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Mechanism of Molybdenum(VI) Complex Formation. Reactions of Molybdate with 1,2-Dihydroxyanthraquinone-3-sulfonate and Nitrilotriacetate

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Equilibria and kinetics of the reactions of molybdate(VI) with 1,2-dihydroxyanthraquinone-3-sulfonate (Has^{2-}) and nitrilotriacetate ($Hnta^{2-}$) have been studied spectrophotometrically in aqueous solution of pH 6–8 at $I = 1.00$ M ($NaClO_4$) and 25 °C. The formation constants of molybdate complexes were determined to be $[MoO_2(OH)_2(as)^{3-}]/([MoO_4^{2-}]\cdot[as^{3-}][H^+]^2) = 10^{20.57\pm0.05}$ M^{-3} and $[MoO_3(nta)^{3-}]/([MoO_4^{2-}][nta^{3-}][H^+]^2) = 10^{18.09\pm0.04}$ M^{-3} ($\Delta H = -79 \pm 2$ kJ mol^{-1} and $\Delta S = 81 \pm 5$ J mol^{-1} K^{-1}). The rate law is expressed in the form: rate $= k_f[MoO_4^{2-}][HX^{2-}][H^+] - k_d[Mo\text{–}X]$ (X $= as^{3-}$ or nta^{3-}), where k_f and k_d were $(1.49 \pm 0.08) \times 10^{10}$ M^{-2} s^{-1} and 0.9 s^{-1} for Has^{2-} and 2.3×10^6 M^{-2} s^{-1} ($\Delta H^\ddagger = 33 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -12 \pm 10$ J mol^{-1} K^{-1}) and 1.8×10^{-3} s^{-1} ($\Delta H^\ddagger = 85 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -12 \pm 10$ J mol^{-1} K^{-1}) for $Hnta^{2-}$, respectively. On the basis of these and the earlier results, we propose a reaction mechanism for these reactions.

Introduction

It is now recognized that the molybdenum found in enzymes in microorganisms, plants, and animals plays an important biochemical role.[1] As a result, interest in coordinated molybdenum has increased recently. The kinetics and mechanism of complex formation between molybdate and chelating ligands have been reported.[2-6] However, because of overlapping protolytic equilibria leading to kinetically indistinguishable paths, no definite conclusion was drawn as to the mechanism of complex formation.

The equilibria of molybdenum(VI) in aqueous solution are complex, and various polynuclear species in addition to the monomeric species MoO_4^{2-}, $HMoO_4^-$, and H_2MoO_4 may exist in acidified molybdate solutions.[7,8] The change of coordination number of molybdenum(VI) in monomeric molybdic acid has been discussed. Honig and Kustin[9] pointed out an increase in the coordination number of Mo(VI) from 4 to 6 in the first step of the protonation of the molybdate ion. Their conclusion was based on slower recombination of H^+ with MoO_4^{2-} than expected for a diffusion-controlled reaction. On the other hand, from consideration of thermodynamic parameters for protonation of molybdate, Cruywagen and Rohwer[10] have suggested that only in the presence of a second proton are six-coordinate molybdate species to be expected. One of our purposes is to investigate the effect of coordination number change on molybdenum complex formation rates.

In the present paper, we used AS[11] and NTA[11] as chelating ligands in order to avoid proton ambiguities in rate laws. We investigated the kinetics of molybdate complex formation over a pH range where both molybdate and ligands exist as only one species stoichiometrically. In accord with the present and earlier results, a reaction mechanism has been proposed. Thermodynamic and kinetic parameters for the Mo(VI)–NTA complex formation have been determined which appears to be the first for molybdate complex formation.

Experimental Section

Reagents. Sodium Alizarinsulfonate. Sodium 1,2-dihydroxyanthraquinone-3-sulfonate hydrate ($C_{14}H_7O_7SNa\cdot H_2O$) (Wakojunyaku Co.) was recrystallized three times from 50% ethanol and then dried at 70 °C under reduced pressure.

Sodium Molybdate. Reagent grade sodium molybdate ($Na_2MoO_4\cdot H_2O$) was recrystallized three times from distilled water and then dried in an air oven at 60 °C. Determination of the molybdate solution was carried out by gravimetry with α-benzoin oxime.[12]

Nitrilotriacetic Acid. NTA (Wakojunyaku) was recrystallized twice from distilled water and then dried in an air oven at 120 °C.

Mo(VI)–NTA Complex. The crystals were prepared according to the directions of Butcher and Penfold.[13] The analysis indicated that the complex was isolated as $K_3[MoO_3(nta)]\cdot H_2O$. Anal. Calcd for $C_6H_8K_3MoNO_{10}$: C, 15.42; H, 1.73; N, 3.00. Found: C, 15.39; H, 1.78; N, 2.93.

MES Buffer. MES (2-(*N*-morpholino)ethanesulfonic acid) (Wakojunyaku) was purified by recrystallization and used as a pH buffer in kinetic studies of the Mo(VI)–AS system.

Solutions of sodium perchlorate and sodium hydroxide were prepared as described previously.[14a] Perchloric acid of special purity (Wakojunyaku) was used without further purification.

