Kinetics of the 1 : 1 Equilibration of Thiocyanate with the Molybdenum(v) Aquo-dimer

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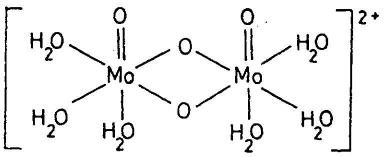
Equilibration kinetic studies on the complexing of thiocyanate with the molybdenum(V) aquo-dimer $[Mo_2O_4]^{2+}$, (I), have been carried out using the temperature-jump technique. With excess thiocyanate the reaction exhibits more than one relaxation effect, and the mechanism cannot be expressed in terms of a single process. With $[Mo_2O_4]^{2+}$ in excess (*ca.* 5 : 1) only one relaxation time corresponding to the formation of the 1 : 1 complex $[Mo_2O_4(NCS)]^+$ is observed, and this is independent of hydrogen-ion concentration in the range 0·5—2·0M, I = 2·0M ($LiClO_4$). Relaxation times, τ, can be expressed in terms of equilibrium concentrations of reactant as in (i), where rate constants k_1 and k_{-1} for the formation and aquation of the 1 : 1 complex are, at 25 °C, (2·9

$$\tau^{-1} = k_1([Mo_2O_4{}^{2+}]_e + [NCS^-]_e) + k_{-1} \qquad \text{(i)}$$

± 0·1) × 10^4 l mol^{-1} s^{-1} and 120 ± 10 s^{-1} respectively. Activation parameters from data at 15—35 °C are $\Delta H_1^\ddagger = 11{\cdot}3 \pm 0{\cdot}9$ kcal mol^{-1}, $\Delta S_1^\ddagger = -0{\cdot}3 \pm 3{\cdot}1$ cal K^{-1} mol^{-1}, $\Delta H_{-1}^\ddagger = 13{\cdot}7 \pm 2{\cdot}5$ kcal mol^{-1}, and $\Delta S_{-1}^\ddagger = -3{\cdot}0 \pm 8{\cdot}0$ cal K^{-1} mol^{-1}. The kinetic value of the equilibrium constant (k_1/k_{-1}) at 25 °C, I = 2·0M ($LiClO_4$), is 240 l mol^{-1}, which is in good agreement with that obtained spectrophotometrically.

SUBSTITUTION and redox behaviour exhibited by the different oxidation states of molybdenum are currently of interest to us, and are of relevance in attempting to evaluate the function of molybdenum in metalloenzymes.[1] As a part of our scheme of study substitution and redox reactions of the molybdenum(V) aquo-dimer, $[Mo_2O_4]^{2+}$, are being investigated. In this paper the kinetics of complexing of thiocyanate to the molybdenum(V) aquo-dimer $[Mo_2O_4]^{2+}$ which, it has been deduced, has the structure (I),[2,3] are reported.



(I)

Previous studies have been concerned with the kinetics of formation and/or dissociation of ethylenediaminetetra-acetate (EDTA),[3,4] oxalate,[5] and iminodiacetate [4,5] to (I). No firm conclusions regarding the lability of H_2O ligands in (I) were possible because of the multistage nature of the reactions and the incidence of protonation equilibria. It was, therefore, decided to investigate the complexing of a unidentate acidic ligand to (I). By far the most versatile of these is thiocyanate which binds strongly to most transition-metal ions. Although visible absorbance changes are small, and indeed were not clearly delineated at an earlier stage in our studies,[4] we now find that u.v.–visible changes are sufficient to permit a full investigation of the equilibrium kinetics.

RESULTS

Spectrophotometric Determination of Equilibrium Constant.—The addition of NCS^- (10^{-3}—10^{-1}M) to solutions of $[Mo_2O_4]^{2+}$ (5×10^{-5}—5×10^{-2}M) with $[H^+]$ in the range 0·5—2·0M resulted in absorption increases in the range 250—550 nm. The peak at 297 nm is shifted to longer wavelengths, and the peak at 384 nm becomes a shoulder. Attempts to determine the equilibrium constant for complex formation between $[Mo_2O_4]^{2+}$ and NCS^- (K_1) with either species in excess were unsuccessful. With excess NCS^- the Benesi–Hildebrand [6] plot of $(\Delta O.D.)^{-1}$ against $[NCS^-]^{-1}$ was curved indicating the presence of more than two absorbing species, and implying that more than one NCS^- is involved. With excess of $[Mo_2O_4]^{2+}$ the absorbance changes (ΔO.D.) were too small to obtain a meaningful value of K_1. However it was possible to determine a value of this quantity by working with equal concentrations of $[Mo_2O_4]^{2+}$ and NCS^- which were in the range (0·13—2·88) × 10^{-3}M (0·2—4·0 cm optical cell path length). Under these conditions a modification of the procedure used to determine the dimerisation constant for molybdenum(VI) [7] could be used. Thus the reaction investigated may be expressed as in (1). At equilibrium

