Relaxation Spectra of Molybdate–Ethylenediaminetetraacetic Acid Complexes[1]

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Abstract: Aqueous molybdate–EDTA solutions were studied by temperature jump in the pH range 7.25–8.25 at 25° and ionic strength 0.1 M ($NaNO_3$). The upper time limit of the apparatus was extended to allow accurate measurement of relaxation times in the 1–3 sec range by interfacing the signal to an on-line averager. The rate constant for the reaction $HMoO_4^- + AH_2^{2-} \rightarrow MoO_3AH^{3-} + H_2O$ is $k_5 = (2.26 \pm 0.23) \times 10^5\ M^{-1}\ sec^{-1}$, where AH_2^{2-} is the diprotonated form of EDTA. The composite rate constant for the reactions $MoO_3A^{4-} + HMoO_4^- \rightarrow O_3MoAMoO_3^{4-} + OH^-$ (k_6) and $MoO_3AH^{3-} + MoO_4^{2-} \rightarrow O_3MoAMoO_3^{4-} + OH^-$ (k_7) is $k_{67} = (3.26 \pm 0.88) \times 10^8\ M^{-2}\ sec^{-1}$. Upper limits for the individual rate constants are $k_6 \leqq 3.26 \times 10^4$ and $k_7 \leqq 1.03 \times 10^1\ M^{-1}\ sec^{-1}$. Comparing k_5 with rate constants for chelation of $HMoO_4^-$ by 8-hydroxyquinoline and catechol shows the EDTA reaction to be slower. Bimolecular steps in the polymerization of molybdenum(VI) are also more rapid. The nature of the rate-limiting step appears to depend on the ligand; for EDTA, the process of forming molybdenum–ligand bonds may be rate limiting.

Until recently, there have been only a few detailed studies of molybdate complex formation equilibria[2] and none on their kinetics. Protonation of reactants and products as well as polymerization of molybdenum(VI) below pH 7 served to hinder progress in solving equilibria problems. The rapidity and complexity of these reactions, likewise, hampered the kineticist. Improved equilibrium data and the application of fast reaction techniques have led to firm conclusions on the number and identities of the species in equilibrium and their kinetics, for example, for molybdate polymerization,[3] formation of 8-hydroxyquinoline complexes[4] and formation of catechol complexes.[5]

Anionic molybdenum(VI) forms ethylenediaminetetraacetic acid complexes,[6] which have been studied extensively with regard to their equilibria and structure.[7-10] Variously protonated 2Mo(VI):A and Mo(VI):A (*i.e.*, 2:1 and 1:1) complexes are present in aqueous solution below pH 9.[9,10] The structure of the 2:1 complex has been determined by X-ray analysis.[7] It was shown that, with respect to MoO_4^{2-}, an oxygen atom is lost on complexation. The coordination is octahedral around each Mo(VI), *i.e.*, MoO_3 moieties with A^{4-} being linked to each Mo(VI) by one nitrogen and two carboxylate oxygen linkages. The formula of the 2:1 complex can be given as $O_3MoAMoO_3^{4-}$. The structure of the 1:1 complex is analogous.[9,10]

We have carried out temperature-jump relaxation studies on Mo(VI)–EDTA complexes in order to study the kinetics and mechanism of these complexation reactions. Offsetting the knowledge of definite Mo(VI) oxygen loss on complexation, however, is the presence in solution of 2:1 and 1:1 complexes. Simple procedures,[11-13] such as graphical analysis,[3,4] for treating the relaxation data are thereby precluded. Direct solution for the kinetics constants of the homogeneous system of linear rate equations applicable to this system requires a fairly extensive number of reliable measurements.[11] To provide this kind of data, the upper time limit of the temperature-jump apparatus was extended by interfacing the signal to an on-line signal averager.

