Kinetics of the Rapid Monomer–Dimer Equilibration of Molybdenum(VI) in Aqueous Perchloric Acid Solutions

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The monomer–dimer equilibration of molybdenum(VI) in 0·2—3·0M perchloric acid solutions, I = 3·0M(LiClO$_4$), has been studied at 25 °C. Spectrophotometric measurements are consistent with the presence of a monomeric species, $[HMoO_3]^+$, and dimeric species, $[H_2Mo_2O_6]^{2+}$ and $[H_3Mo_2O_6]^{3+}$, in agreement with previous work by Krumenacker. Evidence for the further monomeric species $[H_2MoO_3]^{2+}$ has been obtained. Kinetic studies using the temperature-jump technique indicate a major pathway (i) for equilibration, with rate constant k_1 =

$$[HMoO_3]^+ + [HMoO_3]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [H_2Mo_2O_6]^{2+} \qquad \text{(i)}$$

$(1{\cdot}71 \pm 0{\cdot}10) \times 10^5$ l mol^{-1} s^{-1} and $k_{-1} = (3{\cdot}20 \pm 0{\cdot}20) \times 10^3$ s^{-1}. The equilibration (ii), appears to contribute to a small extent with $k_2 = (0{\cdot}3 \pm 0{\cdot}3) \times 10^5$ l mol^{-1} s^{-1} and $k_{-2} = (30 \pm 20)$ s^{-1}.

$$[H_2MoO_3]^{2+} + [HMoO_3]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [H_3Mo_2O_6]^{3+} \qquad \text{(ii)}$$

ONE of the most interesting features of the chemistry of molybdenum is the prevalence of dimeric species. Those of molybdenum(V) are extensive [1] (and present even in >4M-acid solutions), and examples with molybdenum-(II) [2] and -(IV) [3] are now well established. Monomeric and dimeric forms of molybdenum(III) have been identified,[4] while molybdenum(VI) is known to

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[1] See for example, P. C. H. Mitchell, *Co-ordination Chem. Rev.*, 1966, **1**, 315.

[2] A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 3287; C. L. Angell, F. A. Cotton, B. A. Frenz, and T. R. Webb, *J.C.S. Chem. Comm.*, 1973, 399.

[3] M. Ardon and A. Pernick, *J. Amer. Chem. Soc.*, 1973, **95**, 6871.

[4] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, in the press.

exhibit a monomer–dimer equilibration within the $[H^+]$-range 0·2—3·0M. This latter equilibration provides the subject of the present paper. Equilibrium constants have been determined spectrophotometrically under conditions similar to those of Krumenacker,[5] with $LiClO_4$ to adjust the ionic strength to 3·0M. The temperature-jump technique was required for kinetic studies.

The tetrahedral molybdenum(VI) ion, $[MoO_4]^{2-}$, is present in alkaline solutions, pH >7.[6] Acidification of such solutions yields first protonated species $[HMoO_4]^-$ and $[H_2MoO_4]$, and subsequently polymeric species.[7] Kinetic studies on the latter processes have revealed two coupled relaxation times associated with monomer–heptamer and heptamer–octamer equilibria.[8] Species containing one, seven, and eight molybdenum atoms are predominant under these conditions.[9] Cationic species are present in more strongly acidic solutions, $[H^+]/[Mo^{VI}] > 2$.[10] Recently Krumenacker, Byé, and Heitz have published a series of papers,[11-14] on the equilibrium behaviour of molybdenum(VI) in acid solution. They have used a medium of 3M-ionic strength made up with sodium perchlorate. Several techniques have been used including u.v. spectrophotometry,[11] autodiffusion,[12] voltamperometric polarography,[13] and solubility [14] measurements. Chojnacka [15] has shown that the species which exists at high dilution and pH ⩽1 is a monomeric monovalent cation which he writes as $[H_3MoO_4]^+$. Evidence has also been obtained by Krumenacker [5] for dimeric species $[H_2Mo_2O_6]^{2+}$ and $[H_3Mo_2O_6]^{3+}$. The dependence of equilibrium constants for the monomer–dimer interconversion on $[H^+]$ has been shown to be complex,[5] and consistent with either more extensive protonation of the monomer $[HMoO_3]^+$ or a medium effect. Krumenacker has favoured a medium effect based on solubility measurements on MoO_3, and on u.v. absorption measurements at low concentrations of molybdenum(VI).

