Contribution from the Department of Chemistry,
University of the Orange Free State, Bloemfontein, Republic of South Africa

Kinetic Study of the Reaction between *trans*-Dioxotetracyanomolybdate(IV) Ions and 1,10-Phenanthroline

Johann G. Leipoldt,* Stephen S. Basson, Izak M. Potgieter, and Andreas Roodt

Received March 27, 1986

The reaction between the protonated species of *trans*-dioxotetracyanomolybdate(IV) and 1,10-phenanthroline has been studied at $\mu = 0.1$ M from pH 8.5 to 12.5. The rate-determining step is the substitution of the aqua and hydroxo ligands in $[MoO(H_2O)(CN)_4]^{2-}$ and $[MoO(OH)(CN)_4]^{3-}$, respectively. This is followed by the fast closing of the chelate ring, which is accompanied by the substitution of a cyanide ligand. The hydroxo form is the more reactive species. The different rate constants have been determined. A dissociative activation is proposed.

Introduction

It is well-known that *trans*-dioxotetracyanomolybdate(IV) ions can be protonated to form the oxo hydroxo and oxo aqua complexes. These stepwise protonation reactions may be represented by

$$[MoO_2(CN)_4]^{4-} + H^+ \rightleftharpoons [MoO(OH)(CN)_4]^{3-} \quad (1)$$

$$[MoO(OH)(CN)_4]^{3-} + H^+ \rightleftharpoons [MoO(H_2O)(CN)_4]^{2-} \quad (2)$$

The different protonated species were also structurally characterized by means of crystal structure determinations of $K_3Na[MoO_2(CN)_4]\cdot 6H_2O$,[1] $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$,[2] $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$,[2] and $(PPh_4)_2[MoO(H_2O)(CN)_4\cdot 4H_2O$.[3] The Mo═O bond distances in these complexes show an increase in double-bond character ranging from 1.834 (9) Å in the dioxo to 1.698 (7) Å in the oxo hydroxo and 1.668 (5) Å in the oxo aqua complex. This Mo═O bond shortening is accompanied by a large increase in the Mo—O bond length trans to it from the hydroxo to the aqua complex (Mo—OH = 2.077 (7) Å and Mo—OH_2 = 2.27–2.48 Å). Considering these long Mo–O bond distances, especially in the case of the aqua complex, we realized the possibility that these complexes may undergo substitution reactions. It was structurally proved that $[MoO(H_2O)(CN)_4]^{2-}$ reacted with the bidentate ligand phenanthroline with the substitution of the aqua ligand as well as one of the cyanide ligands.[4,5]

In order to determine which of the aqua or cyanide ligands are first substituted in such a stepwise process, we determined the crystal structure of $(AsPh_4)_2[WO(pic)(CN)_3]\cdot 2H_2O$ obtained during the reaction of $[WO(H_2O)(CN)_4]^{2-}$ with 2-picolinic acid (Hpic).[6] The results indicated that the aqua ligand was first substituted during the two-step reaction process. The crystal structure determination of $Cs_2Na[MoO(N_3)(CN)_4]$[7] indicated, in agreement with the above conclusion, that only the aqua ligand was substituted by the azide ion during the reaction with $[MoO(H_2O)(CN)_4]^{2-}$. It is against this background that we performed this kinetic study as these reactions were observed for the first time in our laboratory.

Experimental Section

$K_3Na[MoO_2(CN)_4]\cdot 6H_2O$ was prepared as described previously.[4] All measurements were done in a constant ionic strength medium of 0.1 M. This was achieved by using mixtures of 0.1 M $NaHCO_3$ and 0.033 M Na_2CO_3 as buffer solutions. The determination of the acidity constants of $[MoO(H_2O)(CN)_4]^{2-}$ was performed by spectrophotometric titrations with NaOH at $\lambda = 610$ nm. An Orion pH-meter, Model 701, was used for the pH measurements. All the absorption measurements were done on a Pye Unicam SP 1700 spectrophotometer equipped with a constant-temperature cell holder. The kinetics were studied under pseudo-first-order conditions. The pseudo-first-order rate constants were obtained from plots of log $(A_\infty - A)$ vs. time, where A is the absorbance at time t and A_∞ is the absorbance after about 10 half-lives. The plots of log $(A_\infty - A)$ vs. time were linear for at least 3 half-lives.

