Formation and Dissociation of the Ethylenediaminetetra-acetic Acid Complex of the Molybdenum(v) Dimer $Mo_2O_4^{2+}$ in Aqueous Perchloric Acid Solution

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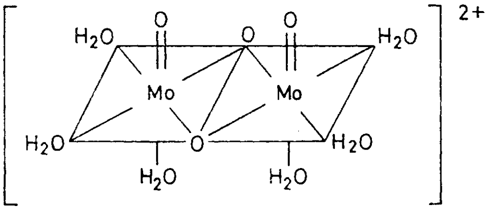
The kinetics of the equilibration of the molybdenum(v,v) complexes $Mo_2O_4^{2+}$ (A) and $Mo_2O_4Y^{2-}$ (B) in the presence of excess of EDTA (H_4Y = ethylenediaminetetra-acetic acid) have been studied by conventional spectrophotometry at 25°, I = 2·0M ($LiClO_4$). At constant hydrogen-ion concentrations in the range $[H^+]$ = 0·5—2·0M investigated, first-order rate constants k_{eq} may be expressed as $k_{eq} = a[\mathrm{EDTA}] + b$. The hydrogen-ion dependences of a and b, corresponding to the formation and dissociation processes respectively are not simple. For the dissociation process the equation $b = b_1[H^+]^4/(1 + b_2[H^+]^3)$ gives a good fit to the experimental data. Contributions from terms in $[H^+]$ and $[H^+]^2$ in the denominator cannot be ruled out however. An inverse hydrogen-ion dependence is apparent for a but the precise form of this is less certain.

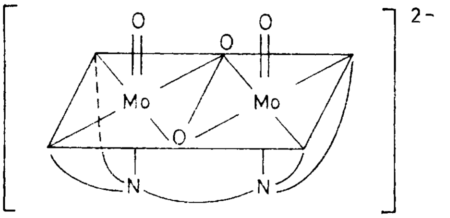
STUDIES relating to the substitution and redox properties of mono- and bi-nuclear complexes of molybdenum with different N, O, and S donor atoms are of interest as models for molybdenum-containing enzymes.[1] It has now been established that most of these enzymes contain two molybdenum atoms which are redox active. The molybdenum atoms are in oxidation state (vi) in the oxidized form, and can utilize other oxidation states, in some cases down to (iii), in the reduced form.[2]

Most of the substitution studies to date have been with molybdenum(vi), and reactions involving complexation of 8-hydroxyquinoline,[3] 8-hydroxyquinoline 5-sulphonate,[4] catechol,[5] and EDTA [6] to molybdate have been studied by fast reaction techniques. A feature of these studies is the expansion in the inner-co-ordination sphere from 4 to 6. The complexing of diethylenetriamine to MoO_4^{2-} is also very rapid.[7] Recently the kinetics of 1 : 1 complex formation of chloride and thiocyanate with $Mo(H_2O)_6^{3+}$ have been studied.[8]

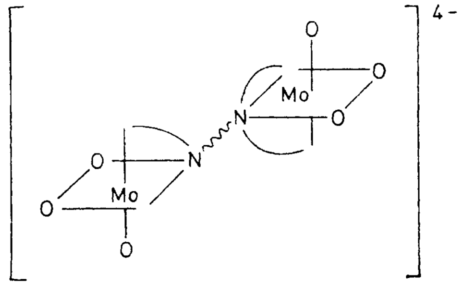


(A)

The molybdenum(v) aquo-dimer (A) hereafter $Mo_2O_4^{2+}$ has now been characterized.[9] Complexes between the (iii),[10], (v),[11] and (vi) [11] oxidation states of molybdenum and EDTA in which the ratio of Mo to EDTA is 2 : 1 have been prepared. The structure † of the molybdenum(v)–EDTA complex (B) has similar features to (A).



(B)



(C)

With molybdenum(vi) the metal atoms are more remote however,[13] (C), and kinetics [6] and equilibrium [14] studies have indicated the existence of a 1 : 1 species.

Kinetic studies on the equilibration of (A) and (B) in the presence of excess of EDTA are reported in this paper.

Properties of $Mo_2O_4Y^{2-}$ *and* $Mo_2O_4^{2+}$.—A crystalline sample of $Na_2Mo_2O_4Y$,‡ the sodium salt of (B), was

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† Haynes and Sawyer [12] have reported preliminary *X*-ray structural data by R. M. Wing, K. P.Callahan, L. V. Haynes, and D. T. Sawyer. More precise information has not been forthcoming and a full crystal study has not been reported due possibly to some disorder in the crystals (personal communication from Professor D. T. Sawyer).

