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Kinetic Study of the 1:1 Equilibration of Thiocyanate with the Molybdenum(IV)–Aquo Ion

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The kinetics of the equilibration of thiocyanate with the molybdenum(IV)–aquo ion

$$MoO^{2+} + NCS^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} MoO(NCS)^+$$

have been studied by conventional spectrophotometry in perchloric acid, $[H^+] = 0.75$–2.0 M, $I = 2.00$ M ($LiClO_4$), at temperatures in the range 10–25 °C. The equilibrium constant K_1 for (i) has been determined spectrophotometrically and has a value 405 ± 35 M^{-1} at 25 °C in 2 M $HClO_4$, with $\Delta H_1 = -6.7 \pm 0.9$ kcal mol^{-1} and $\Delta S_1 = -10.5 \pm 3.0$ cal K^{-1} mol^{-1}. First-order rate constants, k_{obsd}, for equilibration i can be expressed as $k_{obsd} = (k_1 + k_2[H^+]^{-1})([NCS^-] + K_1^{-1})$. At 25 °C, rate constants for the forward reaction are $k_1 \approx 0.23$ M^{-1} s^{-1} and $k_2 = 1.25$ s^{-1}. Activation parameters for the dominant $[H^+]^{-1}$-dependent pathway k_2 are $\Delta H_2^\ddagger = 14.9 \pm 0.25$ kcal mol^{-1} and $\Delta S_2^\ddagger = -8.1 \pm 0.9$ cal K^{-1} mol^{-1}.

Souchay et al.[1] first prepared the aquomolybdenum(IV) ion in 1966 by heating solutions containing Mo(III) and Mo(V) species. The same ion has been obtained from Mo(III) and Mo(VI).[2] Evidence in favor of a mononuclear divalent cationic structure, MoO^{2+}, in noncomplexing aqueous media has been reported.[3] Ardon and Pernick[4] in 1973 suggested that the structure was dimeric. More recent studies in these laboratories have provided conclusive evidence that the ion is monomeric.[5] A formula MoO^{2+}, or less likely $Mo(OH)_2{}^{2+}$, has been assigned in agreement with Souchay et al.[3] The first full kinetic study aimed at evaluating the substitution properties of the molybdenum(IV)–aquo ion is described in this paper. A spectrophotometric study of the reaction of Mo(IV) with thiocyanate has previously been reported.[6] However the conditions used, sulfate buffer pH 1.9, were very different from those in this study, and no kinetic data were presented.

Experimental Section

Reagents. Sodium thiocyanate (GPR, Hopkin and Williams) was recrystallized once from ethanol. Thiocyanate solutions were standardized by titration against mercury(II) with iron alum as indicator or against silver(I) with eosin (tetrabromofluorescein) as indicator. Sodium molybdate, $Na_2MoO_4 \cdot H_2O$ (Analar, BDH), was used without further purification. The complex $(NH_4)_2[MoCl_5(H_2O)]$ was prepared as described previously,[7] and $K_3[MoCl_6]$ was generously provided by the Molybdenum Climax Co. Lithium perchlorate was prepared from 72% perchloric acid (Analar, Hopkin and Williams) and lithium carbonate (Reagent grade, BDH) and purified by recrystallization. *p*-Toluenesulfonic acid (HPTS) (Aldrich Chemical Co.) was purified by recrystallization from water.

Aquomolybdenum(IV). A solution of $Na_2MoO_4 \cdot H_2O$ in 2 M HCl (25 ml, 0.3 M) was added to a solution of $K_3[MoCl_6]$ or $(NH_4)_2[MoCl_5(H_2O)]$ in 2 M HCl (50 ml, 0.3 M). Both solutions were deoxygenated by passing nitrogen through them for 30 min prior to mixing. The reaction mixture was kept for 1 h at 90 °C under N_2, and the resultant stock solution stored in the refrigerator. For normal purposes 5–10 ml of this stock was diluted ca. 50 times with 0.5 M HPTS and left to stand at room temperature for at least 1 day to allow aquation of coordinated chloride. To isolate the aquo ion the solution was transferred to a Dowex 50W-X2 cation-exchange column (12 cm × 1.2-cm diameter). A red band was held on the column and a diffuse yellowish brown band of Mo(V) dimer formed below this. Elution of the Mo(V) was achieved with 0.5 M HPTS. The red band moved slowly under these conditions and in some cases split into two, the first of which was eluted with 1.0 M HPTS and was shown to contain chloride ions. The second band, the aquomolybdenum(IV) ion, was eluted with 2.0 M HPTS. To obtain Mo(IV) in perchlorate medium the HPTS solution was again ion exchanged on Dowex 50W-X2 resin, but this time with a very short (ca. 0.5 cm) column and by eluting with 2 M $HClO_4$ after first moving the band to the bottom of the column with 1 M $HClO_4$. The Mo(IV) was determined by titration against cerium(IV), when oxidation to Mo(VI) occurs, using ferroin indicator.

