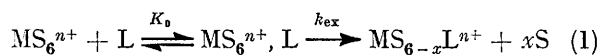


Rates of Formation and Dissociation of Complexes of Manganese(II) with the Ligands 1,10-Phenanthroline, 2,2'-Bipyridine, and 2,2',2''-Terpyridine in Anhydrous Methanol

By D. J. Benton and P. Moore,* Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL

Rate constants for the formation (k_f) and dissociation (k_d) of complexes of Mn^{II} with the ligands 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy), and 2,2',2''-terpyridine (terpy) have been measured, at low temperatures in anhydrous methanol, by the stopped-flow method. At 298.1 K and $I = 0.20 \text{ mol l}^{-1}$ ($NaClO_4$): $\log(k_f/l \text{ mol}^{-1} \text{ s}^{-1})$ (extrapolated) = 4.95, 4.24, and 3.72; $\Delta H_f^\ddagger = 10.6 \pm 0.4$, 11.7 ± 0.1 , and $12.8 \pm 1.0 \text{ kcal mol}^{-1}$; $\Delta S_f^\ddagger = -0.4 \pm 1.6$, 0.1 ± 0.1 , and $1.3 \pm 3.9 \text{ cal K}^{-1} \text{ mol}^{-1}$; $\log(k_d/s^{-1}) = 1.15$, 1.57 , and -1.33 ; $\Delta H_d^\ddagger = 13.5 \pm 0.3$, 13.4 ± 0.5 , and $13.7 \pm 0.6 \text{ kcal mol}^{-1}$; and $\Delta S_d^\ddagger = -8.2 \pm 0.9$, -6.4 ± 1.9 , and $-18 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$ for phen, bipy, and terpy respectively. The kinetically determined stability constants in methanol for the complexes ($\log K_1 = 3.8$, 2.7 , and 5.0 for phen, bipy, and terpy respectively) are very similar to values determined in aqueous solution. Values of ΔH_f^\ddagger are significantly larger than the activation enthalpy associated with Mn^{II} -methanol solvent exchange and possible reasons for this unexpected behaviour are discussed.

THERE is widespread agreement¹⁻⁴ that rates of formation of metal complexes in aqueous solution are controlled largely by the rate of exchange of water molecules between the inner sphere of a metal ion (MS_6^{n+} , where S is a solvent molecule) and the bulk solvent. An interchange mechanism (1) has been proposed in most



cases ($L =$ ligand) in which rapid outer-sphere ion-pair or ion-dipole association (equilibrium constant K_0) is followed by rate-determining solvent exchange (rate constant k_{ex}). If the concentration of metal ion is in a large excess the mono-complex is predominantly formed and the rate law is⁵ as in equation (2). In the simplest

$$d[\text{Complex}]/dt = k_{ex}K_0[MS_6^{n+}][L]/(1 + K_0[MS_6^{n+}]) \quad (2)$$

cases where $K_0[MS_6^{n+}] \ll 1$, the second-order formation rate constant (k_f) is given by equation (3). Although this equation has been extended with some success to

$$k_f = k_{ex}K_0 \quad (3)$$

rates of formation reactions in anhydrous methanol,^{5,6} further studies in a variety of non-aqueous solvents

¹ M. Eigen and R. G. Wilkins, 'Mechanisms of Inorganic Reactions,' *Adv. in Chem. Series*, No. 49, Amer. Chem. Soc., 1965, p. 55.

² R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.

³ D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45.

⁴ K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107.

⁵ R. G. Pearson and P. Ellgen, *Inorg. Chem.*, 1967, **6**, 1379.

indicate that mechanism (1) is not entirely valid in such media.⁷⁻⁹ An alternative model has been presented which takes into account the processes of solvent re-organisation in the vicinity of the metal ion.⁸

Studies in non-aqueous solvents have been largely limited to the less labile of the bivalent first-row transition-metal ions, particularly that of Ni^{II} . However, Ni^{II} is unsuited to studies in a wide variety of different solvents since its d^8 configuration allows it to exist in several different geometries. Therefore we are investigating substitution reactions in non-aqueous solvents of d^0 , high-spin d^5 , and d^{10} metal ions, which are less prone to distortion from a regular octahedral geometry by ligand-field effects. These reactions tend to be too fast to measure by flow methods at ambient temperatures and so a low-temperature stopped-flow technique was developed to try to overcome this problem.^{9,10} The advantage to be gained by cooling metal complexes in this way was demonstrated at an early stage,¹¹ and a low-temperature flow apparatus has been used more recently for investigating the reaction between Cu^{II} and β -diketone ligands.¹²

⁶ F. Dickert, P. Fischer, H. Hoffman, and G. Platz, *J.C.S. Chem. Comm.*, 1972, 106.

⁷ C. H. Langford and H. G. Tsiang, *Inorg. Chem.*, 1970, **9**, 2346.

⁸ H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. (A)*, 1971, 2191, 2198.

⁹ D. J. Benton and P. Moore, *J.C.S. Chem. Comm.*, 1972, 717.

