The trans-Effect in Octahedral Complexes. Part V.[1] Intrinsic Kinetic trans-Effect of Hydroxide Ions in Octahedral Rhodium(III) Complexes [2]

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Data are presented for the kinetics of the reaction of trans-$Rh(en)_2(OH)I^+$ (en = ethylenediamine) with hydroxide ions. The observed pseudo-first-order rate constants fit the expression $k_{obs} = k_1 + k_2[OH^-]$, and activation parameters corresponding to k_1 and k_2 have been obtained. The value of $\Delta H^{\ddagger}_1$ gives a different measure of the kinetic trans-effect of the hydroxide ion, relative to those of ammonia and iodide, from that based on anation reactions, but this ambiguity can be resolved by appropriate allowance for the corresponding values of ΔH^0 for the reactions. When this allowance is made, a measure of the intrinsic kinetic trans-effect of hydroxide ion in such rhodium(III) complexes is obtained and this is found to be very close to that of chloride. This intrinsic kinetic trans-effect is obtainable even though data for the corresponding reactions of the trans-chloroiodo- and -bromoiodo-complexes, etc., are not available.

The reaction path corresponding to k_2 is the first [OH^-]-dependent path observed for such trans-complexes but it is not very important, even in this case, because the value of $\Delta S^{\ddagger}_2$ is relatively unfavourable compared with those usually found for base hydrolysis of amine complexes of cobalt(III) and rhodium(III).

THE reaction of iodide ions with trans-$Rh(en)_2(OH)OH_2^{2+}$ has recently been studied.[1] Comparison of the rate parameters with those for reaction of iodide ions with $Rh(NH_3)_5OH_2^{3+}$ (ref. 3) and trans-$Rh(en)_2I(OH_2)^{2+}$ (ref. 4) provides a quantitative measure of the kinetic trans-effect of hydroxide ion compared with that of iodide and ammonia in these octahedral rhodium(III) complexes, the different cis-effects of four ammonia and two ethylenediamine ligands having been shown to be small.[1,5] On the basis of both relative rate constants

and enthalpies of activation the trans-effect sequence is $I^- > OH^- > NH_3$. It has been shown, however, that kinetic parameters alone do not always provide an unambiguous measure of kinetic trans-effects, but that allowance has to be made for different thermodynamic parameters for the various reactions involved.[3,6] Plots of $\Delta H^{\ddagger}$ against corresponding values of ΔH^0 for a wide variety of reactions of rhodium(III) complexes enabled an unambiguous quantitative measure of the

[1] Part IV, A. J. Poë and K. Shaw, J. Chem. Soc. (A), 1970, 393.

[2] Presented at the Third Northeast Regional Meeting of the American Chemical Society, Buffalo, New York, October 1971.

[3] A. J. Poë, K. Shaw, and M. J. Wendt, Inorg. Chim. Acta, 1967, 1, 371.

[4] H. L. Bott and A. J. Poë, J. Chem. Soc. (A), 1967, 205.

[5] M. V. Twigg and A. J. Poë, Canad. J. Chem., 1972, 50, 1089.

[6] A. J. Poë and K. Shaw, Chem. Comm., 1967, 52.

trans-effects of ammonia, chloride, and bromide to be obtained with respect to that of iodide ion. These trans-effects were named *intrinsic kinetic trans*-effects because they were quite independent of the various thermodynamic contributions to the rates of the individual reactions. In order to place hydroxide ion in this series, we have studied the reaction: *trans*-

$$\text{Rh(en)}_2\text{(OH)I}^+ \xrightarrow{\text{OH}^-} \textit{trans-}\text{Rh(en)}_2\text{(OH)}_2{}^+.$$

EXPERIMENTAL AND RESULTS

trans-[Rh(en)₂ICl]ClO₄ Was prepared by a published method [7] (Found: C, 9·75; H, 3·5. $C_4H_{16}Cl_2IN_4O_4Rh$ requires C, 9·90; H, 3·3%). The electronic spectrum in aqueous 0·1M-sodium chloride solution showed peaks at 490, 440, 301, and 241 nm with extinction coefficients of 260, 160, 4300, and 38,000 1 mol⁻¹ cm⁻¹ respectively, the free chloride being necessary to repress loss of chloride ions from the complex by hydrolysis. Reaction of the complex with iodide ions gave a solution of the *trans*-di-iodo-product which had an extinction coefficient at 466 nm within about 1% of that for a separately prepared and analysed sample of the di-iodo-complex in a similar iodide solution.

