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Articles

Kinetic, Equilibrium, and Ion-Pairing Studies on Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes in Acetonitrile

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The kinetics of the substitution reaction $[ML_7]^{2+} + X^- \rightleftharpoons [ML_6X]^+ + L$ (X = Cl, Br, or I; $L = t\text{-}C_4H_9NC$; M = Mo or W) have been investigated in both directions via conductance studies in acetonitrile. For M = Mo, the reaction is reversible. Overall pseudoequilibrium constants were experimentally determined to be 3.5, 1.3, and 0.12 for X = Cl, Br, and I, respectively, at an X^- concentration of 0.0056 M. A dissociative process with participation of both ion-paired and non-ion-paired complexes is proposed as the mechanism of substitution. Microscopic rate constants are reported. Calculated activation parameters for the reaction with X = I are forward, $\Delta H^* = 20.8 \pm 0.2$ kcal/mol, $\Delta S^* = -14.0 \pm 0.7$ eu; reverse, $\Delta H^* = 15.4 \pm 0.2$ kcal/mol, $\Delta S^* = -27.3 \pm 0.7$ eu. For M = W, the reaction does not proceed at an observable rate in either direction. Ion association constants, K_A, in acetonitrile are 3.2×10^3, 1.5×10^3, and 1.0×10^3 for $[MoL_6X]X$, X = Cl, Br, and I, respectively, and 1.3×10^3 for $[WL_6I]I$ at 40 °C. Values for $[ML_7](PF_6)_2$ are <100 for M = Mo or W at 40 °C.

Introduction

The molybdenum(II) and tungsten(II) isocyanide systems are among the better developed areas of seven-coordination chemistry. Numerous reports on syntheses,[1] characterizations,[2] reactions,[3] and crystal structures[4] have been reported. However, to date, virtually no work has appeared on the kinetic studies of substitution reactions, ion-pairing studies, or equilibrium studies on these isocyanide complexes or any seven-coordination number metal complexes.[5]

Studies of reactions in nonaqueous solvents have been hampered by their inherent complexity. While aqueous solutions are often more desirable due to lesser complexity, studies in such solutions are rather limited in scope and hence less enlightening. Use of nonaqueous solvents allows a more thorough understanding of mechanisms of substitution reactions. The low dielectric constants of these nonaqueous solvents, however, makes ion-pairing an added complication to the studies of reaction mechanisms. The study of ion-pairing is essential to providing both insight into mechanisms of such substitution reactions and also increased understanding of such areas as chemical bonding and the nature of ion–ion interactions. While kinetic studies can be quite revealing in their own right, the ability to elucidate a mechanism by also using the equilibrium data for a reversible substitution reaction is even more powerful a tool. The kinetic and equilibrium data can now be compared for internal consistency. Very few such studies have been reported in the literature.[6]

Detailed studies on seven-coordinate molybdenum(II) and tungsten(II) isocyanide complexes in acetonitrile solution, reported herein, are the first such studies on seven-coordinate metal complexes.

Experimental Section

Reagents. Spectra grade acetonitrile (Aldrich) was dried over molecular sieves and degassed before use for kinetic and equilibrium studies. For ion-pairing studies, the acetonitrile was refluxed with phosphorus pentoxide and distilled. It had a conductance of $<2.5 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$. Tetrabutylammonium chloride, bromide, iodide, and perchlorate (all East-

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Table I. Conductance Parameters in Acetonitrile Solution[a]

cation	anion	$K_A \times 10^{-3}$ [b]	Λ_0	Λ_0^+	Λ_0^- [c]	r^+ [d]	r^- [d]	$r^+ + r^-$
$[Mo(t\text{-}C_4H_9NC)_6Cl]^+$	Cl^-	3.2	255	145.2	109.8	1.82	2.41	4.23
$[Mo(t\text{-}C_4H_9NC)_6Br]^+$	Br^-	1.5	280	167.9	112.1	1.57	2.36	3.93
$[Mo(t\text{-}C_4H_9NC)_6I]^+$	I^-	1.0	220	106.0	114.0	2.49	2.32	4.81
$[Mo(t\text{-}C_4H_9NC)_7]^{2+}$	$2PF_6^-$	0.10[e]	430	99.8	115.2	2.65	2.29	4.94
$[W(t\text{-}C_4H_9NC)_6I]^+$	I^-	1.3	240	126.0	114.0	2.10	2.32	4.42
$[W(t\text{-}C_4H_9NC)_7]^{2+}$	$2PF_6^-$	0.10[e]	400	84.8	115.2	3.11	2.29	5.40

[a] All data at 40.00 °C. Concentration ranges studied ($M \times 10^5$) were $[Mo(t\text{-}C_4H_9NC)_6Cl]Cl$, 0.6–40; $[Mo(t\text{-}C_4H_9NC)_6Br]Br$, 1.3–55; $[Mo(t\text{-}C_4H_9NC)_6I]I$, 1.5–39; $Mo[C_4H_9NC)_7](PF_6)_2$, 1.8–32; $[W(t\text{-}C_4H_9NC)_6I]I$, 3.4–48; and $[W(t\text{-}C_4H_9NC)_7](PF_6)_2$, 1.0–40. [b] Standard deviations were 4–9%. [c] Values at 40.0 °C, converted from literature values at 25.0 °C. See (a) Covington, A. K.; Dickson, T. *Physical Chemistry of Organic Solvent Systems*; Plenum Press: New York, 1973; see also references therein. (b) Janz, G. J.; Tomkins, R. R. T. *Nonaqueous Electrolytes Handbook*: Academic Press: New York, 1972; Vol. 1. [d] Stokes radii, from the equation $10^8 r_\pm = 0.819/\Lambda_0 \pm \eta$. [e] Maximum possible estimated value.

man) were purified by literature methods.[7] *tert*-Butyl isocyanide was prepared by literature methods[8] and distilled prior to use.

