Slow Substitution Reaction of Manganese(II) Ion in Dimethyl Sulphoxide Solution

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Summary The reaction between excess of Mn^{II} ion and 2,6-(2-pyridyl)pyridine (terpy) in dimethyl sulphoxide solution occurs in two stages; a rapid formation of a binuclear intermediate is followed by a very slow reaction attributed to final chelate ring closure.

It is generally recognised that substitution reactions of Mn^{II} ion are very rapid.[1] Most kinetic studies have been made by relaxation methods such as temperature-jump,[2] pressure-jump,[3] and ultrasonic sound absorption,[4] although in favourable cases flow studies are possible,[5] especially in non-aqueous solvents and at reduced temperatures.[6] In dimethyl sulphoxide a significantly different pattern emerges for the reaction between 2,6-(2-pyridyl)pyridine (terpy, 2.5×10^{-5}—10^{-4} mol l^{-1}) and a large excess of Mn^{II} ion (0.02—0.5 mol l^{-1}).

The reaction was investigated with stopped-flow and Cary 14 spectrophotometers between 292 and 314 K. At 335 nm, an initial very rapid reaction was observed at a rate characteristic of other Mn^{II} substitutions in methanol.[6] At 292·1 K, $\mu = 0.20$ (NaClO$_4$), the rate is given by equation (1). A similar rate law has been observed[7] for the reaction

$$\text{Rate/(mol l}^{-1}\text{ s}^{-1}) = \{(46.1 \pm 0.7)$$
$$+ (1.64 \pm 0.06) \times 10^3 [Mn^{II}]\}[\text{terpy}] \qquad (1)$$

of $Mn(dmso)_6{}^{2+}$ with 1,10-phenanthroline [for phen at 291·7 K, k(formation) $= (7.7 \pm 0.6) \times 10^3$ l mol^{-1} s^{-1}; k(dissociation) $= 33.7 \pm 1.7$ s^{-1}]. The large value of k(dissociation) ($= 46.1$ s^{-1}) in equation (1) is in marked contrast to the low value for terpy in methanol,[6] and indicates incomplete chelation in the initial phase. Furthermore, with terpy (but not phen) the initial rapid process was followed by a much slower reaction which was examined by repetitive scan spectrophotometry.† Examination of the slow reaction at 314·1 K gave relationship (2) (k is the observed, pseudo-first-order rate constant). The mechanism shown
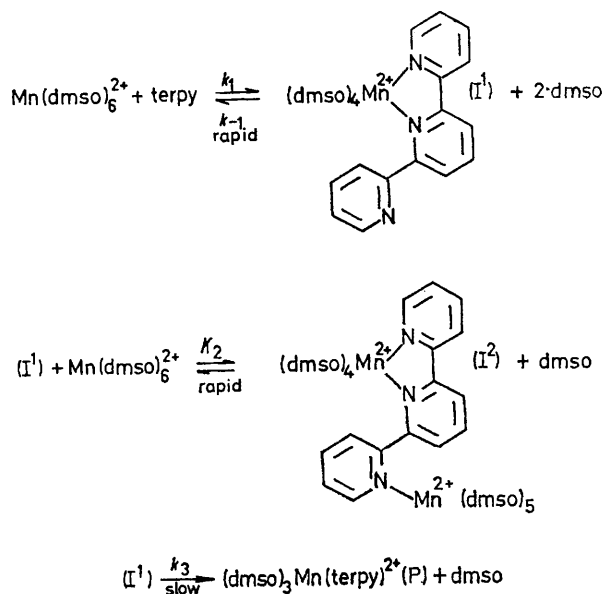
$$1/k = (387 \pm 69) + (6.74 \pm 0.67) \times 10^3 [Mn^{II}] \qquad (2)$$

in the Scheme is consistent with equations (1) and (2).

With this Scheme the initial rapid reaction involves the formation of the mononuclear intermediate (I^1) which rapidly equilibrates with the binuclear intermediate (I^2). From equation (1), $k_1 = (1.64 \pm 0.06) \times 10^3$ l mol s^{-1}, $k_{-1} = 46.1 \pm 0.7$ s^{-1} and the equilibrium constant for the formation of the intermediate (I^1) is $K = 35.6 \pm 0.8$ l mol^{-1}; (I^1) then slowly ring closes to give the final product (P). The presence of (I^2) is necessary to account for the observed relationship (2); if K_2 is defined as the equilibrium constant associated with the formation of (I^2), it can readily be shown that $k = k_3/(1 + K_2[Mn^{II}])$. Hence a plot of k^{-1} vs.

† At the highest [Mn^{II}], four isosbestic points were observed between 320 and 360 nm. At 314 K, [Mn^{II}]$=0.45$ mol l^{-1}, the slow stage was complete in 2—3 h.

[Mn^{II}] should give a straight line from which k_3 and K_2 can be estimated. From equation (2), we find that at 314.1 K, $k_3 = (2.58 \pm 0.46) \times 10^{-3}$ s^{-1}, and $K_2 = (17.4 \pm 1.4)$ l mol^{-1}. The value of k_3 is remarkably low (half-life $ca.$ 4.5

$$Mn(dmso)_6^{2+} + terpy \underset{\underset{rapid}{k_{-1}}}{\overset{k_1}{\rightleftharpoons}} (dmso)_4Mn^{2+}(I^1) + 2 \cdot dmso$$

$$(I^1) + Mn(dmso)_6^{2+} \underset{rapid}{\overset{K_2}{\rightleftharpoons}} (dmso)_4Mn^{2+}(I^2) + dmso$$

$$(I^1) \xrightarrow[slow]{k_3} (dmso)_3Mn(terpy)^{2+}(P) + dmso$$

Scheme. Mechanism of the reaction between excess of Mn-(dmso)₆²⁺ and 2,6-(2-pyridyl)pyridine (terpy) in dimethyl sulphoxide (dmso).

min), although we have found evidence for a rate-determining chelate-ring-closure mechanism during the reaction between Ni(dmso)₆²⁺ and 2,2′-bipyridyl in dmso.[8] The much slower final ring closure of terpy with the more labile Mn^{II} ion presumably arises from the steric strain present in the final product. Terpy is known to bond with all three pyridine rings co-planar,[19a] and final ring closure will result, therefore, in considerable steric strain. This effect, together with the difficulty of twisting the planar pyridine rings against the bulky co-ordinated dmso molecules[8] makes ring closure very difficult in this case. The reaction of Ni-(dmso)₆²⁺ with the more flexible ligands 2-pyridylethyl-amine and 2-pyridylmethylamine is much faster[7] than with 2,2′-bipyridyl and similar to the rate of reaction with pyridine.[8,10] It is also noteworthy that a very slow equilibration was observed during the reaction between excess of Ni(dmso)₆²⁺ and terpy in dmso,[11] although in this case the spectral changes over a period of 24 h were less marked than those observed for Mn^{II}.

The possibility that the slow reaction of Mn^{II} with terpy might arise from oxidation of the complex, as observed for Mn^{II} hematoporphyrin,[12] was eliminated by careful de-oxygenation of our solutions, and by the addition of excess of reducing agent (0.2 mol l^{-1} hydroxylamine) during trial experiments. Equation (2) is also inconsistent with such behaviour.

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