RESULTS

Determination of Equilibrium Constants.—Absorption coefficients, ε_{obs}, per molybdenum increase with increasing total concentration of molybdenum(VI), c_A, at constant $[H^+]$, while at constant molybdenum(VI) and increasing $[H^+]$ they show a decrease. The data obtained is given in Figure 1, where c_A is varied in the range 0·6—240 × 10^{-4}M, and $[H^+]$ in the range 0·2—3·0M. The dependence of ε_{obs} on these concentration variables was determined as follows. At constant hydrogen-ion concentration the absorption of solutions

$$\varepsilon_{obs}c_A = \varepsilon_{MT}[M]_T + 2\varepsilon_{DT}[D]_T \qquad (1)$$

may be expressed as in (1), where ε_{MT} and ε_{DT} are absorption coefficients per Mo^{VI} for total monomer and total dimer at a particular $[H^+]$, and $[M]_T$ and $[D]_T$ are concentrations of these species at a particular $[H^+]$ and c_A. The various concentration terms are related by (2),

$$c_A = [M]_T + 2[D]_T \qquad (2)$$

and, substituting for $[M]_T$ in (1), (3) is obtained. A

$$\varepsilon_{obs}c_A = \varepsilon_{MT}c_A + 2(\varepsilon_{DT} - \varepsilon_{MT})[D]_T \qquad (3)$$

value $\varepsilon_{MT} = 50 \pm 5$ l mol^{-1} cm^{-1} can be estimated from Figure 1 and, within experimental error, is independent of $[H^+]$.

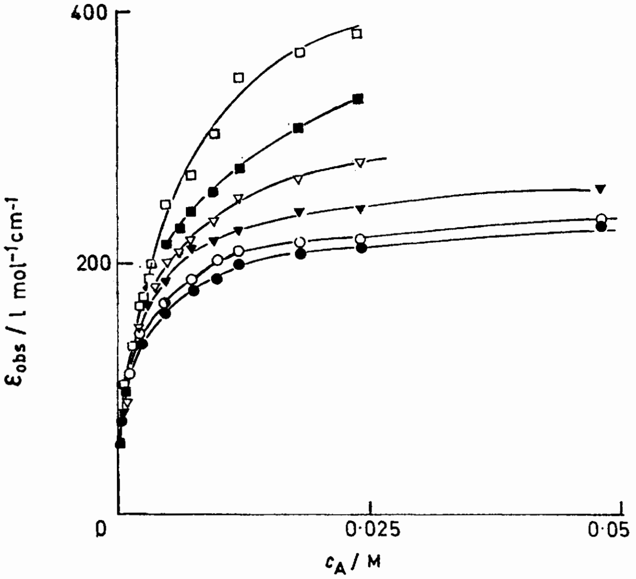

FIGURE 1 Dependence of ε_{obs} on total molybdenum(VI) concentration, c_A, at I = 3·0M ($LiClO_4$) and 25 °C: $[H^+]$ = 3·0M (●), 2·0M (○), 1·0M (▼), 0·4M (▽), 0·3M (■), and 0·2M (□)

Now the monomer–dimer equilibrium constant K at constant $[H^+]$ can be expressed as in (4), and by substituting for $[D]_T$ from (3), and re-

$$K = \frac{[D]_T}{(c_A - 2[D]_T)^2} \qquad (4)$$

arranging, (5) is obtained. Thus a plot of $(\varepsilon_{obs} - \varepsilon_{MT})$

$$(\varepsilon_{obs} - \varepsilon_{MT}) = (\varepsilon_{DT} - \varepsilon_{MT}) - \left\{\frac{(\varepsilon_{DT} - \varepsilon_{MT})}{2K}\right\}^{\frac{1}{2}}\left\{\frac{(\varepsilon_{obs} - \varepsilon_{MT})}{c_A}\right\}^{\frac{1}{2}} \qquad (5)$$

against $\{(\varepsilon_{obs} - \varepsilon_{MT})/c_A\}^{\frac{1}{2}}$ should be linear with intercept $(\varepsilon_{DT} - \varepsilon_{MT})$ and gradient $\{(\varepsilon_{DT} - \varepsilon_{MT})/2K\}^{\frac{1}{2}}$. Such plots are shown in Figure 2. Values of K and ε_{DT} were obtained by a least-squares treatment at each $[H^+]$ (Table 1). The dependence of K on $[H^+]$ is similar to that obtained by Krumenacker *et al.*[11] (Table 1). However since we have used $LiClO_4$ to adjust the ionic strength to 3·0M, it is felt that a medium effect is unlikely (see Discussion), and have therefore interpreted

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[5] L. Krumenacker, *Ann. Chim.*, 1972, **7**, 425.