‡ The symbol Y is used whenever it is possible to specify the degree of protonation of EDTA.

[1] J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475.

[2] R. C. Bray and J. C. Swann, 'Structure and Bonding,' Springer-Verlag, 1972, **11**, 107.

[3] P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, 1968, **64**, 977.

[4] H. Diebler and R. E. Timms, *J. Chem. Soc.* (*A*), 1971, 273.

[5] K. Kustin and S. T. Liu, *J. Amer. Chem. Soc.*, 1973, **95**, 2487.

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

[7] R. S. Taylor, P. Gans, P. F. Knowles, and A. G. Sykes, *J.C.S. Dalton*, 1972, 24.

[8] Y. Sasaki and A. G. Sykes, *J.C.S. Chem. Comm.*, 1973, 767.

[9] M. Ardon and A. Pernick, *Inorg. Chem.*, 1973, **12**, 2484.

[10] J. Kloubek and J. Podlaha, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2981.

[11] R. L. Pecsok and D. T. Sawyer, *J. Amer. Chem. Soc.*, 1956, **78**, 5496.

[12] L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, 1967, **6**, 2146.

[13] J. J. Park, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1969, **91**, 301.

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prepared as described in the Experimental section. The u.v.-visible spectrum in pH 5 acetate buffer solution, Figure 1, has two absorption peaks at 390 ($\varepsilon = 336$ l mol^{-1} cm^{-1}) and 297 nm ($\varepsilon = 8980$ l mol^{-1} cm^{-1}), in satisfactory agreement with reported values.[15] The u.v.-visible spectrum is the same ($\pm 3\%$ at 390 nm) in buffer solutions pH 1—9, and at 25° remains unchanged over periods of at least 1 day. Dissociation of EDTA occurs in perchloric acid solutions, $[H^+] = 0{\cdot}5$—$2{\cdot}0$M, and isosbestic points are observed at 253 and 273 nm during the dissociation. At $[H^+] > 2{\cdot}0$M dissociation is complete, and the final spectrum is the same for solutions 2—5M in $HClO_4$. The dissociation is substantially faster by a factor of *ca.* 2 in 2M-HCl as compared to 2M-$HClO_4$.

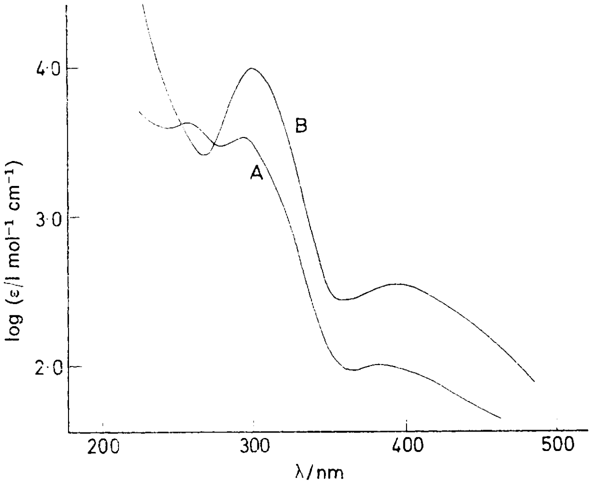

FIGURE 1 U.v.-visible spectra of the di-μ-oxo-molybdenum(V) dimers $Mo_2O_4^{2+}$ (A) and $Mo_2O_4Y^{2-}$ (B)

A number of studies have been made of the behaviour of molybdenum(V) in HCl or HBr solutions,[16] and monomer–dimer equilibria have been proposed. Species present in aqueous perchloric acid solution have been reported to be positively charged.[17] Ardon and Pernick[9] have now shown that structure (A) with charge 2+ applies in aqueous perchloric acid solutions. Our observations that 0·5M-perchloric acid is required to elute the ion from a Dowex 50W-X12 cation exchange resin are consistent with this assignment. The spectrum of (A), Figure 1, has similar features to spectra of other complexes containing the Mo_2O_4 unit,[18] and on this basis it is fairly certain that the terminal oxo-ligands are *cis* to each other. No change in spectrum is observed for $[H^+] = 0{\cdot}5$—$5{\cdot}0$M, and it is concluded that structure (A) is stable over this range. Details of absorption maxima λ/nm (ε/l mol^{-1} cm^{-1}) are: 384 (103), 295 (3546), and 255 (4320) in good agreement with the spectrum of Ardon and Pernick: 293 (3454) and 254 (3998).*

On dilution to $[H^+] < 0{\cdot}1$M a strong absorption is superimposed over the 384 nm band, and the peak at 295 nm shifts to longer wavelengths. At much higher pH a brown precipitate is eventually obtained. These changes are slowly reversible on addition of perchloric acid.