Solutions of sodium hydroxide were prepared by dilution of 2N-sodium hydroxide (Fischer Certified), and anhydrous sodium perchlorate was prepared by dehydration of NaClO₄,H₂O (B.D.H.) at 210 °C.

Kinetics.—Reaction of *trans*-Rh(en)₂ICl⁺ with hydroxide ions was followed by observing the accompanying changes in the electronic spectra. The absorption maxima characteristic of the iodochloro-complex decreased in intensity while new peaks at 274, 402, and 446 nm were observed to grow to maximum intensities, and subsequently to decrease at a substantially slower rate. This second reaction was accompanied by the appearance of stable peaks at 296 and 348 nm. The first reaction was characterised by isosbestic points at 266, 289, 371, and 440 nm but these were eventually replaced by others, characteristic of the second reaction, at 341 and 356 nm. The maximum intensities of the peaks due to the intermediate product gave approximate values for the extinction coefficients of 4000, 160, and 150 1 mol⁻¹ cm⁻¹ at 274, 402, and 446 nm respectively.

The rate of the initial reaction, with 0·10M-sodium hydroxide at 50·2 °C, was followed by observing the increase in absorbance at 277 nm and the decrease at 310 nm, the infinite-time absorbances being taken, respectively, as the maximum and minimum absorbances were reached. These values are, respectively, too low and too high because of the subsequent reaction, and the corresponding observed rate constants of $9·9 \times 10^{-4}$ and $7·6 \times 10^{-4}$ s⁻¹ are therefore, respectively, too high and too low. The mean value of $8·8 \times 10^{-4}$ s⁻¹ is in excellent agreement with values for other reactions of *trans*-Rh(en)₂-ICl⁺ that involve replacement of the chloride ligand and formation of *trans*-iodo-products.[8]

The spectrum of the initial product described above is similar to that of basic solutions of *trans*-Rh(en)₂I(OH₂)²⁺ (prepared previously,[4] by reaction of *trans*-Rh(en)₂I₂⁺ with silver nitrate, preparatory to a study of its anation

[7] E. J. Bounsall and A. J. Poë, *J. Chem. Soc.* (A), 1966, 286.
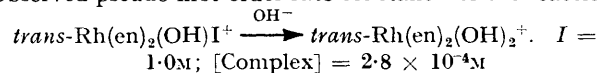[8] H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc.* (A), 1966, 1275.

reactions), but the peaks of the latter were neither as clear nor as intense. It seems probable that the earlier preparation led to mixtures of *trans*-Rh(en)₂(OH₂)₂³⁺ and *trans*-Rh(en)₂I(OH₂)²⁺ (this would not have affected the kinetic studies of the latter complex which reacts very much more rapidly than the diaquo-impurity [1]). Reaction of these solutions with iodide gave solutions with spectra characteristic of the *trans*-di-iodo-complex. The present kinetic and spectroscopic results suggest very strongly that the initial product of the reaction of the *trans*-iodo-chloro-complex with hydroxide ions is the *trans*-iodo-hydroxy-complex.

The absorption peaks of the final product at 296 and 348 nm are in good agreement with those at 298 and 348 nm shown by solutions, at pH 13, of *trans*-Rh(en)₂(OH)OH₂²⁺ prepared by the unpublished method of Basolo and Klabunde,[1] although the corresponding extinction coefficients (101 and 133 1 mol⁻¹ cm⁻¹) are somewhat higher than those from the latter preparation (88 and 117 1 mol⁻¹ cm⁻¹), and than those (88 and 128 1 mol⁻¹ cm⁻¹) inferred from spectra, given by Klabunde,[9] of the products of the reaction of *trans*-Rh(en)₂(OH)Cl⁺ with hydroxide ions. The final reaction can, however, be concluded to involve loss of iodide from the *trans*-iodohydroxy-complex.

