I_a (S_N2) Reactions of Some Octahedral Rhodium(III) Complexes

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MONACELLI and VIEL[1] have recently published data for the H_2O-exchange reaction of the complex $Rh(NH_3)_5OH_2^{3+}$. We report some results[2,3] of anation studies of this and other complexes of rhodium(III) which, when compared with the exchange studies, suggest that there is a significant amount of bond making between the metal and the incoming nucleophile in the transition state; *i.e.* the mechanism is S_N2 or I_a.[4]

The majority of complex formation reactions are thought to go[5] *via* an S_N1 or I_d mechanism[4] in which the observed pseudo-first-order rate constants are given by $k_{obs} = k_1K_a[X]/(1 + K_a[X])$, where K_a is the equilibrium constant for formation of an associated pair involving the nucleophile X and the complex, and k_1 is the first-order rate constant for interchange of the co-ordinated solvent molecule and X. In many cases k_1 is determined mainly by the energy needed to dissociate the solvent molecule, and is usually independent of X but is related closely to the rate constant, k_{ex}, for solvent exchange. Langford and Muir[6] have shown that anation reactions of the complex $Co(NH_3)_5OH_2^{3+}$ with several nucleophiles have $k_1 = ca.\ 0{\cdot}2k_{ex}$. This is because the nucleophile X is suitably oriented to compete for the vacated co-ordination site left by the leaving water molecule only in about 20% of the ion-pairs.

For our anation reactions, plots of k_{obs} against [X] are curved so that ion-pairing is occurring to a significant extent. Graphs of $1/k_{obs}$ against $1/[X]$ are linear with positive intercepts on the $1/k_{obs}$ axis, and weighted least-squares analyses of the data give values of $1/k_1$ and K_a which are listed in the Table, the uncertainties being standard deviations. Where corresponding values of k_{ex} are known, the values of k_1 are significantly *greater* than k_{ex} rather than only 20% as great. The ease of entry into the inner sphere of a chloride or bromide ion from the outer sphere is considerably greater than that of a water molecule. Since it is unlikely that the mere presence of a halide ion in the outer sphere would enhance the rate of release of a water molecule to this extent, it may be concluded that an appreciable amount of bond making is occurring during the formation of the transition state, and the mechanism can be classified as I_a. Previous studies had failed to

Rate parameters for anation of some rhodium(III) *complexes at* $\mu = 1{\cdot}5$ M[a]

			$10^{-2}/k_1$	K_a	10^4k_1 (sec.$^{-1}$)		10^4k_{ex}[c]
Complex	X	T°	(sec.)	(l.mole^{-1})	(i)[b]	(ii)[b]	(sec.$^{-1}$)
$Rh(NH_3)_5OH_2{}^{3+}$	Cl	35	70 ± 21	$0{\cdot}095 \pm 0{\cdot}029$	0·89	0·65	0·5
	Cl	65	$2{\cdot}55 \pm 0{\cdot}34$	$0{\cdot}156 \pm 0{\cdot}022$	31	26	13
	Br	35	45 ± 23	$0{\cdot}054 \pm 0{\cdot}028$	1·1	0·73	0·5
trans-Rh $en_2(OH_2)_2{}^{3+}$ ..	Br	70	$4{\cdot}79 \pm 0{\cdot}31$	$0{\cdot}518 \pm 0{\cdot}034$	18·5	16·6	—
trans-Rh $en_2Br(OH_2)^{2+}$ ..	Cl	45	$2{\cdot}07 \pm 0{\cdot}23$	$0{\cdot}645 \pm 0{\cdot}073$	39	33	—

[a] Maintained with sodium perchlorate.

[b] Lower limits calculated by assuming (i) two and (ii) four standard deviations from the best value of $1/k_1$.

[c] Data from ref. 1; negligible dependence on ionic strength.

clarify the mechanisms of reactions of such rhodium(III) complexes.[7]

The value of K_a for $Rh(NH_3)_5OH_2,Cl^{2+}$ is less than 1/10 of that of $Co(NH_3)_5OH_2,Cl^{2+}$.[6] The overall charge on the complex appears to have little effect on the values of K_a, as seems to be true also for other rhodium(III)[8] and cobalt(III)[9] complexes. Specific effects are, therefore, probably more important and the presence of co-ordinated water molecules appears to enhance ion-pairing. No spectroscopic evidence for ion-pairing of iodide with hexa-aminerhodium(III) complexes has been observed,[10] but K_a for the ion-pair $Rh(OH_2)_6,Cl^{2+}$ is *ca.* 1·2 l.mole^{-1} at 65° and $\mu = 2{\cdot}5$ M.[8] Spectrophotometric studies[3] show that K_a for $Rh(NH_3)_5OH_2,Br^{2+}$ is *ca.* 0·2 l.mole^{-1} at 35° and $\mu = 1{\cdot}5$ M. This is probably not significantly higher than the value obtained kinetically, the precision of determination of such small association constants being quite low.

Studies of the anation reaction of $Rh(NH_3)_5OH_2{}^{3+}$ with chloride at $\mu = 0{\cdot}2$ M shows that fluoride ions retard the reaction although it still goes to completion. The effect is consistent with competitive ion-pairing by fluoride with $K_a = 2{\cdot}6 \pm 0{\cdot}5$ and $11{\cdot}4 \pm 0{\cdot}8$ l.mole^{-1} at 45·4 and 74·8°, respectively; $\Delta H_a^0 = 11 \pm 2$ kcal./mole, and $\Delta S_a^0 = 38 \pm 6$ cal. mole^{-1} deg.$^{-1}$.[3] The rate of anation of *trans*-Rh $en_2Br(OH_2)^{2+}$ with chloride is also retarded by fluoride and K_a is *ca.* 11 l.mole^{-1} at 45° and $\mu = 0{\cdot}2$ M.[2] This reaction is also retarded by nitrate to an extent consistent with a value of K_a = *ca.* 0·8 l.mole^{-1} at 45° and $\mu = 1{\cdot}5$M.

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[1] F. Monacelli and E. Viel, *Inorg. Chim. Acta*, 1967, **1**, 467.

[2] H. L. Bott, Ph.D. thesis, London University, 1966.

[3] K. Shaw, Ph.D. thesis, London University, 1966.

[4] C. H. Langford and H. B. Gray, "Ligand Substitution Process", Benjamin, New York, 1966, ch. 1.

[5] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 2nd edn., 1967, ch. 3.

[6] C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, 1967, **89**, 3141.

[7] A. J. Poë, K. Shaw, and M. J. Wendt, *Inorg. Chim. Acta*, 1967, **1**, 371; H. L. Bott and A. J. Poë, *J. Chem. Soc.* (*A*), 1967, 205; H. L. Bott, E. J. Bounsall, and A. J. Poë, *ibid.*, 1966, 1275.

[8] G. M. Harris and K. Swaminathan, *J. Amer. Chem. Soc.*, 1966, **88**, 4411.

[9] D. W. Archer, D. A. East, and C. B. Monk, *J. Chem. Soc.*, 1965, 720.

[10] H.-H. Schmidtke, Proceedings 8th I.C.C.C., Vienna, 1964, p. 72.