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The *trans*-Effect in Octahedral Complexes. III.[1] The Kinetic and Thermodynamic *trans*-Effects of NH_3 in Rhodium(III) Complexes

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Received September 12, 1967

Kinetic studies have been made of the aquation and anation reactions involved in the equilibria $Rh(NH_3)_5X^{2+} \rightleftharpoons Rh(NH_3)_5OH_2^{3+} + X^-$ *(*X = *Cl, Br, and I), and of the anation of the aquocomplex by thiocyanate. The activation parameters are compared with previously published data on related complexes so as to obtain a measure of the relative kinetic* trans-*effect of* NH_3*. Combination of the appropriate activation parameters enables the thermodynamic parameters for the above equilibria to be estimated and, from them, the thermodynamic* trans-*effect of* NH_3*. The kinetic* trans-*effect is found to depend, qualitatively as well as quantitatively, on the particular reaction chosen to measure it, but this is found to be a result of the dependence of the kinetic behaviour on the thermodynamics of the reactions. When this dependence is allowed for, a measure of the intrinsically kinetic* trans-*effect, can be obtained. This* trans-*effect is in the order* $I > Br > NH_3 \geqslant Cl$*, the increases in the activation enthalpy being* 3.20 ± 0.20*,* 1.52 ± 0.25*, and* 0.30 ± 0.23 *kcal./mole, respectively, along the series. The thermodynamic* trans-*effect is in the order* $I > NH_3 \geqslant Br > Cl > H_2O$ *when measured in terms of the enthalpies of the halide complexes,* i.e. *the "softness" of the ions* RhA_4L^{n+} *decreases as L changes along this series. The position of* NH_3 *in this series is discussed in terms of* trans-*bond weakening effects of L, and the susceptibility to such bond weakening of the rhodium-ligand bond affected. The kinetic parameters of the anation reactions depend very little on the nature of the anion, and a consideration of the kinetic parameters for both the anation and aquation reactions shows that no definite assignment of the mechanisms of these reactions can be made although the results are quite consistent with most of the activation enthalpy's being devoted to breaking the metal-ligand bond,* i.e. *with there being very little contribution from bond-making.*

Introduction

Acido-amine complexes of rhodium(III) have been shown to be suitable for studies of the kinetic and thermodynamic *trans*-effects in octahedral complexes.[1,2]

We have extended earlier kinetic studies to include the anation reactions of the aquopenta-amminerhodium-(III)ion, and the aquation reactions of the penta-amminehalogenorhodium(III) ions, so as to obtain a measure of the kinetic *trans*-effect of ammonia as a ligand, and the dependence of this effect on the nature of the rhodium-ligand bond affected. The reactions were followed spectrophotometrically and free energies, enthalpies, and entropies of activation were estimated. Two independent studies of the aquation reactions have recently been reported but the results obtained do not agree with each other.[3,4]

The kinetic parameters can be combined to give corresponding thermodynamic parameters for the displacement of a coordinated halide ion by a water molecule, or by another halide ion, and a measure of the class (a) or (b) character[5] (*i.e.* "hardness" or "softness"[6]) of the $Rh(NH_3)_5^{3+}$ ion can thus be obtained. This, in turn, can be related to the thermodynamic *trans*-effect[1,2b] of the ammonia molecule in these octahedral complexes.

Results

Aquation of Penta-amminehalogenorhodium(III) Complexes. The rates of aquation of all aminoacidorhodium(III) complexes studied so far have been found to be independent of the nature and concentration of the incoming nucleophile[1-4,7] unless this is the hydroxide ion, when base catalysis is sometimes observed.[4,7,8] The rate determining step is, therefore, the replacement of the acido ligand by a water molecule. Replacement of one halide by another provides a convenient method of studying aquation rates since such reactions can be made to go to completion, and can be followed spectrophotometrically.[1,2a] Details of the visible and ultraviolet spectra of the halogeno complexes are given in Table I, together with those for some other relevent complexes. Large changes in absorbance accompany the interchange of one halide by another.

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[1] Part II, H. L. Bott and A. J. Poë, *J. Chem. Soc.*, A, 205 (1967).

[2] (a) H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc.*, A, 1275 (1966); (b) E. J. Bounsall and A. J. Poë, *J. Chem. Soc.*, A, 286 (1966).

[3] G. B. Schmidt, *Z. Phys. Chem. (Frankfurt)*, *50*, 222 (1966); *Idem, Ibid.*, *41*, 26 (1964).

[4] S. C. Chan, *Aust. J. Chem.*, *20*, 61 (1967).

[5] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, *12*, 265 (1958).

[6] R. G. Pearson, *J. Amer. Chem. Soc.*, *85*, 3533 (1963).

[7] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, *85*, 1741 (1963).

[8] G. W. Bushnell, G. C. Lalor, and E. A. Molwyn-Hughes, *J. Chem. Soc.*, *A*, 719 (1966).

Table I. Visible and ultraviolet spectra of $Rh(NH_3)_5X^{n+}$ complexes.