[6] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.

[7] Y. Sasaki and L. G. Sillèn, *Arkiv Kemi*, 1968, **29**, 253.

[8] D. S. Honig and K. Kustin, *Inorg. Chem.*, 1972, **11**, 65.

[9] J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 735.

[10] E. Pungor and A. Halász, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1187.

[11] L. Krumenacker and J. Byé, *Bull. Soc. chim. France*, 1968, 3099, 3103; L. Krumenacker, *Bull. Soc. chim. France*, 1974, 362, 2820.

[12] L. Krumenacker and C. Heitz, *Bull. Soc. chim. France*, 1971, 365.

[13] L. Krumenacker, *Bull. Soc. chim. France*, 1971, 368.

[14] L. Krumenacker, *Bull. Soc. chim. France*, 1971, 2824.

[15] J. Chojnacka, *Roczniki Chem.*, 1965, **39**, 161.

our equilibrium data in terms of participation of a second monomer species $[H_2MoO_3]^{2+}$. The equilibrium processes are, accordingly, as in reaction (6). Equation

$$\begin{tikzcd} 2[HMoO_3]^+ + H^+ \arrow[r, shift left, "K_1"] \arrow[d, shift right, "K_{MH}"'] & {[H_2Mo_2O_6]^{2+} + H^+} \arrow[l, shift left] \arrow[d, shift right, "K_{DH}"'] \\ {[HMoO_3]^+ + [H_2MoO_3]^{2+}} \arrow[u, shift right] \arrow[r, shift left, "K_2"] & {[H_3Mo_2O_6]^{2+}} \arrow[l, shift left] \arrow[u, shift right] \end{tikzcd} \quad (6)$$

(7) can be derived for the absorbance of dimeric species.

$$(\varepsilon_{DT} - \varepsilon_{DH})^{-1} = (\varepsilon_D - \varepsilon_{DH})^{-1}(1 + K_{DH}[H^+]) \quad (7)$$

The absorption coefficient ε_{DH} for protonated dimer can be estimated from a plot of ε_{DT} (Table 1) against $[H^+]$.

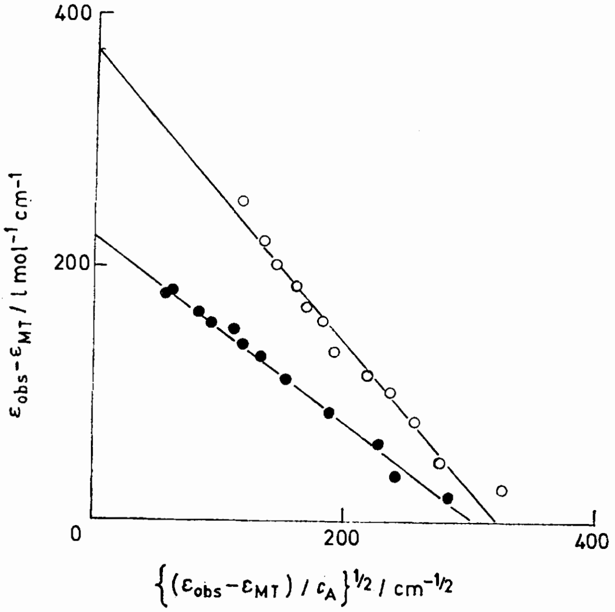

FIGURE 2 Plots to determine K and total absorption coefficient change, equation (5), for the dimerisation of molybdenum(VI) at I = 3·0M ($LiClO_4$) and 25 °C: $[H^+]$ = 3·0M (●) and 0·3M (○)

TABLE 1

Comparison of K and ε_{DT} at 320 nm for the monomer–dimer equilibration of molybdenum(VI) at 25·0 °C, as a function of $[H^+]$, I = 3·0M adjusted with $LiClO_4$,[a] and $NaClO_4$[b]

$[H^+]$ / M	$K(LiClO_4)$ / l mol^{-1}	$K(NaClO_4)$ / l mol^{-1}	ε_{DT}[c]$(LiClO_4)$ / l mol^{-1} cm^{-1}	ε_{DT}[c]$(NaClO_4)$ / l mol^{-1} cm^{-1}
0·20	119 ± 12	119	530 ± 25	575
0·30	136 ± 11		420 ± 15	
0·40	152 ± 7	139	370 ± 5	490
0·80		154		445
1·00	214 ± 7		315 ± 5	
1·50		173		400
2·00	224 ± 5		280 ± 5	
3·00	205 ± 9	204	275 ± 5	365

[a] This work. [b] Ref. 11. [c] Absorption coefficient per molybdenum atom.