Stability and Spectrum of Mo(IV). Solutions of Mo(IV) in 2 M HPTS were quite stable to aerobic oxidation, and the loss of Mo(IV) was less than 10%/day. In the absence of oxygen such solutions appear to be stable indefinitely. Molybdenum(IV) in perchlorate is generally very much less stable and aerobic oxidation of such solutions can be quite rapid. The stability of Mo(IV) in deoxygenated perchlorate solutions is variable since solutions were often stable for over 1 day at room temperature, but at other times only for 1 h or so. Such solutions were much more stable when maintained at <0 °C and with $[H^+]$ as high as possible (ca. 2.0 M). With such precautions small amounts of oxygen could even be tolerated, and in this study it was not always necessary to work in strictly anaerobic conditions.

Attempts were made to determine the acid dissociation constant K_a for the 2+ molybdenum(IV)–aquo ion by measuring absorption changes of solutions $[HClO_4] = 0.02$–0.20 M, $I = 2.00$ M ($LiClO_4$), at 250 nm. However these changes were not always rapidly established and it seems unlikely that protonation alone is important. For example, small (6%) changes in absorbance ($t_{1/2}$ = ca. 3 min) were observed on changing the $[H^+]$ from 0.65 to 0.055 M. Over short time intervals the changes appeared to be reversible. These absorbance changes may reflect polymerization processes in solution, a phenomenon which is not perhaps too surprising in view of the behavior exhibited by some other tetravalent transition metal ions such as Zr(IV) and Hf(IV). To avoid such changes $[H^+]$ values were restricted to ≥0.75 M, although this probably represents an overcautious approach. For such a range of $[H^+]$ values it is assumed that $K_a \ll [H^+]$.

The absorption spectrum of Mo(IV) in 1 M $HClO_4$, Figure 1, has two absorption maxima, λ 303 nm (ϵ 265 M^{-1} cm^{-1}) and 505 nm (ϵ 63 M^{-1} cm^{-1}). Solutions in 1 M HPTS give additional absorption < ca. 300 nm due to the PTS^- ion. The visible spectrum reported here is in good agreement with spectra reported elsewhere.[3,4]

Equilibrium Constants. Absorbance changes for a series of solutions at constant $[H^+]$, constant [Mo(IV)], and varying $[NCS^-]$, $I = 2.00$

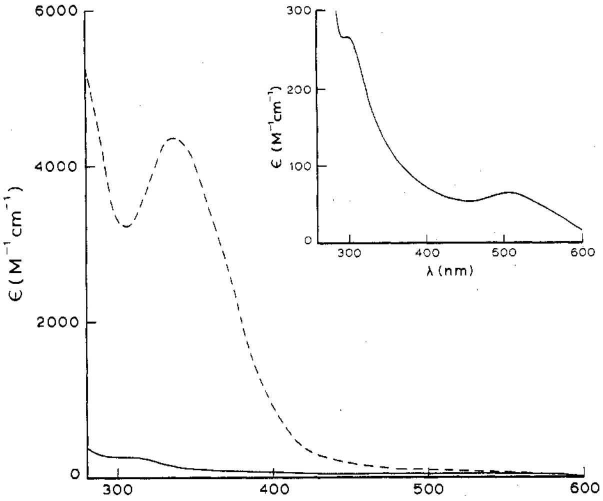

Figure 1. Uv-visible spectrum of the molybdenum(IV)–aquo ion in 1 M $HClO_4$ (lower curve and inset) and of the 1:1 thiocyanato complex extrapolated from a kinetic run at 25 °C, $[H^+] = 2.0$ M, and $[NCS^-] = 3.5 \times 10^{-3}$ M, using a value of $K_1 = 405$ M^{-1}.