X	λ (mμ)	ε (l.mole^{-1}cm.$^{-1}$) This work	ε (l.mole^{-1}cm.$^{-1}$) Other work
Cl	344, 274	104, 113	100, 103 [a]
Br	424 (sh), 360	29, 125	25, 122 [a]
I	419, 381 (sh), 276	276, 230, 3690	270, 230, 3200 [a]
NCS [b]	318	474	460 [c]
OH_2	312, 261	108, 91	105, 89 [a]

[a] C. K. Jørgensen, *Acta Chem. Scand., 10,* 500 (1956). [b] Refers to the N-bonded complex. [c] Ref. 12.

Solubility problems complicate the measurement of absorbance changes in the visible region when halide interchange occurs and the use of thiocyanate or fluoride as substituting anions, although suitable from solubility and spectroscopic points of view, leads to irreproducible results.

The best results were obtained by following the interchange of chloride and bromide in the ultraviolet region at 245 mμ, and the replacement of iodide by chloride at 276 mμ; 4 and 10 cm. silica cells were used, and absorbance values up to ~1.2 were obtained. The ionic strength was usually maintained at 0.2 *M* by using 0.2 *M* solutions of ammonium halides. The use of ammonium salts was found to be essential since the ammonium ion appears to prevent the dissociation of co-ordinated ammonia from the complexes. This loss was most noticeable from the iodo complex, and least from the chloro complex. Thus the reaction of $Rh(NH_3)_5I^{2+}$ with sodium chloride did not give linear rate plots, and the final absorbance in the reaction of sodium bromide with $Rh(NH_3)_5Cl^{2+}$ was 30% lower than theoretical. The reaction of sodium chloride with $Rh(NH_3)_5Br^{2+}$ gave quite good rate plots and the results were in agreement with those obtained by using ammonium chloride. These results are in line with similar behaviour in corresponding platinum(IV) complexes,[9] and with the fact that unless ammonium iodide is used in the preparation of $[Rh(NH_3)_5I]I_2$, $Rh(NH_3)_3I_3$ is formed.[10]

Rate constants were estimated from plots of log-(A_t-A_∞) against time, where A_t and A_∞ were the absorbances at time, t, and after completion of the reaction, respectively. Excellent rate plots were obtained which were linear up to about 90% reaction. The rate constants are reported in Table II, and Table IV gives the activation enthalpies and entropies which were calculated by a "least squares" method,[11] the limits being standard deviations. The assumptions were made that the variance of the rate constants is independent of temperature, and that any uncertainty in the temperature is reflected in the rate constant. The average deviation of the rate constants from the mean values was ±1%. For comparative purposes, values of the rate constants at 50° were calculated from the best enthalpy and entropy values, and are also reported in Table IV, together with the parameters reported by Schmidt[3] and by Chan.[4] Figure 1 shows that our results for the bromo-complex are in excellent agreement with those of Schmidt, but that Chan's results are consistently high, as they are for the other two complexes as well. Schmidt's data for the bromo-complex at 100° show that the standard deviation of an individual measurement is about ±7%, and the limits assigned to his data in Figure 1 correspond to this uncertainty. Apart from some of the points at 100°, at which temperature the possibility of systematic errors is very real, all of Schmidt's points for all three systems

Table II. Rate constants for the aquation of $Rh(NH_3)_5X^{2+}$ ($\mu=0.2M$)

Temp. (°C)	10^6k_{obs} (sec.$^{-1}$) X=Cl	X=Br	X=I
64.9	6.07, 6.06	6.00, 5.96	1.51, 1.55
80.0	31.1, 31.1	30.3, 31.4	7.95, 8.29
94.9	123, 126	128, 131	40.2, 40.5, 38.5 [a]

[a] $\mu=0.1M$ (not used in calculation of activation parameters).

Table III. Rate constants for anation of $Rh(NH_3)_5OH_2^{3+}$ by X^- ($\mu=0.2M$)

Temp. (°C)	X	$[X^-]$ *M*	10^5k (l.mole^{-1}sec.$^{-1}$)
69.9	Cl	0.196	221, 222, 206 [a]
		0.100	233, 231
54.9		0.195	33.3, 35.0
39.9		0.195	5.62, 5.63
69.9	Br	0.198	139, 148, 142
		0.100	146, 153
54.9		0.198	26.3, 25.7
39.9		0.198	3.91, 4.12
79.8	I	0.191	307, 307, 266 [b]
		0.100	319, 307
65.1		0.191	67.6
50.1		0.191	11.8, 11.4
79.6	NCS	0.198	278, 288, 311,[a] 304[c]
		0.100	300,[d] 301 [d]
64.8		0.191	66.9 [e]
50.1		0.191	11.9 [e]

[a,c,d,e] Added $HClO_4$ = 30.4, 5.06, 8.86, and 10.1, $\times10^{-5}M$, respectively. [b] Added hydrazine = 10 mole % with respect to complex.

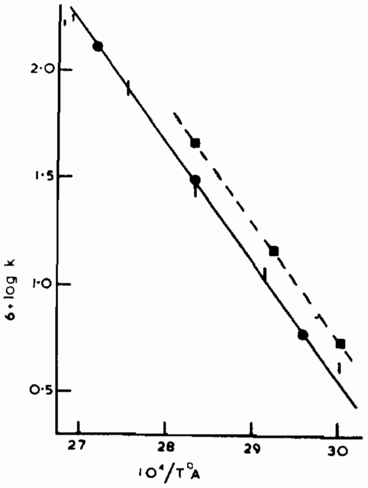

Figure 1. Arrhenius plot for the aquation of $Rh(NH_3)_5Br^{2+}$. ●: this work; |: Schmidt's data (the length of the line is a measure of the standard deviation of the points); ■: Chan's data.