¹⁰ D. J. Benton, Ph.D. Thesis, University of Warwick, 1972.

¹¹ J. Bjerrum and K. G. Poulsen, *Nature*, 1952, **169**, 463.

¹² A. V. Celiano, M. Cefola, and P. S. Gentile, *J. Phys. Chem.*, 1961, **65**, 2194; 1962, **66**, 1132; 1966, **70**, 1358.

EXPERIMENTAL

Materials.—AnalaR 2,2'-bipyridine and 1,10-phenanthroline monohydrate were used without purification. Commercial 2,2',2''-terpyridine was recrystallised from aqueous methanol to remove an unidentified yellow impurity and then sublimed *in vacuo* (m.p. 359.5; lit., 359.5 K).¹³ AnalaR sodium perchlorate was recrystallised from water and dried by heating overnight at 393 K. Hydrated manganese(II) perchlorate was prepared by dissolving high purity manganese metal in perchloric acid, filtering off any undissolved metal, and recrystallising the product several times from water. The anhydrous salt was obtained by heating at 353–373 K and 0.1 mmHg over P₂O₅ for 2 days.¹⁴ AnalaR mercury(II) chloride and silver(I) perchlorate were dried in a similar manner (2 h). Stock solutions of Mn^{II} were estimated by EDTA titration,¹⁵ and NaClO₄ solutions by evaporating aliquot portions to dryness at 393 K and weighing the residue.

AnalaR grade methanol was dried by heating under reflux over magnesium turnings and then distilled.¹⁶ The water content was estimated by Fischer titration and found to be less than 0.01% by weight. Solutions in dry methanol were prepared in a dry-box and stored under an atmosphere of dry nitrogen gas in volumetric flasks sealed with Suba-seal caps. Solutions were transferred to the stopped-flow apparatus using 50 ml hypodermic syringes, and protected from atmospheric moisture at all times. To avoid contamination of the ligand solutions (particularly terpy) caused by metal ions being leached from the glass of the volumetric flasks, the latter were pre-cleaned with a strong solution of EDTA, washed, and dried; solutions were prepared immediately prior to the runs.

Solutions of perchloric acid (*ca.* 0.2 mol l⁻¹) in methanol were prepared by adding perchloric acid (72%, *ca.* 5 ml) dropwise to dry methanol (*ca.* 300 ml). An attempt was made to dry this solution by distillation under vacuum, the condensed vapour being passed through a column of dried molecular sieves before returning it to the solution.¹⁷ Fischer titration indicated a water content of 0.09% by weight. A solution of Hg(ClO₄)₂ in methanol was prepared by reacting HgCl₂ with a stoichiometric amount of AgClO₄.

Low-temperature Stopped-flow Apparatus.—This apparatus is described in detail elsewhere.¹⁰ To avoid contamination by metal ions, the flow-line was constructed entirely of glass and fluorocarbon plastic materials. Solutions, stored under an atmosphere of nitrogen gas in reservoirs, were introduced *via* glass 3-way stopcocks into all-glass driving syringes mounted at room temperature. The solutions were then driven hydraulically through glass capillary tubing (2 mm bore) coiled inside a low-temperature thermostat (similar in design to that of Scott and Brickwedde¹⁸) into a Kel-F mixing chamber and observation tube totally immersed in the thermostat. The 8-jet mixing chamber was similar in design to that of Gibson and Milnes,¹⁹ but eliminated the need for a pre-mixing chamber block. Tests of the mixing efficiency and the apparatus dead-time were found to be similar to our other stopped-flow apparatus.²⁰ The

observation tube (pathlength 14.5 mm) was fitted with quartz windows, and quartz focusing lenses and front-surface aluminised mirrors were used throughout. The light path was in the form of a simple periscope, a design similar to that used in the first low-temperature stopped-flow apparatus²¹ (we thank Professor Caldin for showing us his stopped-flow equipment). Ancillary equipment was similar to that described previously.²⁰ Temperatures were measured (± 0.01 K) with a calibrated platinum resistance thermometer. It was found necessary to thermostat the apparatus for several hours prior to kinetic studies to avoid spurious traces which arose when there was a temperature difference between the incoming solutions and the observation chamber. If this precaution was neglected, large signals could be obtained by simply mixing solvent with solvent. A similar problem has been reported by Gibson, even when working nearer to room temperature.²²

Kinetic Studies.—Spectra of reactants and products recorded on a Cary 14 spectrometer were used to choose suitable monitoring wavelengths. Reactions were followed between 290 and 300 nm. Stopped-flow traces were analysed as described previously.²⁰ Errors are quoted as ± 1 s.d. throughout this paper.