Experimental Section

Solutions of sodium molybdate, sodium hydroxide, nitric acid, and sodium nitrate were prepared as described previously.[3] Reagent grade disodium ethylenediaminetetraacetate (Fisher) was used as is. The pH was finally adjusted to within ±0.01 pH unit on a Corning Model 12 pH meter; ionic strength, μ, was 0.1 M. A sodium ion medium was used, as the stability constants for Mo(VI)–EDTA were determined in such a medium.[10] Hydrogen ion concentrations were obtained from pH readings by assuming the activity coefficient of the hydrogen ion to be 0.83 at the experimental conditions.[4,14] The indicators used were phenol red, cresol red, and thymol blue (Fisher). Belmont Springs distilled water was used throughout.

Details of the temperature-jump apparatus have already been given.[15] The temperature was 25 ± 1°. For analog signal records, each trace was plotted semilogarithmically. In all cases, the resulting curves were simple exponentials. For some experiments, the relaxation times were long enough for thermal convection to interfere with the measurement. (With the cell used, the onset of convection was observed at 3–5 sec.) To allow accurate recording of data at these relatively long times, the observed signal change was either recorded on an on-line signal averaging computer (Fabri-Tek) or the signal was directly converted to digital form and stored on paper tape. All the data stored on tape were processed on a PDP-10 computer.

Molybdenum(VI)–indicator and EDTA–indicator blanks were run at each pH value chosen. With EDTA, the results were nega-

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(1) The authors gratefully acknowledge support from Public Health Service Research Grant No. GM-08893-11, and from the National Science Foundation for Grant GB 33617.

(2) P. C. H. Mitchell, *Quart. Rev., Chem. Soc.*, **20**, 103 (1966).

(3) (a) D. S. Honig and K. Kustin, *Inorg. Chem.*, **11**, 65 (1972); (b) D. S. Honig and K. Kustin, *J. Phys. Chem.*, **76**, 1575 (1972).

(4) (a) P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, **64**, 977 (1968); (b) H. Diebler and R. E. Timms, *J. Chem. Soc. A*, 273 (1971).

(5) K. Kustin and S.-T. Liu, *J. Amer. Chem. Soc.*, **95**, 2487 (1973).

(6) The abbreviation EDTA and the short formula AH_4 are used throughout for ethylenediaminetetraacetic acid.

(7) J. J. Park, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, **91**, 301 (1969).

(8) S. I. Chan, R. J. Kula, and D. T. Sawyer, *J. Amer. Chem. Soc.*, **86**, 377 (1964).

(9) (a) R. J. Kula, *Anal. Chem.*, **38**, 1581 (1966); (b) R. J. Kula and D. L. Rabenstein, *ibid.*, 38, 1934 (1966).

(10) M. Naarova, J. Podlahová, and J. Podlaha, *Collect. Czech. Chem. Commun.*, **33**, 1991 (1968).

(11) M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., Wiley, New York, N. Y., 1963, p 895.

(12) G. Schwarz, *Rev. Mod. Phys.*, **40**, 206 (1968).

(13) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 3, 1 (1964).

(14) J. Podlahová, personal communication. See also J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

(15) (a) P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964); (b) R. Pizer, Ph.D. Thesis, Brandeis University, 1970.