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[9] W. R. Mason III and R. C. Johnson, *Inorg. Chem., 4,* 1258 (1965).
[10] S. M. Jørgensen, *J. Prakt. Chem.,* (2) *34,* 395 (1866).
[11] J. Mandel, «The Statistical Analysis of Experimental Data», Interscience, New York, pp. 272-278 (1964).

Table IV. Kinetic Parameters for aquation of $Rh(NH_3)_5X^{2+}$ at $\mu=0.2M$ (Uncertainties are standard deviations)

	$10^6k_{50^\circ}$(sec.$^{-1}$)			ΔH* (kcal./mole)			ΔS* (cal. mole^{-1} deg.$^{-1}$)
X	This work	Ref. (3)	Ref. (4)	This work	Ref. (3)	Ref. (4)	This work
Cl	1.13	~2	3	24.2±0.3	20.3	22.1	−11.1±0.8
Br	1.00	1	1.7	24.6±0.2	23.3	24.3	−9.9±0.6
I	0.24	3	0.7	26.2±0.2	25.3	26.6	−7.8±0.7

lie within about two standard deviations of the best straight line drawn through our points according to the parameters obtained by the least squares procedure. Schmidt's value for the chloro complex at 70° lies 13% above the best straight line and this causes the low value for ΔH* which he obtained. Apart from this point, his data for the chloro complex agree very well with ours.

Anation Reactions of $Rh(NH_3)_5OH_2^{3+}$. The anation reactions of the aquopenta-amminerhodium(III) ion with chloride, bromide, iodide, and thiocyanate were followed by observing the growth of the absorbance at 360, 365, 419, and 322 mμ, respectively. Ionic strengths were maintained constant at 0 .2 *M* with sodium perchlorate, and sodium salts were used to provide the reacting anion. These reaction were all sufficiently fast for there to be no interference from loss of ammonia from the complexes. Absorbances up to ~1.0 were obtained in 4,5 and 10 cm. silica cells. Good isosbestic points at 329, 294, 264, and 241 mμ, and at 333 and 299 mμ, were obtained when the anions were chloride and bromide, respectively. Values of the rate constants were again obtained graphically. The absorbance at the end of the reaction was obtained experimentally when the anion was chloride, iodide, or thiocyanate, linear rate plots being found over 90% of the reaction. When the anion was thiocyanate, the extinction coefficient of the product was consistent with the formation of 90% isothiocyanato and 10% thiocyanato complex, in agreement with Schmidtke's results.[12] For the anations by chloride and iodide, the extinction coefficients measured at the end of the reactions were within ±3% of those obtained from isolated complexes. When the anion was bromide, the complex formed tended to precipitate, and values of A_∞ were calculated from the concentration of the complex and the known extinction coefficient. Only the first 50% of the reaction was followed in this case.

Knowledge of the acidity of the aquo complex (see below) showed that, even in the most dilute solutions used, less than 3% of the aquo complex had dissociated, and the effect of adding acid to the reaction mixtures was found to be negligible. Addition of hydrazine to solutions of the aquo complex failed to catalyse anation by iodide, although such catalysis of aquation reactions of some similar rhodium(III) complexes has been observed.[2a,13]

The rate constants obtained are reported in Table III. The activation enthalpies and entropies, and the rate constants at 50° calculated from these parameters, are given in Table V.

Table V. Kinetic parameters for anation of $Rh(NH_3)_5OH_2^{3+}$ by X^- at $\mu=0.2M$ (Uncertainties are standard deviations)

X	$10^4k_{50^\circ}$ (l.mole^{-1}sec.$^{-1}$)	ΔH* (kcal./mole)	ΔS* (cal.mole^{-1}deg.$^{-1}$)
Cl	2.01	25.5±0.5	3.2±1.5
Br	1.44	25.3±0.3	1.9±0.9
I	1.15	24.4±0.2	−1.4±0.6
NCS	1.19	23.8±0.4	−3.0±1.2

Acidity of $Rh(NH_3)_5OH_2^{3+}$. The acidity constant of the aquo complex was measured by pH titration with 0.1 *M* sodium hydroxide. The pK_a value was calculated from pH values in the range 5.8 to 6.9. Measurements were made at two temperatures so as to provide approximate values of the enthalpy and entropy changes involved in the acid dissociation. The ionic strength was kept constant at about 0.2 *M*. At 9.4°, $pK_a = 6.63\pm0.04$, and at 35.0° $pK_a = 6.24\pm0.03$ (each result being the average of six separate measurements, and the limits being the maximum spread of the results). From these values we obtain $\Delta H^\circ = 6\pm1$ kcal./mole and $\Delta S^\circ = -9\pm4$ cal.mole^{-1} deg.$^{-1}$ At 15° the value of pK_a has been found to be 6.27 and 6.40, at ionic strengths of 0.06 and 0.12 *M*, respectively.[14]

Discussion

The Mechanism of the Reactions. The trends in the activation parameters for aquation are qualitatively the same as those observed previously[3,4] (Table IV), but the complications found in the absence of free ammonium ions suggest that our results are quantitatively the most reliable. The rates of anation are almost independent of which anion is involved, and this is the result of opposing but equal trends in the activation enthalpies and entropies (Table V).

