The "Unusual" Kinetic *trans*-Effect of Ammonia in Octahedral Rhodium(III) Complexes

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RECENT studies have shown the existence of pronounced thermodynamic[1] and kinetic[2] *trans*-effects in octahedral complexes of the type *trans*-RhA_4LX^+ and *trans*-$RhA_4LOH_2^{2+}$, where L and X are Cl, Br, and I, and A is $en_{\frac{1}{2}}$. We have extended these studies[3] to the case in which $L = NH_3$ and $A = en_{\frac{1}{2}}$ or NH_3. Some of the data are given in the Table. The rate parameters for the reaction of chloride with $Rh(NH_3)_5OH_2^{3+}$ and *trans*-$Rh\ en_2NH_3OH_2^{3+}$ are virtually identical, so

TABLE. *Enthalpy data for reactions of some penta-amminerhodium*(III) *complexes*
(limits are standard deviations)

Reaction	$\Delta H^{\ddagger}$(kcal./mole)	ΔH°(kcal./mole)
$Rh(NH_3)_5OH_2^{3+} + I^- \rightarrow Rh(NH_3)_5I^{2+} + H_2O$	24·2 ± 0·2	−1·9 ± 0·3
$Rh(NH_3)_5OH_2^{3+} + Br^- \rightarrow Rh(NH_3)_5Br^{2+} + H_2O$	25·3 ± 0·3	+0·7 ± 0·4
$Rh(NH_3)_5OH_2^{3+} + Cl^- \rightarrow Rh(NH_3)_5Cl^{2+} + H_2O$	25·5 ± 0·3	+1·3 ± 0·6
trans-Rh $en_2NH_3OH_2^{3+} + Cl^- \rightarrow$ *trans*-Rh $en_2NH_3Cl^{2+} + H_2O$	25·2 ± 0·3	—
$Rh(NH_3)_5Cl^{2+} + H_2O \rightarrow Rh(NH_3)_5OH_2^{3+} + Cl^-$	24·2 ± 0·3	−1·3 ± 0·6
$Rh(NH_3)_5Br^{2+} + H_2O \rightarrow Rh(NH_3)_5OH_2^{3+} + Br^-$	24·6 ± 0·2	−0·7 ± 0·4
$Rh(NH_3)_5I^{2+} + H_2O \rightarrow Rh(NH_3)_5OH_2^{3+} + I^-$	26·2 ± 0·2	+1·9 ± 0·3

that the more extensive studies on the penta-ammine complexes can be compared directly with those on the bisethylenediamine complexes.[2]

The kinetic *trans*-effect of L can be seen in Figure 1 in which the activation enthalpies are plotted as a function of the leaving group. The *trans*-effect of the halides is I > Br > Cl, irrespective of the nature of the leaving group, although the magnitude of the effect decreases as the leaving group becomes softer, *i.e.*, along the series H_2O, Cl, Br, I. This is a consequence of the inter-dependence of the kinetic and thermodynaic *trans*-effects.[2b] The kinetic *trans*-effect of ammonia actually changes *qualitatively* as the leaving group changes. Thus, for the leaving groups water, chloride, and bromide the *trans*-effect order is I > Br > Cl > NH_3, I > Br > NH_3 > Cl, and I > NH_3 > Br > Cl, respectively. This seems to suggest that, compared with the halides, ammonia has an unusual kinetic *trans*-effect.

That this is not the case can be seen from Figure 2 in which the activation enthalpies are plotted against the enthalpy changes for the reactions concerned. The data fall on smooth, parallel curves, each one characterised by a particular *trans*-ligand, L. The curve for L = NH_3 is of the

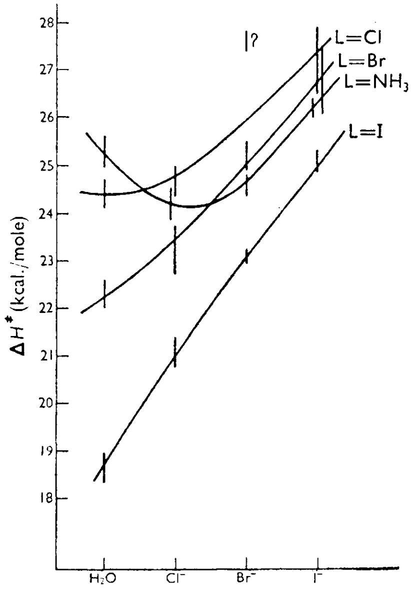

FIGURE 1. *The* trans-*effect as a function of the leaving group. Differences in* ΔH‡ *for a given leaving group give a quantitative measure of the* trans-*effect.*[2] (*Data for* L = Cl, Br, *and* I *are from ref.* 2; *when the leaving group is* OH_2 *the entering group is* Br^-)

