

Spectroscopic and kinetic evidences for the formation of a 1:1 mixed complex of Mo^V and V^{IV} in perchloric medium*

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Summary

The kinetics of interaction of Mo₂O₄²⁺ with VO²⁺ was studied in HClO₄ medium at 25°C and ionic strength of 2 M by the stopped-flow technique. Under conditions of excess VO²⁺ a reaction mechanism is proposed to account for the observed pseudo-first order kinetics. For the overall process, 1/2 [Mo₂O₄(H₂O)₆]²⁺ + VO²⁺ ⇌ C + H⁺, the equilibrium constant ($K = 33 \text{ M}^{1/2}$) was determined by absorbance measurements.

Introduction

The ability of vanadium and molybdenum to form several mixed iso- and heteropolyanions with different stoichiometries both in solution and in the solid state has been the subject of many investigations⁽¹⁾.

In order to learn more about the stability and kinetics of formation of small mixed isopolycomplexes between the d¹ metal ions molybdenum(V) and vanadium(IV), the present study was forwarded in perchloric acid medium, where the reactions of molybdenum(V) are predominantly those of the dimeric μ -oxo complex⁽²⁾ [Mo₂O₄(H₂O)₆]²⁺.

Experimental

Materials

Reagent grade VOCl₂ (Carlo Erba), NaClO₄·H₂O (Merck), and HClO₄ (Merck) were used without further purification. Aqueous solutions of [Mo₂O₄(H₂O)₆]²⁺ were prepared according to Cayley and Sykes⁽³⁾. The (Mo₂O₄)²⁺ concentration was determined at $\lambda = 384 \text{ nm}$ ($\epsilon = 103 \text{ M}^{-1} \text{ cm}^{-1}$)^(4,5). The ionic strength of all the solutions ($\mu = 2.0 \text{ M}$) was controlled by addition of NaClO₄.

Determination of the equilibrium constant

The u.v.–vis. absorption spectra of solutions of VO²⁺ (3.66 and 4 mM), (Mo₂O₄)²⁺ (0.1–0.4 mM) and solutions containing mixtures of both reactants at different concentrations of HClO₄ (1–2 M) were recorded on a Zeiss spectrophotometer model PMQ3 (C. Zeiss, Germany).

Raman spectra

Raman spectra of perchloric solutions ([HClO₄] = 2 M) of (Mo₂O₄)²⁺ (0.25 and 3.3 mM) and VO²⁺ (1 mM) and mixtures containing 0.25 mM (Mo₂O₄)²⁺ and 1 mM VO²⁺ were recorded with a Raman FTIR spectrophotometer (Bruker IFS 66) between 150–3500 cm⁻¹ using a Nd:YAG laser as the excitation source ($\lambda = 1064 \text{ nm}$).

Kinetic measurements

Reactions were monitored with a DURRUM-D110 stopped-flow spectrophotometer at $\lambda = 340 \text{ nm}$. The experiments were done at constant concentration of (Mo₂O₄)²⁺ (0.25 mM) with an excess of VO²⁺ (2.4–11.2 mM) and at different HClO₄ concentrations (0.5–2.0 M).

Results and discussion

Determination of equilibrium constant

The mixtures of VO²⁺ and (Mo₂O₄)²⁺ were accompanied by changes in the u.v.–vis. absorption spectra as shown in Figure 1.

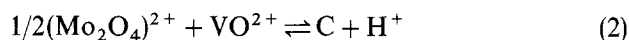
The electronic transitions which are responsible for the shoulder at ca. 300 nm in the absorption spectrum of the di- μ -oxo-dimolybdate(V) group involve orbitals which are mainly located on the molybdenum atoms and should be slightly affected by changing the ligands⁽⁶⁾. Thus, the spectral changes (Figure 1) indicate that the di- μ -oxo-dimolybdate(V) moiety is not present in the reaction product.

The experimental behaviour of the absorbance changes at different wavelengths are well fitted by Equation 1.

$$\Delta A/[D]_0 = \alpha + \beta \cdot [D]_0 \cdot [H^+]^2/[V]_0 \quad (1)$$

where ΔA is the difference between the absorbances of the mixtures and those calculated assuming no interaction between both reactants, and $[D]_0$ and $[V]_0$ are the analytical concentration of (Mo₂O₄)²⁺ and VO²⁺, respectively. The constants α and β depend on the wavelength. Figure 2 shows the linear plots according to Equation 1 at different wavelengths.