Measurements. All measurements were made in a thermostated room. Temperature of the reaction solution was controlled to within ±0.1 °C by using a thermoelectric circulating bath. Ionic strength was maintained at 1.00 M with sodium perchlorate. Spectra were recorded on a highly sensitive spectrophotometer (Type SM401, Union Giken Co., Osaka, Japan) to characterize species spectrally. Hydrogen ion concentration was determined by using a pH meter (Orion Research pH meter 701A or Corning pH meter 130). A 1.000×10^{-2} M perchloric acid solution at an ionic strength of 1.00 M (Na, $HClO_4$) was employed as a standard for hydrogen ion concentration.

The protonation constants of alizarinsulfonate and the formation constant of the Mo(VI)–AS complex were determined by measuring the absorbance at various hydrogen ion concentrations at 25 °C. The formation constants of the Mo(VI)–NTA complex were determined potentiometrically by titrating about 10^{-2} M complex solutions prepared by dissolving $K_3[MoO_3(nta)]\cdot H_2O$ crystals with ca. 1 M sodium hydroxide solution with use of a piston buret (Metrohm, Switzerland).

Formation of the Mo(VI)–NTA complex was followed by recording the spectra or absorbance at some wavelengths as a function of reaction time after starting the reaction by conventional mixing of a molybdate solution and an excess of NTA solution.

For the formation of the Mo(VI)–AS complex, kinetic experiments were carried out with the use of a coaxial cable temperature-jump apparatus (Union Giken RA1200). A discharge of 25 kV from a 0.05 μF condenser corresponding to an increase in temperature of 3 ± 0.5

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(11) Ligand abbreviations: AS, 1,2-dihydroxyanthraquinone-3-sulfonic acid (alizarinsulfonic acid) (H_3as); NTA, nitrilotriacetic acid (H_3nta); IDA, iminodiacetic acid; EDTA, ethylenediamine-*N,N,N',N'*-tetraacetic acid.
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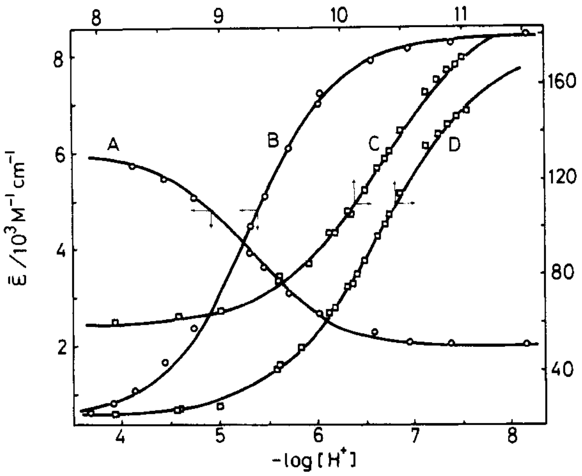

Figure 1. Plots of $\bar{\epsilon}$ against $-\log [H^+]$ [$C_{AS} = 4.98 \times 10^{-5}$ M; I = 1.00 M ($NaClO_4$); 25 °C]: A, 417 nm; B, 508 nm; C, 550 nm; D, 590 nm. The curves are calculated with protonation constants obtained.

°C was used in all experiments. Absorption curves for reactions were stored in a transient recorder (SM-540, Union Giken) and displayed on an X-Y recorder. The curve was monitored with a synchroscope (V-018 Memoriscope, Hitachi, Tokyo, Japan). Mostly the reactions were followed at 495 nm, the wavelength of the maximum absorption for the Mo(VI)–AS complex. The kinetic runs were carried out under pseudo-first-order conditions, i.e., with a large excess of molybdate anion over AS.

Results

Determination of Protonation Constants of Alizarinsulfonate. The protolytic equilibria for alizarinsulfonate are

$$as^{3-} + H^+ \rightleftharpoons Has^{2-} \quad K_1 \tag{1}$$

$$Has^{2-} + H^+ \rightleftharpoons H_2as^- \quad K_2 \tag{2}$$

where H_2as^- is 1,2-dihydroxyanthraquinone-3-sulfonate anion. Visible absorption spectra of AS solutions with various hydrogen ion concentrations have distinct isosbestic points at 365 and 446 nm below pH 8 and at 504 nm above pH 8. An apparent molar absorption coefficient $\bar{\epsilon}$ of AS is given by eq 3, where A, C_{AS}, ϵ_2, ϵ_1, and ϵ_0 are

$$\bar{\epsilon} = \frac{A}{C_{AS}} = \frac{K_1K_2\epsilon_2[H^+]^2 + K_1\epsilon_1[H^+] + \epsilon_0}{K_1K_2[H^+]^2 + K_1[H^+] + 1} \tag{3}$$