A plot of $(\varepsilon_{DT} - \varepsilon_{DH})^{-1}$ against $[H^+]$ is linear assuming ε_{DH} = *ca.* 200 l mol^{-1} cm^{-1}. From this plot K_{DH} and ε_D can be obtained. Equation (8) follows from the definition of K, and by introducing K_{MH} and K_{DH}, as well as $K_1 = [D]/[M]^2$ from (6), this can be written in the form (9). A plot of $\{(1 + K_{DH}[H^+])/K\}^{\frac{1}{2}}$ against $[H^+]$ is linear and yields K_1 and K_{MH}.

$$K = \frac{[D] + [DH]}{([M] + [MH])^2} \quad (8)$$

$$\left(\frac{1 + K_{DH}[H^+]}{K}\right)^{\frac{1}{2}} = \frac{1}{K_1^{\frac{1}{2}}}(1 + K_{MH}[H^+]) \quad (9)$$

The data obtained from the analyses of spectrophotometric measurements are summarised in Table 2.

TABLE 2

A summary of equilibrium constants (25 °C) and absorption coefficients (per molybdenum) as determined from spectrophotometric studies at 320 nm on the monomer–dimer equilibration of molybdenum(VI) species in perchloric acid solutions 0·2—3·0M, I = 3·0M ($LiClO_4$)

K_{DH}	$[H_2Mo_2O_6]^{2+}$ protonation	8 ± 3 (l mol^{-1})
K_{MH}	$[HMoO_3]^+$ protonation	0·52 ± 0·25[b] (l mol^{-1})
K_1	$[HMoO_3]^+$ dimerisation	55 ± 25[b] (l mol^{-1})
ε_M[a]	$[HMoO_3]^+$	50 ± 5[b,c] (l mol^{-1} cm^{-1})
ε_D	$[H_2Mo_2O_6]^{2+}$	790 ± 190 (l mol^{-1} cm^{-1})
ε_{DH}	$[H_3Mo_2O_6]^{3+}$	200 ± 10[b,c] (l mol^{-1} cm^{-1})

[a] ε_{MT} from Figure 1 is independent of $[H^+]$ and therefore equal to ε_M. [b] Errors estimated from those of other parameters. [c] Graphically determined parameters.

Determination of Rate Constants.—Temperature-jump studies on the monomer–dimer equilibration, $[H^+]$ = 0·2—3·0M, yielded only one relaxation time, τ, over the time scale 1 μs—1 s. Plots of τ^{-2} against total molybdenum(VI), c_A, were linear (Figure 3). From the spectrophotometric studies described above the simplest possible mechanism is as in equation (6) with equilibria K_1 (= k_1/k_{-1}) and K_2 (= k_2/k_{-2}) rate determining, and K_{MH} and K_{DH} rapid. For this mechanism, (10) is

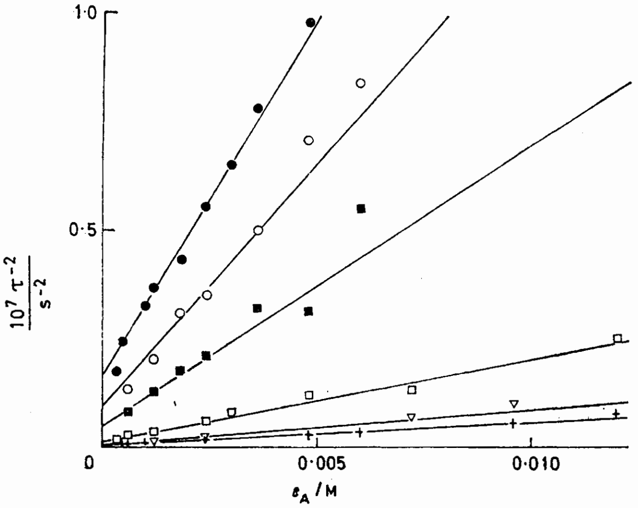

FIGURE 3 Plots of τ^{-2} against c_A for the dimerisation equilibration of molybdenum(VI) at I = 3·0M ($LiClO_4$) and 25 °C; $[H^+]$ = 3·0M (+), 2·0M (▽), 1·0M (□), 0·4M (■), 0·3M (○), 0·2M (●). The straight lines are those for the best fit of data using the values of K determined spectrophotometrically