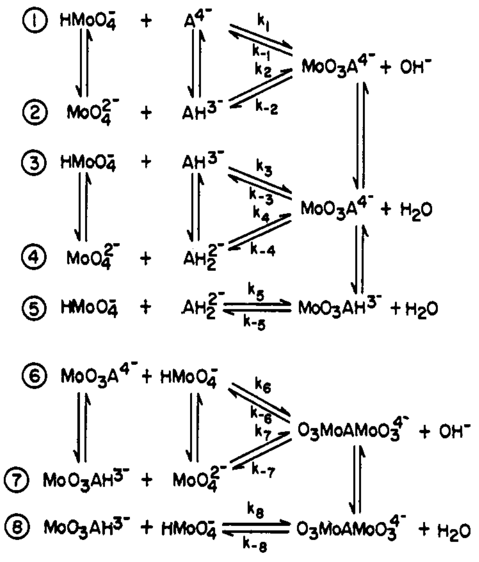

Figure 1. Reaction scheme for Mo(VI)–EDTA complexation. The system of reactions 1–8 possesses two coupled relaxation times representative of the oxyanion-complex mechanism. In scheme 1–5, the (vertical) protolytic reactions equilibrate more rapidly than do reactions of molybdate complexation, for which there is a single relaxation time. Scheme 6–8 may be similarly described, but inclusion of the 2:1 complex introduces another concentration variable; solution for the entire system then yields two relaxation times specifying the relatively slow process of oxyanion-complex formation.

tive for times longer than ~50 μsec. With Mo(VI), the results were also negative. At pH 7.00, solutions of Mo(VI) and indicator might possibly give an effect mixed in with convection (see ref 3a and references therein); consequently, the lowest pH used was 7.25.

Results

Stability constants for the Mo(VI)–EDTA system in aqueous solution (at $7 < \mathrm{pH} < 9$) are given in Table I. Concentrations were calculated on a PDP-10 computer using a Newton–Raphson iteration. Under the experimental conditions, the chemically significant species (in addition to Na^+, NO_3^-, and indicator) are given in Figure 1. Due to the very low concentrations of H_2MoO_4, AH_3^-, AH_4, and possibly $(MoO_3)_2AH_n^{(4-n)-}$, $n = 1$–4, these species were not considered to be important.[3,4,10] Naarova, *et al.*, found no need to take NaA^{3-} into account in determining the stability constants.[10,14] As this species will be a minor constituent at the experimental conditions used,[9,10,14,16–19] it was not taken into account. The complexes that have to be considered in the mechanism are MoO_3A^{4-}, MoO_3AH^{3-}, and $(MoO_3)_2A^{4-}$.[9,10]

The full mechanism for Mo(VI)–EDTA complexation ($7 < \mathrm{pH} < 9$), assuming bimolecular steps involving chemically significant species, is given in Figure 1. The assumption of rapid protolytic reactions, *i.e.*, that such reactions are always equilibrated during the observed response to the temperature-jump perturbation,[11,13] allows us to describe the complexation with three rate equations

$$\mathrm{d}[\mathrm{MoO_3A^{4-}}]/\mathrm{d}t = k_1[\mathrm{HMoO_4^-}][\mathrm{A^{4-}}] + k_2[\mathrm{MoO_4^{2-}}][\mathrm{AH^{3-}}] - (k_{-1} + k_{-2})[\mathrm{MoO_3A^{4-}}][\mathrm{OH^-}] + k_3[\mathrm{HMoO_4^-}][\mathrm{AH^{3-}}] + k_4[\mathrm{MoO_4^{2-}}][\mathrm{AH_2^{2-}}] - (k_{-3} + k_{-4})[\mathrm{MoO_3A^{4-}}] + k_{-6}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}][\mathrm{OH^-}] - k_6[\mathrm{HMoO_4^-}][\mathrm{MoO_3A^{4-}}] \quad (1)$$

$$\mathrm{d}[\mathrm{MoO_3AH^{3-}}]/\mathrm{d}t = k_5[\mathrm{HMoO_4^-}][\mathrm{AH_2^{2-}}] - k_{-5}[\mathrm{MoO_3AH^{3-}}] + k_{-7}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}][\mathrm{OH^-}] - k_7[\mathrm{MoO_3AH^{3-}}][\mathrm{MoO_4^{2-}}] + k_{-8}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}] - k_8[\mathrm{MoO_3AH^{3-}}][\mathrm{HMoO_4^-}] \quad (2)$$

$$\mathrm{d}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}]/\mathrm{d}t = k_6[\mathrm{MoO_3A^{4-}}][\mathrm{HMoO_4^-}] + k_7[\mathrm{MoO_3AH^{3-}}][\mathrm{MoO_4^{2-}}] - (k_{-6} + k_{-7})[(\mathrm{MoO_3})_2\mathrm{A^{4-}}][\mathrm{OH^-}] + k_8[\mathrm{MoO_3AH^{3-}}][\mathrm{HMoO_4^-}] - k_{-8}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}] \quad (3)$$