Table I. Molar Absorptivities of the Compounds Studied

complex ion	λ_{max}, nm	ϵ_{max}, $M^{-1}\,cm^{-1}$
$[MoO(H_2O)(CN)_4]^{2-}$	614	43
$[MoO(OH)(CN)_4]^{3-}$	600	44
$[MoO_2(CN)_4]^{4-}$	603	45
$[MoO(CN)_3(phen)]^-$	455	3800

Table II. Kinetic and Equilibrium Data at 25 °C and $\mu = 0.1$ M

k_1,[a] $M^{-1}\,s^{-1}$	$2.68\ (2) \times 10^{-1}$	pK_{a1}[e]	10.24 (7)
k_{-1},[a] s^{-1}	$4.8\ (2) \times 10^{-4}$	pK_{a1}[f]	10.36 (6)
$K\ (k_1/k_{-1})$,[b] M^{-1}	$5.6\ (3) \times 10^{2}$	pK_{a2}[f]	12.50 (6)
k_2,[c] $M^{-1}\,s^{-1}$	1.01 (3)	pK_{a1}[g]	10.9
k_{-2},[c] $M^{-1}\,s^{-1}$	1.09 (3)	pK_{a2}[g]	12.2
k_2,[d] $M^{-1}\,s^{-1}$	1.04 (4)	$\Delta S^*(k_1)$,[a] cal deg^{-1} mol^{-1}	4.1 (10)
k_{-2},[d] $M^{-1}\,s^{-1}$	1.05 (5)		
k_1,[e] $M^{-1}\,s^{-1}$	$1.9\ (3) \times 10^{-1}$	$\Delta H^*(k_1)$,[a] kcal mol^{-1}	19.5 (3)
k_2,[e] $M^{-1}\,s^{-1}$	1.1 (1)		
k_{-2},[e] $M^{-1}\,s^{-1}$	1.0 (2)		

[a] From data in Figure 3. [b] Overall stability constant. [c] From data in Figure 4. [d] From data in Figure 5. [e] From data in Figure 2. [f] From spectrophotometric titration. [g] Reference 2.

Results

All the compounds studied showed only one maximum in the 400–700-nm region. The wavelengths, λ_{max}, and the molar absorptivities at λ_{max} are reported in Table I. In the spectrophotometric determination of the stability constant of $[MoO(phen)(CN)_3]^-$ (phen = 1,10-phenanthroline) the concentration of the incoming ligand was varied from 0.001 to 0.009 M. The plot of absorbance vs. the concentration of the incoming ligand (Figure 1) revealed that under the experimental conditions $[MoO(H_2O)(CN)_4]^{2-}$ reacts with phenanthroline in a 1:1 ratio. This is in agreement with the results of the structure determination of $[MoO(phen)(CN)_3]^-$.[4,5]

When the pH was changed from 8 to 13 during the pH titration, there was a change in the absorbance between about pH 9 and 11 and again between pH 11 and 13. The data were treated as if there were two independent deprotonation steps. From Beer's law and the mass balance eq 3 can be derived, where A is the

$$A = \frac{A_b K_a + A_a[H^+]}{K_a + [H^+]} \quad (3)$$

absorbance at a particular $[H^+]$, A_b the absorbance of the deprotonated form, and A_a the absorbance of the protonated form. K_a is either K_{a1}, the acid dissociation constant of [MoO(H_2O)-

---

(1) Day, V. W.; Hoard, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 3374.
(2) Robinson, P. R.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1975**, *14*, 2035.
(3) Wieghardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44.
(4) Basson, S. S.; Leipoldt, J. G.; Potgieter, I. M. *Inorg. Chim. Acta* **1984**, *87*, 71.
(5) Basson, S. S.; Leipoldt, J. G.; Potgieter, I. M. *Inorg. Chim. Acta* **1984**, *90*, 57.
(6) Leipoldt, J. G.; Basson, S. S.; Roodt, A.; Potgieter, I. M. *Transition Met. Chem.*, in press.
(7) Basson, S. S.; Leipoldt, J. G.; Potgieter, I. M.; Roodt, A. *Inorg. Chim. Acta* **1985**, *103*, 121.