$$[Mo_2O_4]^{2+} + NCS^- \overset{K_1}{\rightleftharpoons} [Mo_2O_4(NCS)]^+ \qquad (1)$$

the concentration of complex is x, and the concentration of reactant is $(a - x)$, where a represents the initial concentration of reactant. Equation (2) can

$$\frac{\Delta O.D.'}{a} = \Delta\varepsilon - \left(\frac{\Delta\varepsilon}{K_1}\right)^{\frac{1}{2}} \frac{(\Delta O.D.')^{\frac{1}{2}}}{a} \qquad (2)$$

therefore be deduced, where $\Delta O.D.' = \Delta O.D./l$ and $\Delta\varepsilon$ is the difference in absorption coefficient between $[Mo_2O_4(NCS)]^+$ and $[Mo_2O_4]^{2+}$ at the wavelengths investigated (380 and 400 nm). Graphs of $\Delta O.D.'/a$ against $(\Delta O.D.')^{\frac{1}{2}}/a$ are linear and K_1(spec) can be determined from the slope and intercept. Plots of this type are shown in Figure 1 for data at 25 °C, I = 0·5

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[1] See for example, J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475.

[2] M. Ardon and A. Pernick, *Inorg. Chem.*, 1973, **12**, 2484.

[3] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1974, 1968.

[4] Y. Sasaki and A. G. Sykes, Proceedings of the Climax First International Conference on the Chemistry and Uses of Molybdenum, University of Reading, ed. P. C. H. Mitchell, 1973, p. 64.

[5] Y. Sasaki and A. G. Sykes, unpublished work.

[6] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[7] J. F. Ojo, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, in the press.

and 2·0M. Values of K_1(spec) were obtained by applying a least-squares fit of data to equation (2) with each point weighted equally. At 25 °C, $[H^+] = 0{\cdot}5$M and $I = 0{\cdot}5$M, K_1(spec) $= 200 \pm 40$ l mol^{-1}. At the same temperature and $[H^+]$, $I = 2{\cdot}0$M ($LiClO_4$), K_1(spec) $= 260 \pm 25$ l mol^{-1}. A comparison of these values with K_1(kin), see below, is given in Table 3.

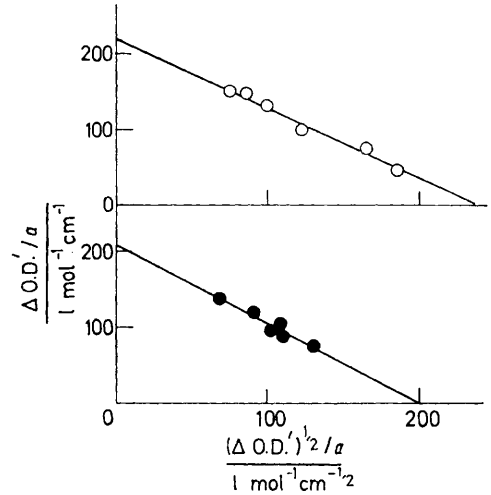


FIGURE 1 Equilibrium constant determination for the reaction of $[Mo_2O_4]^{2+}$ with NCS^- at 25 °C, according to equation (2), $I = 0{\cdot}50$M, $\lambda = 400$ nm (●); $I = 2{\cdot}0$M, $\lambda = 380$ nm (○)

Kinetic Studies.—The reaction appeared to be complete as soon as the reactants were mixed ($t_{\frac{1}{2}} < 10$ s), and further experiments were therefore carried out using the temperature-jump technique. Relaxation times of the order of 0·5—10 ms were observed. At 25 °C, $I = 0{\cdot}5$M ($LiClO_4$), with $[Mo_2O_4^{2+}] = (4$—$50) \times 10^{-5}$M and NCS^- in at least ten-fold excess, temperature-jump experiments revealed at least two relaxation times, τ(fast) being an order of magnitude smaller than τ(slow). Values of τ^{-1}(slow) did not show a linear dependence on the concentration of NCS^- (Figure 2, Table 1), and it was concluded that more than one process was involved in the complexation reaction. Equilibrium studies support this, and the most likely explanation is that NCS^- is complexing more extensively. By working with an excess $[Mo_2O_4^{2+}]$ such problems could be averted.

