J. CHEM. SOC. DALTON TRANS. 1984 1229

Kinetics of the 1 : 1 Complexing of Oxalate to Hexa-aquamolybdenum(III) †

Helen M. Kelly, David T. Richens, and A. Geoffrey Sykes *
Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU

The kinetics of the 1 : 1 equilibration of oxalate with $[Mo(H_2O)_6]^{3+}$ have been investigated spectrophotometrically at 350 nm in aqueous *p*-toluenesulphonic acid (Hpts) at 25 °C, $I = 1.0$ M [Li(pts)]. For the range of $[H^+]$ values studied, 0.35—0.90 M, protonated forms of oxalate are present. The $[H^+]$ dependence, equation (i), is consistent with $HC_2O_4^-$ and not $H_2C_2O_4$ (acid dissociation

$$k_{eq} = \frac{k_1 K_a [Mo^{3+}]}{[H^+] + K_a} + k_{-1}[H^+] \qquad \text{(i)}$$

constant $K_a = 0.084$ M at 25 °C) as the dominant reactant, where k_1 and k_{-1} are as defined in equation (ii). At 25 °C, $k_1 = 0.49 \pm 0.1$ M^{-1} s^{-1} and $k_{-1} = (4.2 \pm 0.2) \times 10^{-4}$ M^{-1} s^{-1}, giving an

$$Mo^{3+} + HC_2O_4^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo(C_2O_4)^+ + H^+ \qquad \text{(ii)}$$

equilibrium constant of 1 170 ± 100, which is in agreement with an independently determined value of 1 230 ± 460. Using trifluoromethanesulphonic acid instead of Hpts, k_1 is 15% higher but k_{-1} remains unchanged. The results are discussed in terms of a model in which the oxalate chelates to the metal.

The preparation of $[Mo(H_2O)_6]^{3+}$ using air-free techniques and avoiding the use of perchlorate is now well documented.[1-3] Kinetic studies on the 1 : 1 substitution reactions of $[Mo(H_2O)_6]^{3+}$ with NCS^- and Cl^- have previously been reported,[3] and are of interest for two reasons: (*a*) a large difference in formation rate constants is observed for NCS^- (0.28 M^{-1} s^{-1}) and Cl^- (4.6×10^{-3} M^{-1} s^{-1}) at 25 °C; and (*b*) $[Mo(H_2O)_6]^{3+}$ reacts ≈ 10^5 times faster with NCS^- than its congenor $[Cr(H_2O)_6]^{3+}$.[4] Both these observations suggest an extensive associative contribution to the substitution process. Here we seek to extend existing information by considering the reaction of $[Mo(H_2O)_6]^{3+}$ with oxalate.

Experimental

Preparation of Reactants.—Hexa-aquamolybdenum(III) was prepared as described previously by aquation of $K_3[MoCl_6]$ in 0.50 M *p*-toluenesulphonic acid (Hpts), and subsequent purification on a Dowex 50WX2 column. Oxalic acid (B.D.H. AnalaR) and Hpts (Sigma) were used without further purification. To prepare Li(pts), 4 M Hpts was neutralised by addition of Li_2CO_3 (B.D.H. Reagent Grade) followed by recrystallisation. Solutions of Li(pts) were standardised by ion exchange onto Amberlite IR(H) 120 resin and titration of the H^+ released. Trifluoromethanesulphonic acid (Htfms) from Aldrich was purified by distillation under reduced pressure (≈ 10 mmHg). A sample of Li(tfms) was prepared by the same procedure as for Li(pts).