The plots shown in Figure 2, as well as the kinetic results (*vide infra*) can be interpreted by assuming the formation of a complex C between (Mo₂O₄)²⁺ and VO²⁺ (Reaction 2):



Under conditions of excess VO²⁺, the concentration of C in equilibrium will be given by Equation 3:

$$[C] = \Delta A / \Delta \epsilon \\ = (-K' + \{K'^2 + 4 \cdot [\text{Mo}_2\text{O}_4^{2+}]_0 \cdot K' \cdot [H^+]^2\}^{1/2}) \\ \times [H^+]^2 \quad (3)$$

where $\Delta \epsilon = \epsilon_C - 1/2 \cdot \epsilon_D - \epsilon_V$; ϵ_C , ϵ_D and ϵ_V are the molar absorptivities of complex C, (Mo₂O₄)²⁺ and VO²⁺, respectively; $K' = K^2 \cdot [\text{VO}^{2+}]^2/4$, and K is the equilibrium constant for Reaction 2.

In order to account for the experimental behaviour shown in Figure 2, the first two terms of the Taylor expansion for the square root in Equation 3 are taken and Equation 4 is obtained:

$$\Delta A / [\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]_0 \\ = 2 \cdot \Delta \epsilon - \{8 \cdot [\text{Mo}_2\text{O}_4^{2+}]_0 \cdot [H^+]^2 / K^2 \cdot [\text{VO}^{2+}]_0^2\} \quad (4)$$

* Dedicated to Professor Pedno J. Aymonino on the occasion of his 65th birthday.

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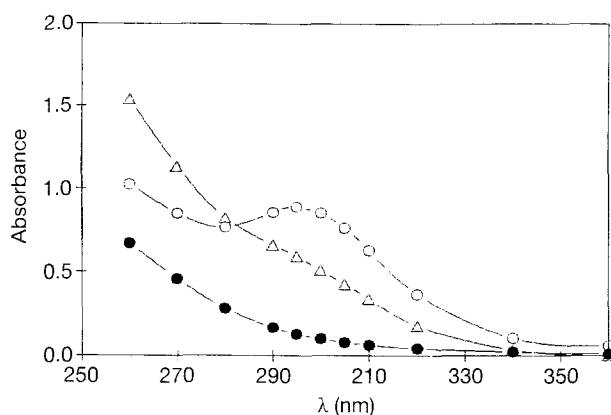


Figure 1. Absorption spectra of aqueous solutions of $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ (0.25 mM) (○), VO^{2+} (3.66 mM) (●) and a solution containing both $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ (0.25 mM) and VO^{2+} (3.66 mM) (△).

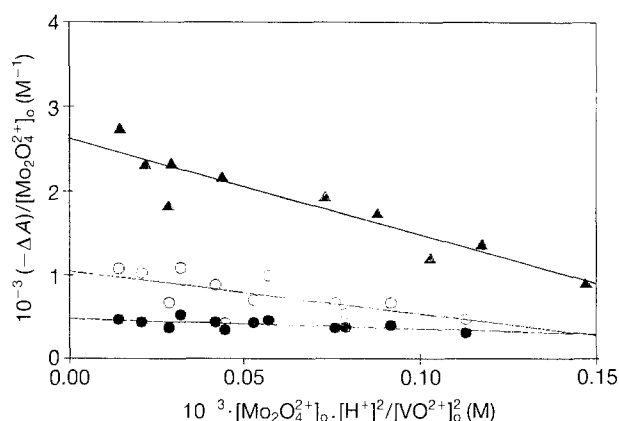


Figure 2. $-\Delta A/[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}_0$ versus $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}_0 \cdot [\text{H}^+]^2/[\text{VO}^{2+}]_0^2$ at different wavelengths. The following values for α and β are obtained: $\lambda = 300 \text{ nm}$ (▲), $\alpha = -2629 \text{ M}^{-1} \text{ cm}^{-1}$, $\beta = 11.54 \text{ M}^{-2}$; $\lambda = 270 \text{ nm}$ (○), $\alpha = -1046 \text{ M}^{-1} \text{ cm}^{-1}$, $\beta = 5.13 \text{ M}^{-2}$; $\lambda = 340 \text{ nm}$ (●), $\alpha = -477 \text{ M}^{-1} \text{ cm}^{-1}$, $\beta = 1.22 \text{ M}^{-2}$.

From the β values indicated in Figure 2, a value of $33 \pm 7 \text{ M}^{1/2}$ is obtained for the equilibrium constant K .

Raman spectra

Raman spectra of perchloric solution of $(\text{Mo}_2\text{O}_4)^{2+}$, VO^{2+} and mixtures of both reactants were recorded in an attempt to characterize reaction product C. Since the formation of different mixed isopoly species of molybdenum and vanadium in solution⁽¹⁾ as well as the nature of the molybdenum(V) complexes^(5,7) strongly depend on the experimental conditions, the spectra were taken in HClO_4 medium and the concentrations of $(\text{Mo}_2\text{O}_4)^{2+}$ and VO^{2+} used (see Experimental) were similar to those employed for the determination of equilibrium constant K (*vide infra*). Under these conditions only those bands assigned to HClO_4 in H_2O could be detected and the characterization of product C by raman was not possible.

Kinetic measurements

The pseudo-first order rate constants (k_{app}) obtained for solutions of various concentration of VO^{2+} and H^+ at constant $[\text{Mo}_2\text{O}_4]_0$ are listed in Table 1.