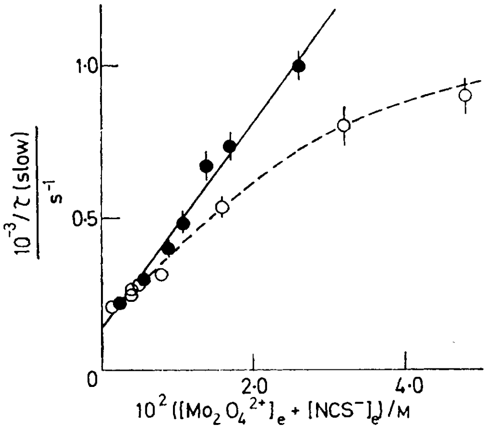


FIGURE 2 The dependence of relaxation times τ (slow process) on equilibrium concentrations of reactants, $[Mo_2O_4]^{2+}$ and NCS^-, at $I = 0{\cdot}5$M and 25 °C, $[NCS^-] \gg [Mo_2O_4^{2+}]$ (○), and $[Mo_2O_4^{2+}] \approx 5[NCS^-]$ (●). Error bars represent ranges of individual values obtained for each set of conditions

Initial experiments with $[Mo_2O_4]^{2+}$ in five-fold excess of NCS^- were carried out at $I = 0{\cdot}5$M ($LiClO_4$). Under these conditions only one measurable relaxation time was observed over the entire concentration range studied (Table 1), with λ in the range 350—530 nm. This corresponded to τ(slow) as observed with NCS^- in excess. Data obtained gave a good fit to (3), where

$$\tau^{-1} = k_1([Mo_2O_4^{2+}]_e + [NCS^-]_e) + k_{-1} \qquad (3)$$

$[Mo_2O_4^{2+}]_e$ and $[NCS^-]_e$ are the equilibrium concentrations of reactants, which could be calculated using K_1(spec) $= 200$ l mol^{-1}. Values of k_1 and k_{-1}, the formation and dissociation (*i.e.* aquation) rate constants in (1), were however determined by a least-squares treatment of data (weighting τ^2) without assuming a value for K_1. This is possible since the equilibrium concentrations in equation (3) can be expressed in terms of made up concentrations and k_1 and k_{-1}. Values of k_1 and k_{-1} so determined are summarised in Table 3. It can be seen that the kinetic equilibrium constant K_1(kin) ($= k_1/k_{-1}$) of 260 l mol^{-1} is in satisfactory agreement with the value of K_1(spec) of 200 ± 40 l mol^{-1}.

TABLE 1

Reciprocal relaxation times, τ^{-1}, for the reaction of $[Mo_2O_4]^{2+}$ with NCS^- at 25 °C, $[H^+] = 0{\cdot}5$M, $I = 0{\cdot}5$M

$10^2[Mo_2O_4^{2+}]$ M	$10^3[NCS^-]$ M	τ^{-1}(obs.) s^{-1}	τ^{-1}(calc.) [a] s^{-1}
NCS^- in excess [b]			
0·005	48·0	900	
0·005	32·0	805	
0·015	16·0	535	
0·015	8·0	318	
0·050	5·0	285	
0·015	4·0	265	
0·005	4·0	250	
0·005	1·2	210	
$[Mo_2O_4]^{2+}$ in excess			
0·19	0·40	217	203
0·57	1·20	302	322
0·95	2·00	398	434
1·15	2·00	482	496
1·51	3·00	668	595
1·89	4·00	738	697
3·02	6·00	1010	1017

[a] Calculated using parameters in Table 3, and equation (3).
[b] Relaxation time quoted is the slower of two observed.