The kinetics of this reaction were followed by measuring the decreasing absorption at 272 nm, absorbance changes of *ca.* 1 unit being easily obtainable in 1 cm cells. Groups of four runs were followed simultaneously *in situ* in cells contained in the thermostatted cell holder of a Perkin-Elmer 402 spectrophotometer. Ionic strength was maintained constant with sodium perchlorate. Temperatures of solutions in the cells were measured directly with a precision thermometer, emergent stem corrections being

TABLE 1

Observed pseudo-first-order rate constants for the reaction:
$$\textit{trans-}\text{Rh(en)}_2\text{(OH)I}^+ \xrightarrow{\text{OH}^-} \textit{trans-}\text{Rh(en)}_2\text{(OH)}_2{}^+. \quad I = 1·0\text{M}; \ [\text{Complex}] = 2·8 \times 10^{-4}\text{M}$$

[OH⁻] (M)	10⁵k_{obs}/s⁻¹					
	55·4	60·9	65·6	70·3	75·7	81·0 °C
0·01	2·63	5·80	10·5	19·0	34·1	61·3
0·01	2·62	5·33	10·6		34·0	61·7
0·01	2·64				34·1	61·2
0·01						62·0
0·01						65·8
0·10	2·71	5·97	10·0	18·9	36·2	62·6
0·10				19·6		
0·20	2·80	6·23	11·3	19·0	38·0	69·8
0·30	3·00	6·06	11·7	20·6	39·5	72·7
0·40	3·07	6·56	11·8	21·0	38·9	77·7
0·40					42·9	
0·50	3·07	7·05	12·9	22·2	42·5	76·2
0·60	3·31	7·04	13·1	23·4	44·4	78·5
0·70	3·34	7·19	13·2	23·3	47·0	75·8
0·80	3·52	7·67	13·8	25·2	46·2	84·2
0·90	3·37	7·51	13·0	27·1	48·3	84·8
1·00	3·82	8·32	15·9	29·1	53·5	95·4
1·00					53·8	

made. The reactions were first order in concentration of complex, good pseudo-first-order rate plots being obtained for at least three half-lives. The observed rate constants (Table 1) were found to increase with increasing hydroxide-ion concentration according to the equation

[9] R. Klabunde, Ph.D. Thesis, Northwestern University, Evanston, Illinois, 1967.

$k_{obs} = k_1 + k_2[OH^-]$. The effect is small but quite real, as was evidenced by groups of runs followed simultaneously for which the absorbance changes were clearly more rapid the greater the hydroxide-ion concentration. Values of k_1 and k_2 (Table 2) were obtained by a weighted least-

TABLE 2

Kinetic parameters derived according to the rate law:
$$k_{obs} = k_1 + k_2[OH^-]$$

$t/°C$	$10^5 k_1/s^{-1}$	$\dfrac{10^5 k_2}{l\ mol^{-1}\ s^{-1}}$	$\sigma(k_{obs})/\%$
55·4	2·619 ± 0·034	1·051 ± 0·072	2·8
60·9	5·57 ± 0·11	2·48 ± 0·22	3·8
65·6	10·26 ± 0·30	4·36 ± 0·59	5·5
70·3	17·99 ± 0·44	9·22 ± 0·90	4·3
75·7	33·95 ± 0·51	17·8 ± 1·0	3·2
81·0	62·2 ± 1·1	27·8 ± 2·5	4·3