0020-1669/87/1326-0057$01.50/0

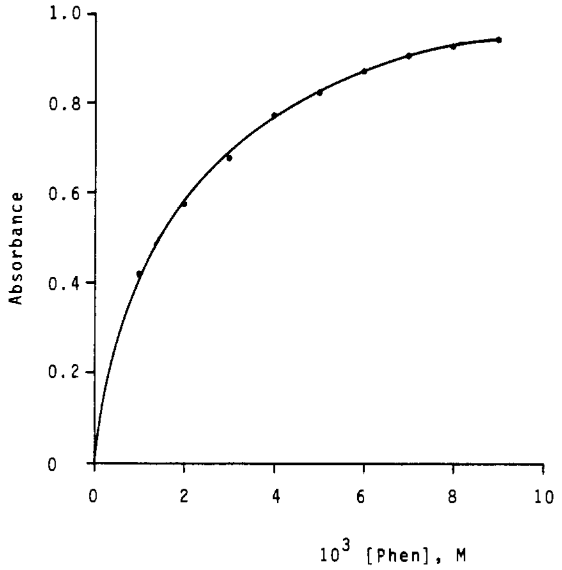


Figure 1. Plot of absorbance vs. [phen] at pH 8.8, $[Mo]_T = 2 \times 10^{-4}$ M, $\mu = 0.1$ M, $T = 25$ °C, and $\lambda = 464$ nm.

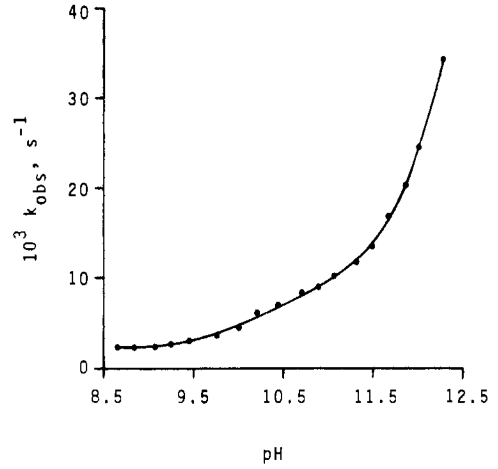


Figure 2. Effect of $[H^+]$ on k_{obsd} at 25, °C, $[Mo]_T = 2 \times 10^{-4}$, $\mu = 0.1$ M, and [phen] = 0.008 M. The solid line is the computer fit of the data to eq 4.

$(CN)_4]^{2-}$, or K_{a2}, the acid dissociation constant of $[MoO(OH)(CN)_4]^{3-}$. The values of K_{a1} and K_{a2} were obtained by fitting the absorbance vs. $[H^+]$ data (by using a nonlinear least-squares program) to eq 3. The values are listed in Table II.

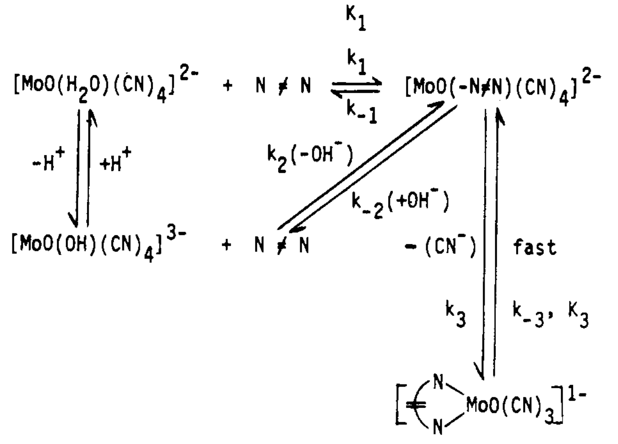
No reaction between $[MoO_2(CN)_4]^{4-}$ and phen took place at a high pH (>13) where $[MoO_2(CN)_4]^{4-}$ is the predominant species. All the reactions observed were monophasic. This, together with the pH dependence (Figure 2) and the results of the structure determination of $[WO(pic)(CN)_4]^{2-}$ (X-ray powder photographs proved that the corresponding molybdenum complex is isomorphous with the tungsten complex), indicates that the aqua ligand is first substituted and that the closing of the chelate ring, which is accompanied by the substitution of a cyanide ligand, is a fast reaction. Scheme I may thus be postulated.