M ($LiClO_4$), were analyzed by the Benesi–Hildebrand method[8] in order to obtain estimates of K_1, the formation constant of the monothiocyanato–molybdenum(IV) complex. Estimates of the molar absorption coefficient ϵ_C for this species were also obtained. The wavelength of these measurements was 340 nm. The temperature dependence of K_1 and the $[H^+]$ dependence at 25 °C were also investigated.

Kinetic Measurements. Kinetic runs were followed on Unicam SP500 and SP8000 spectrophotometers at wavelengths in the range 340–370 nm. Solutions containing thiocyanate were prethermostated for 20 min, while perchlorate solutions of Mo(IV) were thermostated for ca. 5 min since only small amounts (<5% total volume) were generally used. Stock solutions of Mo(IV) in $HClO_4$ were made fresh each day by the procedure described above. Rigorous air-free techniques were not necessary provided the stock Mo(IV) solution was maintained in an inert atmosphere and that cells were filled to the top and securely stoppered to prevent contact of the solution with air. Final absorbances were measured for each run, and first-order plots were linear to at least 80% and sometimes >95% completion. The ionic strength was adjusted to 2.00 M in all cases using $HClO_4$ (as required) and $LiClO_4$.

Analysis of Data. Rate constants (weighting $1/k^2$) and equilibrium data (weighting $\Delta\epsilon^2$ or K_1^{-2} as applicable) were analyzed with the aid of a nonlinear least-squares program.[9]

Separation and Analysis of Thiocyanate Product. A solution of NaNCS (1.0 M, 0.4 ml) was added to a deoxygenated solution of Mo(IV) (5×10^{-3} M) in HPTS (0.5 M, 100 ml). The mixed solution was allowed to equilibrate overnight in a refrigerator. The solution was then transferred onto a column of Dowex 50W-X2 cation-exchange resin in the H^+ form, which was maintained at 0 °C. A reddish band which was held on the column separated into two with deaerated $HClO_4$ (1 M). Initially the eluate was pale yellow-brown presumably due to Mo(V) species. When a separation of ca. 2 cm between the two bands had been achieved, the first band was eluted with 2 M $HClO_4$ and collected under nitrogen. The uv spectrum of the brown-red solution containing NCS⁻ (test with $AgNO_3$ solution) was measured in the range 300–370 nm and the solution stored at 0 °C. The spectrum obtained was in satisfactory agreement with that calculated from the final spectrum of a kinetic equilibration experiment, Figure 1. The elution required ca. 2 h. It is estimated (from kinetic and equilibrium data in this paper) that in aqueous solution at 0 °C the half-life for aquation of the thiocyanato complex is ca. 4 h. Any aquation that occurs will yield MoO^{2+}, which will (presumably) remain on the column, and NCS⁻ which will be eluted more rapidly. It is possible that aquation takes place more slowly on the column since no spreading of the bands was observed during the elution. Equal aliquots of eluent (20 ml) were used for Mo(IV) and thiocyanate determinations. The Mo(IV) was determined by addition of excess Fe(III) and back-titrating the excess with EDTA using variamine blue indicator. Thiocyanate was determined potentiometrically with silver(I) as follows. An aliquot of the molybdenum(IV)–thiocyanate solution was pipetted into an excess of $AgNO_3$. After ca. 1 h aquation of the complexed NCS⁻ was judged to be complete and the unprecipitated Ag(I) was titrated potentiometrically with NaNCS (10^{-2} M) using an Ag electrode relative to a standard sulfate electrode ($Na_2SO_4 \cdot 10H_2O$–Hg_2SO_4–Hg). Under the conditions used it was shown that Mo(IV) does not interfere with the potentiometric titration.