This dependent set of equations can be reduced to two independent equations[11,12]

$$\frac{\mathrm{d}[\mathrm{MoO_3A^{4-}}]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{MoO_3AH^{3-}}]}{\mathrm{d}t} = k_{12}\left([\mathrm{H^+}][\mathrm{A^{4-}}][\mathrm{MoO_4^{2-}}] - \frac{1}{K_{12}}[\mathrm{MoO_3A^{4-}}][\mathrm{OH^-}]\right) + k_{34}\left([\mathrm{H^+}]^2[\mathrm{A^{4-}}][\mathrm{MoO_4^{2-}}] - \frac{1}{K_{34}}[\mathrm{MoO_3A^{4-}}]\right) + k_5\left([\mathrm{HMoO_4^-}][\mathrm{AH_2^{2-}}] - \frac{1}{K_5}[\mathrm{MoO_3AH^{3-}}]\right) + k_{67}\left(\frac{1}{K_{67}}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}][\mathrm{OH^-}] - [\mathrm{MoO_3A^{4-}}][\mathrm{MoO_4^{2-}}][\mathrm{H^+}]\right) + k_8\left(\frac{1}{K_8}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}] - [\mathrm{MoO_3A^{4-}}][\mathrm{HMoO_4^-}]\right) \quad (4)$$

$$\frac{\mathrm{d}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}]}{\mathrm{d}t} = k_{67}\left([\mathrm{MoO_3A^{4-}}][\mathrm{H^+}][\mathrm{MoO_4^{2-}}] - \frac{1}{K_{67}}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}][\mathrm{OH^-}]\right) + k_8\left([\mathrm{HMoO_4^-}][\mathrm{MoO_3AH^{3-}}] - \frac{1}{K_8}[(\mathrm{MoO_3})_2\mathrm{A^{4-}}]\right) \quad (5)$$

where $k_{12} = (k_1K_{\mathrm{HM}} + k_2K_{\mathrm{HA}})$, $k_{34} = (k_3K_{\mathrm{HM}}K_{\mathrm{HA}} + k_4K_{\mathrm{H_2A}})$, $k_{67} = (k_6K_{\mathrm{HM}} + k_7K_{\mathrm{C}})$, and $k_{-12} = k_{12}/K_{12}$, etc.

Application of mass balance and small perturbation constraints to the above rate equations permits their solution by standard methods.[3a,11,12,20] The relaxation times, τ, are readily computed; they are the solutions of a quadratic characteristic equation.

The kinetics results are given in Table II. The data were treated by a nonlinear least-squares routine[21] on a PDP-10 computer to obtain the "best-fit" rate constants. The characteristic equation, with the observed values of τ, was not sensitive to k_{12}, k_{34}, and k_8; consequently, only meaningful values for k_5 and k_{67} could

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(16) G. Schwarzenbach and H. Ackerman, *Helv. Chim. Acta*, 30, 1798 (1947).

(17) J. Botts, A. Chashin, and H. L. Young, *Biochemistry*, 4, 1788 (1965).

(18) J. I. Watters and O. E. Schupp, III, *J. Inorg. Nucl. Chem.*, 30, 3359 (1968).

(19) H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler, *Pure Appl. Chem.*, 20, 93 (1969).

(20) D. S. Honig, Ph.D. Thesis, Brandeis University, 1972.

(21) We wish to thank Dr. D. Toppen for adapting a nonlinear least-squares program for use on the PDP-10.