Chan[4] has argued for a rather extreme form of S_N2 mechanism in which the rate determining step is the formation of a $Rh-OH_2$ bond, and the trend is governed by the relative electronegativity of the halides. This is said to contrast with the case of the analogous cobalt(III) complexes in which a concerted S_N2 interchange mechanism is assumed to be operating, the entering and leaving groups being bound simultaneously only by partial bonds. In fact, the trends shown by the activation energies are essentially identical in the two systems, the values of ΔH* for the cobalt complexes being 22.4, 23.4, and 26.2 kcal./mole for

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[12] H.-H. Schmidtke, *Z. Phys. Chem. (Frankfurt)*, **45**, 305 (1965); *J. Amer. Chem. Soc.*, **87**, 2522 (1965).

[13] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3594 (1963).

[14] J. N. Brønsted and K. Volquartz, *Z. Physik. Chem.*, **134**, 97 (1928).

the chloro,[15] bromo-,[16] and iodo-complexes,[17] respectively. This trend is opposed by a rather more pronounced increase, for the cobalt complexes, in the entropy term so that the lability increases along this series, rather than decreases as it does for the rhodium complexes.

Johnson *et al.*[7] have concluded that a seven coordinate transition state is involved but that the energy required to break the metal-ligand bond is the major factor determining the activation parameters. Langford's arguments[18] concerning analogous cobalt(III) complexes can also be applied to these rhodium complexes and suggest that a significant amount of bond formation has occurred in the transition state. The nucleophilicity difference between bromide and iodide in their associative reactions with planar PtdienCl^+ [19] is certainly greater than that observed in our anation reactions, but this could easily be accounted for by the greater steric effects in the octahedral complexes.

These arguments in favour of an associative mechanism with significant amounts of bond-making are, however, rather tenuous and the data can equally well be interpreted in terms of a predominately dissociative mechanism with the formation of an ion-pair intermediate. The existence of such intermediates has been indicated by spectrophotometric studies of the aquo-complex in concentrated halide solutions.[20] It therefore seems best to acknowledge that there is at present no realiable indication of substantial bond-making, and that the rhodium system behaves, as do most other octahedral complexes, in a way consistent with bond breaking being the major determinant of the activation parameters.[21]

The Thermodynamic trans-*Effect of* NH_3. The kinetic parameters in Tables IV and V are combined in Table VI to give values for corresponding thermodynamic parameters for the dissociation of a halide from these complexes. A comparison of thermodynamic parameters obtained indirectly in this way with those obtained by direct measurements has shown good agreement for other rhodium complexes of this type.[1]

Table VI. Thermodynamic Parameters for the Equilibrium: $Rh(NH_3)_5X^{2+} \rightleftharpoons Rh(NH_3)_5OH_2^{3+} + X^-$

X	$10^3K_{50°}$ (mole/l.)	ΔH° (kcal./mole)	ΔS° (cal.mole^{-1}deg.$^{-1}$)
Cl	5.63	−1.3±0.6	−14.3±1.7
Br	6.94	−0.7±0.4	−11.8±1.1
I	2.08	+1.8±0.3	− 6.4±0.9

The equilibrium constants for interchange of the halide ligands place the $Rh(NH_3)_5^{3+}$ ion on the borderline between classes (a) and (b) but the enthalpies characterise it as quite strongly class(b). Allowance for the enthalpy difference between the free halide ions in aqueous solution[22] enables the differences between the enthalpies of the halogeno complexes in aqueous solution to be calculated.[2,23] These values are a measure of the combined effects of different enthalpies of bonding of the ligands to the metal, and of the solvating water molecules to the complex ion. The enthalpies of the bromo- and chloro-complexes are 7.9±0.5 and 15.2±0.7 kcal./mole less, respectively, than that of the iodo complex if the enthalpies of the free chloride and bromide ions in aqueous solution are taken to be 18.5 and 10.4 kcal./mole less, respectively, than that of the iodide ion.[22] (More recently tabulated values for these differences are 14.9 and 7.0 kcal./mole, respectively,[24] but the older values will continue to be used here to facilitate comparison with earlier studies.[2,23] The trends in the enthalpies of the complexes are what are of interest and these are unaffected by the exact values of the enthalpy differences of the free halide, provided the same are used in each case).