$$\tau^{-1} = \frac{(k_1 + k_2K_{MH}[H^+])[M]_T}{(1 + K_{MH}[H^+])^2} + \frac{k_{-1} + k_{-2}K_{DH}[H^+]}{(1 + K_{DH}[H^+])} \quad (10)$$

obtained, which may be expressed as (11), where k_f

$$\tau^{-2} = 8k_fk_bc_A + k_b^2 \qquad (11)$$

and k_b are as defined in equations (12) and (13).

$$k_f = \frac{k_1 + k_2K_{MH}[H^+]}{(1 + K_{MH}[H^+])^2} \qquad (12)$$

$$k_b = \frac{k_{-1} + k_{-2}K_{DH}[H^+]}{(1 + K_{DH}[H^+])} \qquad (13)$$

The linear plots illustrated in Figure 3 are in accordance with equation (11), and enable k_f and k_b to be determined at each $[H^+]$. The dependences of k_f and k_b on $[H^+]$ are shown in Figures 4 and 5 respectively. Values of k_1, k_2, k_{-1}, and k_{-2} can be determined by a least-squares fit of k_f and k_b, equations (12) and (13), using the values K_{MH} and K_{DH} in Table 2. Rate constants $k_1 = (1{\cdot}71 \pm 0{\cdot}10) \times 10^5$ l mol^{-1} s^{-1} and $k_{-1} = (3{\cdot}20 \pm 0{\cdot}20) \times 10^3$ s^{-1}, as well as $k_2K_{MH} = 0{\cdot}13 \pm 0{\cdot}06$ l^2 mol^{-2} s^{-1}, $k_{-2}K_{DH} = 275 \pm 110$ l mol^{-1} s^{-1} are obtained. Although $k_2 = (0{\cdot}3 \pm 0{\cdot}3) \times 10^5$ l mol^{-1} s^{-1} and $k_{-2} = (30 \pm 20)$ s^{-1} appear to contribute the errors in both are large. If it is assumed that k_2 is not effective a plot of $(k_f)^{-\frac{1}{2}}$ against $[H^+]$ gives satisfactory linearity, and values $k_1 = 1{\cdot}63 \times 10^5$ l mol^{-1} s^{-1} and $K_{MH} = 0{\cdot}41$ l mol^{-1} are obtained, which are not too different from the above.

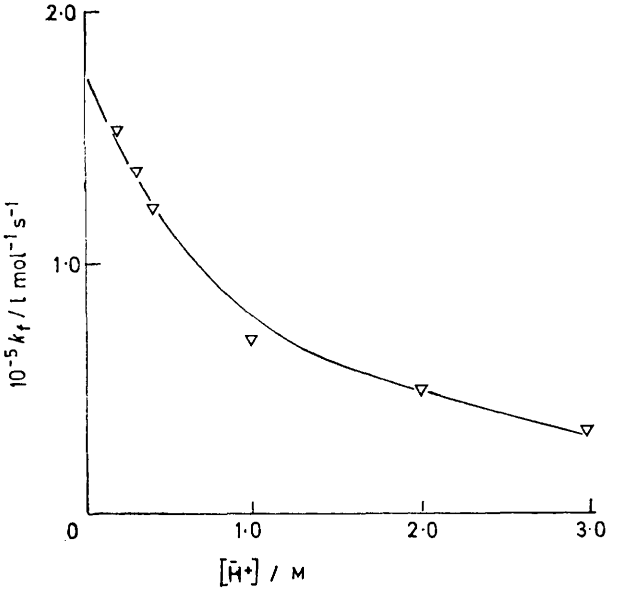

FIGURE 4 Hydrogen-ion dependence of rate constant (k_f) for the dimerisation of molybdenum(VI) at $I = 3{\cdot}0$M (LiClO$_4$) and 25 °C