absorbance of the system, the total concentration of AS, and molar absorption coefficients of H_2as^-, Has^{2-}, and as^{3-}, respectively. Since as^{3-} and Has^{2-} species are predominant at pH's higher than 8, eq 3 is reduced to $\bar{\epsilon} = (K_1\epsilon_1[H^+] + \epsilon_0)/(K_1[H^+] + 1) = \epsilon_1 + (\epsilon_0 - \epsilon_1)/(K_1[H^+] + 1)$. Over the pH range lower than 8, Has^{2-} and H_2as^- prevail. Then eq 3 becomes $\bar{\epsilon} = (K_2\epsilon_2[H^+] + \epsilon_1)/(K_2[H^+] + 1) = \epsilon_2 + (\epsilon_1 - \epsilon_2)/(K_2[H^+] + 1)$. We now determine the protonation constants by the curve-fitting method in the two separate pH ranges. The plots of $\bar{\epsilon}$ against $-\log [H^+]$ (Figure 1) are compared with a normalized function: $Y = p/(X + 1) = f(-\log X)$.[14b] The plot fits well one of a family of the normalized curves (Figure 1). The values of $\log K_1$ and $\log K_2$ at 25 °C and I = 1.00 M were determined to be 10.32 ± 0.02 and 5.32 ± 0.02, respectively. These values compare favorably with the literature values.[15]

Equilibrium between Molybdate and Alizarinsulfonate. Results have shown that the equilibrium between molybdate and AS under the experimental conditions should be written as

$$MoO_4^{2-} + Has^{2-} + H^+ \rightleftharpoons MoO_2(OH)_2(as)^{3-} \quad K' \tag{4}$$

An apparent molar absorption coefficient of AS ($\bar{\epsilon}$) is given as

$$\bar{\epsilon} = \frac{A}{C_{AS}} = \frac{\epsilon_{Has} + \epsilon_c K'[MoO_4^{2-}][H^+]}{1 + K'[MoO_4^{2-}][H^+]} \tag{5}$$

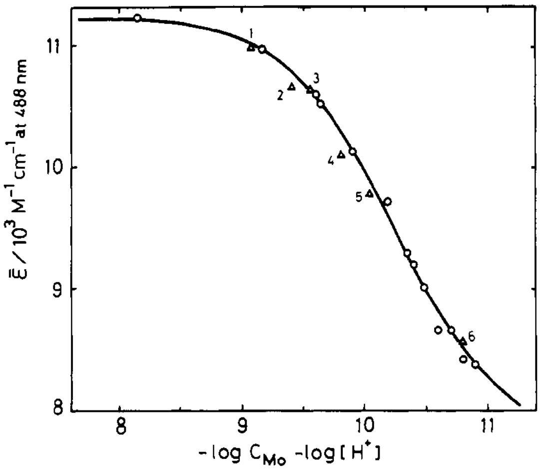

Figure 2. Plots of $\bar{\epsilon}$ against $-\log C_{Mo}[H^+]$ (25 °C; I = 1.00 M ($NaClO_4$); $-\log [H^+]$ = 7.2–7.4): ○, $C_{AS} = 4.25 \times 10^{-5}$ M, $C_{Mo} = 6.40 \times 10^{-3}$ M; △, $C_{AS} = 3.19 \times 10^{-5}$ M, $C_{NH_3} = 1.09 \times 10^{-2}$ M. C_{Mo}: 1, 1.82×10^{-2} M; 2, 10^{-2} M; 3, 6.00×10^{-3} M; 4, 4.00×10^{-3} M; 5, 2.00×10^{-3} M; 6, 3.20×10^{-4} M. The curve is calculated with the formation constant obtained.

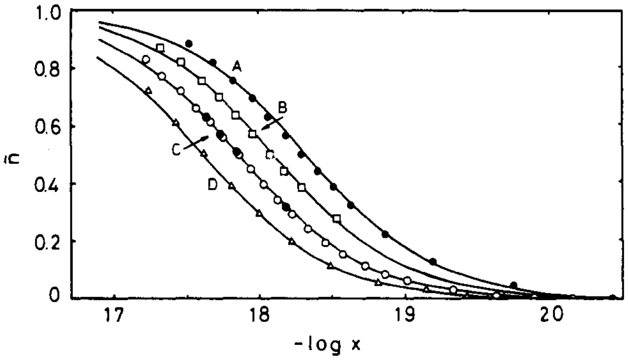

Figure 3. Plots of $\bar{n}$ against $\log x$ [$C_{Mo-NTA} = 10^{-2}$ M, I = 1.00 M ($NaClO_4$)]: A, 20 °C; B, 25 °C; C, 30 °C; D, 35 °C; ● at 30 °C (data points for back-titration). The curves are calculated with formation constants obtained.

where A, C_{AS}, ϵ_{Has}, and ϵ_c are absorbance of the system, the total concentration of AS, and molar absorption coefficients of Has^{2-} and $MoO_2(OH)_2(as)^{3-}$, respectively. In the present case where $C_{Mo} >> C_{AS}$, we have $[MoO_4^{2-}] \simeq C_{Mo}$, and then

$$\bar{\epsilon} = \epsilon_c + \frac{\epsilon_{Has} - \epsilon_c}{1 + K'C_{Mo}[H^+]} \tag{6}$$

The plot of $\bar{\epsilon}$ against $-\log C_{Mo} - \log [H^+]$ is given in Figure 2. We obtain the value $K' = (1.8 \pm 0.8) \times 10^{10}$ M^{-2} by comparison of the plot with a normalized function: $Y = p/(1 + X) = f(-\log X)$.[14b] With $\log K_1 = 10.32$, we have $K = [MoO_2(OH)_2(as)^{3-}]/([MoO_4^{2-}] \cdot [as^{3-}][H^+]^2) = 10^{20.57 \pm 0.05}$ M^{-3} at 25 °C and I = 1.00 M. As apparent from Figure 2, the formation constant K is not affected by variation of molybdate concentrations and the presence of ammonium ion. Thus the system involves no polynuclear species.