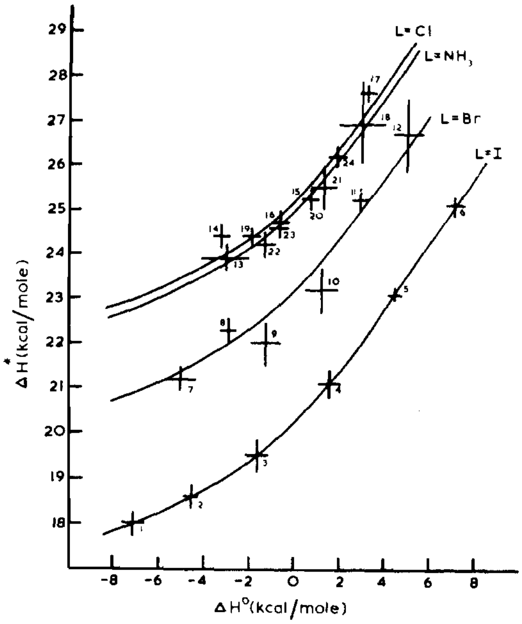

Figure 2. ΔH* versus ΔH° for the following reactions: [LOH_2/X represents the anation of *trans*-$RhA_4LOH_2^{n+}$ by X^- and LX represents the aquation of *trans*-$RhA_4LX^{(n-1)+}$] (1) IOH_2/I, (2) IOH_2/Br, (3) IOH_2/Cl, (4) ICl, (5) IBr, (6) II, (7) $BrOH_2/I$, (8) $BrOH_2/Br$, (9) $BrOH_2/Cl$, (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. 1 and 2a; points (15) and (20) are superimposed).

A plot of the enhtalpies of the complex ions against the enthalpies of the corresponding *trans*-$Rhen_2ClX^+$ complexes (cf. Figure 2, ref. 2b) leads to a good straight line of gradient 0.81, as compared with gradients of 0.85 and 0.65 when L in *trans*-$Rhen_2LX^+$ is Br and I, respectively,[2b] and > 1 when L = H_2O.[1] This type of plot gives a measure of the relative affinity for the

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(15) Calculated from data in S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, 724 (1965); S. H. Laurie, Ph. D. thesis, University of Wales (1962).
(16) J. N. Brønsted and R. J. Livingstone, *J. Amer. Chem. Soc.*, *49*, 435 (1927).
(17) M. J. Wendt, Ph. D. thesis, University of Wales (1967).
(18) C. H. Langford, *Inorg. Chem.*, *4*, 265 (1965).
(19) U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, *4*, 591 (1966).
(20) K. Shaw, Ph. D. thesis, University of London (1966).
(21) M. Eigen and R. G. Wilkins, in «Mechanisms of Inorganic Reactions», Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D.C., p. 55 (1965).
(22) L. Benjamin and V. Gold, *Trans. Farad. Soc.*, *50*, 797 (1954).
(23) A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 3431 (1960).
(24) Technical Note 270 - 1, National Bureau of Standards, Washington, D.C., October (1965).

halide ions of the Lewis acid concerned. The smaller the gradient the greater is the relative affinity for the heavier halide ions and the softer is the Lewis acid. The Lewis acid $Rh(NH_3)_5^{3+}$ is, therefore, very slightly softer than $Rh\,en_2Br^{2+}$. If we assume that having four NH_3 ligands instead of two ethylenediamine ligands in the plane perpendicular to the NH_3–Rh–X axis has no effect on the relative enthalpies, then we can conclude that the thermodynamic *trans*-effect of L in *trans*-$Rh\,en_2LX^{n+}$ is $I > NH_3 \geqslant Br > Cl > H_2O$, *i.e.* the softness of $Rh\,en_2L^{(n+1)+}$ decreases along this series. This is also the order of the thermodynamic *trans*-effect of L which can be defined[1] as being greater the greater the class (b) character of softness of $Rh\,en_2L^{(n+1)+}$

The relative affinities for the halides is not, however, the only way of quantitatively measuring the softness of these Lewis acids. The H_2O ligand is harder than chloride, and an alternative basis for obtaining the softness of these Lewis acids is the relative enthalpies of the ions *trans*-$Rh\ en_2LX^{n+}$ and *trans*-$Rh\ en_2LOH_2^{(n+1)+}$. The softer the Lewis acid $Rh\ en_2L^{(n+1)+}$ the greater would be the relative enthalpy of the aquo complex. On this basis, the softness decreases along the series $L = I > Br > Cl > NH_3$. Thus, the enthalpy of replacement of Cl^- by H_2O increases monotonically from -1.3 to $+1.6$ kcal./mole as L changes along this series. When bromide or iodide are replaced the increase is from -0.7 to $+4.5$, and from $+1.8$ to $+7.1$ kcal./mole, respectively. (This shows that, if the softness of a Lewis Acid is to be measured quantitatively by the relative affinity of the acid for two Lewis Bases, then the greater the difference in softness between these two bases the greater the sensitivity of the estimation). The thermodynamic *trans*-effect of NH_3 is, therefore, qualitatively dependent on which interchange reaction is used to measure it. This is probably because of differences in the solvation changes. When two halide ligands are interchanged the charge on the complex does not change, but when a halide is replaced by H_2O the charge on the complex increases by one unit. When L is a halide the charge increases from $1+$ to $2+$, but when L is NH_3 the charge changes from $2+$ to $3+$. The changes in solvation energy will therefore be quite different in the two cases. For a spherical charge distribution, an increase in charge from $2+$ to $3+$ results in a larger gain in solvation energy than does an increase from $1+$ to $2+$ because of the dependence of solvation energies on the square of the ionic charge. Although the charge distribution in these complexes is far from spherical, solvation effects could reasonably make replacement of a halide by H_2O about 3 to 4 kcal./mole easier when L is NH_3, and this could account for the apparently greater hardness. Since solvation effects are much less when halide interchange is used as the criterion, any interpretation of the degree of softness or hardness in terms of ligand-metal interactions should be confined to that determined by halide interchange, *i.e.* the order of softness $L = I > NH_3 \geqslant Br > Cl > H_2O$ is the one to be considered.