An experiment at a lower $[H^+]$ of 0·1M, $[Mo_2O_4^{2+}] = 4{\cdot}5 \times 10^{-5}$M, $[NCS^-] = 4 \times 10^{-3}$M, gave a 25% decrease in relaxation time. It is possible that this effect is related to changes in the structure of (I), the spectrum of which is $[H^+]$-dependent at $[H^+] \leqslant 0{\cdot}1$M. Furthermore the reaction could not be readily studied over a significant range of $[Mo_2O_4^{2+}]$ at such low $[H^+]$ values, because the concentration of molybdenum stock solutions eluted from the column were too low; attempts to neutralise some of the hydrogen ions in the stock solutions caused precipitation. In order to overcome these problems it was decided to carry out the major part of the study at $I = 2{\cdot}0\text{M}$.

Over the concentration range investigated, the relaxation expression was given by equation (3), and at 25 °C there was no observable [H+]-dependence within the range 0·5—2·0M (Table 2, Figure 3). Values of k_1 and k_{-1} were determined as described above. The reaction was also studied as a function of metal and ligand concentration over the temperature range 15—35 °C, and results of these experiments are also shown in Table 2. Activation parameters computed using a least-squares programme[8] (weighting τ^2) are $\Delta H_1^\ddagger = 11{\cdot}3 \pm 0{\cdot}9$ kcal mol^{-1} and $\Delta S_1^\ddagger = -0{\cdot}3 \pm 3{\cdot}1$ cal K^{-1} mol^{-1} for the formation reaction, and $\Delta H_{-1}^\ddagger = 13{\cdot}7 \pm 2{\cdot}5$ kcal mol^{-1} and $\Delta S_{-1}^\ddagger = -3 \pm 8$ cal K^{-1} mol^{-1} for the aquation process. At $I = 2{\cdot}0\text{M}$ (LiClO$_4$) values of K_1(spec) and K_1(kin), Table 3, are in excellent agreement.

TABLE 2

Reciprocal relaxation times, τ^{-1}, for the reaction of $[Mo_2O_4]^{2+}$ with NCS$^-$ at 25 °C, $I = 2{\cdot}0\text{M}$ (LiClO$_4$)

Temp. / °C	[H+] / M	$10^2[Mo_2O_4^{2+}]$ / M	10^3[NCS$^-$] / M	τ^{-1}(obs.) / s^{-1}	τ^{-1}(calc.) / s^{-1}
15·1	2·0	1·97	3·94	331	298
15·7	2·0	2·30	5·25	365	346
16·0	2·0	1·15	2·62	200	214
16·3	2·0	1·73	3·94	268	292
16·8	2·0	0·57	1·31	166	149
20·4	2·0	1·31	2·62	295	328
20·4	2·0	1·97	3·94	427	441
20·4	2·0	2·63	5·25	546	553
21·0	2·0	0·26	0·52	141	145
25·0	0·5	0·10	0·20	144	151
25·0	0·5	0·29	0·60	210	205
25·0	0·5	0·72	1·40	354	316
25·0	0·5	1·45	2·90	485	492
25·0	0·5	2·18	4·40	660	662
25·0	0·5	2·89	5·80	860	827
25·0	2·0	0·25	0·50	195	194
25·0	2·0	0·51	1·00	290	263
25·0	2·0	1·27	2·50	420	449
25·0	2·0	1·91	3·80	605	600
25·0	2·0	2·54	5·10	800	746
30·8	2·0	0·26	0·53	308	304
31·0	2·0	0·66	1·31	483	464
31·3	2·0	1·31	2·62	630	714
31·4	2·0	1·97	3·94	1050	957
31·4	2·0	2·63	5·25	1250	1192
35·4	2·0	0·26	0·53	430	424
35·4	2·0	0·66	1·31	615	631
35·8	2·0	1·31	2·62	980	970
35·8	2·0	2·63	5·25	1600	1597
35·9	2·0	1·97	3·94	1240	1294

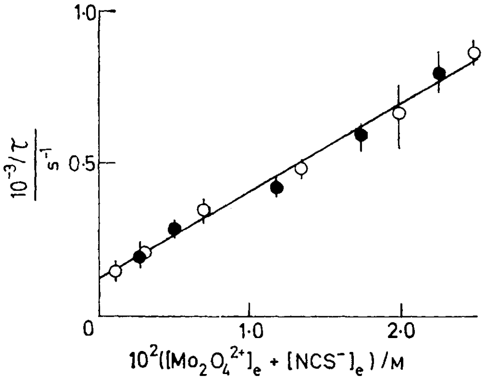


FIGURE 3 The dependence of relaxation times τ on the equilibrium concentrations of reactants, $[Mo_2O_4]^{2+}$ and NCS$^-$, at $I = 2{\cdot}0\text{M}$ and 25 °C, [H+] = 0·5M (○) and 2·0M (●), with $[Mo_2O_4^{2+}] \approx 5[NCS^-]$. Error bars represent ranges