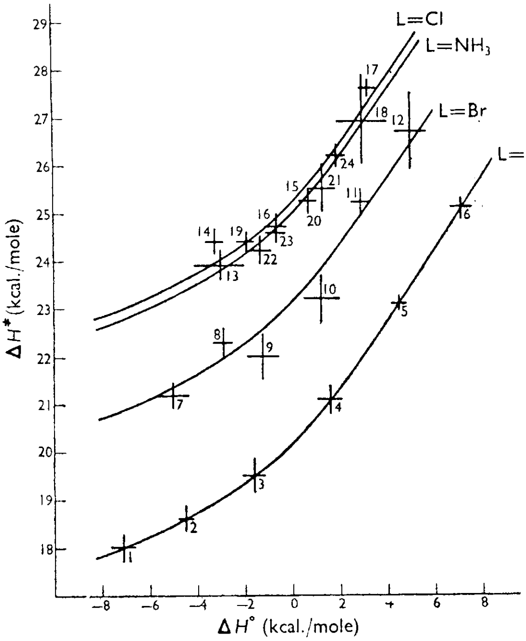

FIGURE 2. ΔH‡versus ΔH° *for the following reactions*: {LOH_2/X *represents the anation of* trans-$RhA_4LOH_2^{n+}$ *by* X^-, *and* LX *represents the aquation of* trans-$RhA_4LX^{(n-1)+}$} (1) IOH_2/I, (2) IOH_2/Br, (3) IOH_2/Cl, (4) ICl, (5) IBr, (6) II, (7) $BrOH_2/I$, (8) $BrOH_2/Br$, (9) $BrOH_2/Cl$, (10) BrCl, (11) BrBr, (12) BrI, (13) $ClOH_2/I$, (14) $ClOH_2/Br$, (15) $ClOH_2/Cl$, (16) ClCl, (17) ClBr, (18) ClI, (19) NH_3OH_2/I, (20) NH_3OH_2/Br, (21) NH_3OH_2/Cl, (22) NH_3Cl, (23) NH_3Br, (24) NH_3I. (*Data from ref.* 2 *and* 3; *points* (15) *and* (20) *are superimposed*).

same form as the others and is almost coincident with that for L = Cl. The fact that the curves are parallel shows that the relative kinetic *trans*-effects of a series of ligands, L, is independent of the particular reaction chosen to measure it, *provided* the thermodynamic driving forces of the different reactions are the same. If, as seems to be the case,[2b,3] the relative activation enthalpies for anation by chloride, bromide, and iodide are the same for all the aquo-complexes then it is logically necessary for the curves to be parallel. The reason why the magnitudes of the relative kinetic *trans*-effects of the halides, and the position of ammonia in the *trans*-effect order, depend on the leaving group is entirely because of the different thermodynamic driving forces involved in the reactions being compared. The parallel curves in Figure 1 enable a measure to be made of the intriniscally kinetic *trans*-effect, independent of the nature of the leaving group and of the thermodynamic *trans*-effect. Thus we have $I > Br > NH_3 \gtrsim Cl$, the increases in the activation enthalpies being 3·0, 1·7, and $\sim$ 0·2 kcal./mole, successively, along the series.

These results illustrate the danger of attempting to explain kinetic data alone in terms of a purely kinetic *trans*-effect. For example, the release of chloride from *trans*-$\mathrm{Rh\,en_2(NO_2)Cl^+}$ and *trans*-$\mathrm{Rh\,en_2(OH)Cl^+}$ is governed by the same activation enthalpy (21·7 kcal./mole) in each case,[4] as compared with the value 24·7 kcal./mole for the dichloro-complex. Until the thermodynamics of the aquation reactions are studied it would be most unwise to attempt to explain what may be only an apparently high kinetic *trans*-effect of hydroxide and nitrite ions in these complexes.

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[3] K. Shaw, Ph.D. Thesis, London, 1966.

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