A further criterion for the softness of an ion is the tendency for it to bond to the sulphur atom of the thiocyanate ion, rather than to the nitrogen atom. Schmidtke[12] has shown that $Rh(NH_3)_5^{3+}$ bonds preferentially to the nitrogen atom although the sulphur bonded form can be made. $Rh(NH_3)_5^{3+}$ is, therefore, slightly hard on this basis but the result reflects free energy differences and even the halide interchange criterion shows much lower softness when free energies are used.[2b,23] The possible importance of steric effects in stabilising the nitrogen bonded form has been emphasised recently, and this might also be a factor here.[25,26]

The thermodynamic *trans*-effect of Cl, Br, and I in these complexes has been explained in terms of the tendency for the ligand to transmit *trans*-bond weakening effects (T.B.W.E.) across the rhodium.[2b] In addition the susceptibility to these *trans*-bond weakening effects (S.T.B.W.E.) must be in the order $Rh–I < Rh–Br < Rh–Cl$ These trends were explained by the greater degree of charge transfer to the rhodium from the more polarisable, soft ligands, coupled with the greater sensitivity of stronger bonds to bond weakening effects. (The bond strengths decrease along the series $Rh–Cl > Rh–Br > Rh–I$).[2a,23] The fact that ammonia has a similar thermodynamic *trans*-effect to bromide does not mean that they both have the same T.B.W.E. and S.T.B.W.E. The T.B.W.E. and S.T.B.W.E. of ammonia could both be lower or both be higher than that of bromide. Since NH_3 has a lower kinetic *trans*-effect than bromide (see below), we suggest tentatively that the T.B.W.E. of NH_3 and, therefore, also the S.T.B.W.E. of the $Rh–NH_3$ bond, are both less than that of bromide.

The Kinetic trans-*Effect of* NH_3. The kinetic parameters for the removal of X^- from $Rh(NH_3)_5X^{2+}$ can be compared with those for *trans*-$Rhen_2LX^+$.[1,2a] If we assume that the two ethylenediamine ligands have the same *cis*-effect as four ammonia ligands, we can obtain an estimate of the relative kinetic *trans*-effects of NH_3 and L as a function of the leaving group X^-. (*trans*-$Rh\,en_2(NH_3)Cl^{2+}$ has almost exactly the same activation enthalpy for loss of chloride as does pentamminechlororhodium(III),[20] so this assumption is quite valid). The data in Table VII show that the *trans*-effect of ammonia depends quantitatively *and* qualitatively on the nature of the leaving group. In terms of enthalpies, the orders are $I > Br > Cl > NH_3$, $I > Br > NH_3 > Cl$, and $I > NH_3 > Br > Cl$ for the leaving groups H_2O*, Cl^-, and Br^-, respectively, and when the leaving group is I^- the *trans*-effect of NH_3 is increased further although it is still less than that of iodide.

The magnitude of the *trans*-effect $I > Br > Cl$ decreases[1] as the leaving group changes along the series H_2O, Cl^-, Br^-, I^- (*i.e.* as the leaving groups becomes softer) but the case of ammonia is the first in which the actual position of a ligand in the series changes with the leaving group. This behaviour is due to the dependence of the kinetic *trans*-effect on the thermo-

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(25) W. H. Baddley, F. Basolo, and J. L. Burmeister, *Inorg. Chem.*, 3, 1202 (1964).

(26) D. J. Hewkin and A. J. Poë, *J. Chem. Soc., A*, 1884 (1967).

(*) When the leaving group was H_2O the entering group was Br^- but the effect of changing the anion would be negligible.

Table VII. Relative rate parameters [a] for removal of X from *trans*-RhA_4LX (k_L and ΔH_L^*) and from *trans*-$RhA_4(NH_3)X$ (k_{NH_3} and $\Delta H^*_{NH_3}$). A_4 = en_2 or $(NH_3)_4$

	X			
	H_2O [b]	Cl	Br	I
$(k_I/k_{NH_3})_{50°}$	5900	730	470	260 [c]
$(k_{Br}/k_{NH_3})_{50°}$	37	3.5	2.7 [c]	—
$(k_{Cl}/k_{NH_3})_{50°}$	4	0.4 [c]	0.3	—
$\Delta H^*_{NH_3} - \Delta H_I^*$	6.7	3.1	1.5	1.1
$\Delta H^*_{NH_3} - \Delta H^*_{Br}$	3.0	1.0	−0.6	—
$\Delta H^*_{NH_3} - \Delta H^*_{Cl}$	1.1	−0.5	−3.0	—

[a] Data taken from references 1 and 2a, and from this work. [b] Measured by anation with bromide. [c] Corrected for statistical effects.

dynamic *trans*-effect but the difficulty can be removed if values of ΔH^* are plotted against the corresponding values of $\Delta H°$ as is done in Figure 2. For a given *trans* ligand, L, the results all lie on a smooth curve, ΔH^* increasing monotonically with $\Delta H°$. The curves for any two *trans* ligands are characterised by having a constant difference in ΔH^* and this must indeed be so if the relative nucleophilic character of the halide ions is independent of L (see appendix). The curve for $L = NH_3$ in Figure 2 behaves in exactly the same way as the others, and the apparently anomalous kinetic *trans*-effect of ammonia is a consequence of thermodynamic, rather than kinetic, factors, the thermodynamic behaviour being affected in a particular way by the charges on the ions.

