Ligand Exchange Kinetics of Tetrahedral Chlorocobalt(II) Species by ^{35}Cl Nuclear Magnetic Resonance

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Summary Ligand exchange kinetics in nitromethane of the $CoCl_3$ (pyridine)$^-$ and $CoCl_4^{2-}$ species provide a probe into the mechanism of exchange in tetrahedral complexes.

RELATIVELY little is known about the mechanisms of ligand substitution in tetrahedral metal complexes of the more labile sorts.[1] A significant cause of this gap is the lack of data on the kinetics of halide exchange in species that are chiefly to be characterized by the presence of halide ligands.[2] We report on kinetics of the exchange of ^{35}Cl between bulk solution chloride and chlorocobalt(II) complexes observed in nitromethane solution by ^{35}Cl n.m.r. transverse relaxation-time measurements.

Visible absorption spectra of $CoCl_4^{2-}$ and related tetrahedral and octahedral complexes are known.[3] Nitromethane solutions containing Co^{II}, excess of tetraethylammonium chloride, and pyridine have visible spectra indicative of an equilibrium between $CoCl_4^{2-}$ and $CoCl_3py^-$ (py = pyridine). The method of Newton and Arcand[4] permits analysis of the spectra to give the equilibrium quotient for conversion of $CoCl_4^{2-}$ into $CoCl_3py^-$ and the extinction coefficient of $CoCl_3py^-$. The equilibrium quotient is $0{\cdot}50 \pm 0{\cdot}05$ at 25·0°. Knowledge of this quotient allows calculation of the distribution among species for interpretation of kinetic experiments.

In the absence of pyridine, $CoCl_4^{2-}$ is the only Co^{II} species in solutions containing 1M-Et_4NCl. The ^{35}Cl line-width in these solutions is 24 Hz, independent of the Co^{II} concentration. The absence of concentration-dependent line-broadening implies that Cl^- exchange is too slow to result in the averaging of the n.m.r. signals from free and bound chloride.[5] Variable-temperature measurements indicate line-width narrowing with increasing temperature much like that observed for the chloride ion in the bulk phase in the absence of Co^{II}. An upper limit of 100 sec^{-1} is placed on the exchange rate constant under these high Cl^- conditions.

Upon addition of pyridine to solutions of $CoCl_4^{2-}$ and Cl^- in $MeNO_2$, formation of $CoCl_3py^-$ is indicated in the visible spectra. ^{35}Cl n.m.r. spectra of these solutions show significant line broadening which must be associated with chloride exchange reactions of $CoCl_3py^-$. This line broadening leads to a maximum line-width of about 300 Hz at $1{\cdot}3 \times 10^{-2}$ M-Co^{II} and 5 M-pyridine. It depends on both the Co^{II} and pyridine concentrations of the solutions. According to standard arguments,[6] this line broadening (shortened transverse relaxation times) can be assigned to chemical exchange by noting that there is a significant decrease in line-width as temperature is increased. The relation,

$$1/T_{2\text{obs}} = 1/T_{2\text{A}} + P_\text{M}/\tau_\text{M}$$

may be applied to solutions dilute in Co^{II}. In this equation, $T_{2\text{obs}}$ is the observed transverse relaxation time derived from the observed line-width,[6] $T_{2\text{A}}$ is the relaxation time for chloride in the bulk solution environment, P_M is the probability that a chloride is in the co-ordination sphere of the metal ion, and $1/\tau_\text{M}$ is the rate constant for exchange between the bulk solution and the co-ordination sphere of the Co^{II} ion. Assuming, on the evidence of pyridine-free solutions, that all exchange is taking place through the $CoCl_3py^-$ species, values of $1/\tau_\text{M}$ for this species may be obtained as a function of pyridine and chloride concentration with the aid of visible spectral data. The Figure shows the values for 1M-chloride as a function of pyridine concentration. The Figure supports a rate law for chloride exchange of the form:

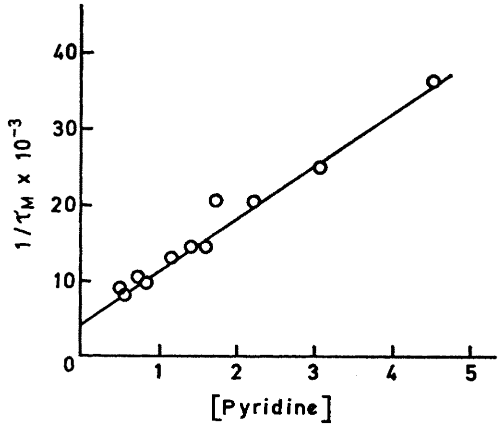

FIGURE. *Dependence of ^{35}Cl exchange rate on pyridine concentration.*

$$\text{rate} = [CoCl_3py^-](k_1 + k_2[py])$$

where k_1 is $4{\cdot}5 \times 10^3$ sec^{-1} and k_2 is $7{\cdot}1 \times 10^3$ M^{-1} sec^{-1} at 25°. Variation of chloride concentration shows k_1 to be, in fact, a pseudo-first-order rate constant dependent upon chloride concentration and properly expressed as $4{\cdot}5 \times 10^3$ M^{-1} sec^{-1}. Thus, there are two paths for chloride exchange, one chloride-dependent and the other pyridine-dependent.

There is a simple but by no means certain mechanistic interpretation of the present results. It would suggest that the substitution reactions of $CoCl_3py^-$ are both associative in character passing through a five-co-ordinate transition state. The pyridine-dependent pathway may be explained by the "slow" formation of $CoCl_2py_2$ which reacts rapidly with Cl^- as would be required by the failure to observe $CoCl_2py_2$ as an equilibrium component of these mixtures. Of course, intermediates (as opposed to transition states) of five-co-ordination cannot be excluded. But, the small difference in reactivity of Cl^- and pyridine toward $CoCl_3py^-$ suggests that bond formation is not predominant and tends to argue against an intermediate of higher co-ordination number. On the other hand, reactivity increases along the series $CoCl_4^{2-} < CoCl_3py^- < CoCl_2py_2$ which corresponds to approach to the ligand arrangement about Co^{II} which favours octahedral co-ordination. It seems likely from these results that the lability of the tetrahedral species is correlated with their tendency to form complexes of higher co-ordination number.

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