Table 1. Apparent rate constants (k_{app}) for the $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}/\text{VO}^{2+}$ reaction; $\mu = 2.0 \text{ M NaClO}_4$, $T = 25^\circ \text{C}$; $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]_0 = 0.25 \text{ mM}$.

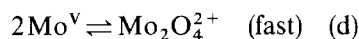
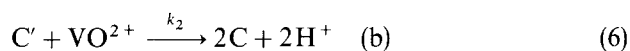
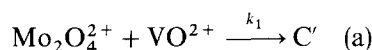
$[\text{HClO}_4]$ (M)	$[\text{VO}^{2+}]_0$ (mM)	k_{app} (s^{-1}) ^a
0.5	10.0	1.14(1.18)
1.0	1.6	0.34(0.37)
1.0	2.4	0.51(0.46)
1.0	3.2	0.60(0.54)
1.5	1.6	0.30(0.47)
1.5	2.4	0.30(0.56)
1.5	3.2	0.50(0.64)
1.5	4.0	0.63(0.72)
1.5	4.8	0.70(0.81)
1.5	8.0	1.02(1.15)
1.5	10.0	1.07(1.37)
2.0	3.2	0.62(0.74)
2.0	4.0	1.11(0.82)
2.0	5.6	0.93(1.00)
2.0	8.0	0.94(1.26)
2.0	11.2	0.78(0.80)

^aThe values within brackets were calculated using Equation 5.

The following expression accounts for the experimental kinetic results:

$$k_{\text{app}}/[\text{H}^+] = 0.197 + 108.0 \cdot [\text{VO}^{2+}]/[\text{H}^+] \quad (r = 0.97) \quad (5)$$

where k_{app} , the pseudo-first order rate constant, is expressed in s^{-1} and $[\text{VO}^{2+}]$ and $[\text{H}^+]$ are molar concentrations. The values of k_{app} calculated using Equation 5 are shown in Table 1. The results can be interpreted in terms of the following mechanism:



where the intermediate C' is a complex ion and Mo^{V} is a monomeric molybdenum species. Monomeric molybdenum(V) species were proposed as intermediates in one-electron reductions by $(\text{Mo}_2\text{O}_4)^{2+}$ ⁽⁵⁾. A reaction mechanism including a 2:1 molybdenum:vanadium intermediate similar to C' was also proposed to account for the reaction of $(\text{Mo}_2\text{O}_4)^{2+}$ with VO^{2+} ⁽⁸⁾.

For this mechanism, rate law 7 can be written:

$$v = d[\text{C}]/dt = 2k_2 \cdot [\text{C}'] \cdot [\text{VO}^{2+}] - k_3 \cdot [\text{C}] \cdot [\text{H}^+] \quad (7)$$

If $[\text{Mo}^{\text{V}}]$ and $[\text{C}']$ are neglected in the equation for the conservation of molybdenum and assuming the steady-state condition for C' , Mechanism 6 predicts the following expression for k_{app} :

$$k_{\text{app}}/[\text{H}^+] = k_3 + 2k_1 \cdot [\text{VO}^{2+}]/[\text{H}^+] \quad (8)$$

The comparison of Equation 8 with Equation 5 yields

$$k_3 = 0.197 \text{ M}^{-1} \text{ s}^{-1} \quad \text{and} \quad k_1 = 54 \text{ M}^{-1} \text{ s}^{-1}.$$

The H_2O exchange rate constant (k_0) for VO^{2+} is 500 s^{-1} ⁽⁹⁻¹¹⁾ at the equatorial positions (k_0 is at least a factor 10^6 higher at the axial position⁽⁹⁻¹¹⁾), which corresponds to a bimolecular rate constant of the order of $10 \text{ M}^{-1} \text{ s}^{-1}$. From the rate constant for the substitution

of an isothiocyanate ligand for one molecule of H₂O at an equatorial position of [Mo₂O₄(H₂O)₆]²⁺ ($2.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ⁽¹²⁾) a value lower than $1 \text{ M}^{-1} \text{ s}^{-1}$ is expected for similar substitution of a positive VO²⁺ ion for a molecule of H₂O by considering the effect of the different ion pair constants on the bimolecular rate constant⁽¹³⁾. Thus, the value $k_1 = 54 \text{ M}^{-1} \text{ s}^{-1}$ indicates that at least the equatorial positions at [Mo₂O₄(H₂O)₆]²⁺ would not be involved in Reaction a.

On the other hand, the high value for the equilibrium constant of the overall Reaction 2 ($K \approx 33 \text{ M}^{1/2}$) supports the formation of a reaction product C in which equatorial positions of both reactants are involved in the coordination. This is compatible with reaction Mechanism 6 if Reaction b is interpreted as the attack of VO²⁺ ion on complex C', which induces the dissociation of the di- μ -oxo-dimolybdate(V) moiety followed by a molecular rearrangement leading to complex C.

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