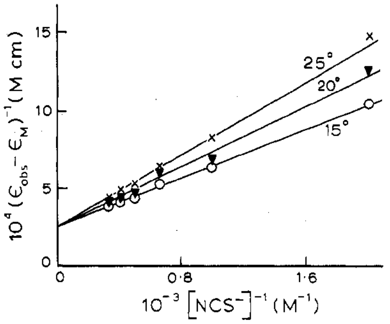

Figure 2. Determination of the formation constant K_1, eq 2, for the reaction of the molybdenum(IV)–aquo ion with thiocyanate at $[H^+] = 2.00$ M and $I = 2.00$ M ($LiClO_4$).

Table I. Formation Constants (K_1) and Absorption Coefficients (ϵ_C) for the 1:1 Aquomolybdenum(IV) Complex with Thiocyanate; $I = 2.00$ M ($LiClO_4$)

Temp, °C	25	20	15	10
K_1(spec),[a] M^{-1}	405 ± 35[b]	500 ± 75	655 ± 45	710 ± 70
K_1(calcd),[c] M^{-1}	415	510	625	760
K_1(kin),[d] M^{-1}	350	405	540	770
ϵ_C M^{-1} cm^{-1} (at 340 nm)	4200 ± 170	4250 ± 350	4050 ± 150	3900 ± 170

[a] At $[H^+] = 2.00$ M. [b] At $[H^+] = 0.40$ M, $K_1 = 460 \pm 40$ M^{-1}; at $[H^+] = 1.00$ M, $K_1 = 430 \pm 35$ M^{-1}. [c] Calculated from $\Delta H_1 = -6.7$ kcal mol^{-1} and $\Delta S_1 = -10.5$ cal K^{-1} mol^{-1}. [d] From kinetics $[H^+] = 0.75$–2.00 M.

Results

Nature of Thiocyanate Complex. Only a single stage was observed in the reaction of Mo(IV) with NCS⁻ at 25 °C, $[NCS^-] = (0.1$–$5.0) \times 10^{-3}$ M. At higher $[NCS^-]$ a further slower reaction was incident and for this reason it was decided to work with $[NCS^-] \leq 3.5 \times 10^{-3}$ M in kinetic runs. The reaction product separated by ion exchange at 0 °C and in 2 M $HClO_4$ gave an absorption maximum at 340 nm (ε 4400 M^{-1} cm^{-1}), Figure 1. Analysis of the product revealed an Mo:NCS ratio of 1:0.95 (±0.05).

Formation Constant for Thiocyanato Complex. The constant K_1 refers to the equilibrium

$$MoO^{2+} + NCS^- \overset{K_1}{\rightleftharpoons} MoO(NCS)^+ \qquad (1)$$

At constant $[H^+]$ and [Mo(IV)] and with a large (>10 times) excess of thiocyanate, absorbance changes for equilibrated solutions were analyzed in order to obtain K_1 and ϵ_C using (2)

$$\frac{1}{\epsilon_{obsd} - \epsilon_M} = \left(\frac{1}{\epsilon_c - \epsilon_M}\right)\left(1 + \frac{1}{K_1[NCS^-]}\right) \qquad (2)$$

where ϵ_M, ϵ_C, and ϵ_{obsd} are the molar absorption coefficients for MoO^{2+}, $MoO(NCS)^+$, and a mixture of the two at any particular thiocyanate concentration. Such plots of (2), Figure 2, are linear and reveal no evidence for higher complexes. Values of K_1 and ϵ_C at various temperatures 10–25 °C are shown in Table I. The possible dependence of K_1 on $[H^+]$ at 25 °C was investigated for $[H^+] = 0.40$–2.00 M. Since the value of $\epsilon_C - \epsilon_M$ may also be $[H^+]$ dependent if K_1 shows a dependence on $[H^+]$, no attempt was made to analyze the

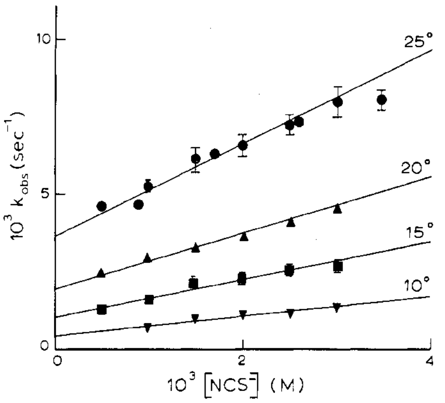

Figure 3. Dependence of pseudo-first-order rate constants k_{obsd} on [NCS⁻] for the reaction of the molybdenum(IV)-aquo ion with thiocyanate at $[H^+] = 1.00$ M and $I = 2.00$ M ($LiClO_4$). The lines drawn are for the best fit of kinetic data to K_1 (calcd).