Table I. Mo(VI)–EDTA Equilibrium Data (25°, $\mu = 0.1\ M$)[a,b]

$K_{HM} = [HMoO_4^-]/[H^+][MoO_4^{2-}] = 1 \times 10^4$[c,d]
$K_{HA} = [AH^{3-}]/[H^+][A^{4-}] = 2.41 \times 10^9$
$K_{H_2A} = [AH_2^{2-}]/[H^+]^2[A^{4-}] = 2.58 \times 10^{15}$
$K_C = [MoO_3AH^{3-}]/[H^+][MoO_3A^{4-}] = 3.16 \times 10^7$[d]
$K_{In} = [H][In]/[HIn] = 1.66 \times 10^{-8}$ (phenol red)[e]
$= 5.62 \times 10^{-9}$ (cresol red)[e]
$K_W = [H^+][OH^-] = 1.1 \times 10^{-14}$[f]
$K_1 = [MoO_3A^{4-}][OH^-]/[HMoO_4^-][A^{4-}] = 7.87 \times 10^{-1}$
$K_2 = [MoO_3A^{4-}][OH^-]/[MoO_4^{2-}][AH^{3-}] = 3.27 \times 10^{-6}$
$K_{12} = [MoO_3A^{4-}][OH^-]/[H^+][MoO_4^{2-}][A^{4-}] = 7.87 \times 10^3$
$K_3 = [MoO_3A^{4-}]/[HMoO_4^-][AH^{3-}] = 2.97 \times 10^4$
$K_4 = [MoO_3A^{4-}]/[MoO_4^{2-}][AH_2^{2-}] = 2.77 \times 10^2$
$K_{34} = [MoO_3A^{4-}]/[H^+]^2[MoO_4^{2-}][A^{4-}] = 7.16 \times 10^{17}$
$K_5 = [MoO_3AH^{3-}]/[HMoO_4^-][AH_2^{2-}] = 8.75 \times 10^5$
$K_6 = [(MoO_3)_2A^{4-}][OH^-]/[MoO_3A^{4-}][HMoO_4^-] = 7.08 \times 10^{-2}$
$K_7 = [(MoO_3)_2A^{4-}][OH^-]/[MoO_3AH^{3-}][MoO_4^{2-}] = 2.24 \times 10^{-5}$
$K_{67} = [(MoO_3)_2A^{4-}][OH^-]/[H^+][MoO_3A^{4-}][MoO_4^{2-}] = 7.08 \times 10^2$
$K_8 = [(MoO_3)_2A^{4-}]/[MoO_3AH^{3-}][HMoO_4^-] = 2.04 \times 10^5$
$K_9 = [MoO_3AH^{3-}]/[H^+]^3[MoO_4^{2-}][A^{4-}] = 2.26 \times 10^{25}$
$K_{10} = [(MoO_3)_2A^{4-}]/[H^+]^4[MoO_4^{2-}]^2[A^{4-}] = 4.61 \times 10^{34}$
$K_{11} = [(MoO_3)_2A^{4-}]/[H^+]^2[MoO_4^{2-}][MoO_3A^{4-}] = 6.44 \times 10^{16}$

[a] Except where noted, data from ref 10. Stability constants determined in Na^+ medium. [b] Stability constants for MoO_3A^{4-} and $(MoO_3)_2A^{4-}$ in ref 10 are given in terms of MoO_3 rather than MoO_4^{2-}. The $[MoO_3]$ was determined from $[MoO_4^{2-}]$ by using the dissociation constants of H_2MoO_4 ($[H_2MoO_4]/[H^+]^2[MoO_4^{2-}] = 10^{7.75}$); G. Schwarzenbach and J. Meier, *J. Inorg. Nucl. Chem.*, **8**, 302 (1958); also J. Podlahová, personal communication. [c] From ref 4 see also E. F. C. H. Rohwer and J. J. Cruywagon, *J. S. Afr. Chem. Inst.*, **16**, 26 (1963); **17**, 145 (1964); **22**, 198 (1969). [d] This value is not as accurately known as the others presented here. [e] K_{In} = indicator dissociation constant, neglecting charge; I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930). [f] L. G. Sillén and A. E. Martell, Ed., *Chem. Soc., Spec. Publ.*, **No. 25**, Suppl. 1 (1971).

be obtained. These constants are given in Table III, along with upper limits for k_6 and k_7.