According to this reaction scheme, the pseudo-first-order rate constant is given by eq 4, ignoring the fast equilibrium, K_3. It

$$k_{obsd} = \frac{(k_1[H^+] + k_2K_{a1})[phen]}{K_{a1} + [H^+]} + k_{-1} + k_{-2}[OH^-] \quad (4)$$

should be noted that the value of the back-reaction rate constants in eq 4 are actually a composite of k_{-1} or k_{-2} (see Scheme I) and the equilibrium constant for the fast ring closure step, K_3. It must be pointed out that no reaction is observed when a slight excess of free cyanide ions is present. The situation is further complicated in that addition of excess free CN^- leads to the formation of $[MoO(CN)_5]^{3-}$.[3]

Scheme I



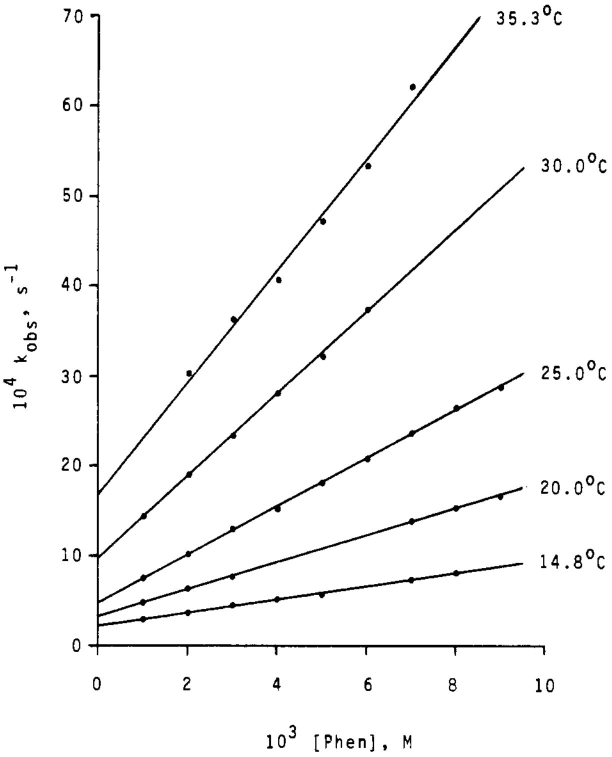


Figure 3. Plot of k_{obsd} vs. [phen] at a pH of 8.8, $[Mo]_T = 2 \times 10^{-4}$ M, and $\mu = 0.1$ M. The solid line is the computer fit of the data to eq 5.

Figure 2 is a plot of k_{obsd} vs. the pH of the medium. It is clear that the reaction is independent of the $[H^+]$ at a low pH in agreement with eq 4 if one assumes that the term $k_{-2}[OH^-]$ becomes negligible at a pH of about 8 due to the low OH^- ion concentration. The very small change in the absorbance at a pH above 12.5 indicates that the total forward reaction proceeds to a very small extent.

At a low pH (where $[H^+] >> K_{a1}$) eq 4 simplifies to

$$k_{obsd} = k_1[phen] + k_{-1} \quad (5)$$

Figure 3 is a plot of k_{obsd} vs. the phenanthroline concentration at a pH of 8.8. The values of k_1 and k_{-1} were obtained from the slope and intercept of these plots, respectively. The values are reported in Table II.