The plots in Figure 2 enable a quantitative estimate to be made of the *intrinsically kinetic* trans-*effect*. This is measured by the vertical distance between the curves because it is only from a reaction (such as H_2O exchange), which exhibits no thermodynamic *trans*-effect, that a measure of the kinetic *trans*-effect can be obtained *free from thermodynamic influences*. The thermodynamic and kinetic data for the complexes *trans*-$Rhen_2IX^+$ are the most accurate and the graph of ΔH_I^* against $\Delta H_I°$ makes the best reference standard. If ΔH_L^* and $\Delta H_L°$ are known for the reaction *trans*-$Rhen_2LX + OH_2 \rightarrow$ *trans*-$Rhen_2LOH_2 + X^-$, the intrinsically kinetic *trans*-effect of L relative to iodide can immediately be obtained from the difference between ΔH_L^* and ΔH_I^* at $\Delta H° = \Delta H_L°$, larger positive values corresponding to lower *trans*-effects. Since there are such data for several reactions of the complexes with L = Cl, Br, or NH_3, several independent measures of the intrinsically kinetic *trans*-effect can be obtained for each ligand (Table VIII). The uncertainties are standard deviations, obtained from the standard deviation assigned to the original parameters by applying the usual statistical rules. The best numerical value is obtained as the weighted average of the separate values. The intrinsically kinetic *trans*-effects are in the order $I > Br > NH_3 \geqslant Cl$, the increases in the activation enthalpy being 3.20±0.20, 1.52±0.25, and 0.30±0.23 kcal./mole, respectively, along this series. The position of ammonia in the *trans*-effect series is not readily explained, since the effect of the different charges on the ligands cannot be easily assessed.

Table VIII. The "intrinsically kinetic *trans*-effects" of Cl^-, Br^-, and NH_3 relative to that of I^- in octahedral tetra-aminerhodium-(III) complexes

L	Reaction [a]	ΔH^* [b] (kcal./mole)	Reference ΔH^* [c] (kcal./mole)	ΔH^* [d] (kcal./mole)
Cl^-	OH_2/Cl	25.3±0.3	20.6±0.2	4.7 ±0.4
	OH_2/Br	24.4±0.3	18.9±0.2	5.5 ±0.4
	OH_2/I	23.9±0.3	19.0±0.4	4.9 ±0.5
	Cl/OH_2	24.7±0.3	20.0±0.2	4.7 ±0.4
	Br/OH_2	27.6±0.3	22.3±0.3	5.3 ±0.4
	I/OH_2	26.9±1.0	22.1±0.7	4.8 ±1.3
			Weighted average =	5.02±0.18
Br^-	OH_2/Cl	22.0±0.5	19.7±0.3	2.3 ±0.6
	OH_2/Br	22.3±0.3	19.0±0.2	3.3 ±0.4
	OH_2/I	21.2±0.3	18.4±0.2	3.8 ±0.4
	Cl/OH_2	23.2±0.5	21.0±0.4	2.2 ±0.7
	Br/OH_2	25.2±0.3	22.0±0.2	3.2 ±0.4
	I/OH_2	26.7±0.8	23.5±0.5	3.2 ±1.0
			Weighted average =	3.20±0.20
NH_3	OH_2/Cl	25.5±0.5	21.0±0.4	4.5 ±0.7
	OH_2/Br	25.3±0.3	20.7±0.3	4.6 ±0.4
	OH_2/I	24.4±0.2	19.3±0.3	5.1 ±0.4
	Cl/OH_2	24.2±0.3	19.7±0.3	4.5 ±0.4
	Br/OH_2	24.6±0.2	19.9±0.2	4.7 ±0.3
	I/OH_2	26.2±0.2	21.4±0.2	4.8 ±0.3
			Weighted average =	4.72±0.15

[a] OH_2/X represents the anation of *trans*-RhA_4LOH_2 by X^-, and X/OH_2 represents the aquation of *trans*-RhA_4LX. [b] Data from ref. 1 and 2a, and from this work. [c] These values are obtained from the plot of ΔH^* against $\Delta H°$ for the *trans*-iodo complex by reading off the value of ΔH^* which corresponds to the value of $\Delta H°$ for the reaction specified in column 2. Values of $\Delta H°$ were obtained from ref. 1 and 2b, and from this work, and the uncertainty in the reference ΔH^* corresponds to the uncertainty in the $\Delta H°$ values. [d] These values give a quantitative measure of the intrinsic kinetic *trans*-effect of L compared with I^-; higher positive numbers correspond to lower *trans*-effects.