RESULTS AND DISCUSSION

Formation Studies.—A preliminary study showed that the rate of formation of the 1,10-phenanthroline (phen) complex decreased with increasing ionic strength (Table 1)

TABLE 1

Variation of the observed pseudo-first-order rate constant (k) with ionic strength (I , adjusted with NaClO₄) for the reaction of Mn^{II} with 1,10-phenanthroline (phen) in anhydrous methanol at 251.8 K ([Mn²⁺] = 1.01 $\times 10^{-2}$; [phen] = 5.0 $\times 10^{-5}$ mol l⁻¹)

k/s^{-1}	43.4	23.7	18.2	14.3
$I/mol\ l^{-1}$	0.03	0.20	0.30	0.40

and so a constant ionic strength of 0.20 mol l⁻¹ was maintained throughout with NaClO₄. Either ion-pairing or the effect of ions on the solvent structure could account for the variation observed. Complex-formation reactions of Ni^{II} have also been reported to be ionic-strength dependent in methanol.⁵ The present reactions were followed under pseudo-first-order conditions with manganese(II) perchlorate (0.001–0.05 mol l⁻¹) in a large excess over the ligand (1 $\times 10^{-5}$ –5 $\times 10^{-5}$ mol l⁻¹). It was necessary to work with relatively high excesses of metal-ion concentrations in order to ensure that mono-complexes were almost exclusively formed, since the stabilities of the manganese(II) complexes are quite small.¹³ Three temperatures in the range 227–273 K were employed and good first-order rate plots were obtained over several half-lives. Pseudo-first-order rate constants (k) are collected in Table 2.

The second-order formation rate constants (k_f) were estimated by linear least-squares analysis from gradients

¹³ R. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1966, **5**, 622; 1965, **4**, 929.

¹⁴ H. Levanon and Z. Luz, *J. Chem. Phys.*, 1968, **49**, 2031.

¹⁵ A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, 3rd edn., 1961, p. 434.

¹⁶ A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, 1957, p. 169.

¹⁷ P. Arthur, W. M. Haynes, and L. P. Varga, *Analyt. Chem.*, 1966, **38**, 1630.

¹⁸ R. B. Scott and R. G. Brickwedde, *J. Res. Nat. Bur. Stand.*, 1931, **6**, 401.

¹⁹ Q. H. Gibson and L. Milnes, *Biochem. J.*, 1964, **91**, 161.

²⁰ T. C. Matts and P. Moore, *J. Chem. Soc. (A)*, 1969, 219.

²¹ C. R. Allen, A. J. W. Brook, and E. F. Caldin, *Trans. Faraday Soc.*, 1960, **56**, 788.

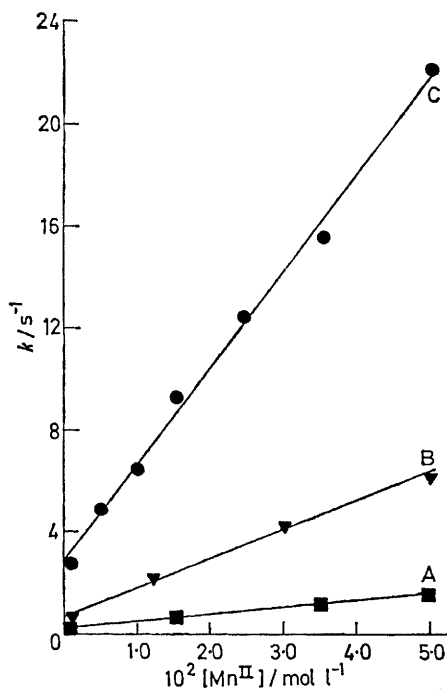
²² Q. H. Gibson, 'Methods in Enzymology,' ed. K. Kustin, Academic Press, 1969, p. 195.

TABLE 2

Observed pseudo-first-order rate constants (k) for the formation of mono-complexes of Mn^{II} in anhydrous methanol ($I = 0.20 \text{ mol l}^{-1}$, NaClO_4). $[\text{phen}] = 5 \times 10^{-5}$; $[\text{bipy}] = 10^{-5}$; and $[\text{terpy}] = 10^{-5} \text{ mol l}^{-1}$

T/K	$10^2[\text{Mn}^{\text{II}}]/\text{mol l}^{-1}$	$k(\text{phen})/\text{s}^{-1}$	$k(\text{bipy})/\text{s}^{-1}$		
226.9	0.10	0.299	0.210		
	1.53	2.05	0.67		
	3.51	6.23	1.14		
	4.96	11.7	1.53		
239.8	0.125	1.24	0.624		
	1.22	8.88	2.13		
	3.01	23.5	4.16		
	5.00	47.3	6.17		
251.8	0.10	3.47	2.72		
	0.50	11.9	4.89		
	0.99	21.7	6.47		
	1.53	32.5	9.29		
	2.44	58.9	12.4		
	3.51	95.7	15.6		
	4.96		22.1		
Terpy					
$10^2[\text{Mn}^{\text{II}}]/\text{mol l}^{-1}$	0.101	1.01	2.02	3.04	5.05
$k(251.5 \text{ K})/\text{s}^{-1}$	0.072	0.819		2.39	3.99
$k(262.4 \text{ K})/\text{s}^{-1}$		2.78		7.56	13.8
$k(273.7 \text{ K})/\text{s}^{-1}$	0.67	7.44	13.9	21.2	

of plots of k against $[\text{Mn}^{\text{II}}]$ at each temperature. For the 2,2'-bipyridine (bipy) complex such plots (Figure)



