

## Redox Properties of Ethylenediaminetetra-Acetic Acid Complex of the Molybdenum(V) $\text{Mo}_2\text{O}_4^{2+}$ in Aqueous Acidic Solution

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**Summary:** The kinetics of the equilibration of molybdenum (V,V) complexes of  $\text{Mo}_2\text{O}_4^{2+}$  (A) and  $\text{Mo}_2\text{O}_4\text{Y}^{2-}$  in the presence of excess of EDTA ( $\text{H}_4\text{Y}$  = ethylenediaminetetra-acetic acid) have been studied by spectrophotometry methods at 25°C, and ionic strength,  $I=1.50\text{M}$  ( $\text{LiClO}_4$ ). First order rate constants at constant hydrogen-ion concentrations in the range  $[\text{H}^+] = 0.2\text{-}1.8\text{M}$  may be expressed as  $k_{\text{eq}} = a[\text{EDTA}] + b$ . The hydrogen dependences of  $a$  and  $b$ , corresponding to the formation and dissociation processes respectively are not simple. For the dissociation process the equation  $b = [\text{H}^+]^3 / (1 + b_2 [\text{H}^+]^2)$  gives a good fit the experimental data. Contributions from terms in  $[\text{H}^+]$  and  $[\text{H}^+]^2$  in the denominator can not be ruled out however. An inverse hydrogen-ion dependence is apparent for  $a$  but the precise form is less certain.

The substitutional and redox properties of mono- and binuclear complexes of molybdenum with different ligands N,O and S atoms are of interest as models for molybdenum enzymes [1]. It has been now established that most of these enzymes contains two molybdenum atoms which are redox active. The molybdenum 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].

### Introduction

Most of the substitution studies have been with molybdenum (VI), and reactions involving complexation of 8-hydroxyquinoline [3], 8-hydroxyquinoline 5-sulphonate [4], catechol [5], EDTA [6], and cabalamine [7] to molybdate have been studied by fast reaction techniques. An important feature of these studies is the extension of inner-coordination sphere from 4 to 6. The kinetic studies of 1:1 complex formation of chloride and thiocyanate with  $\text{Mo}(\text{H}_2\text{O})_6^{3+}$  have been reported [8].

Initially we started to look at the reduction of  $\text{Mo}_2\text{O}_4^{2+}$  with halogen containing oxidizing agents, haloamines,  $\text{NH}_2\text{Cl}$ ,  $\text{NH}_2\text{Br}$ . During the studies, while preparing the complex of  $\text{Mo}_2\text{O}_4^{2+}$  dimer referred below, and looking at its redox properties which were of interest as models for molybdenum containing enzymes [1], we are observed that the kinetics and structure of  $\text{Mo}_2\text{O}_4^{2+}$  has to be verified and investigated, since the kinetic studies were not hitherto reported. This led to our present report of the kinetics studies on the equilibration of  $\text{Mo}_2\text{O}_4^{2+}$  (A)  $\text{Mo}_2\text{O}_4$  -  $\text{EDTA}^{2-}$  (B) in the presence of excess EDTA as complexing agent.

The molybdenum(V) aquo-dimer (A) here after  $\text{Mo}_2\text{O}_4^{2+}$  has 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). With molybdenum (VI) metal atom are more remote, however [12,13], (C), and equilibrium studies [6,14] have indicated the existence of a 1:1 species. Kinetic studies on the equilibrium of (A) and (B) in the presence of excess of EDTA are reported here.

