A Low Temperature Stopped-flow Investigation of Manganese(II) Complex Formation with Bipyridyl-type Ligands in Anhydrous Methanol

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Summary Rates of formation of mono-complexes of manganese(II) ion with 2,2′-bipyridyl, 1,10-phenanthroline and 2,6-bis(2-pyridyl)pyridine (terpy) have been measured in anhydrous methanol by the stopped-flow method between 227 and 273 K; the activation parameters are not in accord with the Eigen-Wilkins mechanism.

THE importance of the manganese (II) ion in metallo-enzyme systems has been stressed,[1] and substitution reactions of Mn^{II} are currently under kinetic investigation.[1,2] Because of the absence of crystal field effects, Mn^{II} is unlikely to distort from a regular octahedral geometry and is therefore more suitable than, say, Ni^{II} for studies in a variety of non-aqueous solvents. In most nonaqueous solvents the Eigen-Wilkins mechanism is not entirely valid[3] although it applies to the majority of formation reactions in aqueous media.

TABLE. *Rate data (at* 298·1 K) *for the formation of manganese*(II) *complexes in methanol and in water*

Ligand	Solvent	μ/medium	log k_f (k_f in l mol^{-1} s^{-1})	ΔH_f* (kcal mol^{-1})	ΔS_f* (cal mol^{-1}K^{-1})
(terpy)	H_2O	~0	5·0[b]	6·0	−15·7
(terpy)	MeOH	0·2 mol l^{-1} $NaClO_4$	3·72[c]	12·8	+1·3
(phen)	H_2O	~0	5·1[b]		
(phen)	MeOH	0·2 mol l^{-1} $NaClO_4$	4·95[d]	10·6	− 0·4
(bipy)	MeOH	0·2 mol l^{-1} $NaClO_4$	4·24[d]	11·7	0·0
8Hq$^-$[a]	H_2O	0·1 mol l^{-1} KNO_3	8·5[e]	~8·8	~+10
8Hq$^-$	MeOH	0·2 mol l^{-1} $NaClO_4$	2·92[f]		
MeOH	MeOH	~0	5·57[g,h]	6·2	−12
H_2O	H_2O	~0	7·49[g,i]	8·1	+2·9

[a] 8Hq$^-$ = 8-hydroxyquinolate ion; [b] at 284·1 K, ref. 4 and 5; [c] Extrapolated to 298·1 K from results between 251 and 273 K (this work); [d] extrapolated to 298·1 K from results between 227 and 252 K (this work); [e] ref. 1; [f] at 226·4 K, this work; [g] solvent exchange rates (s^{-1}); [h] ref. 10; [i] ref. 16.

Unfortunately, the low stability of manganese(II) complexes, together with their relatively high lability have made kinetic investigation of their complex formation reactions difficult. This was the situation found in aqueous solutions for the 2,2′-bipyridyl complexes,[4] although it was possible to investigate by stopped-flow the formation of the more stable mono-[2,6-bis(2-pyridyl)pyridine]manganese (II) ion.[5] Relaxation methods have not so far given accurate activation parameters for manganese(II) complex formation,[6–9] and the determination of accurate activation parameters by these techniques may be difficult.[1]

Since accurate activation parameters are required for a study of substitution reactions in non-aqueous solvents[3], we are investigating several very labile systems by the stopped-flow method at low temperatures (220 to 270 K) and over as wide a temperature range as possible. We report the first of these results in methanol for the reactions of the manganese(II) ion with 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and 2,6-bis(2-pyridyl)pyridine(terpy).

The values of ΔH_f* obtained for the reactions of (phen), (bipy), and (terpy) with manganese(II) ion in methanol are large compared to the results for (terpy) in water (Table) and are 4 to 6 kcal mol^{-1} larger than ΔH_{ex}*, the activation enthalpy assosiated with solvent exchange[10] between the bulk solvent and $Mn(CH_3OH)_6^{2+}$. Until recently[3] the Eigen-Wilkins mechanism[11] was thought to account for the majority of metal complex formation reactions, equation (1), in aqueous solution. In equation (1), rapid outer-sphere ion-pair or ion-dipole interaction (M^{n+} = metal ion, S = solvent L^{m-} = ligand) is followed by rate determining

$$\mathrm{MS}_6^{n+} + \mathrm{L}^{m-} \underset{\text{rapid}}{\overset{K_0}{\rightleftharpoons}} \mathrm{MS}_6\mathrm{L} \longrightarrow \mathrm{MS}_{6-}\mathrm{L}_x{}^{(n-m)+} + x\mathrm{S} \quad (1)$$

metal–solvent exchange. With this mechanism the approximate relationship $k_f \simeq k_{ex}K_0$ holds, and hence one expects $\Delta H^*(k_f) \simeq \Delta H^*(k_{ex}) + \Delta H^0(K_0)$ (constants in brackets indicate the origin of the corresponding enthalpy term).

In general it is found that for uncharged ligands the enthalpy associated with the ion-dipole interaction $[\Delta H^0(K_0)]$ is very small,[3,11] and hence $\Delta H_f^* \simeq \Delta H^*_{ex}$. This behaviour is observed for the majority of reactions in water,[11,12] and for some reactions in methanol.[3] Mechanism (1) is also believed to apply to a number of studies in methanol,[7,9,13] although in other solvents it is definitely not valid.[3] Values of $\Delta\Delta H^*$ $[\Delta\Delta H^* = \Delta H^*(k_f) - \Delta H^*(k_{ex})]$ have been found to vary significantly from solvent to solvent, and to be linearly correlated with values of ΔH_{evap}, the enthalpy of evaporation of the solvent. This behaviour has been attributed[3] to the effects of solvent structure upon ΔH_f*, and although the present results do not fit with the correlations of Bennetto and Caldin, there is little doubt that mechanism (1) is of questionable validity in non-aqueous solvents.

However, factors other than solvent structure may also contribute to the deviations observed. For example, in going from aqueous to methanolic solution a positive value of $\Delta\Delta H^*$ could be accounted for by a switch in the rate-determining step from the first to the second metal–ligand bond formation. Sterically controlled ring-closure mechanisms have already been suggested for reactions in aqueous solutions,[14,15] and it is to be expected that such mechanisms may be even more important in the presence of bulkier solvent molecules. We are extending this work to other systems, including several solvents and various ligand types.

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