Plot of observed rate constants (k) against $[\text{Mn}^{\text{II}}]$ for the formation of the mono-complex of manganese(II) with bipy in anhydrous methanol ($I = 0.2 \text{ mol l}^{-1}$ (NaClO_4)) at 226.9 (A), 239.8 (B), and 251.8 K (C)

showed small positive intercepts at zero $[\text{Mn}^{\text{II}}]$, and for phen an intercept was evident at the highest temperature studied. Values of k_f and the intercepts are given in Table 3. Although intercepts are small and do not markedly effect values of k_f , their origin is uncertain

²³ D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891; W. J. MacKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, 1971, **93**, 4379.

at the present time. It is possible to ascribe them to the reverse (dissociation) reactions,^{5,7} however, in the present case, they are larger than expected from extrapolation of directly measured dissociation rates to the lower temperatures used in the formation studies. Similar unexplained behaviour has been reported recently for reactions of nickel(II) with bipy and 2,2',2''-terpyridine (terpy) in acetonitrile, and with bipy in acetone.⁸

TABLE 3

Second-order formation rate constants (k_f) and intercepts (at $[\text{Mn}^{\text{II}}] = 0$) of plots of k against $[\text{Mn}^{\text{II}}]$ from Table 2

Ligand	T/K	$k_f/\text{l mol}^{-1} \text{ s}^{-1}$	Intercept/ s^{-1}
Bipy	226.9	26.1 ± 1.1	0.25 ± 0.04
	239.8	113 ± 3	0.63 ± 0.07
	251.8	385 ± 7	2.8 ± 0.2
Phen	226.9	231 ± 16	<i>a</i>
	239.8	942 ± 36	<i>a</i>
	251.8	2680 ± 82	1.6 ± 0.2
Terpy	251.5	78.6 ± 0.8	<i>a</i>
	262.4	275 ± 10	<i>a</i>
	273.7	684 ± 9	<i>a</i>

^a Negligible.

Activation parameters associated with values of k_f , together with other relevant data, are presented for comparison in Table 4. If equation (2) applies to these reactions then $\Delta H^\ddagger(k_f) = \Delta H^\ddagger(k_{\text{ex}}) + \Delta H^0(K_0)$ (constants in parentheses indicating the origin of the corresponding enthalpy term). However, from Table 4, it can be seen that $\Delta(\Delta H^\ddagger) [= \Delta H^\ddagger(k_f) - \Delta H^\ddagger(k_{\text{ex}})]$ ⁸ has values of ca. 4.4, 5.5, and 6.6 kcal mol⁻¹ for phen, bipy, and terpy respectively, and these values are much larger than those expected for $\Delta H^0(K_0)$. For uncharged ligands it is suggested that K_0 can be estimated from the pre-exponential factor in the Fuoss equation (4),²³ where

$$K_0 \approx 4\pi a^3 N_A / 3000 \quad (4)$$

a is the distance of closest approach of the ligand to the solvated metal ion and N_A is Avogadro's number. Therefore, K_0 should be nearly temperature independent and $\Delta H^0(K_0) \approx 0$. Studies of reactions of Co^{II} and Ni^{II} in methanol with uncharged ligands support this conclusion since $\Delta H^\ddagger(k_f) \approx \Delta H^\ddagger(k_{\text{ex}})$ (within 2 kcal mol⁻¹),⁸ and even with the 2- ligand benzene-1,3-disulphonate the directly measured value of $\Delta H^0(K_0)$ is only $+3.8 \text{ kcal mol}^{-1}$ for Mg^{II} in methanol.²⁴ Therefore, with uncharged ligands it is to be expected that $\Delta H^0(K_0)$ is very small and it appears that equation (3) is not entirely valid in the present case.⁹ It is tempting to try and correlate the large values of $\Delta(\Delta H^\ddagger)$ with ΔH_{evap} (the enthalpy of evaporation of the solvent) as suggested by Bennetto and Caldin,⁸ but the relatively high ionic strength used in this work probably invalidates such a comparison. Moreover the present results do not fit the correlation found previously²⁵ and it will be necessary to investigate several other solvent systems under the present conditions to see if such a correlation is valid for Mn^{II} .

²⁴ A. Fanelli and S. Petrucci, *J. Phys. Chem.*, 1971, **75**, 2649.

²⁵ Ref. 8, figure 2, p. 2201.