On addition of EDTA (*ca.* 10^{-3}M) to a solution of (A) (*ca.* 10^{-4}M) in 0·1—1·0M- $HClO_4$ isosbestic points are observed at 253 and 273 nm as (B) forms. These isosbestics are identical with those observed for dissociation of EDTA from (B) and are consistent with the equilibrium (1) in aqueous perchloric acid solutions, $0{\cdot}1 < [H^+] < 2{\cdot}0$M.

$$Mo_2O_4Y^{2-} + nH^+ \rightleftharpoons Mo_2O_4^{2+} + H_nY^{(n-4)+} \quad (1)$$

It has been reported that molybdenum(V) is slowly oxidized by oxygen at high pH values.[19] Solutions of (B) at $[H^+] < 0{\cdot}1$M are insensitive to oxygen over periods of 1 day. The reaction of (A) with oxygen was briefly investigated over the $[H^+]$-range relevant to this work. A slow stream of oxygen was bubbled through solutions at $[H^+] = 0{\cdot}5$M and $2{\cdot}0$M for 2 days at 25°, and the decrease in absorbance (O.D.) monitored at 390 nm. For the run with $[H^+] = 2{\cdot}0$M the final absorbance was zero but the latter stages of the run with $[H^+] = 0{\cdot}5$M were slow and the final absorbance was not observed. Plots of log (Δ O.D.) against time were linear for *ca.* 30%

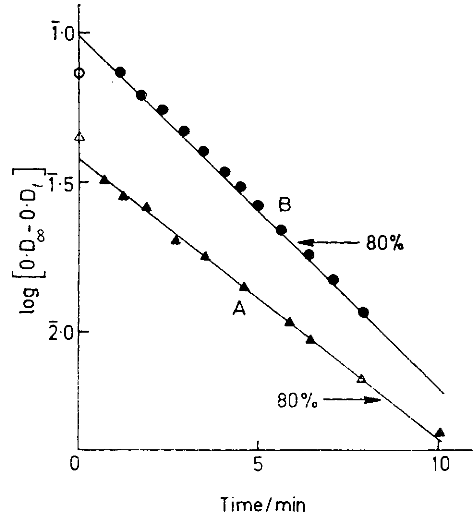

FIGURE 2 Kinetic plots A for the formation and B for the dissociation of $Mo_2O_4Y^{2-}$ at 25°, $I = 2{\cdot}0$M ($LiClO_4$). For A absorbance $O.D._\infty > O.D._t$, $[Mo_2O_4^{2+}] = 3{\cdot}97 \times 10^{-4}$M, $[EDTA] = 6{\cdot}0 \times 10^{-3}$M, and $[H^+] = 0{\cdot}875$M. For B $O.D._\infty < O.D._t$, $[Mo_2O_4Y^{2-}] = 3{\cdot}49 \times 10^{-4}$M, $[EDTA] = 4{\cdot}03 \times 10^{-3}$M, and $[H^+] = 1{\cdot}5$M

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* Absorption coefficients in ref. 9 are very likely per molybdenum atom and are here converted into units per mole of complex, *i.e.* per dimer.

[15] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1962, 4570.

[16] For recent examples see R. Colton and G. G. Rose, *Austral. J. Chem.*, 1968, **21**, 883; B. Jezowska-Trzebiatowska and W. Wojciechowski, 'Transition Metal Chemistry,' ed. R. L. Carlin, 1970, **6**, 6 (and 46) and references therein; Y. Yoshino, I. Taminaga, and S. Uchida, *Bull. Chem. Soc. Japan*, 1971, **44**, 1435.

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[18] D. T. Brown, P. G. Perkins, and J. T. Stewart, *J.C.S. Dalton*, 1972, 1105.

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change and gave rate constants *ca.* 3 × 10^{-5} s^{-1} at 25°, I = 2·0M ($LiClO_4$), which were independent of [H^+]. Subsequent changes were much slower and gave an inverse [H^+]-dependence, the nature of which was not investigated.