$k_1(50\ °C) = 1·2 \times 10^{-5}\ s^{-1}$, $\Delta H^{\ddagger}_1 = 27·93 \pm 0·16\ kcal\ mol^{-1}$ (116·9 ± 0·7 kJ mol^{-1}), $\Delta S^{\ddagger}_1 = 5·33 \pm 0·48\ cal\ mol^{-1}\ K^{-1}$ (22·3 ± 2·0 J mol^{-1} K^{-1}); $k_2(50\ °C) = 4·6 \times 10^{-6}\ l\ mol^{-1}\ s^{-1}$, $\Delta H^{\ddagger}_2 = 29·9 \pm 0·8\ kcal\ mol^{-1}$ (125·1 ± 3·3 kJ mol^{-1}), $\Delta S^{\ddagger}_2 = 9·5 \pm 2·3\ cal\ mol^{-1}\ K^{-1}$ (39·8 ± 9·6 J mol^{-1} K^{-1})

squares treatment in which the percentage uncertainty of each value of k_{obs} at a given temperature was assumed to be constant. The estimated uncertainties in k_1 and k_2, and in an individual measurement of k_{obs} at a given temperature, were corrected for the appropriate number of degrees of freedom so that 95% confidence limits can be obtained by doubling the quoted standard deviations.

ion relative to that of ammonia or iodide. The *trans*-effect order is then $I^- > OH^- > NH_3$ in terms of rate constants, and $I^- > NH_3 > OH^-$ in terms of activation enthalpies. The latter is a generally preferable measure of the *trans*-effect since it is independent of temperature, but the order obtained is different from that found for the reactions of iodide ion with *trans*-Rh(en)$_2$I(OH$_2$)$^{2+}$, *trans*-Rh(en)$_2$(OH)OH$_2$$^{2+}$, and Rh(NH$_3$)$_5OH_2$$^{3+}$ (Table 3). The qualitative ordering of the *trans*-effect, as well as its magnitude, is therefore dependent on which reaction is being used to measure it. In addition, neither set of data allows one to compare the *trans*-effect of hydroxide ion with that of chloride or bromide because the reactions   *trans*-Rh(en)$_2$XI$^+$ + OH$_2$ $\rightleftharpoons$ *trans*-Rh(en)$_2$-XOH$_2$$^{2+}$ + I$^-$ (X = Cl or Br) are subject to catalytic effects and cannot be studied for comparison.[8]

These difficulties are similar to those obtained before and can be resolved in the same way.[3,6] A combination of the kinetic parameters for the forward and reverse reactions of the equilibrium *trans*-Rh(en)$_2$-(OH)I$^+$ + OH$_2$ $\rightleftharpoons$ *trans*-Rh(en)$_2$(OH)OH$_2$$^{2+}$ + I$^-$ leads to the parameters $\Delta H^0 = +4·1 \pm 0·2$ kcal mol^{-1} (17·1 ± 0·8 kJ mol^{-1}), $\Delta S^0 = 0·1 \pm 0·8$ cal mol^{-1} K^{-1} (0·4 ± 3·3 J mol^{-1} K^{-1}), and $K(50\ °C) = 2 \times 10^{-3}$ mol l^{-1} at $I = 0·2$M. The kinetic parameters for the aquation reaction are not affected by a change of

TABLE 3

Kinetic parameters [a] for reactions of some rhodium(III) complexes

Aquation [b] of:	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal mol^{-1} K^{-1}	$10^4 k$ (50 °C) s^{-1}	Reference
trans-Rh(en)$_2$(OH)I$^+$	27·93 ± 0·16	5·33 ± 0·48	0·12	This work
Rh(NH$_3$)$_5$I^{2+}	26·2 ± 0·2	−7·8 ± 0·7	0·0024	3
trans-Rh(en)$_2$I$_2$$^+$	25·1 ± 0·2	1 ± 1	1·24	8

Anation,[c] by iodide, of:			$\dfrac{10^4 k(50\ °C)}{l\ mol^{-1}\ s^{-1}}$	
trans-Rh(en)$_2$(OH)OH$_2$$^{2+}$	23·81 ± 0·15	5·21 ± 0·48	72·6	1
Rh(NH$_3$)$_5$OH$_2$$^{3+}$	24·4 ± 0·2	−1·4 ± 0·6	1·15	3
trans-Rh(en)$_2$I(OH$_2$)$^{2+}$	18·0 ± 0·3	0·3 ± 1·1	5800	4