Kinetic Studies.—Runs were slow enough to monitor in a conventional manner using Perkin-Elmer Lambda 5 and Pye-Unicam SP500 instruments. The $[Mo(H_2O)_6]^{3+}$ reactant was in large 10-fold excess of the total oxalate to avoid formation of higher oxalate complexes. Ionic strengths were adjusted to 1.0 M (pts). Kinetic plots of absorbance (A) changes at 350 nm, $\ln (A_\infty - A_t)$ against time t, where A_∞ was the observed final absorbance for equilibrated solutions, were linear to 90% completion. The slope of such plots gave first-order equilibration rate constants k_{eq}. Because of the sensitivity of $[Mo(H_2O)_6]^{3+}$ to air oxidation, and possibility of air leakage giving incorrect A_∞, the Guggenheim method was also used to evaluate rate constants.[5] The previously determined acid dissociation constant K_a, equation (1), of 0.084 M at 25 °C,

$$H_2C_2O_4 \overset{K_a}{\rightleftharpoons} HC_2O_4^- + H^+ \qquad (1)$$

$I = 1.0$ M ($NaClO_4$),[6] has been used. The second acid dissociation constant, pK_a 3.55, indicates that for $[H^+] \geqslant 0.35$ M amounts of $C_2O_4^{2-}$ are small and can probably be neglected.

Equilibrium Constant.—Solutions of $[Mo(H_2O)_6]^{3+}$ and oxalate, under the same conditions as for kinetic runs, were allowed to equilibrate and final absorbance A_∞ values at 350 nm recorded. For the equilibrium (2) equation (3) can be

$$Mo^{3+} + HC_2O_4^- \overset{K_1}{\rightleftharpoons} Mo(C_2O_4)^+ + H^+ \qquad (2)$$

$$\frac{[ox]_T}{(A_\infty - A_0)} = \frac{[H^+]([H^+] + K_a)}{K_a(\varepsilon_1 - \varepsilon_0)[Mo^{3+}]} \cdot \frac{1}{K_1} + \frac{1}{(\varepsilon_1 - \varepsilon_0)} \qquad (3)$$

derived, where ε_0 is the absorption coefficient for $[Mo(H_2O)_6]^{3+}$ (15 M^{-1} cm^{-1}), ε_1 is for the 1 : 1 oxalate complex at 350 nm, and $[ox]_T$ represents total oxalate. From a plot (Figure 1) of $[ox]_T/(A_\infty - A_0)$ against $[H^+]([H^+] + K_a)/K_a[Mo^{3+}]$ the equilibrium constant K_1 for (2) is 1 230 ± 460, with $\varepsilon_1 = 544 \pm 105$ M^{-1} cm^{-1}.

Treatment of Data.—A non-linear least-squares fit of data was used (weighting unity) to obtain K_1, k_1, and k_{-1}.

Results

Equilibrium rate constants, k_{eq}, are listed in Table 1. These give a good fit to the expression (4) which can be derived from consideration of (1) and (2) with k_1 and k_{-1} the forward and back rate constants in (2). Figure 2 is a plot of k_{eq} against $[Mo^{3+}]$ illustrating this behaviour. The intercepts give a first-

---

† *Non-S.I. units employed:* M = mol dm^{-3}, mmHg ≈ 133 Pa.

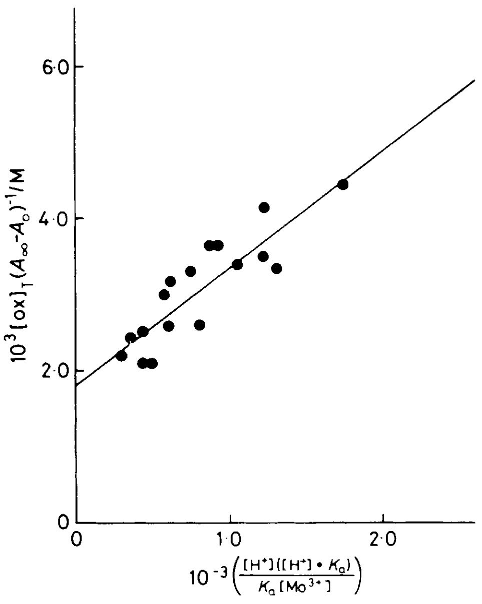

Figure 1. Determination of the equilibrium constant (25 °C) for the equilibration of $[Mo(H_2O)_6]^{3+}$ with oxalate from equation (3), I = 1.0 M [Li(pts)]