Preparation of Compounds. Metal complexes $[ML_7](PF_6)_2$ and $[ML_6X]X$ (X = Cl, Br, or I; M = Mo or W; L = $t\text{-}C_4H_9NC$, *tert*-butyl isocyanide) were prepared by literature methods.[1c]

Conductance Measurements. Conductance measurements were taken on a Beckman RC-18A conductivity bridge with a Beckman CEL-3A conductivity cell. A Lauda K-4/R constant-temperature bath was used to maintain a constant temperature (±0.01 °C). All measurements were taken at 40.00 ± 0.01 °C.

General Procedures: Ion-Pairing Studies. Studies were performed at concentrations ranging from 5.5×10^{-4} to 6.0×10^{-6} M, well below the concentration appropriate for the formation of ion triplets (3.2×10^{-7} D^3).[9] Such aggregate formation was apparent at concentrations $>5 \times 10^{-3}$ M. All solution preparations and measurements were carried out with a rigorous exclusion of oxygen, water, and light. Solutions of (1–10) $\times 10^{-3}$ M were prepared by dissolving weighed amounts of an appropriate salt in a known volume of solvent. Solutions of lower concentration were prepared by diluting these above solutions. Fresh solutions were prepared for each set of measurements, which were made within 1–2 h. All glassware was recalibrated at 25 °C. The correction for the solvent never exceeded 1–2% of the total conductance for even the most dilute solutions. K_A and Λ_0 were obtained from least-squares plots of $1/\Lambda S(Z)$ vs $\gamma_\pm^2 c\Lambda S(Z)$ in the Shedlovsky function for a 1:1 electrolyte

$$1/\Lambda S(Z) = 1/\Lambda_0 + \gamma_\pm^2 c\Lambda S(Z)K_A/\Lambda_0^2 \qquad (1)$$

using the Debye–Hückel limiting law:

$$-\ln \gamma_\pm = e^2\kappa/2DkT(1 + \kappa a I^{1/2}) \qquad (2)$$

All symbols have their usual meanings.[10] This method has the advantage of not requiring the high precision needed for other types of conductance analyses while at the same time being accurate for systems where ion association is relatively large. This is especially important in the systems under study where possible sensitivity to air, light, and water caused a good deal of scatter in the data, despite the precautions taken. The standard deviation in Λ_0 was of the order of 1–3%, while the standard deviation in K_A ranged from 4% to 9%. For 2:1 electrolytes, the equations were modified according to literature methods.[11] Actual K_A values for the 2:1 electrolytes could not be accurately determined by this method due to the small values, but were calculated to be <100.

General Procedures: Kinetic and Equilibrium Measurements. Reactions were typically run at 2.4×10^{-4} M in $[ML_7]^{2+}$ or $[ML_6X]^+$ in acetonitrile solution with a large excess of halide (0.0022 to 0.0056 M) and/or *tert*-butyl isocyanide (0.0033 to 0.0312 M) to ensure that the reaction was pseudo-first-order in metal complex at all times. Tetrabutylammonium perchlorate was added as an electrolyte to bring all solutions used to a constant initial ionic strength of 0.0063. Small changes in ionic strength as the reactions proceeded were negligible. Solutions of reactants of the approximate temperature of the kinetic studies (40.0 °C) were mixed, added to a conductivity cell, and placed in a constant-temperature bath. Complete thermal equilibrium was generally established within 15 min of placing the cell in the bath. Only one kinetic experiment was performed at a time to ensure minimum fluctuation in the bridge and to keep exposure to light and small temperature changes to a minimum.

The three measured conductance parameters, Λ_0, Λ_t, and Λ_e represent the initial conductance, the conductance at time t, and the conductance at equilibrium, respectively. An accurate reading for Λ_e was needed for the determination of rate constants, and thus every effort was made to ensure that the solution was at equilibrium before being removed from the bath. Only data from the first two half-lives of the reaction were used in the calculation of rate constants in order to minimize any error in Λ_e. Rate constants were calculated from plots of $\ln[(\Lambda_0 - \Lambda_e)/(\Lambda_t - \Lambda_e)]$ or $\ln[(\Lambda_e - \Lambda_0)/(\Lambda_e - \Lambda_t)]$ vs time for the forward and reverse directions, respectively.

Overall pseudoequilibrium constants, K_{eq}, were measured by mixing various amounts of $[MoL_7]^{2+}$, $[MoL_6X]^+$, X^- (0.0056 M), and L. The mixture at which no change in conductance was observed was considered to be an equilibrium mixture. Mixtures slightly on either side of equilibrium were also observed to ensure a relatively accurate measurement of K_{eq}. Mixtures slightly to the left side of equilibrium (excess X^- and/or $[MoL_7]^{2+}$) showed a decrease in conductance with time, while mixtures slightly to the right side of equilibrium (excess $[MoL_6X]^+$ and/or L) showed an increase in conductance with time. All measurements were perfored at an ionic strength of 0.0063. Errors in K_{eq} were estimated to be ±10%. It should be noted that this "equilibrium constant" is specific to halide concentrations of 0.0056 M and is dependent on halide concentration.

Activation parameters were determined in their usual ways from plots of log k vs $1/T$ and log (k/T) vs $1/T$. Studies were performed over the temperature range 20–55 °C.

The products of the forward and reverse reactions were well characterized by NMR, IR, and elemental analyses and found to be $[MoL_6X]^+$ and L, and $[MoL_7]^{2+}$ and X^-, respectively. No stable six- or eight-coordinate complexes were observed in any of the systems studied.

Results and Discussion

Ion-Pairing Studies. All complexes studied were found to be associated to some degree in acetonitrile. Conductance parameters are listed in Table I. Data for the complexes $[Mo(t\text{-}C_4H_9NC)_7](PF_6)_2$ and $[W(t\text{-}C_4H_9NC)_7](PF_6)_2$ showed a large degree of scatter due to the small values of K_A which enabled only a rough estimate of K_A values for these complexes.