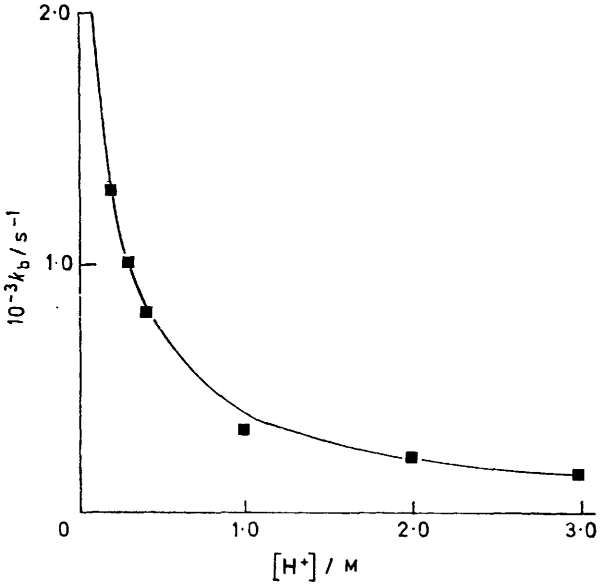

FIGURE 5 Hydrogen-ion dependence of rate constant (k_b) for the aquation of molybdenum(VI) dimer at 25 °C, $I = 3{\cdot}0$M (LiClO$_4$)

DISCUSSION

Information obtained from spectrophotometric studies on the monomer–dimer equilibration, $I = 3{\cdot}0$M (LiClO$_4$), is in good agreement with previous data, $I = 3{\cdot}0$M (NaClO$_4$).[5] It is felt that the presence of a second monomeric species rather than medium effects provides a better explanation of the non-linear dependence of K on $[H^+]$ over the range 0·2—3M. This point will be elaborated on later in the discussion. Thus molybdenum(VI) in 0·2—3·0M perchloric acid solutions is present as monomeric species $[HMoO_3]^+$ and, to a lesser extent, $[H_2MoO_3]^{2+}$, and dimeric species $[H_2Mo_2O_6]^{2+}$ and $[H_3Mo_2O_6]^{3+}$. The precise formulae and geometries of the complexes are uncertain however, and each complex may contain co-ordinated water molecules, for example $[HMoO_3]^+$ may be $[H_3MoO_4]^+$, or $[H_5MoO_5]^+$ *etc.* The most common geometries for molybdenum(VI) are tetrahedral and octahedral. Whereas molybdate $[MoO_4]^{2-}$ is known to be tetrahedral,[16] it has been suggested that the protonated form $[HMoO_4]^-$ may be octahedral.[17] Polymeric forms are known to contain octahedrally co-ordinated molybdenum(VI).[18] The identity of bridging groups in the dimeric species, written $[H_2Mo_2O_6]^{2+}$ and $[H_3Mo_2O_6]^{3+}$, is uncertain at present. If two terminal oxo-groups are retained on each molybdenum the dimer $[H_3Mo_2O_6]^{3+}$ must be bridged by a single hydroxo-group.

Temperature-jump studies by Honig and Kustin[8] on molybdenum(VI) solutions at pH 5·50—6·75 have provided information on the monomer–heptamer and heptamer–octamer interconversions. No information on the rate of the monomer–dimer interconversion was forthcoming in their study. We have shown that information on such a process is obtained by working under more strongly acidic conditions, when polymeric species higher than the dimer are not formed, and cationic species prevail. The equilibrium (14), where any co-ordinated

$$[HMoO_3]^+ + [HMoO_3]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [H_2Mo_2O_6]^{2+} \qquad (14)$$

water molecules are omitted, is found to carry the bulk of reaction for conditions $[H^+] = 0{\cdot}2$—$3{\cdot}0$M, with $k_1 =$

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[16] H. Siebert, *Z. anorg. Chem.*, 1962, **4**, 199.

[17] G. Schwarzenbach and J. Meier, *J. Inorg. Nuclear Chem.*, 1958, **8**, 302.

[18] I. Lindquist, *Arkiv. Kemi*, 1949, **2**, 325, 349.

$(1{\cdot}71 \pm 0{\cdot}10) \times 10^5$ l mol^{-1} s^{-1} and $k_{-1} = (3{\cdot}20 \pm 0{\cdot}20) \times 10^3$ s^{-1}. The path (15), may also contribute $k_2 =$

$$[H_2MoO_3]^{2+} + [HMoO_3]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [H_3Mo_2O_6]^{3+} \quad (15)$$

$(0{\cdot}3 \pm 0{\cdot}3) \times 10^5$ l mol^{-1} s^{-1} and $k_{-2} = (30 \pm 20)$ s^{-1}.