The importance, in principle and also sometimes in practice, of obtaining thermodynamic data at the same time as kinetic data is clearly illustrated here. Thus, the release of chloride from *trans*-$Rhen_2(NO_2)Cl^+$ and *trans*-$Rhen_2(OH)Cl^+$ is governed by the same activation enthalpy (21.7 kcal./mole) in each case,[27] as compared with the value of 24.7 kcal./mole for the dichloro-complex.[2a] It would be unwise, however, to try to explain what might be only an apparently high kinetic *trans*-effect of nitrite and hydroxide ions until suitable thermodynamic data have been obtained.

Experimental Section

Penta-amminechlororhodium(III)chloride was supplied by Johnson, Matthey and Co., Ltd., and used as received. It was also used to prepare the aquopenta-amminerhodium(III)perchlorate complex[10] which was in turn used to prepare the iodo-, bromo-, and thiocyanato-complexes by heating on a steam bath with ammonium salt solutions. The precipitated products

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(27) F. Basolo and U. Klabunde, personal communication.

were recrystallised from water or, in the case of the thiocyanato-complex, from ammonium thiocyanate solution. The precipitates were filtered and washed with cold water, dry alcohol, and acetone, and vacuum dried over silica gel. The purity of the complexes was shown by spectrophotometric analyses, and by the excellent and reproducible kinetic behaviour which was observed.

The kinetics were followed in the presence of a large excess of the appropriate free anion by standard spectrophotometric methods. The anation reactions of the aquopenta-ammine complex with iodide and thiocyanate were followed continuously in silica cells contained in a thermostatted cell holder in the cell compartment of a Unicam S.P. 500 spectrophotometer. All the other reactions were followed by keeping the reaction mixtures in stoppered flasks placed in a thermostat bath. At convenient times small samples were withdrawn from the flasks, cooled rapidly to room temperature, and the optical density measured in cells of suitable path length to give absorbance in the range 0.2 to 1.2. Thermostatting was within ±0.1° in all cases. The presence of isosbestic points during the reactions was looked for by means of a Perkin Elmer 350 recording spectrophotometer.

The pH titrations were performed with a Radiometer pH meter 4, a G-200B glass electrode, and a K601 calomel reference electrode. The solutions were contained in a double walled beaker, thermostatted with water pumped continuously from a thermostat bath. 0.001 *M* sodium hydroxide was added from a 1 ml. burette, in small quantities, to the rapidiy stirred solution, and the pH measured after each addition. The pK_α values were calculated from the equation: $pH = pK_\alpha + \log[m/(m'-m)]$, where m = the number of ml. of sodium hydroxide added, and m′ = the number of ml. of sodium hydroxide required to reach the equivalence point. The latter was calculated from the weight of the sample used to make up the solution.

Appendix. Each curve in Figure 2 must lie the same vertical distance above the reference curve (L=I) at all values of ΔH° provided only that the relative nucleophilic character of the halide ions is independent of L. This is shown in Figure 3. L and L′ are the two ligands whose *trans*-effects are being compared by the replacement of either X^- or Y^- by H_2O. Both pairs of reactions are unaffected by thermodynamic *trans*-effects, *i.e.* the values of ΔH° for the replacement of X^- or Y^- by H_2O are unaffected by whether L or L′ is in the *trans* position. The relative kinetic *trans*-effects of L and L′ is given by C−B=E−D when X^- is involved in the reactions, and by H−G=J−I when Y^- is involved. If the relative nucleophilic characters of X^- and Y^- are the same whichever of L or L′ is in the *trans* position, then D−I=E−J, E−D=J−I and hence, C−B=H−G, *i.e.* the *trans*-effects of L and L′ are independent of the reaction chosen to measure them provided the reactions show no thermodynamic *trans*-effects.

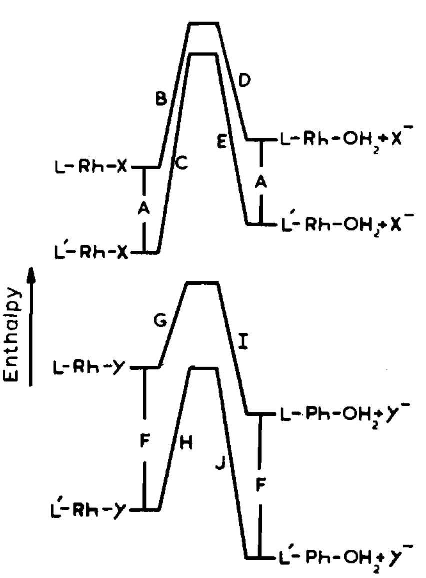

Figure 3. Diagrammatic representation of the enthalpy changes during hypothetical substitution reactions for which there are no thermodynamic *trans*-effects. *i.e.* the values of ΔH° for the replacements of X^- or Y^- by H_2O are each unaffected by whether the *trans* ligand is L or L′. (Only the two relevent ligands *trans* to each other are shown).

Acknowledgments. One of us (K.S.) acknowledges the award of an S.R.C. studentship, and another (M.J.W.) the award of an S.R.C. research assistantship. The spectrophotometers used were also bought with a grant from the S.R.C. We are also very grateful to Professor F. Basolo and Dr. U. Klabunde for communicating their results to us prior to publication.