The electrostatic center-to-center value, a, is typically obtained from[12]

$$1/K_A = (3000/4\pi Na^3)\exp(-e^2/aDkT) \qquad (3)$$

Equation 3, however, does not hold for asymmetrical ions or acetonitrile solutions. For such solvents of high dielectric constant, the Coulombic association described by this equation is relatively insensitive to ion size.[13,14] Indeed, varying a from 2 to 10×10^{-8} cm in the Debye–Hückel limiting law showed a change of less than 2% in the values obtained for Λ_0 or K_A in all systems studied. Best-fit values in eq 2 were obtained by using a values between

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Table II. Reaction of $[Mo(t\text{-}C_4H_9NC)_7]^{2+}$ with X^- [a]

$[X^-]$, M × 10^3 [b]	k^f_{obs} × 10^6, s^{-1} [c]
$X^- = Cl^-$	
5.6	9.65[d]
2.8	7.90
2.2	7.33
$X^- = Br^-$	
5.6	8.33[e]
4.2	8.02
2.8	7.81
$X^- = I^-$	
5.6	6.11[f]
5.1	6.31
4.4	5.88
4.1	5.98
3.6	5.60
2.8	4.95

[a] Initial concentration of $[Mo(t\text{-}C_4H_9NC)_7](PF_6)_2$ was 2.4×10^{-4} in acetonitrile. Initial ionic strength was 0.0063 in all cases studied. Tetrabutylammonium perchlorate was added as an electrolyte when necessary. Changes in ionic strength during the reaction were insignificant. T = 40.0 °C. [b] As tetrabutylammonium halide. [c] Standard deviations on k^f_{obs} were 1–3%. Plots of $k^f_{obs}[1 + K(X^-)]$ vs $K[X^-]$ which were used to calculate k_1 (intercept) and k_3 (slope) for the chloride and bromide systems via eq 9 are shown in Figure 1. [d] First-order rate constants obtained from a plot of $\ln[(\Lambda_0 - \Lambda_e)/(\Lambda_t - \Lambda_e)]$ vs time. The reaction was >98% complete. [e] The reaction proceeds from 91% to 97% completion depending on bromide concentration and using an overall equilibrium constant of 1.3. k was obtained from a plot of $[x_e]/[2a_0 - x_e] \ln[(a_0x_e + x_t(a_0 - x_e))/a_0(x_e - x_t)]$ vs time, where a_0 is the initial concentration of the $[ML_7]^{2+}$ species and x_e and x_t are the concentration of the $[ML_6X]^+$ species at equilibrium and time t, respectively. Differences in ion-paired and non-ion-paired pathways were neglected. See (a) Hughes, Moelwyn, E. A. *Chemical Statics and Kinetics of Solutions*; Academic Press: New York, 1971. (b) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley and Sons: New York, 1981. (c) Reference 5a from text. [f] Same as *e*, except K_{eq} was 0.12 and the reaction proceeded from 67% to 78% completion depending on iodide concentration.

4 and 6 × 10^{-8} cm. The hydrodynamic radii listed in Table I were calculated from the Stokes' law equation

$$10^8 r_\pm = 0.819/\Lambda_{0\pm}\eta \qquad (4)$$

Values obtained for K_A, the ion association constant, were $[MoL_6X]X$, X = Cl, 3.2×10^3, X = Br, 1.5×10^3, X = I, 1.0×10^3; $[WL_6I]I$, 1.3×10^3 all at 40 °C. Values for $[MoL_7](PF_6)_2$ and $[WL_7](PF_6)_2$ were <100 at 40 °C.

Two trends are apparent from these values: first, there is greater association for the 1:1 electrolytes than for the 2:1 electrolytes, and second, there is increased ion association in the order X = Cl > Br > I for the 1:1 electrolytes. Values obtained from purely electrostatic approximations indicate that K_A for a 2:1 electrolyte should be approximately an order of magnitude larger than for a 1:1 electrolyte, from the equation[15]

$$K_A = 4\pi N a^3 \exp(-z_1 z_2 e^2/DkTa + E_s/kT)/3000 \qquad (5)$$

The asymmetrical nature of the $[ML_6X]^+$ cation vs the symmetrical $[ML_7]^{2+}$ cation is apparently the overriding factor. This effect of asymmetry is well documented in the literature in cases involving acetonitrile solutions. Yeager and Kratochvil reported association constants of 4–60 for a series of alkali-metal tetrafluoroborate, perchlorate, hexafluorophosphate, and tetraphenylborate salts.[16] D'Aprano, Goffredi, and Triolo reported K_A values for alkali-metal and quaternary ammonium perchlorates in acetonitrile ranging from 10 to 35.[13] However, Darensbourg and Borman reported K_D ($=1/K_A$) values of (2.7–3.6) × 10^{-3} for $[\eta^5\text{-}C_5H_5Fe(CO)_2PMe_2Ph]BPh_4$, $[\eta^6\text{-}C_6H_6Mn(CO)_3]ClO_4$, and $[\eta^6\text{-}C_6H_6Mn(CO)_3]BPh_4$ in acetonitrile solution.[14] The relatively high association constants for these complexes were attributed to lower symmetry of the (arene)- and (cyclopentyldienyl)metal carbonyl cations, as compared to the more symmetrical alkali-metal and quaternary ammonium cations. This asymmetry caused sites of charge delocalization which increased the association of metal complexes in their study. Indeed, very small K_D values were also reported in acetonitrile solution for the chloride salt of the asymmetrical cation $[Ph_2(NH_2)P]_2N^+$ ($K_D = 3.2 \times 10^{-4}$)[17] and for salts of less symmetrical anions NO_3^- and ClO_3^- ($K_D(AgNO_3) = 0.014$ and $K_D(LiCO_3) = 0.0025$).[18] Although the ML_7^{2+} cations are not technically perfectly symmetrical, they are fluctional in solution,[1e] which apparently causes them to appear as a perfectly symmetrical cation from the point of view of the cation.