Equilibrium between Molybdate and NTA. The equilibria and equations of (7)–(11) were considered in the Mo(VI)–NTA system

$$MoO_4^{2-} + nta^{3-} + 2H^+ \rightleftharpoons MoO_3(nta)^{3-} + H_2O \quad K_f \tag{7}$$

$$nta^{3-} + H^+ \rightleftharpoons Hnta^{2+} \quad K_{Hnta} \tag{8}$$

$$C_H = 2[MoO_3(nta)^{3-}] + [Hnta^{2-}] + [H^+] - [OH^-] \tag{9}$$

$$C_{NTA} = [MoO_3(nta)^{3-}] + [nta^{3-}] + [Hnta^{2-}] \tag{10}$$

$$C_{Mo} = [MoO_3(nta)^{3-}] + [MoO_4^{2-}] \tag{11}$$

under our experimental conditions. Combining these expressions, one

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[15] Zittel, H. E.; Florence, T. M. *Anal. Chem.* **1967**, *39*, 320: $\log K_1$ = 10.85 ± 0.03 and $\log K_2$ = 5.49 ± 0.01 at 25 °C and I = 0.5 M.

obtains eq 12 where $x = [\mathrm{nta}^{3-}][\mathrm{H}^+]^2$ and $[\mathrm{nta}^{3-}] = ([\mathrm{H}^+] - C_\mathrm{H} + 2C_\mathrm{NTA} - [\mathrm{OH}^-])(2 + K_\mathrm{Hnta}[\mathrm{H}^+])^{-1}$.

$$\bar{n} = \frac{[\mathrm{MoO_3(nta)}^{3-}]}{[\mathrm{MoO_3(nta)}^{3-}] + [\mathrm{MoO_4}^{2-}]} = \frac{C_\mathrm{NTA} - [\mathrm{nta}^{3-}](1 + K_\mathrm{Hnta}[\mathrm{H}^+])}{C_\mathrm{Mo}} = \frac{K_\mathrm{f}x}{K_\mathrm{f}x + 1} \quad (12)$$

The plots of $\bar{n}$ vs. log x are shown in Figure 3. By a curve-fitting method, in which we compared the plot with the normalized function $Y = 1/(1 + X^{-1}) = \mathrm{f}(-\log X)$, the values of log K_f were determined to be 18.30 ± 0.03 at 20 °C, 18.09 ± 0.04 at 25 °C, 17.86 ± 0.02 at 30 °C, and 17.61 ± 0.04 at 35 °C. ΔH and ΔS for K_f were estimated to be −79 ± 2 kJ mol^{-1} and 81 ± 5 J mol^{-1} K^{-1}, respectively.

Reaction of Molybdate with Alizarinsulfonate. Under our experimental conditions the reaction system is expressed as in eq 13.

$$\mathrm{MoO_4}^{2-} + \mathrm{Has}^{3-} \underset{k_\mathrm{d}}{\overset{k_\mathrm{f}'}{\rightleftharpoons}} \mathrm{MoO_2(OH)_2(as)}^{3-} \quad (13)$$

The experimentally determined relaxation time τ for the reaction of molybdate with AS is summarized in Table I. Each value is the mean of 4–5 individual measurements. At a given pH the dependence of τ on the molybdate concentration is of the form

$$\tau^{-1} = k_\mathrm{f}'C_\mathrm{Mo} + k_\mathrm{d} \quad (14)$$

The variations of k_f' with hydrogen ion concentration are given in Table II. k_f' is linear in hydrogen ion concentration: $k_\mathrm{f}' = k_\mathrm{f}[\mathrm{H}^+]$ with $k_\mathrm{f} = (1.49 \pm 0.08) \times 10^{10}$ M^{-2} s^{-1} at 25 °C and I = 1.00 M. The contribution of k_d to relaxation is small, and the value of k_d is not accurate. The value of k_d is independent of hydrogen ion concentration and estimated to be $\lesssim 5$ s^{-1}, which agrees with that of 0.9 s^{-1} expected from the formation constant of the Mo(VI)–AS complex within experimental errors.