TABLE 3

Summary of rate and equilibrium data for the reaction of $[Mo_2O_4]^{2+}$ with thiocyanate at 25 °C

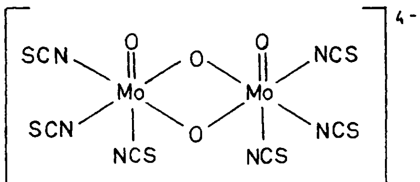
I / M	[H+] / M	$10^{-4}k_1$ [a] / l mol^{-1} s^{-1}	$10^{-2}k_{-1}$ [a] / s^{-1}	K_1(kin) / l mol^{-1}	K_1(spec) / l mol^{-1}
0·5	0·5	3·4 ± 0·3	1·3 ± 0·3	260	200 ± 40 [b]
2·0	0·5	3·0 ± 0·2	1·2 ± 0·1	250	260 ± 25 [c]
2·0	2·0	2·9 ± 0·2	1·2 ± 0·2	230	—
2·0	0·5—2·0	2·9 ± 0·1	1·2 ± 0·1	240	—

[a] Computed from data at 25 °C only. [b] Determined at 400 nm. [c] Determined at 380 nm.

DISCUSSION

The agreement between equilibrium and kinetic data when NCS$^-$ is not in excess strongly suggests that the product of the reaction is a monothiocyanato-complex. This is supported also by the fact that the reciprocal relaxation time shows a linear dependence on concentration. With an excess of thiocyanate further complexing of NCS$^-$ occurs. If the two metal atoms in the $[Mo_2O_4]^{2+}$ ion can be treated as completely independent as regards their substitution properties, the value of K_2 for the complexing of the second thiocyanate should be *ca.* 60 l mol^{-1}, *i.e.* $K_1/4$, on statistical grounds. By working with a five-fold excess of total $[Mo_2O_4]^{2+}$ the amount of disubstituted product cannot therefore be >5% of the total thiocyanate.

The dimeric species $[Mo_2O_4(NCS)_6]^{4-}$, (II),[9] has been characterised, and it seems safe to assume that the $[Mo_2O_4]^{2+}$ unit is retained on complexing of a single thiocyanate. Oxo-bridge cleavage, if it occurred, might be expected to introduce a direct [H+]-dependence, which is certainly not apparent in our studies. Other thiocyanato-complexes of molybdenum(V) are known in which thiocyanate co-ordinates more extensively than in (II). These are $[Mo_2O_3(NCS)_8]^{4-}$, (III),[10] and $[MoO(NCS)_5]^{2-}$, (IV).[11,12] I.r. studies of the complexes (II)—(IV) indicate N-bonded thiocyanate, and we have no reason for supposing that thiocyanate in $[Mo_2O_4(NCS)]^+$ is S-bonded.



(II)

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[8] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler. We are grateful to Dr. A. T. Thornton for helpful comments.

[9] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, **1962**, 4570.

[10] B. Jezowska-Trzebiatowska, M. F. Rudolf, L. Natkaniec, and H. Sabat, *Inorg. Chem.*, 1974, **13**, 617.

[11] H. Sabat, M. F. Rudolf, and B. Jezowska-Trzebiatowska, *Inorg. Chim. Acta*, 1973, **7**, 365.

[12] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.

From a number of *X*-ray crystal studies of di-μ-oxo-[13] and di-μ-sulphido-[14,15] molybdenum(V) complexes it is well established that there is multiple bonding between the molybdenum and terminal oxo-groups. This results in a distortion of the octahedral geometry, with the metal atoms displaced towards the two terminal oxo-groups, and a consequent lengthening of bonds to the *trans*-ligands. The effect is similar to that observed in complexes of vanadium(IV), VO^{2+}, where weak bonding at the position *trans* to the oxo-group is also observed.[16] Five-co-ordinate complexes of vanadium(IV), *e.g.* [VO(acac)$_2$] (acac = acetylacetonate), have been characterised by *X*-ray crystal studies.[17] Similarly it has been possible to prepare molybdenum(V) dimers, *e.g.* the di-μ-oxo-bis[oxo-(L-cysteinato ethyl ester-*N*,*S*)-molybdenum(V)][18] and di-μ-sulphido-bis[oxo-(L-cysteinato methyl ester-*N*,*S*)-molybdenum(V)],[19] which have been shown to be five-co-ordinate from *X*-ray crystal investigations.

