference in the values for k can be accounted for by the difference in the ionic strength. Details of the mechanism for the oxidation of $\text{Mo}_2\text{O}_4^{2+}$ by Fe^{III} have been discussed in an earlier paper.³

The kinetics of the oxidation of Mo^{3+} by the one-equivalent oxidizing agents IrCl_6^{2-} , $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$, and VO^{2+} have also been reported recently.¹⁸ In contrast to the present investigation, these studies have been carried out with Mo^{3+} in excess over the oxidants, and consequently $\text{Mo}_2\text{O}_4^{2+}$ was always the final Mo product. Also, these reactions were monitored by following the disappearance of the oxidants, not the formation of the Mo products. A slow dimerization process, $\text{Mo}^{\text{V}} + \text{Mo}^{\text{V}} \longrightarrow \text{Mo}_2\text{O}_4^{2+}$, would not have been observable therefore. In all cases the time course of the decay of the oxidant absorbance was consistent with rate-determining first electron transfer (formation of Mo^{IV}). The reaction is fast for oxidation by IrCl_6^{2-} (half-lives near 10 ms) but slow for oxidation by $[\text{Co}(\text{C}_2\text{O}_4)_3]^{2-}$ and VO^{2+} (minutes).¹⁸ For a complete understanding of the mechanism of such redox processes it seems desirable to study both the time course of the disappearance of the oxidant, and that of the formation of the Mo products.

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References

- 1 E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22**, 1.
- 2 J. S. Olson, D. P. Ballou, G. Palmer, and V. Massey, *J. Biol. Chem.*, 1974, **249**, 4363.
- 3 C. Millan and H. Diebler, *Inorg. Chem.*, 1985, **24**, 3729.
- 4 H. Diebler and C. Millan, *Polyhedron*, 1986, **5**, 539.
- 5 A. R. Bowen and H. Taube, *Inorg. Chem.*, 1974, **13**, 2245.
- 6 Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1973, 767.
- 7 K. H. Lohmann and R. C. Young, *Inorg. Synth.*, 1953, **4**, 97.
- 8 'Vogel's Textbook of Quantitative Inorganic Analysis,' 4th edn., Longman, London and New York, 1978, pp. 363 and 399.
- 9 M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, 1973, **95**, 6871.
- 10 G. Charlot, 'Oxidation-Reduction Potentials, Tables of Constant and Numerical Data,' Pergamon Press, Oxford, 1958, vol. 8, pp. 12 and 18.
- 11 W. P. Griffith and T. D. Wilkins, *J. Chem. Soc., A*, 1967, 675; J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 735; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley Interscience, New York, 1972, pp. 951 and 967.
- 12 G. P. Haight, jun., *J. Inorg. Nucl. Chem.*, 1962, **24**, 663; J. P. Simon and P. Souchay, *Bull. Soc. Chim. Fr.*, 1956, 1402.
- 13 S. Himeno, A. Saito, and M. Hasegawa, *Inorg. Chim. Acta*, 1984, **88**, 93.
- 14 H. N. Po and N. Sutin, *Inorg. Chem.*, 1968, **7**, 621; C. F. Wells, *J. Chem. Soc. A*, 1969, 2741.
- 15 Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1975, 1048.
- 16 M. Ardon and A. Pernick, *Inorg. Chem.*, 1973, **12**, 2484; Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1974, 1468.
- 17 D. T. Richens and A. G. Sykes, *Comments Inorg. Chem.*, 1981, **1**, 141; G. P. Haight and D. R. Boston, *J. Less-Common Met.*, 1974, **36**, 95; G. P. Haight, jun., *Acta Chem. Scand.*, 1961, **15**, 2012.
- 18 D. T. Richens, M. A. Harmer, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1984, 2099.

- 19 M. Eigen, *Z. Phys. Chem. (Neue Folge)*, 1954, **1**, 176; M. Eigen, *Z. Elektrochem. Ber. Bunsenges. Physik. Chem.*, 1960, **64**, 115; R. Fuoss, *J. Am. Chem. Soc.*, 1958, **80**, 5059.
- 20 H. M. Kelly, D. T. Richens, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1984, 1229.
- 21 M. Grant and R. B. Jordan, *Inorg. Chem.*, 1981, **20**, 55; B. Perlmutter-Hayman and E. Tapuhi, *J. Coord. Chem.*, 1986, **6**, 31.
- 22 A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 166 and p. 173 *et seq.*
- 23 S. W. Provencher, *Biophys. J.*, 1976, **16**, 27.
- 24 Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1975, 396.

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