It is also apparent that charge delocalization decreases for the $[MoL_6X]^+$ cations in the order Cl > Br > I, causing a decrease in K_A. This is not surprising in light of electronegativity considerations. Part of this decrease is also likely due to the nature of the anion. In previous studies, K_A decreased in the order Cl > Br > I by a factor of ~2–3 in acetonitrile solutions.[19] The overall decrease for the $[ML_6X]^+$ systems was by a factor of 3.2. The best-fit ion association constants for $[MoL_7]^{2+}\cdots X^-$ (three dots denote an ion pair), obtained from kinetic studies, were 250, 150, and 40 for X = Cl, Br, or I, respectively. These values are consistent with previous work where association constants were measured in acetonitrile for a given series of anions including halide and hexafluorophosphate[19,20] and with the ion-pairing values for $[ML_6X]^+\cdots X^-$ and for $[ML_7]^{2+}\cdots PF_6^-$ obtained in this work. The reaction of the two ions $[MoL_7]^{2+}$ and X^- makes direct measurement of K_A impossible.

The specific points of cation–anion interaction are not readily obtainable from these studies nor is the exact role of the solvent in the solvation of the cations. It does appear, however, from the Stokes' radii (Table I) that solvent interaction is at most very small. Values obtained were similar to previous studies of metal complexes in acetonitrile solution where solvation of the cation was small.

Kinetic and Equilibrium Studies. A. Results. The reaction

$$[ML_7]^{2+} + X^- \rightleftharpoons [ML_6X]^+ + L \qquad (6)$$

(M = Mo or W; $X^- = Cl^-, Br^-$, or I^-; L = C_4H_9NC, *tert*-butyl isocyanide) was studied in acetonitrile under pseudo-first-order conditions in metal complex via conductance studies. A decrease in conductance is observed as the reaction proceeds from left to right (forward direction) while an increase is noted as the reaction proceeds from right to left (reverse direction). The reaction is reversible in the case where M = Mo (at 40 °C), proceeding essentially to equilibrium in both directions under the experimental conditions used, except in the forward direction with $X^- = I^-$ (67–78% complete) and $X^- = Br^-$ (91–97% complete), and in the reverse direction with $X^- = Cl^-$ (71–95% complete). For M = W, the reaction does not proceed at an observable rate in either direction at 40.0 °C.

Kinetic data are listed in Tables II (k^f_{obs} vs $[X^-]$, forward direction), III (k^r_{obs} vs [L], reverse direction), and IV (k_{obs} vs $[X^-]$ and [L], reverse direction). Microscopic rate constants and equilibrium data for the molybdenum systems are listed in Tables V and VI. The temperature dependence of the reactions and activation parameters are listed in Table VII for the case where X = I.

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Table III. Reaction of $[Mo(t\text{-}C_4H_9NC)_6X]^+$ with $t\text{-}C_4H_9NC$[a]

$[t\text{-}C_4H_9NC]$, M × 10^3	$k^r_{obs} \times 10^5$, s^{-1} [b]
$X^- = Cl^-$	
25.4	3.78
16.2	3.23
6.0	2.79
3.3	2.80
$X^- = Br^-$	
20.4	9.88
9.6	9.88
$X^- = I^-$	
19.3	10.2
13.9	9.72[c]
13.9	9.92[d]
13.2	11.2
11.6	10.0
7.4	9.92
5.9	10.6

[a] Initial concentration of $[Mo(t\text{-}C_4H_9NC)_6X]X$ was 2.4×10^{-4} M in acetonitrile unless otherwise noted. Initial ionic strength was 0.0063 in all cases studied. Tetrabutylammonium perchlorate was added as an electrolyte. Changes in ionic strength during the reaction were insignificant. $T = 40.0$ °C. [b] First-order rate constants obtained from plots of $\ln[(A_e - A_0)/(A_e - A_t)]$ vs time. Reactions proceeded to nearly 100% completion for the bromide and iodide systems. Standard deviations on k^r_{obs} were 1–3%. k^r_{obs} equals k_{-2} (via eq 10) for the bromide and iodide systems. For an analysis of the chloride system (71–95% completion); see text. [c] 4.8×10^{-4} M in $[Mo(t\text{-}C_4H_9NC)_6I]I$. [d] 1.2×10^{-4} M in $[Mo(t\text{-}C_4H_9NC)_6I]I$.

For the molybdenum systems, a mechanism consistent with all experimental data is

$$\begin{tikzcd}[row sep=large, column sep=huge]
{[ML_7]^{2+}} \arrow[r, shift left, "K(+X^-)"] \arrow[d, shift right, "{k_1\ (-L)}"'] & {[ML_7]^{2+}\cdots X^-} \arrow[l, shift left, "(-X^-)"] \arrow[d, shift left, "{k_3\ (-L)}"] \\
{[ML_6]^{2+}} \arrow[u, shift right, "{k_{-1}\ (+L)}"'] \arrow[r, shift left, "K''(+X^-)"] \arrow[d, shift right, "{k_2\ (+X^-)}"'] & {[ML_6]^{+}\cdots X^-} \arrow[l, shift left, "(-X^-)"] \arrow[u, shift left, "{k_{-3}\ (+L)}"] \arrow[d, shift left, "{k_4\ (+X^-)}"] \\
{[ML_6X]^{+}} \arrow[u, shift right, "{k_{-2}\ (-X^-)}"'] \arrow[r, shift left, "K'(+X^-)"] & {[ML_6X]^{+}\cdots X^-} \arrow[l, shift left, "(-X^-)"] \arrow[u, shift left, "{k_{-4}\ (-X^-)}"]
\end{tikzcd} \tag{7}$$