[a] Uncertainties are standard deviations.   [b] Ionic strength, 0·1—1·0M (negligible dependence of kinetic parameters on ionic strength).   [c] Ionic strength, 0·2M.
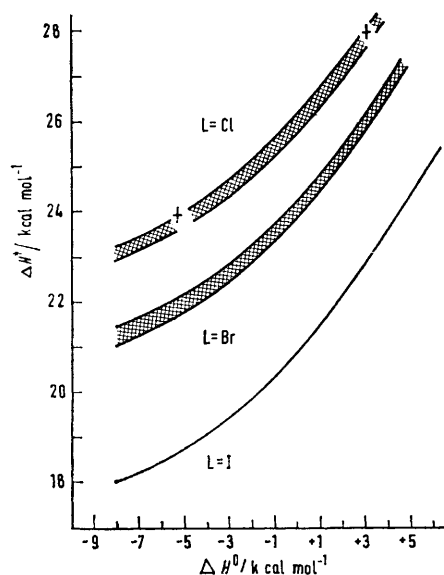
The variation of $\sigma(k_{obs})$ with temperature is not systematic and it seems likely that the variation is itself a reflection of random errors. Values of the activation parameters (Table 2) were obtained from a weighted least-squares analysis of the linear dependence of $\log(k_1/T)$ and $\log(k_2/T)$ on $1/T$, the uncertainties in $\log(k_1/T)$ and $\log(k_2/T)$ being derived from the uncertainties found for k_1 and k_2.

DISCUSSION

The reaction path governed by the rate constant k_1 can be considered to be a simple loss of iodide ion by aquation, the presence of hydroxide being required simply to drive the reaction to completion by transforming the hydroxy-aquo-product into the dihydroxy-form. The values of k_1 (50 °C) and $\Delta H^{\ddagger}_1$ can be compared with corresponding values for the loss of iodide ion from Rh(NH$_3$)$_5$I^{2+} [3] and *trans*-Rh(en)$_2$I$_2$$^+$ [8] (Table 3) to provide a new measure of the *trans*-effect of hydroxide

ionic strength from 1·0 to 0·2M (at 69 °C, [OH$^-$] = 0·01M, and $I = 0·22$M: $10^4 k = 1·65$ and $1·66$ s^{-1}; at $I = 1·02$M: $10^4 k = 1·64$ and $1·68$ s^{-1}). The intrinsic kinetic *trans*-effect of hydroxide ion can now be obtained, in terms of relative enthalpies of activation, by comparing the values of $\Delta H^{\ddagger}$ for the reactions of the *trans*-hydroxy-iodo- and *trans*-hydroxy-aquo-complexes with the values of $\Delta H^{\ddagger}$ for the hypothetical reactions of *trans*-iodo-complexes which have the corresponding values of ΔH^0, *i.e.* +4·1 and −4·1 kcal mol^{-1} (+ or − 17·1 kJ mol^{-1}) respectively.[3,6] These reference values of $\Delta H^{\ddagger}$ can be obtained by interpolation from a plot of $\Delta H^{\ddagger}$ against ΔH^0 for the aquation of the complexes *trans*-Rh(en)$_2$IX$^+$, and for the anation reactions of *trans*-Rh(en)$_2$IOH$_2$$^{2+}$ with X$^-$ (X = Cl, Br, and I).[3] Such a plot is shown in the Figure. The values obtained are 22·85 ± 0·15 and 18·65 ± 0·06 kcal mol^{-1} (95·5 ± 0·6

and 78.0 ± 0.3 kJ mol^{-1}) respectively. Thus the $\Delta H^{\ddagger}$ values for the hydroxy-complexes are 5.08 ± 0.27 and 5.16 ± 0.16 kcal mol^{-1} (21.2 ± 1.1 and 21.6 ± 0.7 kJ mol^{-1}) higher than the reference values for the hypothetical trans-iodo-complexes. These two values are not significantly different, and the weighted average is 5.14 ± 0.14 kcal mol^{-1} (21.5 ± 0.5 kJ mol^{-1}) as compared with the corresponding values of 5.02 ± 0.18, 4.72 ± 0.15, and 3.20 ± 0.20 kcal mol^{-1} (21.0 ± 0.8, 19.7 ± 0.6,