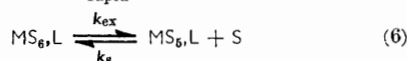
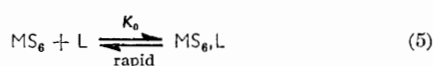
TABLE 4

Comparison of rate and thermodynamic data at 298.1 K ($I = 0.2 \text{ mol l}^{-1}$, NaClO_4) for the formation and dissociation of Mn^{II} complexes in methanol (values in parentheses represent results in aqueous solution, *I ca.* 0 unless specified)

Ligand ^a	$\log(k_t/\text{mol}^{-1} \text{ s}^{-1})$	$\frac{\Delta H_t^\ddagger}{\text{kcal mol}^{-1}}$	$\frac{\Delta S_t^\ddagger}{\text{cal K}^{-1} \text{ mol}^{-1}}$	$\log(k_d/\text{s}^{-1})$	$\frac{\Delta H_d^\ddagger}{\text{kcal mol}^{-1}}$	$\frac{\Delta S_d^\ddagger}{\text{cal K}^{-1} \text{ mol}^{-1}}$	$\log(K_1/\text{mol}^{-1})^b$	$\frac{\Delta H^\circ}{\text{kcal mol}^{-1}}$	$\frac{\Delta S^\circ}{\text{cal K}^{-1} \text{ mol}^{-1}}$
Phen	4.95 (5.1) ^c	10.6 ± 0.4	-0.4 ± 1.6	1.15 (1.5) ^e	13.5 ± 0.3 (9.8)	-8.2 ± 0.9 (-16.6)	3.8 (3.6) ^c	-3	+8
Bipy	4.24	11.7 ± 0.1	0.1 ± 0.1	1.57 (>2.3) ^e	13.4 ± 0.5	-6.4 ± 1.9	2.7 (2.6) ^d	-2	+6
Terpy	3.72 (5.0)	12.8 ± 1.0	$+1.3 \pm 3.9$ (-15.7)	-1.33 (0.6)	13.7 ± 0.6 (11.7)	-18 ± 2 (-16.1)	5.0 (4.4)	-1(-6)	+19 (0)
Quinolin-8-olate(1-)	2.92 ^e (8.0) ^f	(8.8) ^f	(+10) ^f	(2.1) ^f			(5.9) ^f		
Benzene-1,3-disulphonate(2-)	5.04			1.04			4.0		
Cl^-	7.43 ^h (7.2) ⁱ	(9) ⁱ	(4) ⁱ	4.64 ^h (7.49) ^k 5.67 ^l	(8.8) ^k 6.2 ^l	(+5) ^k -12	2.9 ^h		

^a Phen = 1,10-phenanthroline; bipy = 2,2'-bipyridine; and terpy = 2,2',2''-terpyridine. ^b Kinetically determined values; $K_1 = k_t/k_d$. ΔH° and ΔS° only approximate. ^c At 284.1 K; ref. 13. ^d From equilibrium studies (W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135). ^e At 226.4 K; ref. 9. ^f At 289.1 K, $I = 0.10 \text{ mol l}^{-1}$ (KNO_3) (M. S. Zetter and D. N. Hague, *Trans. Faraday Soc.*, 1970, **66**, 1176). ^g G. Macri and S. Petrucci, *Inorg. Chem.*, 1970, **9**, 1009. ^h At 293.1 K; ref. 6. ⁱ Ref. 3. ^j Solvent-exchange data. ^k T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; M. Grant, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1971, **10**, 71. ^l Data taken from F. W. Breivogel, *J. Chem. Phys.*, 1969, **51**, 445 (see also Ref. 14).

Although effects of solvent structure could be important in these reactions,⁸ other factors may also make equation (3) a gross approximation in most cases. Consider, for example, the mechanism depicted by Scheme 1 (L = unidentate ligand and charges are omitted



SCHEME 1

for convenience). If the solvated metal ion (MS_6) is present in large excess, application of the steady-state approximation to the intermediate of reduced co-ordination number (MS_5L where L is in the outer-sphere of the metal ion) gives equation (8). Here $k_{\text{ex}} = x_c k_{\text{ex}}^{\text{I}}$,

$$k_t = x_c k_{\text{ex}}^{\text{I}} k_L K_0 / [(k_s[\text{S}] + k_L)(1 + K_0[\text{MS}_6])] \quad (8)$$

where x_c is the co-ordination number of the metal ion,* assumed to be six in Scheme 1, and k_{ex}^{I} is the normally quoted first-order rate constant for the loss of one solvent molecule from the complex MS_6 .⁸

If $K_0[\text{MS}_6] \ll 1$ and $k_L \gg k_s[\text{S}]$, equation (8) reduces to (3), whereas if $k_s \simeq k_L$ (*i.e.* no discrimination is shown by MS_5L for L over S) so that $k_s[\text{S}] \gg k_L$, equation (8) reduces to that of (9), where $f (= k_L/k_s[\text{S}])$ is a discrimination factor.^{5,7,8} If $k_L = k_s$ this equation further simplifies to (10), which only differs from equation (3)