Table 1

Rate constants, k_{eq}, for the equilibration of the molybdenum(V) complexes $Mo_2O_4^{2-}$ (A) and $Mo_2O_4Y^{2-}$ (B) with EDTA. The equilibration was studied in two ways designated f and d, which correspond to formation and dissociation of (B) respectively. Temperature 25°, I = 2·0M ($LiClO_4$), λ = 390 nm except as stated

[H^+] / M	10^4[$Mo^{V,V}$] / M	10^3[EDTA] / M	Procedure	10^3k_{eq} / s^{-1}
0·50	0·24	0·45	f	1·02 [a]
0·50	0·24	1·79	f	2·62 [a]
0·50	0·24	4·47	f	6·80 [a]
0·50	3·09	5·04	f	7·87 [b]
0·50	3·09	6·04	f	8·83 [b]
0·50	4·12	8·06	f	11·7 [b]
0·50	4·21	8·20	f	12·8
0·50	4·12	10·1	f	15·6 [b]
0·50	6·2	10·1	f	15·2 [b]
0·50	4·12	12·1	f	23·0 [b]
0·50	4·21	12·3	f	23·0
0·50	4·12	14·1	f	24·6 [b]
0·50	4·12	16·1	f	24·8 [b]
0·50	4·21	16·4	f	23·4
0·50	4·21	16·4	f	24·0
0·625	3·39	4·04	f	4·18
0·625	2·51	6·10	f	5·97
0·625	2·88	8·19	f	8·05
0·625	2·51	10·2	f	10·8
0·625	2·89	12·3	f	11·1
0·75	4·15	8·09	f	5·75 [b]
0·75	4·15	10·1	f	6·92 [b]
0·75	4·15	11·1	f	7·68 [b]
0·75	4·15	12·1	f	8·07 [b]
0·875	3·97	6·0	f	3·65
0·875	2·65	8·17	f	4·50
0·875	3·97	10·0	f	5·40
0·875	2·64	12·3	f	5·98
1·00	4·25	10·1	d	3·98
1·00	3·43	12·2	d	3·99
1·00	4·14	15·1	f	4·60
1·00	3·43	16·3	d	4·70
1·00	4·25	20·1	f	5·83
1·00	4·25	30·1	f	7·43
1·25	2·92	6·0	f	3·65
1·25	3·52	8·13	f	4·07
1·25	2·92	10·0	f	3·99
1·25	3·52	12·2	f	4·35
1·25	2·92	14·0	f	4·35
1·25	3·52	16·3	f	4·48
1·5	3·49	4·03	d	4·60
1·5	3·49	8·25	d	4·72
1·5	3·49	16·50	d	5·03
2·0	4·35	10·1	d	6·75 [b]
2·0	4·35	10·1	d	6·83 [b]
2·0	3·30	16·3	d	6·91
2·0	3·30	16·3	d	7·10 [c]
2·0	4·35	20·1	d	6·23 [b]
2·0	4·35	30·1	d	6·22 [b]
2·0	4·35	40·2	d	6·57 [b]

[a] λ = 297 nm. [b] Air-free conditions not used. [c] [NaCl] = 3·51 × 10^{-3}M.

Kinetic Studies.—The kinetics of the equilibration, (1), were studied at 25° [H^+] = 0·5—2·0M, I = 2·0M ($LiClO_4$), with uncomplexed EDTA in at least ten-fold excess of the molybdenum reactant. Depending on the time required to reach equilibrium some runs were carried out under nitrogen. Both (A) and (B) were used as starting material, and absorbance (O.D.) changes were monitored at 390 nm. At this wavelength ε = 102 for (A) and 336 l mol^{-1} cm^{-1} for (B). Plots of log|$O.D._\infty - O.D._t$| against time, Figure 2, were linear for 6—10 half-lives, and the gradient (×2·303) gave rate constants k_{eq}, Table 1. It was also possible to follow absorbance changes at 297 nm using a different range of reactant concentrations. Agreement with data obtained at 390 nm was good. The initial absorbance values corresponding to the intercept time t = 0 of first-order plots for both formation and dissociation reactions are different from the expected values for the initial concentrations of (A) and (B). Observed values are 5—10% higher in both cases. No evidence was obtained for ion-pair formation between EDTA and $Mo_2O_4^{2+}$ under conditions, [H^+] = 2·0M, when complex formation is negligible.