The most relevant comparison to make is with data obtained for the equilibration of the tetrahedral chromate–dichromate ions. The latter reaction has been investigated under two ranges of $[H^+]$.[19,20] Haim[21] has expressed the reactions as in (16) ($k_3 = 9 \times 10^5$

$$H^+ + [CrO_4]^{2-} + [HCrO_4]^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Cr_2O_7]^{2-} + H_2O \quad (16)$$

l^2 mol^{-2} s^{-1} and $k_{-3} = 2{\cdot}7 \times 10^{-2}$ s^{-1}),[19] and (17) ($k_4 =$

$$H^+ + [HCrO_4]^- + [HCrO_4]^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Cr_2O_7]^{2-} + H_2O + H^+ \quad (17)$$

$6{\cdot}2 \times 10^5$ l^2 mol^{-2} s^{-1} and $k_{-4} = 6{\cdot}3 \times 10^3$ l mol^{-1} s^{-1}).[20] The close similarity of k_3 and k_4 to rate constants for other hydrogen-ion dependent substitution reactions of $[HCrO_4]^-$ is consistent with an S_N1 process. We are not able to test whether the same mechanism applies to substitution reaction of molybdenum(VI) in acid solution, because, whereas (15) can be reformulated in the desired form (since the acid dissociation constant for $[H_2MoO_3]^{2+}$ has been determined, Table 2), the acid dissociation constant for $[HMoO_3]^+$ is not known, and we are unable to evaluate the forward rate constant when (14) is expressed as in (18).

$$H^+ + [MoO_3] + [HMoO_3]^+ \rightleftharpoons [H_2Mo_2O_6]^{2+} \quad (18)$$

Other studies which should be mentioned in this context are those of Diebler *et al.*[22] on the complexing of 8-hydroxyquinoline (and its 5-sulphonic acid derivative[23]) with molybdate. The rate constants for the reaction of $[HMoO_4]^-$ with unprotonated and protonated reactant (20 °C) are *ca.* 10^8 l mol^{-1} s^{-1} and *ca.* 4×10^6 l mol^{-1} s^{-1} respectively, where the product is in each case octahedral. The rate constant for the reaction of $[HMoO_4]^-$ with singly deprotonated (1−) ion of catechol is likewise *ca.* 10^8 l mol^{-1} s^{-1}.[24] Similarly for the heptamer–octamer interconversion,[8] the rate constant (25 °C) for the reaction of the heptamer with the monomeric species $[MoO_4]^{2-}$ (which also involves a change to octahedral geometry) is in the range 2×10^7—5×10^9 l mol^{-1} s^{-1}. These rate constants would seem to be in a different range from those obtained for k_1 and k_2 in the present study. A comparable rate is observed for the complexing of $[H_2edta]^{2-}$ to $[HMoO_4]^-$, rate constant $2{\cdot}26 \times 10^5$ l mol^{-1} s^{-1} at 25 °C.[25]

Other monomer–dimer equilibrations which have been studied are with the aquo- or hydroxo-ions of Fe^{III},[26-27] Ga^{III},[28] In^{III},[29] Sc^{III},[30] U^{VI},[31-33] V^{III},[34] V^{IV},[27,35] and V^{V}.[36] While bridge-cleavage reactions of the dimers generally show marked contributions from first-order $[H^+]$ dependent pathways, those of Ga^{III}, In^{III}, and Sc^{III} do not. Thus dimeric species, written $[M_2(OH)_2]^{4+}$ cleave without assistance of H^+ to form $[MOH]^{2+}$. Unfortunately it is not always possible to make detailed comparisons between such studies because the precise form of the dimeric species is not known. This is certainly true for the present molybdenum(VI) study where the geometries (of monomer and dimer species) and nature of the bridging ligands (in the case of the dimeric species) are uncertain.

Finally returning to the non-linear dependence of K on $[H^+]$, and our favouring an explanation in terms of a second monomer species rather than a medium effect. The latter explanation was favoured by Krumenacker[5] on the basis of solubility measurements on $[MoO_3]{\cdot}2H_2O$ which level off at perchloric acid concentrations between 2 and 3M. The latter had been observed before and also occurs in the absence of added $NaClO_4$.[7,37] The solubility in fact passes through a maximum and then decreases, an effect which cannot be due to changes in the activity coefficients of H^+. The reason for this is that in high $[H^+]$ the activity coefficient of H^+ increases dramatically even at constant ionic strength when $NaClO_4$ is present. This is reflected in Hammett acidity functions determined from indicated pK values which have been tabulated.[38] The use of $LiClO_4$ does not generally give rise to significant medium effects. For example Templeton and King[39] have shown that in solution $I = 4{\cdot}0$M the rate of an $[H^+]$-catalysed aquation of azidopenta-aquochromium(III) is a linear function of $[H^+]$ in $LiClO_4$ up to 4·0M, while this is not observed for $NaClO_4$. It seems reasonable then that similar effects would occur in the protonation and dimerisation of molybdenum(VI), and therefore that the form of the

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[21] A. Haim, *Inorg. Chem.*, 1972, **11**, 3147.