### *Properties of $\text{Mo}_2\text{O}_4\text{Y}^{2-}$ and $\text{Mo}_2\text{O}_4^{2+}$*

A crystalline sample of  $\text{Na}_2\text{Mo}_2\text{O}_4\text{Y}$ , the sodium salt of (B), was prepared as described in the experimental section. The U.V. visible spectrum in pH 5.5 acetate buffer solution, Fig. 1, has two absorption peaks at 390 nm ( $E=3381 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 297 nm ( $E=9000 \text{ mol}^{-1} \text{ cm}^{-1}$ ), in satisfactory agreement with reported values [15]. The U.V.-visible spectrum is the same ( $\pm 5\%$  at 390 nm) in buffer solution of pH=1.8, and at 25°C remain unchanged over periods of at least 1 day. Dissociation of EDTA occurs in perchloric acid solution,  $[\text{H}^+]=0.2\text{-}1.8 \text{M}$ ; and isosebestic points are observed at 25.3 and 27.3 nm during the dissociation. At  $[\text{H}^+]>1.8 \text{M}$  dissociation is complete, and the final spectrum is the same for

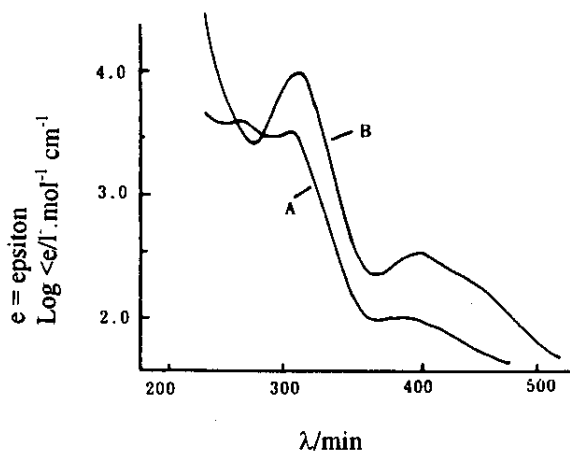


Fig. 1: UV-visible spectra of the di-u-oxo-molybdenum(V) dimers  $\text{Mo}_2\text{O}_4^{2+}$  (A) and  $\text{Mo}_2\text{O}_4\text{Y}^{2-}$  (B).

solutions 1.8-4.0 M in  $\text{HClO}_4$ . The dissociation is substantially faster by a factor of ca. 2.5 in 2 M HCl as compared to 2 M  $\text{HClO}_4$ .

Molybdenum complexes present in aqueous perchloric acid solution have been reported to be positively charged [16]. Ardon and Pernick [9] have shown that structure (A) with charge  $2^+$  applies in aqueous perchloric acid solution. The spectrum of (A) Fig. 1, has similar features to spectra of other complexes containing the  $\text{Mo}_2\text{O}_4$  unit [17] 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  $[\text{H}^+]=0.5\text{-}5.0$  M, and it is concluded that structure (A) is stable over this range. Details of absorption maxima  $\lambda/\text{nm}$  ( $E/l$   $\text{mol}^{-1} \text{cm}^{-1}$ ) are ; 384(103), 295 (3546), and 255 (4320) in good agreement with spectrum of Ardon and Pernick : 293(3454) and 254 (3998).

On dilution to  $[\text{H}^+]$ , 0.1 M a strong absorption is superimposed over the 384 nm band, and the peak at 295 nm shifts to longer wavelength. 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 0.1-1.0 M  $\text{HClO}_4$  isosebestic points are observed at 253 and 273 nm as (B) forms. These isosebestic points are identical with those observed for dissociation of EDTA form (B)

and are consistent with the equilibrium (1) in aqueous perchloric acid solutions,  $0.1 < [\text{H}^+] < 2.0$  M.