Even though a system of coupled reactions can give rise to two relaxation times, only one may be observed.[11,12] This relaxation time may not be equally sensitive to all the rate constants of interest.[11,12] As can be seen in Table II, we are observing τ_+, which is apparently only sensitive to k_5 and k_{67}. This observation does not necessarily mean that the other pathways are unimportant; it only means that the observed response is only sensitive to some, not all, pathways.

The fit of τ_{obsd} to τ_+ is reasonably good except at pH 8.25. The reasons for this are not clear. As can be seen, τ_+ at pH 8.25 does not fit the trend of τ_+ with pH. Effects of NaA^{3-}, the back reactions (dependent on OH^-), pathways k_{12} and k_{34} (which would be more important here than at lower pH), and the increasingly larger contribution of convection at this pH are probably all factors contributing to the poor fit. Use of the characteristic equation with only τ_{obsd} at pH 8.25, instead of the entire data set, did not improve the fit.

Table II. Relaxation Spectra of Mo(VI)–EDTA Solutions[a,b] (25°, $\mu = 0.1\ M$)

pH	[Mo(VI)]$_0$ × 10^2	[EDTA]$_0$ × 10^2	[In]$_0$ × 10^5[c]	Sec τ_{obsd}	 τ_+	 τ_-
7.25	3.00	0.101	1.03	0.535	0.395	1.86
	2.00	1.00	1.03	0.512	0.483	3.60
	2.00	0.199	1.03	0.572	0.421	2.64
	1.00	0.101	1.03	0.755	0.585	4.14
	1.00	2.00	1.03	0.854	0.752	6.69
	0.10	1.00	1.03	2.19	2.01	11.8
	0.10	2.00	1.03	1.85	1.84	12.1
	0.20	2.00	1.03	1.43	1.48	11.0
	0.50	2.00	1.03	1.06	1.02	8.80
7.50	2.00	0.501	1.03	0.788	0.658	3.03
	3.00	0.10	1.03	0.614	0.515	2.39
	2.00	1.00	1.03	0.737	0.703	3.21
	2.00	0.20	1.03	0.716	0.642	2.91
	1.00	0.101	1.03	1.02	1.01	3.86
	1.00	2.00	1.03	0.945	1.15	4.57
	0.10	1.00	1.03	2.82	3.42	7.05
	0.10	2.00	1.03	2.15	3.25	7.10
	0.20	2.00	1.03	1.80	2.54	6.64
	0.50	2.00	1.03	1.13	1.66	5.60
	2.00	0.099	1.03	0.733	0.661	2.86
7.75	3.00	0.099	1.17	1.15	0.712	3.14
	2.00	1.00	1.17	1.21	1.02	3.38
	2.00	0.199	1.17	1.39	0.978	3.34
	1.00	0.10	1.17	1.44	1.77	3.66
	1.00	2.00	1.17	1.73	1.88	3.71
	0.20	2.00	1.17	2.43	3.98	4.91
	0.50	2.00	1.17	1.78	2.96	3.98
8.00	3.00	0.101	1.02	1.45	0.985	4.55
	2.00	1.01	1.02	1.42	1.35	4.73
	2.00	0.202	1.02	1.61	1.34	4.78
	1.00	0.099	1.02	1.89	1.92	6.00
	1.00	2.00	1.02	1.89	1.94	5.82
	0.20	2.00	1.02	~3.5	2.33	9.98
	0.50	2.00	1.02	2.08	2.22	7.62
8.25	3.00	0.099	1.05	~2.6	1.04	9.45
	2.00	1.00	1.05	~2.3	1.16	10.8
	2.00	0.20	1.05	~2.3	1.16	11.0
	1.00	2.00	1.05	~2.6	1.27	14.0
8.49	2.00	1.00	1.05	Too slow and too small to observe		

[a] All concentrations *M;* subscript "0" denotes total stoichiometric concentration. Concentration of Mo(VI) expressed as $[MoO_4^{2-}]$. Concentration of EDTA expressed as $[\Sigma A]$. [b] Convection prevents accurate measurement of τ_{obsd} longer than ~3 sec. [c] Phenol red used at pH 7.25–7.75, cresol red at pH 8.00 and 8.25, and thymol blue at pH 8.49.