A steady-state approximation has been assumed for the two six-coordinate intermediates $[ML_6]^{2+}$ and $[ML_6]^+\cdots X^-$. $K = K_A$ for the $[ML_7]^{2+}$, $[ML_7]^{2+}\cdots X^-$ system; K' refers to K_A for the $[ML_6X]^+$, $[ML_6X]^+\cdots X^-$ system; and K'' refers to the $[ML_6]^{2+}$, $[ML_6]^{2+}\cdots X^-$ system. Although K'' cannot be experimentally measured, it is not needed for the calculation of the microscopic rate constants. Contributions of solvent, perchlorate, and hexafluorophosphate and preassociation of the isocyanide were neglected in the mechanistic analysis of the reaction scheme (eq 7). These topics will be discussed later.

The pathway on the left (k_1, k_2, k_{-1}, k_{-2}) is a dissociative pathway involving non-ion-paired species, while the pathway on the right (k_3, k_4, k_{-3}, and k_{-4}) is also dissociative but involves only ion-paired species. The rate-determining steps involve k_1, k_{-2}, k_3, and k_{-4}, while only the ratios of the other (faster) rate constants k_2/k_{-1} ($=R$) and k_4/k_{-3} ($=Q$) can be experimentally determined.

For the molybdenum systems the following rate equation may be derived from the proposed mechanism in the reverse direction:

Table IV. Reaction of $[Mo(t\text{-}C_4H_9NC)_6X]^+$ with X^- and $t\text{-}C_4H_9NC$[a]

$[X^-]$, M × 10^3 [b]	$[t\text{-}C_4H_9NC]$, M × 10^3	$k_{obs} \times 10^5$, s^{-1} [c]	best-fit $k \times 10^5$, s^{-1} [d]
		$X^- = Cl^-$ [e]	
5.6	31.2	2.18	2.16
5.6	27.1	1.95	2.02
5.6	14.8	1.65	1.58
		$X^- = Br^-$ [f]	
2.5	19.5	3.78	3.85
5.6	16.8	2.26	2.10
5.6	4.8	1.14	1.25
		$X^- = I^-$ [g]	
2.2	19.3	6.57	6.53
5.6	22.2	4.20	3.95
5.6	10.5	2.52	2.73
5.6	7.95	2.40	2.40
5.6	5.28	1.88	2.01
5.6	4.07	1.78	1.88

[a] Initial ionic strength 0.0063. Tetrabutylammonium perchlorate was added as an electrolyte. Changes in ionic strength during the reaction were insignificant. $T = 40.0$ °C. [b] As tetrabutylammonium halide. [c] From plot of $\ln[(A_e - A_0)/(A_e - A_t)]$ vs time. Standard deviations on k_{obs} were 1–3%. [d] χ^2 best fits using eq 8; probabilities were 0.97, 0.88, and 0.99 for the chloride, bromide, and iodide systems, respectively. For a complete analysis, see text. [e] 2.4×10^{-4} M in $[Mo(t\text{-}C_4H_9NC)_6Cl]Cl$. [f] 2.4×10^{-4} M in $[Mo(t\text{-}C_4H_9NC)_6Br]Br$. [g] 2.4×10^{-4} *M* in $[Mo(t\text{-}C_4H_9NC)_6I]I$.

$$k_{obs} = \frac{\dfrac{k_{-2}[L]}{k_2[X^-]/k_{-1} + [L]} + \dfrac{k_{-4}K'[L][X^-]}{k_4[X^-]/k_{-3} + [L]}}{1 + K'[X^-]} + \frac{\dfrac{(k_2k_1/k_{-1})[X^-]}{k_2[X^-]/k_{-1} + [L]} + \dfrac{(k_4k_3K/k_{-3})[X^-]^2}{k_4[X^-]/k_{-3} + [L]}}{1 + K[X^-]} \tag{8}$$

An analogous rate equation can be derived for the forward direction.

For data taken in the forward direction (Table II), a large excess of X^- was used with no L initially present. Although small amounts of L (2.4×10^{-4} M) were formed during the reaction, this amount was much too small to have any effect on the rate. Equation 8 for the molybdenum systems thus simplifies to

$$k^f_{obs} = \frac{k_1 + k_3K[X^-]}{1 + K[X^-]} \tag{9}$$

For similar reasons data taken in the reverse direction (Table III) may also be handled by a simplified version of eq 8:

$$k^r_{obs} = \frac{k_{-2} + k_{-4}K'[X^-]}{1 + K'[X^-]} \tag{10}$$

B. Data Analysis. k_1 and k_3. A linear least-squares plot of $k^f_{obs}[1 + K(X^-)]$ vs $K[X^-]$ for the chloride and bromide systems in the forward direction via eq 9, using the specific value of K obtained in the final overall data analysis, yielded values for k_1 (intercept) and k_3 (slope). For the iodide system, the value for k_3 could not be calculated with confidence via this method since such a small fraction of the reaction was occurring via this ion-paired pathway (9–17%). The value for k_3 (and also K) was obtained for this system as a best fit in the final data analysis using eq 8. These values for k_3 and K were then used to calculate k_1 for the iodide system from data for the forward direction using eq 9. Values for k_1 were identical within experimental error for the three systems: $(5.5 \pm 1.5) \times 10^{-6}$ s^{-1}. Plots of $k^f_{obs}[1 + K(X^-)]$ vs $K[X^-]$ for the chloride and bromide systems are shown in Figure 1. Kinetic data are listed in Table II, and k_1 and k_3 values are included in Table V.