#### Kinetic studies

The kinetics of the equilibrium (1), were investigated at  $25^\circ\text{C}$ ,  $[\text{H}^+]=0.2\text{-}1.8$  M,  $I=1.5$  M ( $\text{LiClO}_4$ ), with uncomplexed EDTA in at least ten-fold excess of 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  $E=102$  for (A) and  $336$   $1 \text{ mol}^{-1} \text{cm}^{-1}$  for (B). Plots of  $\log(\text{OD}-\text{OD}_t)$  against time, Fig. 2, were linear for 6-10 half-lives, and the gradient ( $\times 2.303$ ) gave rate constants  $k_{\text{aq}}$ , 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

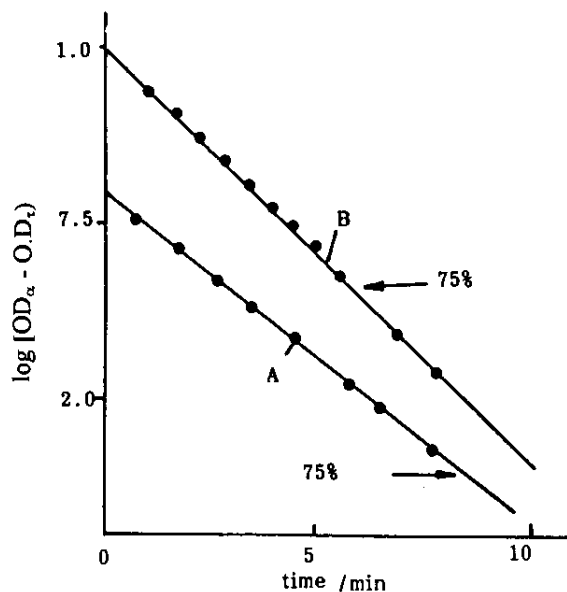


Fig. 2: Kinetic plots, A, for the formation and, B, for the dissociation of  $\text{Mo}_2\text{O}_4\text{Y}^{2-}$  at  $25^\circ\text{C}$ ,  $I=1.80$  M ( $\text{LiClO}_4$ ). For A absorbance  $\text{OD}_2/\text{OD}_1$ ,  $[\text{Mo}_2\text{O}_4^{2+}]=3.07 \times 10^{-4}$  M,  $[\text{EDTA}]=5.0 \times 10^{-3}$  M, and  $[\text{H}^+]=0.87$  M, For, B,  $\text{OD}_\alpha < \text{OD}_t$ ,  $[\text{Mo}_2\text{O}_4\text{Y}^{2-}]=3.49 \times 10^{-4}$  M,  $[\text{EDTA}]=4.03 \times 10^{-3}$  M, and  $[\text{H}^+]=1.5$  M.

Table-1:

1	Column 1 [H]/M	Column 2 [Mo(v,v)]/10	Column 3 [EDTA]/M	Column 4 Procedure	Column 5 10 keq/s
2					
3	0.51	0.24	0.45	f	1.02 a
4	0.51	0.24	1.79	f	2.68 a
5	0.51	0.24	4.49	f	6.89 a
6	0.51	3.00	5.14	f	7.97 b
7	0.51	3.00	6.12	f	8.92 b
8	0.51	4.12	10.19	f	15.71 b
9	0.51	6.25	10.19	f	15.28 b
10	0.51	4.12	12.18	f	23.15 b
11	0.51	4.22	12.38	f	23.15
12	0.51	4.22	16.48	f	23.48
13	0.51	3.34	16.48	f	24.12
14	0.625	2.51	4.12	f	4.28
15	0.625	2.98	6.18	f	5.97
16	0.625	2.98	8.19	f	8.18
17	0.75	4.20	8.28	f	5.84 b
18	0.75	4.20	10.18	f	6.98 b
19	0.75	4.20	11.19	f	7.28 b
20	0.75	4.20	12.19	f	8.18 b
21	1.00	4.25	10.19	d	4.18
22	1.00	3.43	12.28	d	4.19
23	1.00	4.18	15.19	f	4.21
24	1.00	3.48	16.38	d	4.81
25	1.25	2.95	6.10	f	3.75
26	1.25	3.58	8.20	f	4.18
27	1.25	2.98	10.12	f	4.01
28	1.25	3.58	12.28	f	4.45
29	1.5	3.58	4.13	d	4.60
30	1.5	3.58	8.35	d	4.78
31	1.5	3.58	10.58	d	5.08
32	2.00	3.39	10.38	d	6.98
33	2.00	3.39	20.25	d	7.21c
34	2.00	4.40	20.25	d	6.28 b

36 a<sup>1</sup> = 298, b - Air-fee conditions not used, c[NaCl] = 3.51 10<sup>3</sup>M.