TABLE 4

A summary of kinetic data for water exchange and unidentate complex formation reactions of VO^{2+} and $[Mo_2O_4]^{2+}$

Metal	Ligand	$10^{-3}k$(25 °C) / l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal K^{-1} mol^{-1}	I / M	Ref.
$[Mo_2O_4]^{2+}$	NCS^-	29	11·3 ± 0·9	−0·3 ± 3·1	2·0	This study
VO^{2+}	NCS^-	11·5	10·8	−3·7	→ 0 corr	23
VO^{2+}	H_2O exch	0·52 [a]	13·3 ± 0·3	−1·5 ± 1·0	—	22
VO^{2+}	Hgly [b]	1·30	12·0 ± 0·9	−4·0 ± 2·1	0·2	*c*
VO^{2+}	SO_4^{2-}	1·50 [a]	—	—	→ 0 corr	***d***

[a] Units s^{-1}. [b] Glycine zwitterion. [c] H. Tomiyasu, K. Dreyer, and G. Gordon, *Inorg. Chem.*, 1962, **11**, 2409. [d] H. Strehlow and H. Wendt, *Inorg. Chem.*, 1963, **2**, 6.

N.m.r. studies on the water exchange reactions of the VO^{2+} aquo-ion have indicated that the water *trans* to the oxo-group is extremely labile.[20-22] Its exchange characteristics are similar to those of the axial water ligands of the Cr^{2+} and Cu^{2+} aquo-ions, and indeed the behaviour exhibited is not too different from that of a water molecule in the outer-co-ordination sphere. Although similar information concerning the exchange rates of the axial waters of $[Mo_2O_4]^{2+}$, (I), is not available we are inclined to regard the position *trans* to the terminal oxo-groups as being extremely labile in view of the lengthening of bonds to the *trans* ligands. It is unlikely that a stability constant as high as 250 l mol^{-1} would apply to co-ordination in the axial position. Indeed the rate constants (25 °C) of $k_1 = 2{\cdot}9 \times 10^4$ l mol^{-1} s^{-1} and $k_{-1} = 120$ s^{-1}, equation (1), strongly suggest that an equatorial position is involved in the substitution process. This does not necessarily rule out an initial rapid equilibration in which thiocyanate bonds to the axial position, and then subsequently (in a slower process) isomerises to give the equatorially substituted product.

It has previously been concluded that in the complexing of NCS^- to VO^{2+} substitution is occurring at an equatorial co-ordination position.[23] From Table 4 it is seen that rate constants and activation parameters are of similar magnitude for VO^{2+} and $[Mo_2O_4]^{2+}$, although it must be noted that the ionic strength for the two studies do differ considerably. Both vanadium(IV) and molybdenum(V) are d^1 metal ions. An important structural difference is that molybdenum(V) dimers, $[Mo_2O_4]^{2+}$, exhibit diamagnetic behaviour which is indicative of metal–metal bonding. This does not appear to have a marked influence on the complexing with thiocyanate however; thus equilibrium constants 250 l mol^{-1} ($[Mo_2O_4]^{2+}$) and 210 l mol^{-1} (VO^{2+}) like the kinetic parameters, Table 4, are of similar magnitude. From the activation parameters for k_1 and k_{-1} it can be concluded that thermodynamic parameters for the formation of $[Mo_2O_4(NCS)]^+$ (corresponding to K_1) are $\Delta H_1 = -2{\cdot}4$ kcal mol^{-1} and $\Delta S_1 = 2{\cdot}7$ cal K^{-1} mol^{-1}.