Rate constants k_{eq} give the dependence (2) on total

$$k_{eq} = a[\text{EDTA}] + b \qquad (2)$$

EDTA concentration, as illustrated in Figure 3. Values of a and b so defined correspond to the formation and dissociation of (B) respectively. From the gradient and intercepts, Figure 3, individual values of a and b at different [H^+] values were evaluated, and are given in Table 2. Errors were determined by a least-squares treatment with no weighting.

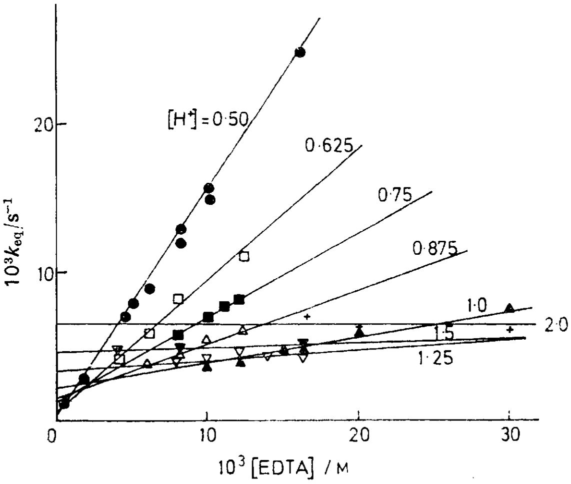

Figure 3 The dependence of first-order rate constants, k_{eq}, for the equilibration of $Mo_2O_4^{2+}$ (A) and $Mo_2O_4Y^{2-}$ (B) on the concentration of uncomplexed EDTA at 25°, I = 2·0M ($LiClO_4$)

Table 2

Rate constants a and b as defined in equation (2), for the formation and dissociation of $Mo_2O_4Y^{2-}$ at 25°, I = 2·0M ($LiClO_4$)

[H^+] / M	a / l mol^{-1} s^{-1}	10^3b / s^{-1}
0·50	1·50 ± 0·03	0·10 ± 0·23
0·625	0·93 ± 0·04	0·37 ± 0·23
0·75	0·59 ± 0·04	0·96 ± 0·36
0·875	0·38 ± 0·03	1·43 ± 0·32
1·00	0·18 ± 0·01	1·99 ± 0·21
1·25	0·075 ± 0·01	3·32 ± 0·17
1·50	0·035 ± 0·023	4·45 ± 0·03
2·00	Very small	6·86 ± 0·26

DISCUSSION

The unit Mo_2O_4 is common in molybdenum(V) chemistry in aqueous media and is present in both complexes (A) and (B). Reaction (1) can therefore be regarded as a co-ordination of EDTA to the Mo_2O_4 unit rather than co-ordination of EDTA to two separate molybdenum centres, as is the case in the formation of the molybdenum(VI)–EDTA complex (C). The molybdenum(V)–EDTA complex, and possibly also the molybdenum(III)–EDTA complex, are at present quite unique since EDTA bridges two metal ions which are bridged by two other groups. Although several other binuclear complexes with EDTA as a bridging ligand are known,[20] none of them have additional bridging ligands between the two metal ions.

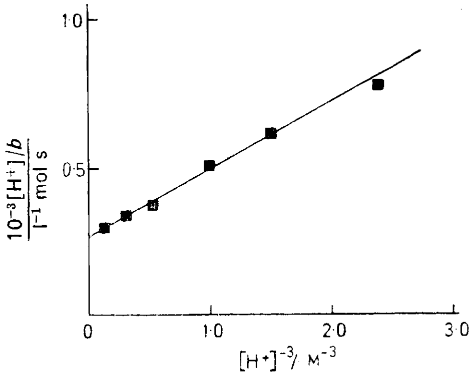

FIGURE 4 Plot of $[H^+]/b$ against $[H^+]^{-3}$ demonstrating the applicability of equation (4) (with $n = 4$)

Over the range $[H^+] = 0{\cdot}75$—$2{\cdot}0$M the rate constant b in (2) for dissociation shows an apparent first-order dependence on $[H^+]$. This dependence gives a large negative intercept which clearly has no meaning. At $[H^+] < 0{\cdot}75$M (however) the first-order dependence decreases dramatically to give $b = 0$ at small $[H^+] \longrightarrow 0$ values. The data give a good fit to (3), with $n = 4$.