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). The observed values are 5-10 % higher in both cases. No evidence was obtained for ion-pair formation between EDTA and Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup> under conditions, [H<sup>+</sup>]=1.8 M, when complex formation is negligible.

Rate constants k<sub>aq</sub> give the dependence (2) on total EDTA concentration, as illustrated in Fig. 3. k<sub>aq</sub>=a[EDTA] + b (2). Values of a and b so defined correspond to the formation and dissociation of (B) respectively. From the gradient and intercept Fig. 3, individual values of a and b at different [H<sup>+</sup>] values were evaluated, and are given in Table-2.

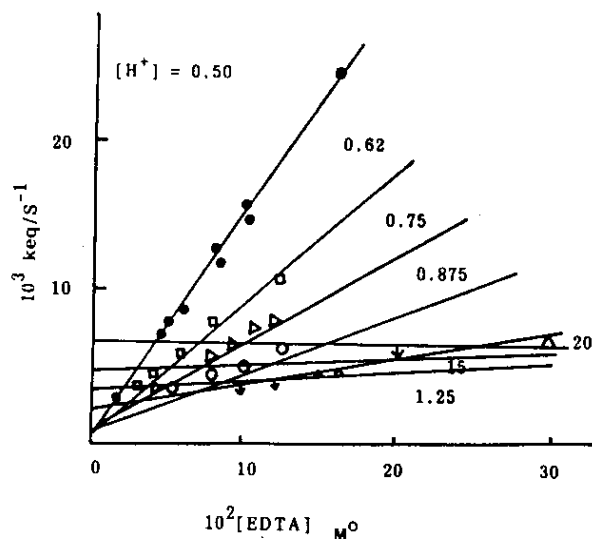


Fig. 3: The dependence of first order rate constants k<sub>eq</sub>, for the equilibration of Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup> (A) and Mo<sub>2</sub>O<sub>4</sub>Y<sup>2-</sup> (B), are the concentration of uncomplexed DTA at 25°C, I=8.0 M(LiClO<sub>4</sub>).

Table-2: Rate constants a and b as defined in equation (2), for the formation and dissociation of Mo<sub>2</sub>O<sub>4</sub>Y<sup>2-</sup> at 25°C, I=1.5 M (LiClO<sub>4</sub>)

[H <sup>+</sup> ]/M	a/ mol <sup>-1</sup> s <sup>-1</sup>	10 <sup>3</sup> b/s <sup>-1</sup>
0.50	1.51 ± 0.04	0.1 ± 0.24
0.65	0.95 ± 0.04	0.41 ± 0.24
0.78	0.59 ± 0.04	0.97 ± 0.32
0.875	0.38 ± 0.03	1.44 ± 0.32
1.00	0.20 ± 0.02	2.04 ± 0.25
1.35	0.08 ± 0.02	3.42 ± 0.20
1.65	0.040 ± 0.025	4.52 ± 0.04
2.00	very small	6.88 ± 0.29

## Results and Discussion

The unit Mo<sub>2</sub>O<sub>4</sub> is common in molybdenum (V) chemistry in aqueous medium and is present in both complexes (A) and (B). Reaction 1 can be regarded as a coordination of EDTA to the Mo<sub>2</sub>O<sub>4</sub> unit rather than coordination of EDTA to two separate molybdenum centers, as is the case in the formation of molybdenum-(VI)-EDTA complex, are quite unique since EDTA bridges two metal ions which are bridged by two other groups. Although several other binuclear complexes with EDTA as bridging ligand are known [18,19], none of them have additional bridging ligands between the two metal ions.