Table 1. Equilibration rate constants at 25 °C for the complexing of oxalate with $[Mo(H_2O)_6]^{3+}$ (present in ⩾ 10-fold excess), I = 1.0 M [Li(pts)]

$[H^+]$/M	$10^3[Mo^{3+}]$/M	$10^4k_{eq}/s^{-1}$
0.35	2.0	3.8
	4.0	5.2
	5.0	6.3
	6.0	7.2
0.50	2.0	3.9
	4.0	5.3
	6.0	6.5
	8.0	7.9
	10.0	9.1
0.60	2.0	4.1
	4.0	5.2
	6.0	6.0
	8.0	7.5
	10.0	8.9
0.75	2.0	4.6
	6.0	6.2
	8.0	7.2
	10.0	8.0
	14.0	10.2
0.90	4.0	5.2
	6.0	6.3
	8.0	6.7
	10.0	7.5
	12.0	8.3
	14.0	9 0
	16.0	10.1

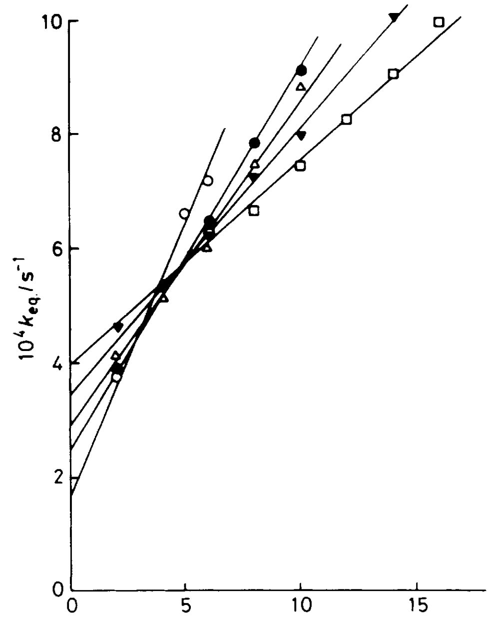

Figure 2. Dependence of equilibration rate constants (25 °C) for the complexing of $[Mo(H_2O)_6]^{3+}$ (reactant in large excess) with oxalate, I = 1.0 M [Li(pts)]; $[H^+]$ = 0.35 (○), 0.05 (●), 0.60 (△), 0.75 (▼), and 0.90 M (□)

Table 2. Summary of rate constants for the 1 : 1 anation (k_1) and aquation (k_{-1}) of $[Mo(H_2O)_6]^{3+}$, I = 1.0 M [Li(pts)]

Ligand	$k_1/M^{-1}\,s^{-1}$	$k_{-1}/M^{-1}\,s^{-1}$	Ref.
$HC_2O_4^-$	0.49	0.00042	This work
NCS^-	0.27	small	3
Cl^-	0.0046	0.00043 *	3

* Units s^{-1}.

order dependence on $[H^+]$ with a small $[H^+]$-independent contribution of (0.38 ± 0.08) × 10^{-4} s^{-1} (which may be spurious), and the slopes a linear plot against $([H^+] + K_a)^{-1}$. Alternatively a plot of $k_{eq}/[H^+]$ against $K_a[Mo^{3+}][H^+]^{-1}/(K_a + [H^+])$ is linear.

$$k_{eq} = \frac{k_1K_a[Mo^{3+}]}{[H^+] + K_a} + k_{-1}[H^+] \qquad (4)$$

From a non-linear least-squares fit to (4), $k_1 = 0.49 \pm 0.1$ M^{-1} s^{-1} and $k_{-1} = (4.2 \pm 0.2) \times 10^{-4}$ M^{-1} s^{-1}. These results are shown in Table 2 alongside data for the reactions with NCS^- and Cl^-.

On replacing Hpts by Htfms, k_1 increases by 15% whereas k_{-1} remains unchanged. An effect of similar magnitude has been observed in check runs on the reaction of $[Mo(H_2O)_6]^{3+}$ with NCS^-.