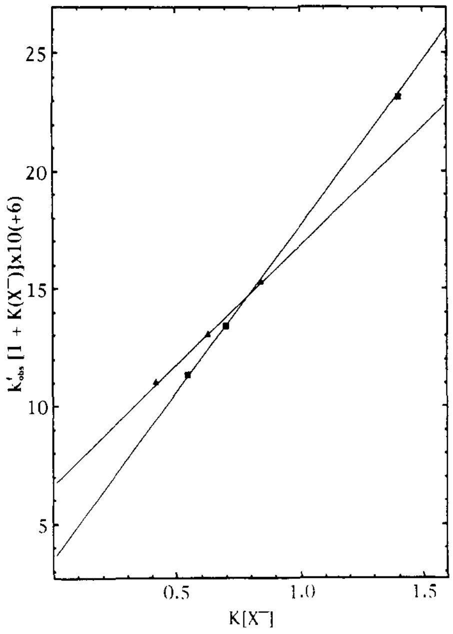

Figure 1. $k^f_{obs}[1 + K(X^-)]$ vs $K[X^-]$ for the reaction of $[MoL_7]^{2+}$ with chloride (■) and with bromide (▲) using the data from Table II.

Table V. Kinetic Data for the Reaction[a] $[Mo(t\text{-}C_4H_9NC)_7]^{2+} + X^- \rightleftharpoons [Mo(t\text{-}C_4H_9NC)_6X]^+ + t\text{-}C_4H_9NC$

X^-	$k_1 \times 10^6$, s^{-1}	$k_{-2} \times 10^5$, s^{-1}	$R = k_2/k_{-1}$	$k_3 \times 10^6$, s^{-1}	$k_{-4} \times 10^5$, s^{-1}	$Q = k_4/k_{-3}$
Cl^-	4.0	4.5	5.0	14	15.3	61
Br^-	7.0	9.9	3.6	10	15.8	40
I^-	6.0	10.2	0.38	5.0	14.4	16

[a] 40.0 °C. See text for procedures used to calculate various parameters.

k_{-2} and k_{-4}. k_{-2} values were measured directly from kinetic experiments in the reverse direction for the bromide and iodide systems using eq 10, since the $k_4/k_{-3}[X^-]$ and $K'[X^-]$ terms in eq 8 were insignificant. This yields $k^r_{obs} = k_{-2}$. For the chloride system, these terms were not insignificant and a slight L dependence on reaction rates was observed. To add to the complication of the chloride system, the reaction did not proceed to 100% completion (maximum 95%, where the L concentration was the greatest) and the halide concentration was increasing throughout the reaction. k_{-2} here was estimated as 4.5×10^{-5} from extrapolation of rates obtained in reactions when the L value was very large. k_{-4} values were not obtainable in the kinetic studies in the reverse direction for any of the three systems since only a small fraction of the reaction was occurring by the ion-paired pathway ($k_{-4}K'[X^-]$). k_{-4} was obtained in the final overall data analysis. Kinetic data are listed in Table III, and k_{-2} and k_{-4} values are included in Table V.

K and K'. K' was experimentally measured. Values are included in Table VI. K, the ion association constant for $[MoL_7]^{2+}\cdots X^-$ could not be measured due to the chemical reaction occurring between the two species. Values were obtained in the χ^2 best fits for the overall final data analysis using eq 8. Best-fit values were K = 250, 150, and 40 for X = Cl, Br, and I, respectively. These constants are defined as

$$K = \frac{[MoL_7\cdots X]^+}{[MoL_7]^{2+}[X^-]} \qquad K' = \frac{[MoL_6X\cdots X]}{[MoL_6X]^+[X^-]} \tag{11}$$

K_{eq}. This pseudoequilibrium constant is defined as

$$K_{eq} = \frac{([MoL_6X\cdots X] + [MoL_6X]^+)[L]}{([MoL_7\cdots X]^+ + [MoL_7]^{2+})[X^-]} \tag{12}$$

Values were experimentally measured for $[X^-] = 0.0056$ M with an estimated error of ±10%. Values were 3.5, 1.3, and 0.12 for $X^- = Cl^-$, Br^-, and I^-, respectively (Table VI).

Table VI. Equilibrium and Ion-Pairing Data for the Reaction[a] $[Mo(t\text{-}C_4H_9NC)_7]^{2+} + X^- \rightleftharpoons [Mo(t\text{-}C_4H_9NC)_6X]^+ + t\text{-}C_4H_9NC$

X^-	K_{eq}[b]	K^*[c]	K^{**}[c]	$K \times 10^{-3}$[d]	$K' \times 10^{-3}$[e]
Cl^-	3.5	0.44	5.6	2.5	3.2
Br^-	1.3	0.25	2.5	1.5	1.5
I^-	0.12	0.022	0.56	0.40	1.0

[a] All data at 40.0 °C. See text. [b] Overall pseudoequilibrium constants obtained from equilibrium measurements. See text. [c] $K^* = k_1k_2/k_{-1}k_{-2}$; $K^{**} = k_3k_4/k_{-3}k_{-4}$. Obtained from K_{eq}. See text. [d] Ion-pairing constants for $[Mo(t\text{-}C_4H_9NC)_7]^{2+}\cdots X^-$. Obtained from best-fit values in the final data analysis. See text. [e] Ion-pairing constants for $[Mo(t\text{-}C_4H_9NC)_6X]^+\cdots X^-$.

