The Catalysis of Substitutions in the Complexes *trans*-$[Rh\,py_4X_2]^+$

By R. D. GILLARD,* B. T. HEATON, and D. H. VAUGHAN

(*University Chemical Laboratory, The University, Canterbury, Kent*)

Summary The rates of halogen interchange in *trans*-$[Rhpy_4X_2]X$ (X = Cl or Br) have been found to be markedly inhibited by oxygen and to be catalysed by both primary and secondary alcohols.

IT has been shown[1] that the rhodium(III) complexes *trans*-$[Rhpy_4X_2]X$ (X = Cl, Br) have a high level of antibacterial activity, whereas the corresponding bisethylenediamine complexes, *trans*-$[Rhen_2X_2]X$, have none. As part of a comprehensive study of these complexes, an investigation into the kinetics of the halide interchange reactions of the complexes *trans*-$[Rhpy_4X_2]X$ was undertaken. The results are compared with those of the careful study[2] of the halide interchanges found for *trans*-$[Rhen_2X_2]X$.

A detailed study of the kinetics at 81° of the reactions in equation (1) has been completed. It was found that the

$$trans\text{-}[Rhpy_4Cl_2]^+ \rightleftarrows trans\text{-}[Rhpy_4BrCl]^+ \rightleftarrows trans\text{-}[Rhpy_4Br_2]^+ \qquad (1)$$

rates were all independent of the concentration of the incoming ligand and were very similar to those in the corresponding ethylenediamine system. However, if nitrogen, argon, or hydrogen was bubbled into the reactant solutions, or if the solutions were made up in water saturated with nitrogen or argon, then the rates of the reactions of the pyridine complexes were greatly increased, whereas no corresponding effect was found in the ethylenediamine system. Oxygen was found to have an inhibiting effect on the rate, but the kinetics were not as clean, as shown by the absence of isosbestic points during the reaction; some decomposition also occurred. Complete removal of oxygen by degassing aqueous solutions under high vacuum gave a rate too fast to be measured by conventional techniques. We have also shown that part of the catalysis found using gases (*e.g.* H_2) for the formation of *trans*-$[Rhpy_4Cl_2]Cl$ from aqueous pyridine and rhodium trichloride arises from the de-oxygenation.

If 30% *v/v* ethanol was used as the solvent for the reactions, the rates were again greatly increased and plots of absorbance against time of the type shown in the Figure were obtained. Both n-propanol and isopropyl alcohol, when used instead of ethanol, gave similar plots whereas t-butyl alcohol, which lacks the α-C–H group, did not increase the rate. Good reproducibility of these plots was obtained and it was found that the induction period and the pseudo-first-order rate constants obtained from the latter

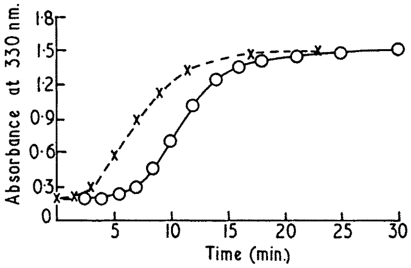

FIGURE. (------) *Absorbance at* 330 *nm. against time for the reaction trans*-$[Rhpy_4Cl_2]^+ \longrightarrow$ *trans*-$[Rhpy_4Br_2]^+$ *at* 81° *in* 30% *ethanol–water* v/v; [Br] = 0·2M; [Rh] = 10^{-3}M. (———) *as above but* O_2 *bubbled into the solution.*

part of these plots were independent of the concentrations of both the incoming halide and ethanol. However, when the ethanol concentration was below *ca.* 3% or when oxygen was bubbled into the reactant solution, the induction period was increased, but the pseudo-first-order rate constants were unaffected.

In contrast, addition of 30% ethanol decreased the rate of reaction (2) at 81° from $4\cdot2 \times 10^{-5}$ sec.$^{-1}$ to $3\cdot0 \times 10^{-5}$ sec.$^{-1}$ in 0·2M-NaBr.

$$trans\text{-}\mathrm{Rhen_2Cl_2^+} \rightarrow trans\text{-}\mathrm{Rhen_2Br_2^+} \qquad (2)$$

The autocatalytic nature of the plots shown in the Figure can be explained by the build up in concentration of a reactive intermediate. This probably contains $\mathrm{Rh^I}$, as there is an increasing amount of evidence[3] pointing to the existence of such $\mathrm{Rh^I}$ species in certain reactions of $\mathrm{Rh^{III}}$ complexes. The $\mathrm{Rh^I}$ intermediate can then react rapidly with the $\mathrm{Rh^{III}}$ complex by means of a bridged two-electron (d^8–d^6) redox mechanism similar to that found[4] in reactions of some cationic $\mathrm{Pt^{IV}}$ complexes. No appreciable concentration of the $\mathrm{Rh^I}$ intermediate is formed in solution since (a) the reactions were all stoicheiometric and (b) rhodium(I) species would be expected to yield metal on disproportionation; none was found. The effect of oxygen on the induction period is due to its oxidising the $\mathrm{Rh^I}$ species.

Further studies are under way to elucidate the mechanism of this interesting reaction, the first "fast reaction," involving $\mathrm{Rh^{III}}$. Clearly, however, on dissolution of salts of the type *trans*-$[\mathrm{RhL_4X_2}]^+\ \mathrm{Y^-}$ (L = pyridine or a 3-, 4-, or 5-substituted pyridine; X = Cl, Br or I; Y is any anion) in water an equilibrium is established with an $\mathrm{Rh^I}$ species (the water or possibly the ligands being the oxidisable moiety). Our current view is that the essential difference between *trans*-$[\mathrm{Rhpy_4X_2}]^+$ and *trans*-$[\mathrm{Rhen_2X_2}]^+$ resides in their redox properties; the pyridine compounds are more readily reducible; in particular the polarographic half-wave potential[5] for *trans*-$[\mathrm{Rhpy_4Cl_2}]^+$ is $-0\cdot39$ v whereas for *trans*-$[\mathrm{Rhen_2Cl_2}]^+$ it is $-0\cdot79$ v *versus* S.C.E.

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