At a high pH ($[H^+] << K_{a1}$) eq 4 simplifies to

$$k_{obsd} = k_2[phen] + k_{-1} + k_{-2}[OH^-] \quad (6)$$

Figure 4 is a plot of k_{obsd} vs. [phen] at a pH of 11.8. k_{obsd} is, as at a pH of 8.8, linearly dependent on [phen], as expected from eq 6. The value of k_2 was obtained from the slope and the value of k_{-2} from the intercept of this plot. Figure 5 is a plot of k_{obsd} vs. the OH^- ion concentration at the high-pH region (pH 11–12).

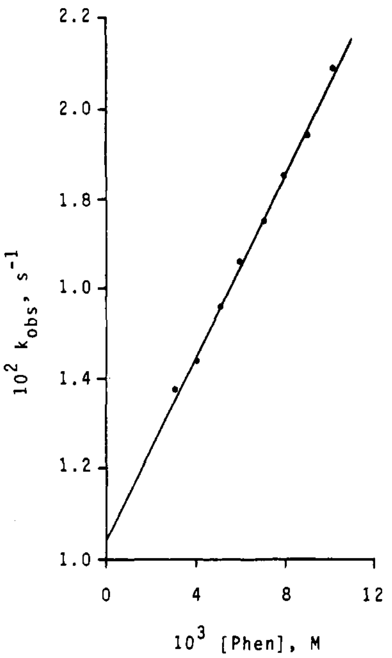


Figure 4. Plot of k_{obsd} vs. [phen] at pH 11.8, $[Mo]_T = 2 \times 10^{-4}$ M, μ = 0.1 M, and T = 25 °C. The solid line is the computer fit of the data to eq 6.

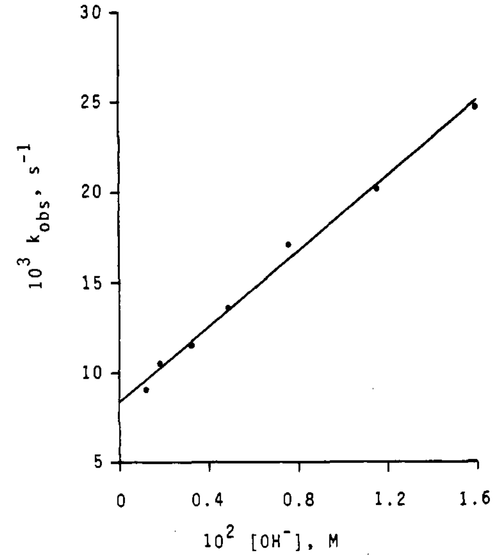


Figure 5. Plot of k_{obsd} vs. $[OH^-]$ at 25 °C, $[Mo]_T = 2 \times 10^{-4}$ M, μ = 0.1 M, and [phen] = 0.008 M. The solid line is the computer fit of the data to eq 6.

The plot is linear in agreement with eq 6. The values of k_2 and k_{-2} were determined from the intercept and slope of this plot, respectively. The values of k_2 and k_{-2} obtained by these independent methods are in excellent agreement; see Table II.

Equation 4 may be written as follows:

$$\frac{k_{obsd} - k_{-1}}{[phen]} = \frac{k_1[H^+]^2[phen] + (k_2K_{a1}[phen] + k_{-2}K_w)[H^+] + k_{-2}K_{a1}K_w}{[phen][H^+]^2 + K_{a1}[phen][H^+]} \qquad (7)$$

The values of k_1, k_2, k_{-2}, and K_{a1} were also determined by means of the nonlinear least-squares fit of the k_{obsd} vs. pH data (Figure 2) to eq 7. These values are also given in Table II. The kinetic parameters defined in Scheme I that were obtained by the different methods are in good agreement.