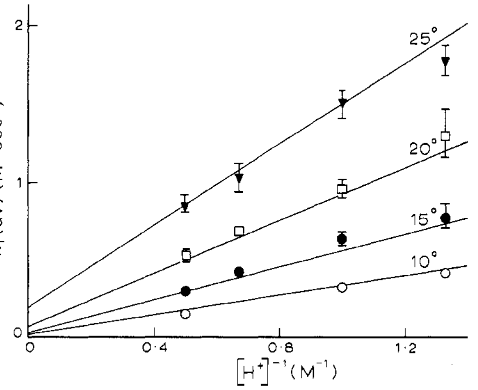

Figure 4. Dependence of average values of k_f, eq 4, on $[H^+]^{-1}$ for the reaction of the molybdenum(IV)-aquo ion with thiocyanate at $I = 2.00$ M ($LiClO_4$).

small (ca. 10%) observed decrease in K_1 over the $[H^+]$ range investigated. From the temperature dependence of K_1 at $[H^+] = 2.00$ M, values of $\Delta H_1 = -6.7 \pm 0.9$ kcal mol⁻¹ and $\Delta S_1 = -10.5 \pm 3.0$ cal K⁻¹ mol⁻¹ were obtained. From these parameters better estimates of K_1 at each temperature, designated K_1(calcd), as required in the kinetic analyses, were calculated and are given in Table I.

Table II. Dependence of Pseudo-First-Order Rate Constants for the Reaction of Mo(IV) with Thiocyanate on $[H^+]$ and $[NCS^-]$; $[Mo(IV)] = (0.48\text{–}2.46) \times 10^{-4}$ M, $I = 2.00$ M ($LiClO_4$)[a]

$10^3[NCS^-]$, M	10^3k_{obsd}, s⁻¹ $[H^+] = 0.75$ M	$[H^+] = 1.00$ M	$[H^+] = 1.50$ M	$[H^+] = 2.00$ M
		25.0 °C		
0.50		4.60		2.66
0.87	6.21	4.64		2.75 (2)
1.00	6.22	5.25 (2)	3.64	2.92 (3)
1.50	7.19	6.11 (2)	4.03	3.25 (2)
1.73	7.86	6.36		3.53
2.00	7.50	6.59 (2)	4.43	3.70 (2)
2.50	8.30 (2)	7.25 (2)	4.75	4.14 (2)
2.60	9.12	7.36		4.06
3.00	9.20	8.02 (2)	5.06	4.41 (2)
3.47	10.2	9.06 (2)		4.75
		20.0 °C		
0.50	3.60	2.48 (2)		1.34
1.00	3.85 (2)	2.95	2.00	1.61 (2)
1.50	4.85	3.24	2.37	1.93 (2)
2.00	5.18	3.62	2.69	2.11 (2)
2.50	5.42	4.11	2.92 (2)	2.21
3.00	5.73 (3)	4.52	3.36	2.39 (2)
		15.0 °C		
0.50	1.80	1.25	0.86	0.60 (2)
1.00	2.24	1.61	1.15	0.80 (2)
1.50	2.41	2.08	1.35	0.91 (2)
2.50	2.88	2.62 (2)	1.76 (2)	1.09
3.00	3.30	2.70 (2)	1.81 (2)	1.22 (2)
3.50			2.09	
		10.0 °C		
1.00	1.00	0.70		0.36
1.50	1.17	1.00		0.42
2.00	1.41	1.13		0.50 (2)
2.50	1.56	1.17		0.63
3.00	1.80	1.40		0.66

[a] Numbers of runs averaged are indicated in parentheses.

