Evidence for a Reaction Intermediate in Nucleophilic Substitution in Rhodium(I) Planar Complexes

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THE kinetic behaviour of amines towards platinum(II) and gold(III) planar substrates has been recently discussed[1] and we are now extending such investigations to rhodium(I) and iridium(I) planar complexes. The few results available for nucleophilic displacements on complexes of these d^8 transition-metal ions indicate that they react by an associative process, occasionally with unusually stable five-co-ordinated intermediates.[2]

We report here the data relevant to the kinetics of the reactions of [Rh(cy) (SbR$_3$)Cl] (cy = 1,5-cyclo-octadiene, R = *p*-tolyl) with different amines (am) in acetone at 25°, followed spectrophotometrically. An attempt to follow the kinetics by conductivity measurements failed because there is no significant change in the molar conductivity during the time required to complete the reaction. The product has been identified for am = pyridine and we assume that all the reactions are of the type:

$$[\mathrm{Rh(cy)\ (SbR_3)Cl}] + \mathrm{am} \rightarrow [\mathrm{Rh(cy)\ (am)Cl}] + \mathrm{SbR_3} \qquad (1)$$

In all kinetic experiments the concentration of the complex was less than 5×10^{-4} M and that of the amine was varied from 5×10^{-3} M to 1 M, in order to realize first-order conditions and to force the reactions to go to completion. The rate of reaction is independent of the concentration of the amine in this region, but the first-order rate constants change with the nature of the amine. The experimental values of *k* are collected in the Table.

These results appear quite interesting since they represent a departure from the general rate law for nucleophilic substitution of ligands in other square-planar complexes where:

$$\text{rate} = (k_1 + k_2[\text{Y}])\ [\text{complex}]$$

(Y = entering group) and both the rate constants k_1 and k_2 are related to bimolecular processes of replacement of the leaving group by the solvent and Y respectively,[2] so that the k_1 is independent of the nature of Y.

The data reported in the Table suggest a reaction scheme of the type:

$$\begin{tikzcd} \text{complex} + \text{amine} \arrow[dr, "\text{fast}"'] & & \\ & \text{intermediate} \arrow[r, "\text{slow}"] & \text{products} \end{tikzcd}$$

The possible existence of an unstable five-co-ordinated intermediate has been proposed and discussed for other planar complexes[2,3] on the basis of indirect evidence.

The extinction coefficient in the range 340—380 mμ calculated by extrapolating back to zero time plots of $\log_{10}(D_\infty - D_t)$ against time (D = optical density at the appropriate wavelength) differ significantly from those of the starting material and the immediate change in the spectra can be related to the fast associative reaction. Moreover, by studying the kinetics at very low concentrations of 3-cyanopyridine the rate of the first step appears to be reduced and the two processes are superimposed. The rate constants in the Table are in a linear free-energy relationship with the values of basicity of the amines, indicating a direct influence of the nature of the entering group on the relatively slow reaction of the intermediate to give the products.

TABLE. *First-order rate constants for the reactions* (1) *in acetone at* 25°. (k_1 *is the average of closely agreeing values obtained in several kinetic runs over a range of concentration.*)

Amine	$10^2 \times k_1$ (sec.$^{-1}$)
3-Cyanopyridine	1·58
3-Chloropyridine	1·93
Pyridine	2·42
4-Methylpyridine	2·66
Morpholine	3·68
n-Butylamine..	4·57

In order to ascertain how far the nature of the solvent can be responsible for this behaviour, we also followed the kinetics with pyridine in methanol and 1,2-dichloroethane and obtained similar results, with just a small change in the reactivity ($k = 1{\cdot}65 \times 10^{-2}$ and $2{\cdot}03 \times 10^{-2}$ sec.$^{-1}$ respectively.)

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[1] L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, 1966, **5**, 1517; L. Cattalini, M. Nicolini, and A. Orio, *ibid.*, p. 1674; L. Cattalini, A. Doni, and A. Orio, *ibid.*, 1967, **6**, in the press.

[2] C. H. Langford and H. B. Gray "Ligand Substitution Processes", Benjamin, New York, 1965, and references therein.

[3] H. B. Gray, "Advances in Chemistry Series", No. 49, American Chemical Society, Washington, D.C., 1965, p. 103. U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, 1966, **5**, 591; L. Cattalini, and M. L. Tobe, *ibid.*, p. 1145.