Ligand Exchange Kinetics of Metal Dimethyl Sulphoxide Complexes, ML_6^{2+}, in Mixed Solvents

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Summary The ligand exchange kinetics of ML_6^{2+} [M = Co^{II} or Ni^{II}, L = dimethyl sulphoxide (DMSO)] in DMSO and the mixed solvents DMSO–$MeNO_2$ and DMSO–CH_2Cl_2 are independent of the composition of the solvent.

IN all previous reports, ligand exchange reactions of octahedral Co^{II} and Ni^{II} have been studied in pure solutions of the ligand. Under these conditions the ligand concentration dependence can not be studied. We report a study of ML_6^{2+} (L = DMSO) in DMSO and in admixtures of nitromethane and methylene chloride. The latter two solvents are inert in the sense that they are nonco-ordinating.

The composition of the bulk solutions used was pure DMSO; 2·2 M, 1·1 M and 0·6 M-DMSO in nitromethane and 1·1 M-DMSO in methylene chloride. Analysis of the variable temperature ^1H n.m.r. spectra by standard techniques[1] shows that the transverse relaxation rate data fall on a common line. This implies a constant value for the ligand exchange rate. The following kinetic parameters are obtained: NiL_6^{2+}, $k(25°) = 3{\cdot}2 \times 10^3$ sec.$^{-1}$, $\Delta H^* = 13{\cdot}0$ Kcal/mole, $\Delta S^* = 3{\cdot}2$ e.u. CoL_6^{2+}, $k(25°) = 1{\cdot}7 \times 10^5$ sec.$^{-1}$, $\Delta H^* = 9{\cdot}6$ Kcal/mole $\Delta S^* = -0{\cdot}4$ e.u. The exchange parameters for NiL_6^{2+} is in reasonable agreement with data previously reported in DMSO.[2]

That nitromethane was not co-ordinated was established by integrating the co-ordinated DMSO peak from the metal complex in a pure solution of nitromethane. The solvation numbers, measured at the extreme temperatures of the kinetic data, were 5·9 ± 0·2 for Ni and 6·0 ± 0·2 for Co.

The dielectric constant of methylene chloride will greatly increase the concentration of outer-sphere perchlorate-ion pairs. Since the same ligand exchange parameters are obtained, a mechanism which involves an outer-sphere ion-pair is very unlikely.

The independence of the exchange rate on the ligand concentration, composition, and fluidity[3] is consistent with a dissociative mechanistic pathway.[4] This implies there is an intermediate in the substitution pathway.

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