Over the range  $[H^+] = 0.7-1.8$  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  $[H^+] < 0.7$  M the first-order dependence decreases dramatically to give  $b=0$  at small  $[H^+] = 0$  values. The data give a good fit to (3), with  $n=4$ .

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

Thus (3) can be rearranged to give (4), and Fig. 4 is a plot of  $[H^+]/b$  against  $[H^+]^{-3}$ .  $[H^+]/b = 1/b_1[H^+]^3 + b_2/b_1$  (4).

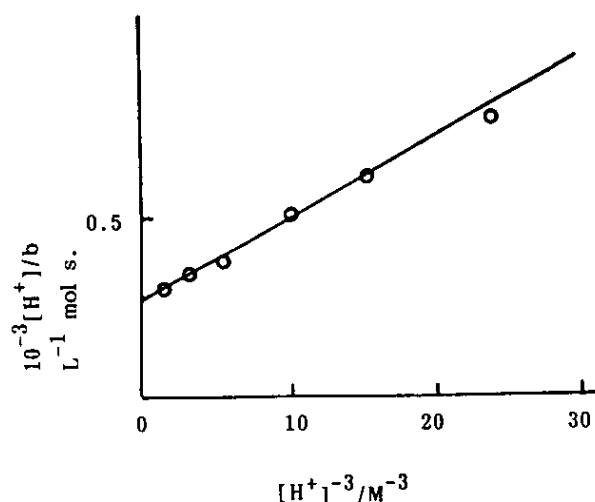
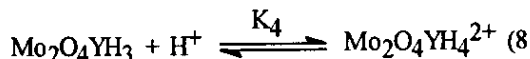
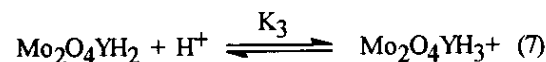
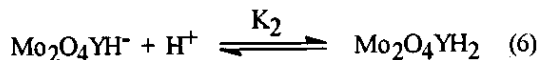
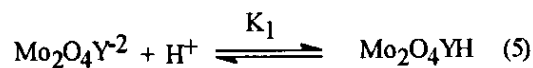


Fig. 4: Plots of  $[H^+]/b$  against  $[H^+]^{-3}$  demonstrating the applicability of equation (4) (with  $n=4$ ).

The corresponding plots with  $n=3$  and  $5$ , respectively show curvature. Data points for  $[H^+] = 0.625$ , and  $0.5$  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 slope and intercept in Fig. 4 and are  $220 \pm 6 \text{ l}^{-4} \text{ mol}^4 \cdot \text{s}$  and  $271 \pm 7 = \text{l}^{-1} \text{ mol} \cdot \text{s}$  respectively.

The mechanism (5)-(8) will account for the hydrogen-ion dependence 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 rapid then the overall rate dissociation,  $k_a$ , will be given by (a). Assuming the equations,



$$K_a = K_4 K_1 K_2 [H^+]^4 / 1 + K_1 [H^+] + K_1 K_2 [H^+]^2 + K_1 K_2 K_3 [H^+]^3 \quad (9)$$

$K_1 K_2 K_3 [H^+]^3$ , (9) simplifies to (10), which is of the same form as the dependence observed, equation (3), with  $n=4$ . This relationship give  $K_a = k_4 K_1 K_2 K_3 [H^+]^4 / 1 + K_1 K_2 K_3 [H^+]^3$  (10)

$k_4 = 3.69 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$  and  $K_1 K_2 K_3 = 1.23 \text{ l}^3 \text{ mol}^{-3}$  equation (4) remains an adequate fit to our data despite attempts of many complicated expression to fit the equations.