$$b = \frac{b_1[H^+]^n}{1 + b_2[H^+]^{n-1}} \qquad (3)$$

Thus (3) can be rearranged to give (4), and Figure 4 is a

$$\frac{[H^+]}{b} = \frac{1}{b_1[H^+]^3} + \frac{b_2}{b_1} \qquad (4)$$

plot of $[H^+]/b$ against $[H^+]^{-3}$. The corresponding plots with $n = 3$ and 5 respectively show curvature. Data points for $[H^+] = 0{\cdot}625$ and $0{\cdot}50$M are omitted from this plot because they are not sufficiently sensitive and small errors in b give rise to large errors. Values of $1/b_1$ and b_2/b_1 can be evaluated from the slope and intercept in Figure 4 and are 220 ± 6 l^{-4} mol^4 s and 271 ± 7 l^{-1} mol s respectively.

The mechanism (5)—(8) will account for the hydrogen-ion dependence observed for b. Protonation occurs as each group of the EDTA ligand is dissociated; H_2O ligands are omitted. If all the equilibria (5)—(7) are

$$Mo_2O_4Y^{2-} + H^+ \overset{K_1}{\rightleftharpoons} Mo_2O_4YH^- \qquad (5)$$

$$Mo_2O_4YH^- + H^+ \overset{K_2}{\rightleftharpoons} Mo_2O_4YH_2 \qquad (6)$$

$$Mo_2O_4YH_2 + H^+ \overset{K_3}{\rightleftharpoons} Mo_2O_4YH_3^+ \qquad (7)$$

$$Mo_2O_4YH_3^+ + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Mo_2O_4YH_4^{2+} \qquad (8)$$

rapid then the overall rate of dissociation, k_d, will be given by (9). Assuming $K_1[H^+] + K_1K_2[H^+]^2 \ll 1 +$

$$k_d = \frac{k_4K_1K_2K_3[H^+]^4}{1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3} \qquad (9)$$

$K_1K_2K_3[H^+]^3$, (9) simplifies to (10), which is of the same

$$k_d = \frac{k_4K_1K_2K_3[H^+]^4}{1 + K_1K_2K_3[H^+]^3} \qquad (10)$$

form as the dependence observed, equation (3), with $n = 4$. This relationship gives $k_4 = 3{\cdot}69 \times 10^{-3}$ l mol^{-1} s^{-1} and $K_1K_2K_3 = 1{\cdot}23$ l^3 mol^{-3}. However in view of the difficulty of obtaining sufficiently accurate (small) b values at $[H^+] < 0{\cdot}75$M, which can be used in fitting data to (4), we do not consider the above assumption to be implicit in our treatment. Equation (4) remains an adequate fit to our data and we are unable to demonstrate whether or not a more complicated expression is applicable.

The hydrogen-ion dependence of the rate constant a in (2) for the formation of $Mo_2O_4Y^{2-}$ is illustrated in Figure 5. A graph of a against $[H^+]^{-2}$ also exhibits linearity over the range $[H^+] = 0{\cdot}5$—$1{\cdot}0$M. Attempts to fit precise equations [of complexity similar to that in (3) for the dissociation] to the variation of a with $[H^+]$ did not yield a satisfactory solution. The problem is basically one of considering different degrees of protonation of the EDTA reactant (H_6Y^{2+}, H_5Y^+, H_4Y forms are relevant) as well as intermediates with partially co-ordinated EDTA, over the range of hydrogen-ion concentration ($[H^+] = 0{\cdot}5$—$2{\cdot}0$M) investigated. Protonation constants for the EDTA ions Y^{4-}, *etc.*, have been determined at 20 °C and $I = 1{\cdot}0$M ($NaClO_4$) [21] but not

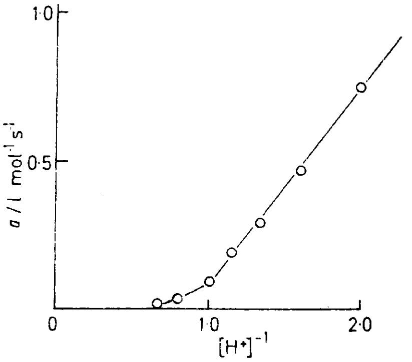

FIGURE 5 The dependence of a on $[H^+]$, at 25° $I = 2{\cdot}0$M ($LiClO_4$)

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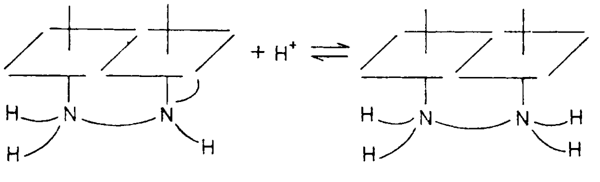
[20] D. W. Margerum and H. M. Rosen, *Inorg. Chem.*, 1968, **7**, 299, and references therein.