K^* and K^{**}. The microscopic equilibrium constants for the molybdenum system $K^* = k_1k_2/k_{-1}k_{-2}$ and $K^{**} = k_3k_4/k_{-3}k_{-4}$ (both included in Table VI) can also be represented by the following equilibrium expressions:

$$K^* = \frac{[MoL_6X]^+[L]}{[MoL_7]^{2+}[X^-]} \qquad K^{**} = \frac{[MoL_6X\cdots X][L]}{[MoL_7\cdots X]^+[X^-]} \tag{13}$$

These are "real" equilibrium constants which do not depend on the X^- concentration. Combining these equations with the K, K', and K_{eq} expressions yields

$$K^* = K_{eq}\frac{[1 + K(X^-)]}{[1 + K'(X^-)]} \qquad K^{**} = K_{eq}\frac{[1/K(X^-) + 1]}{[1/K'(X^-) + 1]} \tag{14}$$

Substituting the value of $X^- = 0.0056$ M in eq 15 yields these true microscopic equilibrium constants. Note that K_{eq} is really only a necessity due to the experimental limitations which makes a direct calculation of K^* and K^{**} impossible. Thus, these equilibrium constants can be calculated purely on the basis of equilibrium measurements or calculations and then used in conjunction with the kinetic measurements to give a detailed mechanistic analysis.

R ($=k_2/k_{-1}$) and Q ($=k_4/k_{-3}$). R was calculated from the expression $R = k_{-2}K^*/k_1$. Q ($=k_{-4}K^{**}/k_3$) was obtained in the final data analysis via eq 8. Values for R and Q are included in Table V.

Final Data Analysis. All values except Q, k_{-4}, and K (and k_3 for the iodide system) were known from experimental measurements for each system. A χ^2 best fit was performed via eq 8 (using these previously calculated parameters) and by setting $k_{-4} = k_3Q/K^{**}$ and varying both Q (and necessarily k_{-4}) and K in the kinetic reactions involving the reaction of an excess of both halide and isocyanide with $[MoL_6X]^+$. This involves fitting with only two unknowns (three in the iodide case), K and k_{-4}/Q, since Q and k_{-4} are directly related. This yields values for Q, k_{-4}, and K (and k_3 for the iodide system). Kinetic data and χ^2 best fits are listed in Table IV.

Values for k_1, k_3, k_{-2}, k_{-4}, $k_2/k_{-1} = R$, and $k_4/k_{-3} = Q$ for X = Cl, Br, or I and M = Mo are listed in Table V. For M = W, these k values are for all practical purposes equal to zero, since the reaction does not proceed at an observable rate in either direction under the conditions used.

C. Discussion. Values for k_1 for this mechanism are, as expected, independent of the halide concentration (within experimental error) since this pathway involves only the dissociation of the non-ion-paired $[ML_7]^{2+}$ species. The k_3 term follows the order $Cl^- > Br^- > I^-$, in order of decreasing nucleophilic strength of the anion involved in the ion pair. Distortions in the electron cloud about the metal ion should follow this order, allowing for a greater ease in breaking of the M–L bond. This may be viewed as an "ion-assisted" bond breakage.

The reaction in the reverse direction is approximately an order of magnitude faster (under the experimental conditions used in

Table VII. Temperature Dependence of Reaction Rates and Activation Parameters[a]

reaction	t, °C	$k_{obs} \times 10^4$, s^{-1} [a]	E_a, kcal/mol	ΔH^*, kcal/mol	ΔS^*, eu
$[MoL_7]^{2+} + I^{-}$ [b] $\rightarrow [MoL_6X]^+ + L$	55	0.296	21.4 ± 0.2	20.8 ± 0.2	−14.0 ± 0.7
	50	0.180			
	45	0.109			
	40	0.0611			
$[MoL_6I]^+ + L$ [c] $\rightarrow [MoL_7]^{2+} + X^-$	55	3.50	16.1 ± 0.2	15.4 ± 0.2	−27.3 ± 0.7
	50	2.45			
	45	1.66			
	40	1.00			
	30	0.455			
	20	0.188			

[a] Standard deviations were 1–3%. [b] 2.4×10^{-4} M in $[MoL_7](PF_6)_2$ and 0.0056 M in tetrabutylammonium iodide in acetonitrile. K_{eq} was assumed to equal 0.12 at all temperatures (reaction proceeds to 78% completion). [c] 2.4×10^{-4} M in $[MoL_6I]I$ and 0.0116 M in L in acetonitrile. Tetrabutylammonium was added to bring the ionic strength up to 0.0063.

the study) than in the forward direction. This could be attributable to the fact that the metal complex has a +1 charge for the reaction in the reverse direction and a +2 charge for the forward direction. The k_{-2} term involves the dissociation of the halide from the $[ML_6X]^+$ species and follows the expected order for such a dissociative process: $I^- > Br^- > Cl^-$ (although in this case $Br^- \approx I^-$). The k_{-4} term is perhaps the least accurate one calculated since it is not directly measurable and is obtained from the final best fit of the data (Table IV). Of significance is the larger increase in rate for the chloride system ($k_{-4} > k_{-2}$) than for the bromide and iodide systems. This term involves the breakage of the bond of the ion-paired species and is especially difficult to assess. It is assumed here that the halide is lost from the metal ion and not from the ion pair. The scenario where the halide ion is lost as the ion pair with subsequent loss of X^- on the metal to form an ion pair involves the "crossover" pathway. This "inner-sphere–outer-sphere" mechanism will be discussed shortly.

Apparently the presence of the more strongly ion-paired chloride ion causes an increase in rate, presumably by polarizing the metal complex, thus easing the breakage of the M–Cl bond. For the bromide and iodide systems, the presence of the ion pair (presumably less tightly bonded and farther apart) is less effective in breaking the bond. The smaller $r^+ + r^-$ distance for the bromide in Table I is likely an anomaly in experimental values.