We consider in detail processes which might correspond to rate-determining step (8) in the dissociation mechanism. It is assumed that carboxylate bond cleavage gives a hydrogen-ion dependence where as nitrogen does not necessarily do so, possible processes to consider are as shown in (11)-(14), where the extent of coordination and protonation of EDTA ligand are indicated. Equation (13) might seem least likely since cleavage of the third and not the fourth carboxylate ring is the 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 carboxylate and amine group might be operative. While we might tentatively favour (12), this discussion is somewhat speculative since extent of protonation of the partly coordinated 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 formation reaction.

Coordination of EDTA to  $\text{Mo}_2\text{O}_4^{+2}$  does not appear to follow the general pattern of complex formation of carbohydrate group to the metal [20]. Instead, in the present case rapid bond formation between  $\text{Mo}_2\text{O}_4^{+2}$  and EDTA takes place before the rate-determining step. Such behavior may be

related to the possible lability of the position trans to the terminal oxo-groups of the  $\text{Mo}_2\text{O}_4$  unit. Trans-labilization is well established in the case of the  $\text{VO}^{2+}$  ion where exchange of the  $\text{H}_2\text{O}$  ligand trans to the oxo-group is much faster than the exchange in the cis-position [21]. The bridging oxo-ligands presumably have a weaker trans-labilization effect than terminal ones since the bridging oxo is shared by two metal ions [18,19].

## Experimental

### *Preparation of diammonium pentachloro-oxomolybdenum (V) [22]*

Analar sodium molybdate (0.1M in 2.0M HCl) was reduced by shaking vigorously with freshly distilled mercury for 15 min [23]. The resulting deep brown molybdenum (V) solution was decanted and filtered. Ammonium chloride (2.2g) was added to 200 ml of above solution, which was then reduced in volume to ca. 10 ml of rotary evaporator at 40-50°C. Some white precipitate was deposited and this was filtered off and discarded. This solution was cooled in an ice bath and saturated with HCl which was generated by dropping ca. 9M- $\text{H}_2\text{SO}_4$  on to concentrated HCl. Green crystals of  $(\text{NH}_4)_2\text{-MoOCl}_5$  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 10M-HCl absorption coefficient at peak position were  $\lambda/\text{nm}$  ( $E/1 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 241 (5718), 310 (4948), 355 (530), 444 (15.38), and 700 (16.8). These are reasonable agreement with literature values [15,24].

### *Preparation of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ solution*

Solution of the aquo-ion,  $\text{Mo}_2\text{O}_4^{2+}$ , A, were obtained by dissolving  $(\text{NH}_4)_2\text{MoOCl}_5$  in the aqueous perchloric acid. Chloride-free solution 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  $\text{Mo}_2\text{O}_4^{2+}$  however, and a kinetic run in the presence of free chloride, table 1, latter does not produce a significant effect. The concentration of molybdenum (V) was determined by filtration with cerium (IV) standard solution ferrin indicator.

### *Preparation of the sodium salt of the EDTA complex of the molybdenum (V) dimer*

The Analar salt of EDTA (1.2 g) was dissolved in water (50 ml) and  $(\text{NH}_4)_2\text{MoOCl}_5$  (2 g) was slowly added to it. When the latter had dissolved the solution was filtered to remove insoluble purity. To the filtrate several drops of 10 M NaOH was added very slowly to neutralize the solution to pH ca. 6. The solution are 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.

### *Buffer solution*

Buffer solution 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 hydrogen phosphate; and pH 9, boric acid/sodium hydroxide.

### *Kinetic studies*

For kinetic runs in which the formation of  $\text{Mo}_2\text{O}_4^{2+}$  was studied, solutions containing the reactants  $\text{Mo}_2\text{O}_4^{2+}$  and EDTA (disodium salt) respectively were made up with concentrations of  $\text{HClO}_4/\text{LiClO}_4$  as required for the reactant solution. For these studies of the equilibration process commencing with EDTA complex, a solution of the latter was used instead of  $\text{Mo}_2\text{O}_4^{2+}$ . The approximate time required for solutions to equilibrate generally determined whether or not 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 other work in this laboratory.

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