$$k_t = x_c k_{\text{ex}}^{\text{I}} K_0 f \quad (9)$$

$$k_t = x_c k_{\text{ex}}^{\text{I}} K_0 / [\text{S}] \quad (10)$$

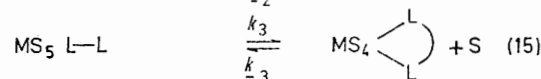
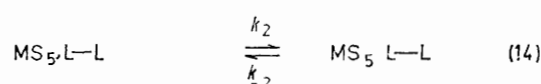
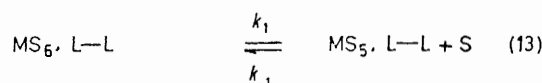
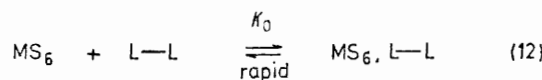
by the factor $1/[\text{S}]$ and therefore cannot account for the relatively large values of $\Delta(\Delta H^\ddagger)$. However, it can be seen from equation (9) that when $\Delta H(K_0) \simeq 0$ equation (11) holds. Therefore, if $\Delta H^\ddagger(k_L) > \Delta H^\ddagger(k_s)$, which is possible in the presence of bulkier co-ordinated solvent

$$\Delta(\Delta H^\ddagger) \simeq \Delta H^\ddagger(k_L) - \Delta H^\ddagger(k_s) \quad (11)$$

molecules, the large values of $\Delta(\Delta H^\ddagger)$ can be partly accounted for without invoking solvent-structure parameters.⁸

One additional factor which also needs to be taken into account for polydentate ligands is a possible switch in the rate-determining step from the first to the second or

subsequent bond formation. This mechanism is illustrated for a bidentate ligand (L-L) in Scheme 2. 'Normally' $k_3 \gg k_{-2}$ and the rate-determining step² has a rate constant k_1 . However, for very labile metal ions k_{-2} will be larger and this reaction may then compete with the chelate ring closure (rate constant k_3). This situation has been termed 'sterically controlled



SCHEME 2

substitution'.⁴ If we neglect the ring-opening reaction (rate constant k_{-3}) and apply the steady-state approximation to the intermediates, equation (16) is obtained.

$$k_t = \frac{k_1 k_2 k_3 K_0 / (1 + K_0[\text{MS}_6])}{k_{-1}[\text{S}](k_{-2} + k_3) + k_2 k_3} \quad (16)$$

If $k_3 \gg k_{-2}$ and substituting $k_1 = x_c k_{\text{ex}}^{\text{I}}$, $k_2 = k_L$, and $k_{-1} = k_s$, it can be seen that equation (16) agrees with (8). However, in the extreme case of a sterically controlled ring closure $k_{-2} \gg k_3$ and in this situation it can be seen from equation (16) that (17) applies. Therefore,

$$k_t \simeq x_c k_{\text{ex}}^{\text{I}} k_L k_3 K_0 / (k_s k_{-2}[\text{S}] + k_L k_3) \quad (17)$$

if $k_s[\text{S}] \gg k_L$, $k_t \simeq x_c k_{\text{ex}}^{\text{I}} k_L k_3 K_0 / k_s k_{-2}[\text{S}]$ and we obtain equation (18). An additional energy barrier to form-

$$\Delta(\Delta H^\ddagger) \simeq \Delta H^\ddagger(k_L) - \Delta H^\ddagger(k_s) + \Delta H^\ddagger(k_3) - \Delta H^\ddagger(k_{-2}) \quad (18)$$

ation could, therefore, arise from the chelate ring closure. However, although a relatively large value of $\Delta H^\ddagger(k_3)$ could account for the observed values of $\Delta(\Delta H^\ddagger)$ for the bipy and terpy complexes in methanol, it seems unlikely for the inflexible ligand phen unless there is a considerable distortion in the bonding of one end of this

* In ref. 8 the symbol N_c is used.

ligand to a metal ion.²⁶ In the case of bipy (and presumably terpy) some further support for a rate-determining ring-closure mechanism comes from the study of the reverse (dissociation) reactions in acidic and neutral conditions discussed in the next section.

It can be seen from equation (10) that even when $k_L = k_s$ three other factors need to be taken into account when comparing values of k_t in different solvents. These are the solvent-exchange rates (k_{ex}^I), the ion-dipole or ion-pair constants (K_0), and the factor $1/[S]$. The latter is difficult to estimate, but it seems reasonable to assume that it will be proportional to $1/[S]_{bulk}$, where $[S]_{bulk}$ is the bulk solvent concentration (55.5 mol l⁻¹ for H₂O and 24.7 mol l⁻¹ for MeOH). With this assumption, it is instructive to compare the relative rates of formation of Mn^{II} complexes in methanol and in water using equation (10). The ratio $K_0(\text{H}_2\text{O}) : K_0(\text{MeOH})$ can be approximated²³ to $a^3(\text{H}_2\text{O}) : a^3(\text{MeOH})$ for neutral ligands using the Fuoss equation. For Ni^{II}, ratios of $a(\text{H}_2\text{O}) : a(\text{MeOH})$ of 4 : 5 and 5 : 6 have been suggested^{5,23} and similar values are to be expected for the slightly larger Mn^{II}. Using a ratio of 4 : 5, from data in Table 4 the following estimation can be made for Mn^{II} at 298.1 K:

$$k_t(\text{H}_2\text{O})/k_t(\text{MeOH}) = (10^{7.49}/10^{5.57}) \times (24.7/55.5) \times (4^3/5^3) \simeq 19 \quad (19)$$