[21] G. Anderegg, *Helv. Chim. Acta*, 1967, **50**, 2333.

under the conditions of these experiments. A computer fit to possible equations for the dependence of *a* on [H$^+$] was not therefore attempted.

We now consider in detail processes which might correspond to the rate-determining step (8) in the dissociation mechanism. If it is assumed that carboxylate bond cleavage gives a hydrogen-ion dependence whereas nitrogen cleavage does not necessarily do so, possible processes to consider are as shown in (11)—(14), where the extent of co-ordination and protonation of the EDTA ligand are indicated. Both N atoms are unco-ordinated throughout in (14). Equation (13) might seem least likely since cleavage of the third and not the fourth carboxylate ring is rate determining. Protonation of a nitrogen atom remote from the metal is possible in (12) for the range of [H$^+$] investigated, although sharing of a proton between a carboxylate and amine group might be operative. While we might tentatively favour (12), this discussion is somewhat speculative since the extent of protonation of the partly co-ordinated ligand is not known. If (12) is rate determining for dissociation then the reverse of (12) must be rate determining (*i.e.* the highest barrier) for the formation reaction. An alternative possibility is that the slow rate-determinimg step corresponds to bridging by the second nitrogen (for the formation), and dissociation of the first nitrogen (for the reverse). At this juncture we find this mechanism less appealing because of the expected lability (see below) of the positions *trans* to the terminal oxo-ligands (which the nitrogens occupy). Furthermore the [H$^+$] dependence in (9) and (10) is not entirely consistent with such a process.



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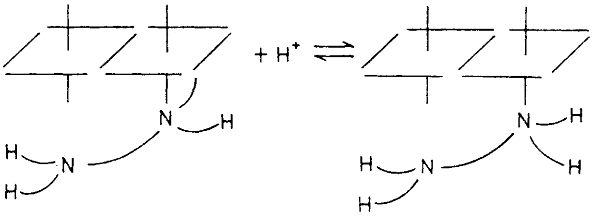

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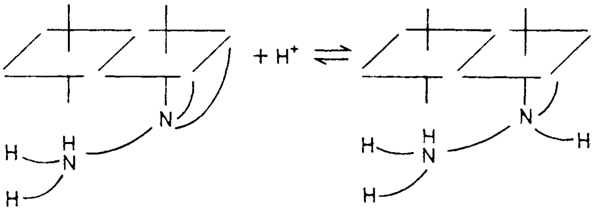
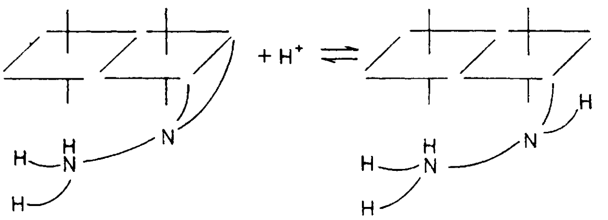


(13)



(14)

Co-ordination of EDTA to Mo$_2$O$_4^{2+}$ does not appear to follow the general pattern of complex formation of EDTA to metal ions where the first step is bonding of a carboxylate group to the metal.[22] Instead, in the present case rapid bond formation between Mo$_2$O$_4^{2+}$ and EDTA takes place before the rate-determining step. Such abnormal behaviour may be related to the possible lability of the positions *trans* to the terminal oxo-groups of the Mo$_2$O$_4$ unit. *trans*-Labilization is well established in the case of the VO^{2+} ion where exchange of the H$_2$O ligand *trans* to the oxo-group is much faster than the exchange in the *cis*-positions.[23] For the Mo$_2$O$_4$ unit such lability is suggested from *X*-ray crystal studies which provide substantial evidence for weak bonding at the positions *trans* to the terminal oxo-group.[18,24] The bridging oxo-ligands presumably have a weaker *trans*-labilizing effect than terminal ones since the bridging oxo is shared by two metal ions.[25]