Reaction of Molybdate with NTA. The reaction of molybdate ion with a large excess of NTA was followed spectrophotometrically at 250 nm. The slope of the plot of ln $(A_\infty - A_t)/(A_\infty - A_0)$ against t gives the conditional first-order rate constant k_0. Values of k_0 under various conditions are summarized in Table III. The plot of k_0 at constant NTA concentration vs. hydrogen ion concentration yields a straight line with an intercept (Figure 4). The slope was proportional to C_NTA. Then the rate law for the molybdate complex formation is expressed as eq 15, and we have the relation $K_\mathrm{f}/K_\mathrm{Hnta} = k_\mathrm{f}/k_\mathrm{d}$.

$$\frac{\mathrm{d}[\mathrm{MoO_3(nta)}^{3-}]}{\mathrm{d}t} = k_\mathrm{f}[\mathrm{MoO_4}^{2-}][\mathrm{Hnta}^{2-}][\mathrm{H}^+] - k_\mathrm{d}[\mathrm{MoO_3(nta)}^{3-}] \quad (15)$$

Values of k_f and k_d were determined by the least-squares method by fixing the ratio $k_\mathrm{f}/k_\mathrm{d}$ at $K_\mathrm{f}/K_\mathrm{Hnta}$. Rate constants k_f and k_d at various temperatures and corresponding activation parameters are tabulated in Table IV.

Discussion

The molybdate anion $\mathrm{MoO_4}^{2-}$ maintains a tetrahedral configuration in neutral and alkaline solutions.[7] Complexes of molybdate with chelating ligands have an octahedral configuration. The complex formation therefore will have to occur by an addition of the ligand to the molybdate ion, thereby increasing its coordination number from 4 to 6. First- and second-protonation constants for $\mathrm{MoO_4}^{2-}$ ($K_{1(\mathrm{Mo})} = 2.95 \times 10^3$ M^{-1}, $K_{2(\mathrm{Mo})} = 5.50 \times 10^3$ M^{-1} at 25 °C and I = 1.0 M (NaCl))[10] are the reverse of the normally expected trend. It has been postulated that the monoprotonated species $\mathrm{HMoO_4}^-$ exists in the form of an octahedral hydrate species in solution. From consideration of thermodynamic parameters for protonation of molybdate, Cruywagen and Rohwer[10] have suggested that it is the second-protonation constant which is anomalous and that the change in coordination number occurs with addition of the second proton. Whichever of these viewpoints is correct, the diprotonated species $\mathrm{H_2MoO_4}$ should be octahedral.

Table I. Relaxation Time for Formation of the 1:1 Mo(VI)–AS Complex[a]

−log [H$^+$]	10^2C_Mo/M	τ/s	−log [H$^+$]	10^2C_Mo/M	τ/s
7.40	3.02	0.048	7.92	3.02	0.14
7.41	6.05	0.024	7.92	6.05	0.070
7.42	9.07	0.017	7.94	9.07	0.049
7.74	3.02	0.088	8.02	3.02	0.14
7.75	6.05	0.053	8.06	6.05	0.084
7.76	9.07	0.036	8.06	9.07	0.059

[a] At 25.0 ± 0.5 °C, ionic strength 1.00 M (NaClO$_4$), $C_\mathrm{AS} = 2.80 \times 10^{-4}$ M, and $C_\mathrm{MES} = 10^{-2}$ M.

Table II. Variations of k_f' and k_d with Hydrogen Ion Concentration

10^8[H$^+$]/M	k_f'/M^{-1} s^{-1}	k_d/s^{-1}
3.9	630 ± 60	2 ± 2
1.8	290 ± 30	2 ± 1
1.2	220 ± 20	2 ± 1
0.89	160 ± 10	1 ± 1

Table III. Conditional First-Order Rate Constants for Formation of the Mo(VI)–NTA Complex at Various Hydrogen Ion Concentrations[a]

−log [H$^+$] (±0.01)	10^3k_0/s^{-1}	−log [H$^+$] (±0.01)	10^3k_0/s^{-1}
	15.0 ± 0.1 °C		
6.43	3.4 ± 0.3	6.66	2.0 ± 0.1
6.54	2.3 ± 0.2	6.97	0.76 ± 0.08
6.59	2.5 ± 0.2	7.02	1.1 ± 0.1
	20.0 ± 0.1 °C		
6.29	6.0 ± 0.5	6.53	4.2 ± 0.4
6.31	5.2 ± 0.5	6.56	4.1 ± 0.3
6.43	5.5 ± 1.0	6.87	2.4 ± 0.1
6.50	4.0 ± 0.4		
	25.0 ± 0.1 °C		
6.11	11 ± 1	6.55	4.5 ± 0.3
6.12	10 ± 1	6.79	3.3 ± 0.3
6.25	8.0 ± 0.2	6.81	3.0 ± 0.2
6.27	9.0 ± 0.5	6.90	3.1 ± 0.3
6.30	7.9 ± 0.5	7.07	2.7 ± 0.1
6.30	7.4 ± 0.3		
	30.0 ± 0.1 °C		
6.28	13 ± 1	6.67	6.2 ± 0.5
6.28	11 ± 2	6.79	4.6 ± 0.5
6.31	11 ± 1	6.84	5.6 ± 0.2
6.32	10 ± 1	6.91	4.0 ± 0.5
6.33	11 ± 1		

[a] I = 1.00 M (NaClO$_4$); $C_\mathrm{NTA} = 4.97 \times 10^{-3}$ M; $C_\mathrm{Mo} = 6.62 \times 10^{-5}$ M; $C_\mathrm{NH_4Cl} = 3.96 \times 10^{-2}$ M.