Table III. Rate Constants for Mo(VI)–EDTA Complexation (25° μ, = 0.1 M)

$k_5 = (2.26 \pm 0.23) \times 10^6\ M^{-1}\ sec^{-1}$
$k_{67} = (3.26 \pm 0.88) \times 10^8\ M^{-2}\ sec^{-1}$
$= (k_6K_{HM} + k_7K_C)$
$k_6 \leq 3.26 \times 10^4\ M^{-1}\ sec^{-1}$
$k_7 \leq 1.03 \times 10^1\ M^{-1}\ sec^{-1}$

Discussion

Comparison of the rate constants found for the Mo(VI)–EDTA system with those obtained for other systems is not straightforward, owing to the various protonated forms of the complexing ligands. The most meaningful comparison between different systems is for reactions where the degrees of protonation of ligand and Mo(VI) are respectively identical. Ligands having similar degrees of protonation may still differ in overall charge; charge distribution, rather than overall charge on the ligand, is a more important factor.

Within most molybdate–ligand systems studied, ambiguities arise in the interpretation of the data because of the presence of two or more kinetically indistinguishable paths. Thus, if a ligand can exist in two forms, H_2X and HX^-, the indistinguishable pairs of reactants are $MoO_4^{2-} + H_2X$ and $HMoO_4^- + HX^-$. In the following, comparisons will be based on results obtained with 8-hydroxyquinoline or oxine (HOx) and catechol (H_2Cat). Valid conclusions with respect to trends in the rate data can be drawn, as long as consistent sets of reaction partners are selected for comparison. It should also be borne in mind that, in these systems, EDTA is bifunctional; thus, AH_2^{2-} should be regarded as presenting a monoprotonated, mononegative attacking site.

The upper-limit, bimolecular rate constants for complexation of MoO_3OH^- by HOx and $HCat^-$ are 4.5×10^6 and 1.9×10^8 M^{-1} sec^{-1}, respectively. For the reaction $MoO_3OH^- + Ox^-$ the rate constant is 1.5×10^8 M^{-1} sec^{-1}. (Rate constants for MoO_4^{2-} and the more protonated species in these systems are smaller, being 4.1×10^2 M^{-1} sec^{-1} for HOx and 2.9×10^2 M^{-1} sec^{-1} for H_2Cat.) The value for the reaction $MoO_3OH^- + AH_2^{2-}$ is $k_5 = 2.26 \times 10^5$ M^{-1} sec^{-1}, which is less than the above even allowing for relatively more charge repulsion. A lack of contribution from k_4 owing to an even lower value for this rate constant would be consistent with these results.

The reactions corresponding to k_6 and k_7 can be viewed as complex formation between the second functional group on the bound EDTA and another molybdate anion. As expected from the increased coulombic repulsion, these constants are less than k_5, and, as seen for both oxine and catechol, $k_6 > k_7$ is consistent with larger rate constants for the reaction of MoO_3OH^-.

We therefore conclude that Mo(VI)-EDTA complex formation is slower than that of Mo(VI) with oxine and Mo(VI) with catechol. The observed relaxation times are one to two orders of magnitude longer (under similar conditions) with EDTA than with the other ligands; this fact in itself suggests EDTA complexation is slower.