The values of R and Q are about as one might expect for such a mechanism. R is a measure of the relative reactivity of the non-ion-paired six-coordinate intermediate for X^- vs. L while Q is the same measure for the ion-paired six-coordinate intermediate. Both R and Q values follow the order $Cl^- > Br^- > I^-$, while within a given halide system $Q > R$ by a factor of between 11 and 42. The ligand preference follows the order $Cl^- > Br^- > I^- > L$ for the ion-paired species (Q), and $Cl^- > Br^- > L > I^-$ for the non-ion-paired species (R). This is not unexpected on the basis of the nucleophilic nature of the ligands. The fact that $Q > R$ likely indicates that the X^- is not completely lost from the sphere of influence of the metal ion upon dissociation—likely an entropy effect. Once the halide is lost from the metal center in the ion pair, it is still very difficult for the isocyanide to get to this metal center. The relatively large values of Q and k_{-4} give a picture of an ion pair in which the halide bond is dissociating more rapidly and then reforming more rapidly than in the non-ion-paired species.

Some additional topics are also worthy of discussion:

(a) Crossover pathways involving ion-paired reactants forming non-ion-paired intermediates or non-ion-paired reactants forming ion-paired intermediates must be considered to satisfy microscopic reversibility. These pathways would be represented by diagonals in the overall mechanistic scheme (eq 7). The two pathways where an ion-paired reactant forms a non-ion-paired intermediate are mechanistically and theoretically not viable since both involve a very unlikely termolecular pathway. The two pathways where a non-ion-paired reactant forms an ion-paired intermediate are more difficult to assess:

$$[ML_7]^{2+} + X^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [ML_6]^{2+}\cdots X^- + L \tag{15}$$

$$[ML_6X]^+ \underset{k_6}{\overset{k_{-6}}{\rightleftharpoons}} [ML_6]^{2+}\cdots X^- \tag{16}$$

The pathway shown in eq 15 is difficult to distinguish experimentally from the k_1 and k_3 pathways. However, to be significant, k_5 must be at least 2 orders of magnitude greater than k_3. This possibility is deemed theoretically unlikely. An analysis of the pathway shown in eq 16 is fruitful only in the reverse direction where the following term is added to the numerator in eq 8:

$$k_{-6}[L]/(k_6/k_{-3} + [L]) \tag{17}$$

Via an analysis of experimental data, one can make the approximation that $k_{-6} < 3 \times 10^{-5}$ s^{-1}. This compares with k_{-2} and k_{-4} values of $\sim 1 \times 10^{-4}$ s^{-1}. Thus, k_{-6} must not be a significant factor in this reaction. Another interesting result is that k_6/k_{-3} must be small, and thus k_6 is not an important pathway either. The analysis yields $0.003 > k_6/k_{-3}$ compared with the values of Q of between 16 and 61. The ion pair is not reacting rapidly with the metal center on the time frame of the overall reaction to form a non-ion-paired product. In addition, a halide which dissociates from a metal complexs is likely not ending up as an ion pair.

(b) The actual participation of the perchlorate ion in the reaction pathway is difficult to assess. The estimated ion-pairing constants with ClO_4^- are <100 for $[MoL_7]^{2+}\cdots ClO_4^-$ and likely in the 500–1000 range for $[MoL_6X]^+\cdots ClO_4^-$ as approximated from literature values of similar systems.[19,20] These values are smaller than the analogous halide ion-pairing values (except for $[MoL_7]^{2+}$ with I^-). Any effect is thus likely to be small, but due to the complexity of the systems under study, a detailed evaluation is impossible. The hexafluorophosphate concentration is so small in all cases that it can be neglected.

(c) The preassociation of the isocyanide ligand in the reverse direction is likely much smaller than for the negatively charged halide anions on the basis of electrostatic grounds. The lack of an L dependence on k^r_{obs} in the reverse direction indicates that this preassociation is not a factor in the reaction.

(d) The participation of the acetonitrile in the reaction is a matter which is nearly impossible to sort out considering the complexity of the system under study. Certainly if the activation entropies are any indication, the solvent must be strongly involved in the solvation of the two transition states. Definitive evaluations must come from other works involving solvent dependence of rates.

(e) At first glance, the large negative values for the activation entropies for the reaction of the molybdenum iodide system (ΔS^* = −14 to −27 eu) is somewhat disturbing considering the proposed dissociative process. Although a great deal is often made of this parameter (ΔS^* negative for associative, positive for dissociative pathways), these interpretations are often subject to much overuse in the literature.[21] All that can really be analyzed is a comparison of the relative $\Delta S^{\ddagger}$ values among similar systems. The large negative values can be easily explained by invoking a degree of solvent participation in the transition states and hence a great deal of solvation and ordering of the system. An additional factor is the formation of the six-coordinate intermediate which may also contribute to the negative $\Delta S^{\ddagger}$ term. This is consistent with other literature work.[22] The change in geometry in going from reactant to product should not be a major contributing factor since both reactant complex and product complex are capped trigonal prisms.[1a] The values of $\Delta H^{\ddagger}$ indicate that the rupture of the Mo–L bond takes ~5 kcal/mol more than the rupture of the Mo–I bond to reach the transition state. The $\Delta S^{\ddagger}$ is ~13 eu more negative in the reverse direction than in the forward direction as might be expected since the $[ML_6X]^+$ system should have a more positive entropy than the $[ML^7]^{2+}$ system.

(f) A comparison of the molybdenum and tungsten systems tends to support expected trends. Previous studies of rates of bimolecular substitution reactions tend to follow the order $Cr < Mo > W$ for these three transition metals.[23] This is also generally true for all transition-metal groups.[24] The little data that exist on seven-coordination compounds also support this trend.[5] Both systems under study are 18-electron systems (seven-coordinate d^4), and such systems invariably have been found to undergo substitution by a dissociative process.[25] The 20-electron, eight-coordinate intermediate needed to provide for an associative process is not observed. This is not surprising in light of the lack of any report of a stable eight-coordinate complex for either molybdenum(II) or tungsten(II).

Certainly more work needs to be done with different solvents, different metal ions, and different ligands to obtain a thorough understanding of these systems and similar systems. Currently, work has begun on studies of analogous complexes with methyl isocyanide, a more reactive ligand from the point of view of substitution reactions.

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