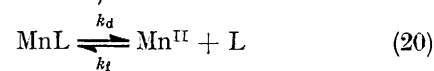
In view of the approximations involved it would seem that this estimate is in remarkable agreement with the observed ratio of 19 for the complex Mn(terpy)²⁺ (Table 4). However, because of the large values of $\Delta(\Delta H^\ddagger)$ there is an obvious danger in making such a comparison at one temperature. For example, at 298.1 K one can estimate from equation (10) that for Mn^{II} in methanol $k_t = 2.7 \times 10^4$ l mol⁻¹ s⁻¹ which is well within the range observed (Table 4) (using a value of K_0 of 0.3 l mol⁻¹ calculated from the Fuoss equation with $a = 5 \text{ \AA}$ and setting $[S] = 24.7$ mol l⁻¹, an assumption which may be wrong⁷). However, at 227 K the agreement is not so good since the observed and calculated values of k_t are *ca.* 26 and 768 l mol⁻¹ s⁻¹ respectively.

Dissociation Studies.—The reverse (dissociation) reactions were investigated in methanol for a number of reasons. A knowledge of the dissociation rate constant (k_d) enables the stability constants to be estimated from the relation¹³ $K_1 = k_t/k_d$, and this information was required since there is a dearth of such data in non-aqueous media. Values of k_d were also required for comparison with the intercepts in Table 3 and with other studies in non-aqueous media.^{6,27}

Attempts were made to induce the dissociation reactions with Co^{II}, Ag^I, Hg(ClO₄)₂, HgCl₂, and HClO₄. Co^{II} has been used for this purpose in an aqueous medium,¹³ but in methanol the rate of reaction of the released ligand with Co^{II} is slower⁸ so that competition between Co^{II} and Mn^{II} for the released ligand is apparent. A similar problem was observed with Ag^I.

²⁶ M. L. Sanduja and W. MacF. Smith, *Canad. J. Chem.*, 1969, **47**, 3773.

Our results for Co^{II} induced dissociations could be accounted for by the following general scheme (L = bipy or terpy and charges and solvent molecules have been omitted for convenience):



With this scheme the observed pseudo-first-order rate constant, k (with Mn^{II} and Co^{II} in large excesses over L) is given by equation (22). For example, at 298.1 K with

$$k = k_d k_1 [\text{M}] / (k_t [\text{Mn}^{II}] + k_1 [\text{M}]) \quad (22)$$

$[\text{Mn}^{II}] = 6.34 \times 10^{-3}$ mol l⁻¹ and $[\text{Co}^{II}] = [\text{M}] = 7.45 \times 10^{-3}$ mol l⁻¹, $10^2 k = 1.43$ s⁻¹ for L = terpy ($I = 0.2$ mol l⁻¹). Since $k_t = 5.3 \times 10^3$ l mol⁻¹ s⁻¹ (Table 4, $I = 0.2$ mol l⁻¹) and $k_1 = 1.07 \times 10^3$ l mol⁻¹ s⁻¹ ($I \simeq 0$),⁸ from equation (22) the value $10^2 k_d = 7.5$ s⁻¹ can be calculated which is significantly larger than the observed rate constant (k). This calculated value of k_d is only a little larger than the directly measured rate constant (Table 5) using Hg^{II} in place of Co^{II}. With Hg^{II} k_1 is

TABLE 5

Observed rate constants (k) for the dissociation of mono-complexes of Mn^{II} in anhydrous methanol ($I = 0.20$ mol l⁻¹, NaClO₄). $[\text{Mn}^{II}]$ *ca.* 10⁻² mol l⁻¹ unless otherwise specified

Ligand	Electrophile	$10^2[\text{Electrophile}]$ mol l ⁻¹	T K	k s ⁻¹
Bipy ^a	H ⁺	5.8	262.9	1.54
	H ⁺	5.8	274.2	5.0
	H ⁺	5.8	274.2	6.0 ^b
	H ⁺	1.25	274.2	6.4 ^b
	H ⁺	5.8	287.7	15.5
	Hg ^{II}	1.0	289.9	11.8
	Hg ^{II}	0.2	289.9	11.6
Phen ^c	H ⁺	5.8	262.9	0.58
	H ⁺	5.8	274.2	1.82
	H ⁺	5.8	274.2	1.66 ^b
	H ⁺	12.5	274.2	1.77 ^b
	H ⁺	5.8	278.7	5.9
Terpy ^d	Hg ^{II}	0.32	289.8	0.0230
	Hg ^{II}	0.80	289.8	0.0238
	Hg ^{II}	0.80	296.4	0.0395
	Hg ^{II}	0.80	303.4	0.0759
	Hg ^{II}	0.80	309.2	0.110