It is to be noted that the value of k_2 is about 4 times greater than the value of k_1. It is difficult to explain why the oxo hydroxo complex is more reactive towards substitution than the aqua complex. It is usually found that an aqua ligand is much more labile than a hydroxo ligand. The rate constant for the substitution of an aqua ligand in $[CrTPPS(OH)(H_2O)]^{4-}$ by NCS^- is for example 0.285 M^{-1} s^{-1} at 25 °C while no reaction between $[CrTPPS(OH)_2]^{5-}$ and NCS^- is observed.[8] There are, however, examples where the substitution of a hydroxo ligand has about the same or even higher rate than the substitution of an aqua ligand. It was for example observed[9] that the anation reaction of $[Fe(CN)_5OH]^{3-}$ with NCS^- is faster than the reaction of $[Fe(CN)_5(H_2O)]^{2-}$ with NCS^-, although it was later established that the observed rate constant for the reaction of $[Fe(CN)_5OH]^{3-}$ was too high, probably as a result of catalysis by small amounts of $[Fe(CN)_5OH]^{4-}$.[10] Similarly the substitution reactions of $[Fe(CN)_5(OH)]^{4-}$ and $[Fe(CN)_5(H_2O)]^{3-}$ with thiourea have rate constants of the same order of magnitude.[11]

Although the plots of k_{obsd} vs. [phen] are linear, the positive value of ΔS^{*} for the k_1 path suggests a dissociative activation. Molybdenum(IV) is known to form complexes with coordination numbers greater than 6, but the coordination of a large incoming ligand, such as phenanthroline in the vicinity of the aqua ligand, is not likely due to the distortion of the $[MoO(H_2O)(CN)_4]^{2-}$ ion.[2] The molybdenum atom is displaced by a significant 0.34 Å out of the plane formed by the four carbon atoms of the cyanide ligands toward the oxo ligand, with the result that the C–Mo–OH_2 angles are significantly smaller than 90°. This phenomenon of distortion isomers was observed for a number of molybdenum(IV) complexes containing one Mo=O bond.[4,5,7,12-14] According to this manner of distortion, the coordination of the phenanthroline molecule in an associative mechanism is unlikely. On the other hand, we may expect that this distortion mode of the $[MoO(H_2O)(CN)_4]^{2-}$ ion, together with the large trans influence of the oxo ligand, will promote dissociation of the aqua ligand and thus a dissociative activation in agreement with the positive value of ΔS^{*}. To this effect the volume of activation for the reaction $[WO(H_2O)(CN)_4]^{2-} + N_3^- \rightarrow [WO(N_3)(CN)_4]^{3-} + H_2O$ was found to be +10.6 (5) cm^3 mol^{-1}, which is indicative of a dissociatively activated substitution process.[15] The large trans influence of the oxo ligand is clearly observed in the Mo–N bond distances in $[MoO(phen)(CN)_3]^-$: The Mo–N bond distance trans to the oxo ligand is 2.363 (7) Å, while the Mo–N bond distance trans to the cyanide ligand is only 2.174 (7) Å.[4]

Acknowledgment. We thank the South African CSIR and the Research Fund of this university for financial support.

Registry No. phen, 66-71-7; $[MoO(H_2O)(CN)_4]^{2-}$, 55493-45-3; $[MoO(OH)(CN)_4]^{3-}$, 52920-70-4.

---

(8) Ashley, K. R.; Leipoldt, J. G.; Joshi, V. K. *Inorg. Chem.* **1980**, *19*, 1608.
(9) Espenson, J. H.; Wolenuk, S. G., Jr. *Inorg. Chem.* **1972**, *11*, 2034.
(10) James, A. D.; Murray, R. S.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1273.
(11) Macartney, D. H.; McAuley, A. *Inorg. Chem.* **1979**, *18*, 2891.
(12) Chatt, J.; Manojlovic-Muir, L.; Muir, K. *J. Chem. Soc., Chem. Commun.* **1971**, 655.
(13) Manojlovic-Muir, L. *J. Chem. Soc. A* **1971**, 2796.
(14) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686.
(15) Leipoldt, J. G.; van Eldik, R.; Basson, S. S.; Roodt, A. submitted for publication in *Inorg. Chem.*