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[25] D. S. Honig and K. Kustin, *J. Amer. Chem. Soc.*, 1973, **95**, 5525.

[26] T. C. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Amer. Chem. Soc.*, 1965, **87**, 926; B. A. Sommer and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 2517; H. N. Po and N. Sutin, *Inorg. Chem.*, 1971, **10**, 428.

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$[H^+]$-dependence in Krumenacker's study[5] is more consistent with protonation of $[HMoO_3]^+$ to $[H_2MoO_3]^{2+}$ than with medium effects.

EXPERIMENTAL

Perchloric acid and sodium molybdate dihydrate were of analytical reagent grade. Lithium perchlorate was prepared from perchloric acid (AnalaR) and lithium carbonate (G.P.R.) and was recrystallised until free of impurities. Stock solutions of sodium molybdate (0·12M) in perchloric acid (1·0M) were made up as required; run solutions were made up to the required ionic strength (3·0M) and acidity using stock $LiClO_4$ (4·0M) and perchloric acid (5·0M) solutions. Allowance was made for the consumption of hydrogen ions by (18).

$$[MoO_4]^{2-} + 3H^+ \rightleftharpoons [HMoO_3]^+ + H_2O \qquad (19)$$

Changes in hydrogen-ion concentration due to further equilibria can be neglected. After *ca.* 3 weeks molybdate stock solutions showed definite signs of deterioration, and it seemed preferable therefore to make up a fresh stock solution for each series of measurements. Check experiments on such solutions showed that there was no significant deterioration during a period of 2—3 days. Stock solutions made up initially at different hydrogen-ion concentrations (0·6—1·2M) gave identical absorbance values when diluted to the same final hydrogen-ion concentration and ionic strength.

Equilibrium constants were determined using a Unicam SP 500 visible–u.v. range spectrophotometer, and cells with path lengths from 0·11 to 10·0 cm, at 320 nm. The path lengths for the smaller cells ($\leqslant$0·2 cm) were determined by absorbance measurements on solutions of molybdenum(VI) and chromate(VI). The linearity of the absorbance scale of the spectrophotometer over the range 0—1·3 was confirmed, by absorbance measurements of a molybdenum(VI) solution in a series of cells (path length 0·5—4·0 cm).

Kinetic measurements were performed on a standard thermostatted temperature-jump apparatus (Messanlagen Instruments, Göttingen, W. Germany). The temperature in the cell was raised 5·9 °C by a 40 kV discharge of a 0·05 μF capacitor, to give a final temperature of 25·0 ± 0·2 °C. The heating time can be estimated to be of the order of 1 μs at 3·0M-ionic strength. Only one relaxation time was observed in the range 1 μs–1 s at $\lambda = 320$ nm; an unresolvably fast process was observed in some solutions especially at high concentrations of acid and molybdenum(VI), possibly due to the predominance of dimer protonation effects under these conditions. Experimental difficulties were encountered at $[H^+] = 0{\cdot}2M$, with $[Mo^{VI}] > 5 \times 10^{-3}M$, and at correspondingly higher concentrations of molybdenum(VI) with $[H^+] > 0{\cdot}2M$. Molybdenum Blue was produced in the cell while thermostatting such solutions. On jumping these solutions the blue colour became much more pronounced. The reason for this effect is not clear. Solutions in which the blue colour was formed were discarded. Consequently the range of molybdenum concentrations which could be investigated at lower hydrogen-ion concentrations (<1·0M) was lessened.

Relaxation effects were photographed on either polaroid or standard 35 mm film, and curves were analysed in the first case by semilogarithmic plots of absorbance amplitude against time, and in the second with the aid of a calibrated exponential simulator.[40] The relaxation times quoted in the text are averages of between four and seven individual determinations on a particular solution. The range of individual values around the mean are <±10%. Least-squares analyses of all data were performed on a Seiko S-301 desk-top computer by linear-regression analysis. Errors on rate constants, equilibrium constants *etc.* are standard deviations unless indicated otherwise.

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