Table IV. Rate Constants and Activation Parameters for the Mo(VI)–NTA Complex Formation[a]

temp/°C	$10^{-6}k_\mathrm{f}$/M^{-2} s^{-1}	10^3k_d/s^{-1}
15	1.5	0.55
20	2.0	1.1
25	2.3	1.8
30	3.0	3.4

[a] $\Delta H^\ddagger$ (kJ mol^{-1}): k_f, 33 ± 4; k_d, 85 ± 4. $\Delta S^\ddagger$ (J mol^{-1} K^{-1}): k_f, −12 ± 10; k_d, −12 ± 10.

Formation constants of 1:1 molybdate complexes with IDA,[11] NTA, and EDTA[11] are of the same order of magnitude,[16] and these complexes have analogous structures. The three coordination sites of the central metal coordinating unit $\mathrm{MoO_3}$ are occupied by one nitrogen and two acetate oxygen atoms of ligands. This was confirmed, at least in the solid state, by the crystal structure of $\mathrm{K_3MoO_3(nta)\cdot H_2O}$.[13] Pro-

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Table V. Kinetic Data for Molybdate Complex Formation[a]

no.	X	log (k_f/M^{-2} s^{-1})	k_d/s^{-1}	log (K_{HX}/M^{-1})	pH range, ionic strength	ref
1	Hox^{b}	10.65	1.95	4.96	7.92-8.91, 0.2 M ($NaClO_4$)	2
2	ox^-	12.18		9.57	c	2
3	$Hoxs^{-\,d}$	10.59	0.85	3.89	7.50-8.50, 0.2 M ($NaNO_3$)	3
4	oxs^{2-}	11.60		8.21	c	3
5	$Hcat^{-\,e}$	12.0	7.76	9.54	7.30-7.80, 0.1 M (KNO_3)	4
6	$H_2edta^{2-\,f}$	9.35	7.59	2.0	7.25-8.49, 0.1 M ($NaNO_3$)	5
7	$Hthb^{2-\,g}$	13.72		11.82	7.3-9.0, 0.5 M (NH_4Cl)	6
8	H_2thb^-	11.82		9.08	c	6
9	$Hpg^{2-\,h}$	13.54		11.43	c	6
10	H_2pg^-	12.32		9.28	c	6
11	$Hep^{3-\,i}$	12.58		10.0	7.3-8.3, 0.5 M (NH_4Cl)	6
12	H_2ep^{2-}	11.56		8.7	c	6
13	$Hdopa^{3-\,j}$	12.32		9.8	7.3-9.0, 0.5 M (NH_4Cl)	6
14	H_2dopa^{2-}	11.61		8.8	c	6
15	$H_2ga^{2-\,k}$	12.01		8.38	7.3-8.3, 0.5 M (NH_4Cl)	6
16	$Co(NH_3)_5(OH)^{2+}$	8.37		6.39	7.1-8.0, 1.0 M ($NaClO_4$)	20
17	Has^{2-}	10.17	0.9	5.32	7.4-8.1, 1.0 M ($NaClO_4$)	this work
18	$Hnta^{2-}$	6.36	1.8×10^{-3}	2.41	6.1-7.0, 1.0 M ($NaClO_4$)	this work

[a] Rate law = $k_f[MoO_4^{2-}][H^+][X]$ at 25 °C. [b] Hox is 8-hydroxyquinoline (oxine). [c] Same conditions as above. [d] H_2oxs is 8-hydroxyquinoline-5-sulfonic acid. [e] H_2cat is catechol. [f] H_4edta is ethylenediamine-*N,N,N′,N′*-tetraacetic acid. [g] H_3thb is 1,2,4-trihydroxybenzene. [h] H_3pg is 1,2,3-trihydroxybenzene (pyrogallol). [i] H_4ep is (3,4-dihydroxyphenyl)-2-(methylamino)ethanol (L-epinephrine). [j] H_4dopa is (3,4-dihydroxyphenyl)alanine. [k] H_4ga is 3,4,5-trihydroxybenzoic acid (gallic acid).