The relative thermodynamic stability of a complex can usually be gauged from a comparison of stepwise stability constants.[22] The relative stabilities of 2:1 and 1:1 Mo(VI)-EDTA complexes cannot be determined this way, however. Examination of Table I shows that if one compares K_{34} with K_{11}, K_I with K_6, and K_{12} with K_{67} then MoO_3A^{4-} is more stable than $(MoO_3)_2A^{4-}$; the reverse is true, however, if one compares K_7 with K_2 and K_8 with K_3. The order of stability constants may often be based on kinetic phenomena. For many oxyanion-ligand complexes, for example, $K_2 > K_1$. This order is a result of more-or-less similar formation rate constants but much larger dissociation rate constants for the monocomplex.[5] This analysis cannot be applied here, since k_{-5} (equal to k_5/K_5) is first order but the composite k_{-67} (equal to k_{67}/K_{67}) is second order. No value was obtained for k_{-8}, for which a comparison would have been possible. The thermodynamic stability constants, which provide the sole criteria for determining relative stability, are of two kinds: overall stability constants (*e.g.*, K_{34} and K_{11}) and stability constants in terms of reacting species (*e.g.*, K_7 and K_2). The two types are related by the acid dissociation constants of the species involved, changes in the values of which can shift the order one way or another. The most reasonable assessment appears to be that MoO_3A^{4-} and $(MoO_3)_2A^{4-}$ are of roughly comparable stability.[8,10]

Studies on Mo(VI) isopolyanion formation indicate that Mo(VI) oxygen loss and coordination expansion are very rapid; bimolecular polymerization steps are estimated to be $\geq 10^7$ M^{-1} sec^{-1}.[3] It was proposed that, instead of involving MoO_4^{2-} directly, the polymerization proceeds by reaction of the oxygen-labile protonated monomeric molybdate,[3a] which has octahedral coordination ($OMo(OH)_5^-$). The evidence for $OMo(OH)_5^-$ is indirect (see ref 3 and references therein); the evidence for very rapid oxygen loss as H_2O (or OH^-) and coordination expansion on polymerization is not. Molybdenum(VI) isopolyanion formation is analogous to Mo(VI) anionic complexation, and proton involvement appears to be necessary.[2-7] Thus, comparison of Mo(VI) complexation rates with polymerization rates is of interest. (As the estimated polymerization rates are for protonated reactants, comparison should be made with reactions of protonated ligand and protonated Mo(VI) monomer.)

With the 8-hydroxyquinolines as ligands, the occurrence of Mo(VI) oxygen loss has not been clearly established.[4] Oxygen loss occurs with EDTA[7,9,10] and with catechol.[5] With all these ligands, $HMoO_4^-$ (or $OMo(OH)_5^-$) seems to be more reactive. Complexation with EDTA is slower than isopolyanion formation, as well as being slower than complex formation with oxine or catechol. Interestingly, preliminary studies on Mo(VI)-nitrilotriacetic acid indicate that observed relaxation times are at least an order of magnitude longer than with EDTA, under similar conditions.[23]

Solid-state structural studies show that Mo(VI)-EDTA complexes can be approximately viewed as having three coordinating linkages, which substitute for a MoO_4^{2-} oxygen. The proposed structure for the 1:1 Mo(VI)-nitrilotriacetic acid complex has four coordinating linkages substituting for a MoO_4^{2-} oxygen.[7] The 8-hydroxyquinolines, which are probably bidentate and are somewhat more reactive than the catechols, may simply "add" to MoO_4^{2-}; the rate determining process would then be formation of ligand-metal linkages by coordination expansion. By implication, both the process of coordination and oxygen loss would appear to require approximately comparable activation for the catechols. For EDTA and NTA, the slowest process in the overall condensation reaction may be formation of coordinating linkages, as oxygen loss appears to be a more rapid process.

Therefore, the mechanism of molybdate complex formation appears to be associative. Ligand geometry and protonation have important parts to play in binding and in oxygen loss. Either process—bond formation or oxygen elimination—may be rate limiting.

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(22) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, pp 646-650.

(23) D. S. Honig and K. Kustin, unpublished results; see also ref 9b.