Table III. Temperature Dependence of k_1 and k_2 (Eq 5) for the Reaction of the Molybdenum(IV)-Aquo Ion with Thiocyanate; $I = 2.00$ M ($LiClO_4$)

Temp, °C	k_1, M⁻¹ s⁻¹	k_2, s⁻¹
25.0	0.235 ± 0.025	1.21 ± 0.04
20.0	0.089 ± 0.022	0.87 ± 0.03
15.0	−0.016 ± 0.017	0.615 ± 0.025
10.0	−0.009 ± 0.007	0.33 ± 0.01

Kinetic Studies. Under the conditions used in this investigation the formation of the monothiocyanato complex never reaches completion and equilibrium kinetics apply. By working with at least a tenfold excess of thiocyanate the pseudo-first-order rate constant, k_{obsd}, conformed to (3), where k_f and

$$k_{\text{obsd}} = k_f[NCS^-] + k_b \tag{3}$$

k_b are the forward and back rate constants in (1). The dependence of k_{obsd} (Table II) on [NCS⁻] at $[H^+] = 1.00$ M is shown in Figure 3. The straight lines indicated correspond to the best fit of k_{obsd} to values of K_1(calcd). Kinetic values, K_1(kin), have also been obtained as the ratio of k_f/k_b from the least-squares fit of data to (3). Mean values of this quantity at each temperature are given in Table I. The terms k_f and k_b exhibit marked $[H^+]^{-1}$ dependences. In order to investigate the effect of $[H^+]$ in more detail, k_b in (3) is replaced by the equivalent term k_f/K_1(calcd) to give (4). Plots

$$k_{\text{obsd}} = k_f([NCS^-] + K_1^{-1}) \tag{4}$$

of $k_{\text{obsd}}/([NCS^-] + K_1^{-1})$, i.e., k_f(av), against $[H^+]^{-1}$ are illustrated in Figure 4, where $[H^+]$ was confined to the range 0.75–2.00 M. Under such conditions k_f exhibits a linear dependence on $[H^+]^{-1}$, (5). Values of k_1 and k_2 are shown

$$k_f = k_1 + k_2[H^+]^{-1} \tag{5}$$

in Table III. Although at 25 and 20 °C k_1 is significant, at 15 and 10 °C slightly negative values are obtained with relatively large errors. There seem to be two possible explanations. Either k_1 makes no contribution at all, in which case the values at 25 and 20 °C are spurious, or the values at 25 and 20 °C are real and those at 15 and 10 °C are not large enough to detect. Of these possibilities the latter gives a better statistical fit and we feel describes the system more precisely. If values of k_1 at 25 and 20 °C are real, we can obtain k_1 at 10 and 15 °C by extrapolating a plot of log (k_1/T) against $10^3/T$ (T in K). These values are 0.034 and 0.013 M⁻¹ s⁻¹, respectively, and are within three standard deviations of those quoted in Table III. Since they are numerically <5% of k_2, experimental detection might be expected to be difficult. At 25 °C rate constants are $k_1 = 0.23$ M⁻¹ s⁻¹ and $k_2 = 1.25$ s⁻¹. Activation parameters for k_2 are $\Delta H_2^{\ddagger} = 14.9 \pm 0.25$ kcal mol⁻¹ and $\Delta S_2^{\ddagger} = -8.1 \pm 0.9$ cal K⁻¹ mol⁻¹. Approximate values for k_1 are $\Delta H_1^{\ddagger} \approx 33$ kcal mol⁻¹ and $\Delta S_1^{\ddagger} \approx 48$ cal K⁻¹ mol⁻¹. If alternatively (and we feel much less likely) k_1

is assumed to be zero at all temperatures, $\Delta H_2^\ddagger = 16.5 \pm 0.25$ kcal mol^{-1} and $\Delta S_2^\ddagger = -2.4 \pm 0.9$ cal K^{-1} mol^{-1}.

Discussion

Evidence for a mononuclear divalent cationic structure for the molybdenum(IV)–aquo ion has been presented elsewhere.[5] The analysis of the molybdenum(IV)–thiocyanate product presented in this paper and the agreement between the absorption coefficient for the product and that obtained from an equilibrium study of the reaction with excess thiocyanate support the mononuclear assignment. For the conditions chosen a 1:1 complex is formed, the most acceptable formulation being $MoO(NCS)^+$.