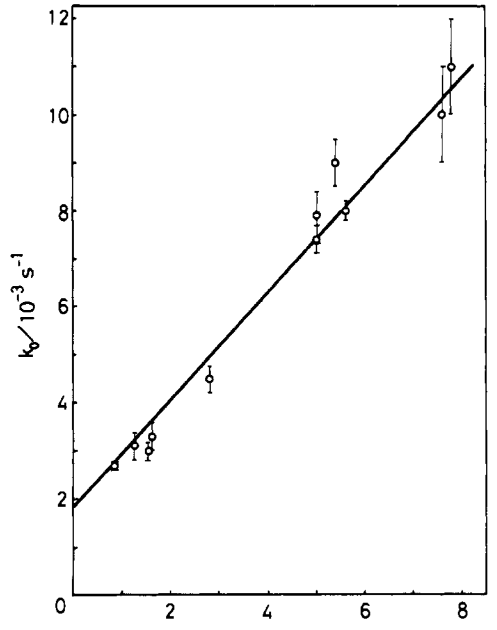

Figure 4. Hydrogen ion dependence of k_0 for the reaction of molybdate anion with NTA at 25 °C and I = 1.00 M ($NaClO_4$): $C_{NTA} = 4.97 \times 10^{-3}$ M, $C_{Mo} = 6.62 \times 10^{-5}$ M, $C_{NH_4Cl} = 3.96 \times 10^{-2}$ M, and $C_{NH_3} = (2\text{-}9) \times 10^{-4}$ M.

tonation of the nonbonded group was not observed potentiometrically under our experimental conditions. Thermodynamic parameters obtained for the Mo-NTA complex appear to be the first for molybdate complex formation. If we accept the thermodynamic parameters for the first and second protonation of molybdate (ΔH_1 = 22.5 kJ mol^{-1}, ΔS_1 = 143 J mol^{-1} K^{-1}; ΔH_2 = −46.5 kJ mol^{-1}, ΔS_2 = −85 J mol^{-1} K^{-1}),[10] the parameters for the reaction $H_2MoO_4 + nta^{3-}$ are ΔH = −55 kJ mol^{-1} and ΔS = 23 J mol^{-1} K^{-1}.

Comparison of the rate constants obtained for various systems of molybdate complex formation is not straightforward, owing to various protonated forms of the reactants. Ambiguities arise in the interpretation of the data because of the presence of two or more kinetically indistinguishable paths. As described above, the present systems were investigated over a pH range where both molybdate and ligands exist as only one species stoichiometrically. The rate law obtained shows the first-order dependence with respect to hydrogen ion concentration. All of the rate laws now available on the kinetics of molybdate complex formation can be represented in the form of eq 16 where X denotes a ligand. The available values of k_f are presented in Table V.

$$\text{rate} = k_f[MoO_4^{2-}][H^+][X] \qquad (16)$$

If we attribute the proton dependence to the ligand protonation, reactivities of Has^{2-} and $Hnta^{2-}$ are, at least, 3 and 5 orders of magnitude, respectively, lower than those of H_2as^- and H_2nta^- (protonated Has^{2-} and $Hnta^{2-}$). This is quite unreasonable. On the other hand, if the proton dependence is attributed to the protonation of molybdate prior to the rate-determining step, the activation parameters for the reaction of $HMoO_4^-$ with $Hnta^{2-}$ are estimated to be $\Delta H^{\ddagger}$ = 10.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −155 J mol^{-1} K^{-1} with knowledge of thermodynamic quantities for the first protonation of molybdate ion.[10] This $\Delta H^{\ddagger}$ of 10.5 kJ mol^{-1} is comparable to activation energy for a diffusion-controlled reaction. Since the rate constants for other reaction systems listed in Table V are larger than that of NTA, $\Delta H^{\ddagger}$ values tend to be smaller than activation energy for diffusion-controlled reactions. This seems unrealistic. Thus the proton dependence attributed to molybdate is also not acceptable.

We propose the nucleophilic attack by the entering ligand at a face of the tetrahedron of molybdate as a monodentate ligand to form an intermediate with a weak bond between the metal and the ligand. Addition of a proton to oxo groups of the intermediate would lengthen the metal-oxygen bond and strengthen the Mo-ligand bond, thereby lowering the activation energy required to form an activated complex with increased coordination number. The rate limiting step may involve both processes—bond formation and configuration change.

Recently in the reaction of hydrogen peroxide with the octahedral $VO_2(nta)^{2-}$ complex to produce the pentagonal-bipyramidal $VO(O_2)(nta)^{2-}$ complex,[17] the first-order proton dependence is accounted for by a mechanism involving protonation to the oxo group in the activated complex, a process which is believed to facilitate association and rearrangement processes. This mechanism is similar to that proposed for molybdate complex formation.

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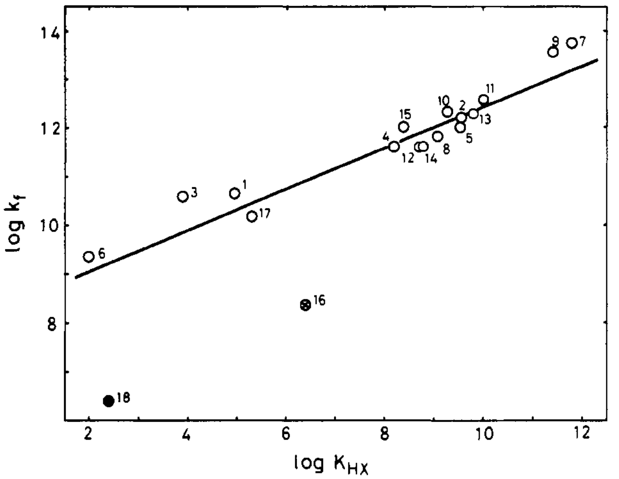

Figure 5. Relationship between log k_f and log K_{HX}. For the numbers, Table V should be referred to.