EXPERIMENTAL

Preparation of Diammonium Pentachloro-oxomolybdate(v).[26]—AnalaR sodium molybdate (0·1M in 2·5M-HCl) was reduced by shaking vigorously with freshly distilled mercury for 15 min,[27] The resulting deep brown molybdenum(v) solution was decanted and filtered. Ammonium chloride (2·2 g) was added to 200 ml of the above solution, which was then reduced in volume to *ca.* 10 ml on a rotary evaporator at 40—50 °C. Some white precipitate was deposited and this was filtered off and discarded. The solution was cooled in an ice bath and was saturated with HCl which was generated by dropping *ca.* 9M-H$_2$SO$_4$ onto concentrated HCl. Green crystals of (NH$_4$)$_2$MoOCl$_5$ were obtained, and after being filtered off were washed with small amounts of cold HCl and dried *in vacuo* over KOH; yield *ca.* 3 g. For a solution in 10·8M-HCl absorption coefficients at peak positions were λ/nm (ε/l mol^{-1} cm^{-1}) 241 (5700), 310 (4940), 355 (537), 444 (14·3), and 700 (15·3). These are in reasonable agreement with literature values.[15,28]

Preparation of Mo$_2$O$_4$(H$_2$O)$_6^{2+}$ *Solution.*—Solutions of the aquo-ion Mo$_2$O$_4^{2+}$, (A), were obtained by dissolving (NH$_4$)$_2$MoOCl$_5$ in aqueous perchloric acid. Chloride-free solutions were prepared by addition of silver perchlorate and removal of the resulting silver chloride. Amounts of chloride present do not appear to complex extensively with Mo$_2$O$_4^{2+}$ however, and a kinetic run in the presence of free

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[22] See introduction to B. J. Fuhr and D. L. Rabenstein, *Inorg. Chem.*, 1973, **12**, 1868; also R. K. Wharton and A. G. Sykes, *J.C.S. Dalton*, 1972, 2404.

[23] J. Reuben and D. Fiat, *Inorg. Chem.*, 1967, **3**, 179; K. Wüthrich and R. E. Connick, *ibid.*, p. 583.

[24] M. C. B. Drew and A. Kay, *J. Chem. Soc.* (*A*), 1971, 1846.

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[26] 'Handbook of Preparative Inorganic Chemistry,' ed. G. Brauer, Academic Press (N.Y.), 2nd edn., 1963, 1413.

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[28] C. K. Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73.

chloride, Table 1, showed that the latter does not produce a significant effect. The concentration of molybdenum(v) was determined by titration with cerium(IV) standard solution using ferroin as indicator.

Preparation of the Sodium Salt of the EDTA Complex of the Molybdenum(v) *Dimer*.—The AnalaR disodium salt of EDTA (1·2 g) was dissolved in water (50 ml) and $(NH_4)_2$-$MoOCl_5$ (2 g) was slowly added to it. When the latter had dissolved the solution was filtered to remove insoluble impurity. To the filtrate several drops of 10M-NaOH was added very slowly to neutralize the solution to pH *ca.* 6. The solution was then evaporated on a water bath to *ca.* 20 ml and cooled. Ethanol was added until crystallization commenced. The crystals were filtered off and washed with ethanol and ether. Recrystallization from a saturated solution was induced by addition of ethanol (Found: C, 20·4; H, 2·2; N, 4·7%. Calc. for $Na_2Mo_2O_4$-$N_2C_{10}H_{12}O_8$: C, 20·4; H, 2·05; N, 4·75%).

Buffer Solutions.—Buffer solutions used in the investigation of the stability of the EDTA complex were pH 1—3, sodium acetate/HCl; pH 5, sodium acetate/acetic acid; pH 7, potassium dihydrogen phosphate/sodium hydroxide; and pH 9, boric acid/sodium hydroxide.

Kinetic Studies.—For kinetic runs in which the formation of $Mo_2O_4Y^{2-}$ was studied, solutions containing the reactants $Mo_2O_4^{2+}$ and EDTA (disodium salt) respectively were made up with concentrations of $HClO_4/LiClO_4$ as required for the reactant solution. For these studies of the equilibration process commencing with the EDTA complex, a solution of the latter was used instead of $Mo_2O_4^{2+}$. The approximate time required for solutions to equilibrate generally determined whether or not air-free conditions were used. For those runs in which air-free conditions were used, solutions were deoxygenated by bubbling nitrogen through solutions for *ca.* 30 min. Techniques using serum caps, nylon syringes, and stainless-steel needles were essentially as used in these laboratories for studies involving chromium(II).

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