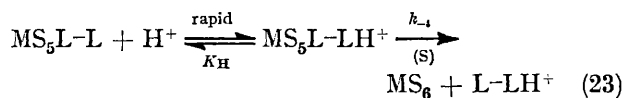
^a 1.03×10^{-5} mol l⁻¹. ^b $[\text{Mn}^{II}]$ *ca.* 10⁻³ mol l⁻¹. ^c 5.2×10^{-5} mol l⁻¹; acid catalysis is not expected for phen (ref. 28). ^d $[\text{Terpy}] = 6 \times 10^{-5}$; $[\text{Mn}^{II}] = 1.6 \times 10^{-3}$ mol l⁻¹.

larger and we find $k_1[\text{M}] \gg k_t[\text{Mn}^{II}]$. Therefore, from equation (22), $k = k_d$ and the dissociation rate constant can be measured directly. Both Hg(ClO₄)₂ and HgCl₂ gave the same results and rate constants were independent of the mercury(II) concentration as expected. Activation parameters associated with values of k_d are given in Table 4.

For L = bipy the HClO₄ induced dissociation rates were also measured for comparison with those obtained using Hg^{II} (Table 5). Acid catalysis was insignificant on increasing the acidity to 0.06 mol l⁻¹ in methanol,

²⁷ F. Dickert, H. Hoffmann, and W. Jaenike, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 500.

a behaviour which was unexpected for bipy in view of previous results in aqueous solution.²⁸⁻³¹ For a bidentate ligand the dissociation reaction corresponds to a reversal of the reactions in Scheme 2. Acid catalysis is expected²⁸ whenever the intermediate MS_5L-L (in which the bidentate ligand $L-L$ is bound in a unidentate fashion) can accept a proton, reaction (23).^{*} If we



include reaction (23) in Scheme 2 and define $K_H = [MS_5L-LH^+]/[MS_5L-L][H^+]$, it is readily shown that equation (24) applies.^{2,28} Since values of k_d for $L = \text{bipy}$ were found not to vary significantly with $[H^+]$

$$k_d = \frac{k_3(k_{-2} + k_4K_H[H^+])}{(k_{-2} + k_3 + k_4K_H[H^+])} \quad (24)$$

(Table 5), we assume $k_4K_H[H^+] \gg (k_{-2} + k_3)$ and the limiting rate constant at high acidity (k_a) is equal to k_3 . If we equate the value of k_d measured with Hg^{II} under neutral conditions (k_n) to $k_3k_{-2}/(k_{-2} + k_3)$, then one expects^{2,4} $k_a/k_n = (k_{-2} + k_3)/k_{-2}$. Hence for $L = \text{bipy}$ the value $k_3/k_{-2} = 0.73$ can be estimated (from Table 5) at 289.9 K, and it would appear that a rate-determining ring-closure mechanism is operative.⁴

An alternative explanation of the lack of acid catalysis

* Deprotonation of MS_5L-LH^+ will be relatively slow and so the term $k_4K_H[H^+]$ in equation (24) will become $k_{H^+}[H^+]$, where k_{H^+} is the rate constant for protonation of the intermediate MS_5L-L (H. Diebler, personal communication).

²⁸ F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 218.

for $L = \text{bipy}$ is also possible from equation (24) if K_H is very small. This is a distinct possibility if pK_H is close to the second pK_a of bipy,²⁹ for which a value of -0.5 has been estimated in aqueous solution.³² (The pK_a of phen in methanol is similar to that in water,²⁶ and ammonia is an order of magnitude more basic in methanol than in water.²³) However, this explanation is made less likely by the recent separation³¹ of the complex $[Cr(\text{bipy})(\text{bipyH})(H_2O)_3]^{4+}$ from an aged solution of *cis*- $[Cr(\text{bipy})_2(H_2O)_2]^{3+}$ in $0.12 \text{ mol l}^{-1}\text{-HNO}_3$, and we believe that the former explanation is to be preferred.

Stability Constants.—Values of the kinetically determined stability constants for the Ni^{II} complexes in methanol are very similar to those determined in aqueous solution (Table 4). In aqueous solution, because of the constancy of k_f values for ligands of the same charge, variation in the stability constants is largely reflected in variations in values of k_d .² In contrast, in methanol, the phen and bipy complex-formation rates differ by a greater factor than do the dissociation rates (Tables 3 and 5).

We thank the S.R.C. for a grant to build the low-temperature stopped-flow apparatus and for a maintenance grant (to D. J. B.).

[2/1906 Received, 11th August, 1972]

²⁹ R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, 1968, **7**, 170; T. S. Roche and R. G. Wilkins, *Chem. Comm.*, 1970, 1681.

³⁰ H. Diebler, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 268.

³¹ S. Y. J. Ng and C. S. Garner, *Inorg. Chim. Acta*, 1971, **5**, 365.

³² W. A. E. McBryde, *Canad. J. Chem.*, 1965, **43**, 3472.