Plots of $\Delta H^{\ddagger}$ against ΔH^0 for the reactions: trans-Rh(en)$_2$LX$^+$ + OH$_2$ ⇌ trans-Rh(en)$_2$LOH$_2$$^{2+}$ + X$^-$ (L = Cl, Br, or I). The line for L = I is a reference drawn through the appropriate data points [3] and the areas for L = Cl and Br show the uncertainties (standard deviations) in the relative values of $\Delta H^{\ddagger}$ as derived from the individual data points.[3] The results for the trans-hydroxy-complexes are shown by crosses, the lengths of the lines indicating the standard deviations of the values.

and 13.4 ± 0.8 kJ mol^{-1}) for the trans-chloro-, trans-ammine- and trans-bromo-complexes respectively.[3] The values for the trans-chloro- and trans-bromo-complexes are also shown diagrammatically in the Figure where the standard deviations for L = Cl and Br are indicated by the vertical distance between the lines defining the shaded areas. The order of the intrinsic kinetic trans-effects is therefore OH$^-$ $\leqslant$ Cl$^-$ < NH$_3$ < Br < I.

This method of analysing the kinetic data allows an estimate of relative intrinsic kinetic trans-effects, independent of any complications from different thermodynamic contributions to the kinetics, even though corresponding reactions of complexes differing only in their trans-ligand cannot be, or have not been, studied.

Although activation parameters are available for aquation reactions of trans-Co(en)$_2$LX^{n+} (L = NH$_3$, OH, Br, or Cl; X = Br or Cl),[10-12] these reactions are complicated by widely varying degrees of trans $\longrightarrow$ cis rearrangement, and this is known to have a large effect on the activation parameters.[12] Activation parameters for aquation of trans-Co(cyclam)LCl$^+$ (L = OH or Cl; cyclam = 1,4,8,11-tetra-azacyclotetradecane) are also available [13] and no rearrangement occurs during these reactions. $\Delta H^{\ddagger}$ (L = OH) Is over 6 kcal mol^{-1} (25 kJ mol^{-1}) less than $\Delta H^{\ddagger}$ (L = Cl) and, although corresponding values of ΔH^0 are not known, it seems likely that the intrinsic kinetic trans-effect of hydroxide ion is genuinely much greater than that of chloride in these cobalt(III) complexes in contrast with the virtual equality in the rhodium(III) complexes. It is not clear whether this can be ascribed to different σ- or π-bonding effects but it has been pointed out that rhodium(III) seems less susceptible to π-bonding effects than cobalt(III).[14] These results may therefore be a consequence of the greater importance, in cobalt(III) complexes, of the more pronounced π-donor character of hydroxide ion compared with that of chloride.

The second-order term in the rate law has not previously been observed for trans-dihalogenobisethylene-diaminerhodium(III) complexes, only those with N–H groups co-ordinated trans to the leaving halide ion showing pronounced second-order reactions with hydroxide ion.[9,14] This is simply due to the low concentrations of hydroxide ion used previously. The activation parameters show that the relative unimportance of the second-order term is due to the fact that $\Delta S^{\ddagger}_2$ is only very slightly more positive than $\Delta S^{\ddagger}_1$, $\Delta H^{\ddagger}_2$ being 2 kcal mol^{-1} (8 kJ mol^{-1}) higher than $\Delta H^{\ddagger}_1$. In cases where base hydrolysis of amine complexes is relatively much more pronounced this is usually due to a much more favourable value of $\Delta S^{\ddagger}_2$ (up to ca. 40 cal mol^{-1} K^{-1} on 170 J mol^{-1} K^{-1} more positive) that more than offsets the difference berween $\Delta H^{\ddagger}_2$ and $\Delta H^{\ddagger}_1$.[15] The significance of the different pattern in the present rhodium complex is not clear and we are extending our studies of the base hydrolysis of such complexes to see how general the pattern is.

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