The present data can usefully be compared with the results of other kinetic studies of molybdate(VI) complexation in weakly basic solution. The plot of log k_f against log K_{HX} is shown in Figure 5, where K_{HX} is a constant for protonation to a ligand X given by eq 16. Points lie nearly along a straight line, except for NTA and $Co(NH_3)_5(OH)^{2+}$ systems (vide infra). This fact clearly indicates that the rate constants depend on the nature of the ligand involved. Greater reactivity of more basic ligands would then be due to stronger bonding of more nucleophilic ligands.[18] Furthermore, for the ^{18}O-exchange reaction between MoO_4^{2-} and water,[19] rate = $(k_0 + k_1[OH^-])[MoO_4^{2-}]$ was obtained with $k_0 = 0.33$ s^{-1} ($\Delta H_0^{\ddagger} = 62.8$ kJ mol^{-1}, $\Delta S_0^{\ddagger} = -43.5$ J mol^{-1} K^{-1}) and $k_1 = 2.22$ M^{-1} s^{-1} ($\Delta H_1^{\ddagger} = 70.3$ kJ mol^{-1}, $\Delta S_1^{\ddagger} = -2.5$ J mol^{-1} K^{-1}). These activation energies are much higher than that for Mo–NTA complex formation. Therefore, the mechanism of molybdate complex formation appears to be associative and a proton plays an important role in binding and in rearrangement.

It should be noticed that the product $Co(NH_3)_5MoO_4^+$ of the reaction of MoO_4^{2-} with $Co(NH_3)_5(H_2O)^{3+}$ contains tetrahedrally coordinated molybdate(VI), in which there is retention of tetrahedral geometry.[20] k_f for $Co(NH_3)_5(OH)^{2+}$ is much smaller than those observed for addition of ligands to tetrahedral molybdate(VI) to give products of increased coordination number (see Figure 5). The reaction of $Co(NH_3)_5(H_2O)^{3+}$ with MoO_4^{2-} is not the same as the coordination of other ligands to MoO_4^{2-} and can be viewed as the coordination of MoO_4^{2-} to $Co(NH_3)_5(H_2O)^{3+}$. This may explain why k_f for $Co(NH_3)_5(OH)^{2+}$ is exceptional in the correlation given in Figure 5.

There is an example of complex formation with retention of tetrahedral geometry. In the formation of a chromium(VI)–substrate complex formed by reaction of tetrahedral chromate anion with various substrates, the rate law is expressed in the form[21] $k_f^H[HCrO_4^-][H^+][X]$, which is the same as for molybdate systems. The chromium(VI) complexes retain tetrahedral geometry. In contrast with molybdate systems, all rate constants determined for such reactions have values in the range 10^5–7×10^5 M^{-2} s^{-1}. It has been pointed that independence of k_f^H to the nature of incoming ligands invokes the loss of a water molecule from chromic acid after the weak addition of a substrate X to the chromium center as the most important feature of the activation process.[21]

The available rate constants for dissociation of molybdate complexes are listed in Table V. It should be noted that there is a very large difference in reactivity for both formation and dissociation of molybdenum complexes of NTA and EDTA, although formation constants of these complexes are nearly identical. According to results obtained by ^1H NMR, with the exception of the Mo(VI)–NTA complex, all the molybdenum(VI)–aminopolycarboxylate complexes display AB splitting in the resonance due to the methyl proton, whereas the singlet is observed in the ^1H NMR spectrum of $MoO_3(nta)^{3-}$.[22] Recently, elegant studies of Miller and Wentworth[23] have clearly indicated that the unbound glycinate arm of the NTA ligand in Mo(VI)–NTA exchanges rapidly with the bound arms at room temperature through dissociation of the Mo–N bond followed by coordination of the previously unbound acetate group. Therefore the exceptional behavior of the NTA complex may be due to the competition between chelating group-metal bond rupture and new bond formation. The dissociating iminodiacetate segment of the EDTA complex is not available for intramolecular interaction. It is also interesting to point out that rates of dissociation are independent of hydrogen ion concentrations and that there is not so much difference in dissociation rate constants (from 0.85 to 7.76 s^{-1}) apart from NTA in comparison with a large difference in formation rate constants. We feel this suggests that water molecules play an important role in dissociation. The negative activation entropy for dissociation of the Mo(VI)–NTA complex may reflect a solvent-assisted dissociation.

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Registry No. MoO_4^{2-}, 14259-85-9; Has^{2-}, 76756-36-0; $Hnta^{2-}$, 75203-70-2; $MoO_2(OH)_2(as)^{3-}$, 76757-54-5; $K_3[MoO_3(nta)]$, 76757-55-6.

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[18] Gilbert and Kustin[6] have pointed out a relationship of the rate and ligand basicity from investigation of kinetics of molybdate complex formation with catechol derivatives. "If the oxyanion is protonated the most basic ligand is most reactive. If the oxyanion is unprotonated, the least basic ligand is most reactive."

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