Information is now available regarding the magnitude of formation constants (25 °C) for the 1:1 complexes of aquo ions of Mo(III) (ca. 10^5 M^{-1}),[7] Mo(IV) (405 M^{-1}), and the Mo(V) dimer $Mo_2O_4^{2+}$ (240 M^{-1}).[10] These values would seem to illustrate a quite striking affinity of molybdenum for thiocyanate, almost certainly N bonded.[11] The decreasing affinity of the higher oxidation states for thiocyanate is also noted, although here some allowance may be necessary for the different charge on the cation.

As far as the kinetics of the equilibration of NCS^- with Mo(IV) are concerned, a dominant feature of both the k_f and k_b terms is the sensitivity to $[H^+]$, where for the range of values studied the $[H^+]^{-1}$ pathway accounts for a large fraction (generally >85%) of the reaction. The complexing of NCS^- with the vanadium(IV) aquo ion VO^{2+} exhibits only a relatively small contribution from an $[H^+]^{-1}$ term,[12] which might stem from a smaller acid dissociation constant for VO^{2+} ($K_a = 4.4 \times 10^{-6}$ M at 25 °C)[13] as compared to MoO^{2+}. Since absorbance changes for Mo(IV) solutions at low $[H^+]$, 0.02–0.20 M, cannot be unambiguously assigned to a protolytic equilibrium (see Experimental Section), we place little reliance on our value for K_a of ca. 0.04 M at 25 °C determined under such conditions.

A structure, MoO^{2+}, has been suggested[2] and seems most probable for the molybdenum(IV)–aquo ion. X-ray crystallographic studies of the Mo(IV) complexes $[MoO(H_2O)(CN)_4]^{2-}$ and $[MoO(OH)(CN)_4]^{3-}$ have indicated relatively short Mo–O bond distances to the oxo ligand,[14] and in each case the molybdenum atom is not coplanar with the four cyanides. As observed with the VO^{2+} ion, elongation and labilization of the water ligand trans to the oxo group are expected. Substitution of the axial position is essentially diffusion controlled in the case of VO^{2+}.[15] If these structural features are also present in the case of the molybdenum(IV)–aquo ion, then the reaction which is observed is likely to correspond to substitution of an equatorial water ligand, where the conjugate-base mechanism is operative from an equatorial site. These comments presuppose a coordination number of 6, which is not as yet established. Coordination numbers as high as 8 and as low as 5 have been reported for Mo(IV).[16]

The rate constant k_2 is a composite term and allowance for the acid dissociation constant must be made before the activation parameters can be fully assessed. It seems certain however that the enthalpy of activation associated with the k_2 process (observed value 14.9 kcal mol^{-1}) is much less than that for k_1 (~33 kcal mol^{-1}). The negative entropy term which is likely to result after correction for acid dissociation (<–8.1 cal K^{-1} mol^{-1}) might suggest associative character, although this would be inconsistent with a dissociative process as is generally invoked to explain conjugate-base pathways.

It is now possible to comment on substitution properties exhibited by aquo ions of molybdenum in oxidation states III–VI. A wide range of rate constants of some ten orders of magnitude is observed, and the trend is to increasing lability with the higher oxidation states. No dependence on $[H^+]$ is observed for the complexing of Mo^{3+} with NCS^- and Cl^-, $[H^+] = 0.5$–2.0 M, rate constants 0.28 M^{-1} s^{-1} (NCS^-) and 4.6×10^{-3} M^{-1} s^{-1} (Cl^-) at 25 °C,[7] and an associative mechanism has been assigned. For Mo(IV) (present study) a hydrogen ion dependence $k_1 + k_2[H^+]^{-1}$ is observed with k_2 dominant. Both these aquo ions require conventional techniques to study their substitution properties, while for the much more labile molybdenum(V)–aquo dimer[10] and for Mo(VI) species fast-reaction techniques are necessary.[17,18]

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Registry No. Mo, 7439-98-7; thiocyanate, 302-04-5.

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