Discussion

The range of formation rate constants for substitution on $[Mo(H_2O)_6]^{3+}$ is now ≈ 100, Table 2, consistent with an associative mechanism. It is of interest to compare the reaction of $[Mo(H_2O)_6]^{3+}$ with oxalate to that of $[Fe(H_2O)_6]^{3+}$, for which $K_1 = 1.1 \times 10^4$.[6] In the latter, complexation proceeds *via* the conjugate base $Fe(OH)^{2+}$ as well as Fe^{3+}. A small $[H^+]$-independent contribution to k_{-1} has been noted in the present study. Since in the complexing of NCS^- and Cl^- no participation of $Mo(OH)^{2+}$ was observed, we are inclined to view this effect as spurious, and certainly too small to quantify in a more meaningful way. That there is no contribution from the conjugate-base form can be understood if an associative pathway involving the hexa-aqua-ion is very much more favourable, so that it excludes any significant contribution from the conjugate-base form. Similar behaviour has been observed with $[V(H_2O)_6]^{3+}$ [7,8] and $[Ti(H_2O)_6]^{3+}$,[9] and appears to be a feature of metal ions having low *d*-electron populations, which can react in an associative manner.

The $[H^+]$ dependence for k_{-1} suggests that the oxalate chelates to the metal and in the process deprotonates to give $[Mo(H_2O)_4(C_2O_4)]^+$, a situation which would not arise if the oxalate remained monodentate. A two-stage process can be written as in equations (5) and (6), and its implications examined. If it is assumed that the concentration of the monodentate species is given by the steady-state approximation, it can be shown that expressions (7) and (8) hold. On arranging

$$[Mo(H_2O)_6]^{3+} + HC_2O_4^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [Mo(H_2O)_5(HC_2O_4)]^{2+} + H_2O \quad (5)$$

$$[Mo(H_2O)_5(HC_2O_4)]^{2+} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} [Mo(H_2O)_4(C_2O_4)]^+ + H_2O + H^+ \quad (6)$$

$$k_1 = \frac{k_a k_b}{k_{-a} + k_b} \quad (7)$$

$$k_{-1} = \frac{k_{-a} k_{-b}}{k_{-a} + k_b} \quad (8)$$

equation (7) it follows that $k_a = k_1(1 + k_{-a}/k_b)$, or alternatively that k_a is always greater than k_1. Making the assumption $k_b \gg k_{-a}$ to the reverse reaction, it follows that $k_{-1} = k_{-a}/(k_b/k_{-b})$. The implication of the experimental k_{-1} value (0.00042 M^{-1} s^{-1}) is that k_b/k_{-b} for chelation/dechelation is numerically much bigger than k_{-a} for dissociation of $HC_2O_4^-$.

The value of k_1 for $HC_2O_4^-$ (0.49 M^{-1} s^{-1}) is similar to the rate constant (0.34 M^{-1} s^{-1}) for the oxidant-dependent pathway in the $[Co(C_2O_4)_3]^{3-}$ oxidation of $[Mo(H_2O)_6]^{3+}$.[10] For the reasons given it has been suggested that the latter is a substitution-controlled redox process.

The 15% difference in rate constant k_1 when Htfms replaces Hpts suggests that the relevant anions may to some (possibly small) extent be complexing to the metal, or alternatively that there is a medium effect.

Acknowledgements

We thank Climax Molybdenum for support under an S.E.R.C. C.A.S.E. studentship (to H. M. K.).

References

1 A. R. Bowen and H. Taube, *J. Am. Chem. Soc.*, 1971, **93**, 3287.
2 A. R. Bowen and H. Taube, *Inorg. Chem.*, 1974, **13**, 2245.
3 Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, **1973**, 767; *J. Chem. Soc., Dalton Trans.*, 1975, 1048.
4 J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 1554.
5 A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 49.
6 E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1866.
7 R. C. Patel and H. Diebler, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 1035.
8 B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, 1967, **6**, 1948.
9 H. Diebler, *Z. Phys. Chem.* (*Frankfurt am Main*), 1969, **68**, 64.
10 D. T. Richens and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1983, 616; D. T. Richens, M. A. Hamer, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, in the press.

Received 31*st August* 1983; *Paper* 3/1517