Other data for water exchange and complexing of unidentate ligands to VO^{2+} are shown in Table 4, and as has previously been suggested[23] support an S_N1 assignment for this ion. Entropies of activation $\Delta S^{\ddagger}$, Table 4, clearly indicate a similar mechanism for both $[Mo_2O_4]^{2+}$ and VO^{2+}. If the mechanism were associative in character more negative values of $\Delta S^{\ddagger}$ would be expected. Thus for the water exchange reactions of $[Ti(H_2O)_6]^{3+}$[24] and $[V(H_2O)_6]^{3+}$[25] the entropies of activation are both −15 cal K^{-1} mol^{-1}, and for NCS^- complexing with V^{3+} the entropy term is −23·8 cal K^{-1} mol^{-1}.[26] The tentative assignment of an S_N1 mechanism to the reaction of $[Mo_2O_4]^{2+}$ with NCS^- is of considerable interest when it is recalled that molybdenum(V) is capable of exhibiting co-ordination numbers as high as *eight*, *e.g.* $[Mo(CN)_8]^{3-}$.[27] An S_N2 process might have

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[27] H. W. Willard and R. C. Thielke, *J. Amer. Chem. Soc.*, 1935, **57**, 2609.

been more in keeping with the size of the molybdenum atom, the low population of the 4*d* orbitals, as well as the tendency to utilise higher co-ordination numbers. The conclusion that in this one study the data supports an S_N1 mechanism suggests that the terminal oxo- or bridging oxo- ligands may be having a profound influence on the mechanism of substitution. Clearly there is a need for other studies to further establish the position.

Finally for a range of $[H^+] = 0·5—2·0$M an $[H^+]^{-1}$ conjugate-base path is not observed in the complexing of NCS^- to $[Mo_2O_4]^{2+}$. Such a path is a dominant feature for the complexing of NCS^- with the molybdenum(IV) aquo-dimer.[28] Also it is now possible to compare the labilities of H_2O ligands complexed to molybdenum in different oxidation states. Whereas the molybdenum-(III)[4] and -(IV)[28] states exhibit substitution inert properties, labile behaviour would seem to prevail with molybdenum-(V) and -(VI).[7]

EXPERIMENTAL

Previously[3] ammonium pentachloro-oxomolybdenum(V), $[NH_4]_2[MoOCl_5]$, was used as a starting material. In this study it was preferable to use the more easily prepared pyridinium salt, $[pyH]_2[MoOCl_5]$, which can be obtained in higher yield. This was prepared by dissolving sodium molybdate (AnalaR grade, 8·2 g) in 10M-HCl (180 ml).[11,29] The solution was warmed to 80 °C and hydrazine hydrochloride, $N_2H_4·2HCl$ (6·6 g) was added and the mixture heated for a further 2—3 h. The solution was filtered and pyridine (9 ml) was added to the filtrate. On cooling in ice, green needles of $[pyH]_2[MoOCl_5]$ were deposited. They were filtered off and stored at 0 °C.

To prepare solutions the above crystals were dissolved in 0·05M-$HClO_4$ sufficient to give molybdenum concentrations of *ca.* 10^{-3}M. The solution (200 ml) was transferred to a Dowex 50W-X12 cation exchange column (10-cm high, 1·2-cm diameter). A brown band remained on the column, which was then washed with 0·2M-$HClO_4$ (100 ml). The brown band consisting of the aquo-ion, $[Mo_2O_4]^{2+}$, was eluted with 2M-perchloric acid to give a *ca.* 0·2M-solution, the precise concentration of which was determined spectrophotometrically at 384 nm ($\varepsilon = 103$ l mol^{-1} cm^{-1}). The acidity was determined by an ion-exchange technique.

Lithium perchlorate was prepared from perchloric acid (AnalaR) and lithium carbonate (G.P.R.), and was recrystallised until free of impurities. AnalaR grade ammonium thiocyanate was used without recrystallisation and was standardised by titration against Hg^{2+}.

Spectrophotometric studies were carried out using Unicam SP 500 and SP 800 spectrophotometers fitted with thermostatted cell housings. All kinetic studies were performed using the temperature-jump technique.[30] The temperature dependence of the reaction was investigated over the range 15—35 °C, and the cell temperature was measured before and after a series of jumps on each solution. Temperatures quoted are accurate to ±0·3 °C. Relaxation effects were recorded on either Polaroid or 35 mm film, and in the latter case relaxation times were measured with the aid of an exponential simulator.[31] Relaxation times quoted in the Tables are the average of at least three, and usually five, individual determinations. The reaction was monitored at wavelengths in the range 300—500 nm. Care was taken to exclude oxygen from solutions. Air-free techniques were used at all times although no effect of oxygen could be detected on exposing cell contents to the atmosphere for several minutes.

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[30] M. Eigen and L. de Maeyer, *Progr. Org. Chem.*, 1963, **VIII/2**, 904.

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