Base Hydrolysis of *trans*-Bis(ethylenediamine)dihalogenorhodium(III) Complexes

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Base hydrolysis of the complexes *trans*-$[Rh(en)_2X_2]^+$ (X = Cl, Br, and I) obeys the rate equation $k_{obs.} = k_1 + k_2[OH^-]$ at an ionic strength of 1·0 mol dm^{-3} where $k_2/k_1 \approx 1$ dm^3 mol^{-1}. Activation parameters for the $[OH^-]$-independent path are essentially the same as those for aquation. The $[OH^-]$-dependent path leads to virtually complete *trans* ⟶ *cis* isomerisation when X = Cl or Br, and to *ca.* 50% when X = I. The values of $\Delta H_2^‡$ and $\Delta S_2^‡$ lie at the upper end of an isokinetic plot that includes data for the *trans*-$[Rh(en)_2(OH)X]^+$ complexes. An excellent ' pseudo-isokinetic plot ' of $\Delta H_2^‡ - \Delta H_1^‡$ against $\Delta S_2^‡ - \Delta S_1^‡$ has also been obtained. The isokinetic plot lies above the corresponding plot for complexes with co-ordinated NH groups *trans* to the leaving group, the respective isokinetic temperatures being *ca.* 100 and 190 °C. It seems probable that the reactions that lead to extensive stereochemical rearrangement occur by an S_N1 CB mechanism but that reactions of complexes further down the isokinetic plot may well have a mechanism closer to the S_N1 IP end of an S_N1 CB–S_N1 IP mechanistic spectrum.

EARLY studies [1,2] of base hydrolysis of amine complexes of rhodium(III) suggested that a co-ordinated NH group *trans* to the reaction site was necessary in order for there to be a significant $[OH^-]$-dependent term in the rate equation. However, the complex *trans*-$[RhCl(en)_2(py)]^{2+}$ was shown [2] to undergo $[OH^-]$-dependent base hydrolysis and, more recently,[3,4] so were the complexes *trans*-$[Rh(en)_2(OH)X]^+$ (X = Cl,[3] Br,[3] and I [4]; en = ethylenediamine, py = pyridine). The $[OH^-]$-dependent terms in the rate equation for reactions of the *trans*-halogenohydroxo-complexes were much smaller than those for complexes with a co-ordinated amine group in the *trans* position. This was due to small values of $\Delta S_2^‡ - \Delta S_1^‡$ (−8 to +17 J K^{-1} mol^{-1} compared to more typical values [5] of 80—170 J K^{-1} mol^{-1}) which were not offset by more favourable values of $\Delta H_2^‡ - \Delta H_1^‡$. No detectable *trans* ⟶ *cis* isomerisation was found during these reactions. We now report studies of the base hydrolysis of the complexes *trans*-$[Rh(en)_2X_2]^+$ (X = Cl, Br, and I) that were undertaken in order to see whether it was some unique feature of the *trans*-hydroxo-complexes that caused them to undergo second-order reactions with base.

EXPERIMENTAL AND RESULTS

The complexes *trans*-$[Rh(en)_2X_2][ClO_4]$ were prepared by published methods.[6] Satisfactory analyses were obtained.[3b] The electronic spectra in aqueous solution showed peaks at 410, 289, *ca.* 240sh, and 207 nm (X = Cl; ε 82, 121, 1 700, and 39 600 dm^3 mol^{-1} cm^{-1}), 431, 277, and 234 nm (X = Br; ε 115, 2 900, and 37 800 dm^3 mol^{-1} cm^{-1}), and 467, 342, and *ca.* 270 nm (X = I; ε 271 and 16 000 dm^3 mol^{-1} cm^{-1}, respectively, for the first two bands. The band at 270 nm was not so clearly defined due to interference from free iodide present to prevent hydrolysis.) These are in good agreement with published values,[6] although there are some slight differences in the absorption coefficients, particularly that of the highest-energy band of the dibromo-complex (*cf.* ε 31 000 dm^3 mol^{-1} cm^{-1} in ref. 6*b*).

Spectroscopic Changes.—During reaction of *trans*-$[Rh(en)_2X_2]^+$ (X = Cl or Br) with 0.1 mol dm^{-3} hydroxide the spectra changed smoothly to those of the final products (Figure 1), and good isosbestic points were maintained at 283 and 386 nm (X = Cl) and 328 and 394 nm (X = Br). Reaction with 1.0 mol dm^{-3} hydroxide showed spectroscopic changes of the same form, but the isosbestic points moved to 276 and 384 nm (X = Cl) and 325 and 392 nm (X = Br). In addition, the minimum in the product absorbance at *ca.* 250 nm was much more pronounced for reactions with 1.0 mol dm^{-3} hydroxide. The spectroscopic changes occurring during the hydrolysis of the di-iodo-complex are clearly associated with two distinct reactions. During the first, the absorbances due to the peaks at 467, 342, and 269 nm decrease and an isosbestic point appears at 253 nm. The second stage is characterised by the appearance of isosbestic points at 346 and 362 nm, and these spectroscopic changes correspond to those occurring during reaction (1).[4] The final product of reaction with 0.1 mol dm^3 hydroxide had peaks at 347 and 297 nm (ε 100 and 132 dm^3 mol^{-1} cm^{-1}), while that from reaction with 1.0 mol dm^{-3} hydroxide had peaks at 345 and 294 nm (ε 108 and 138 dm^3 mol^{-1} cm^{-1}), the change with hydroxide concentration being less pronounced than with the dichloro- and dibromo-complexes.

$$trans\text{-}[RhI(en)_2(OH)]^+ + OH^- \longrightarrow trans\text{-}[Rh(en)_2(OH)_2]^+ + I^- \quad (1)$$

Kinetics.—The reaction of the dichloro-complex was much slower than that of either the *cis*- [2] or the *trans*-chlorohydroxo-complexes [3] so the reaction was followed by observing the overall decrease in absorbance at 245 nm, where changes of at least 0.7 units were obtained in 10-mm cells. Excellent first-order rate plots were obtained, linear for three half-lives. The rate of reaction of the dibromo-complex was also much slower than that of the corresponding *trans*-bromohydroxo-complex and excellent linear rate plots were obtained when the decrease (*ca.* 1 unit) in absorbance at 250 nm was monitored. Evidently

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

[2] U. Klabunde, Ph.D. Thesis, Northwestern University, Evanston, Illinois, 1967.

[3] (*a*) A. J. Poë and C. P. J. Vuik, *Canad. J. Chem.*, 1975, **53**, 1842; (*b*) C. P. J. Vuik, Ph.D. Thesis, London University, 1974.

[4] A. J. Poë and C. P. J. Vuik, *J.C.S. Dalton*, 1972, 2250.

[5] (*a*) F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, ch. 3; (*b*) M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377; (*c*) C. H. Langford and V. S. Sastri, ' Reaction Mechanisms in Inorganic Chemistry,' *M.T.P. Internat. Rev. Sci.*, Butterworths, London, 1973, vol. 9, ed. M. L. Tobe, ch. 6; (*d*) J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47.

[6] (*a*) S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925; (*b*) E. J. Bounsall and A. J. Poë, *J. Chem. Soc.* (*A*), 1966, 286; (*c*) C. Burgess, F. R. Hartley, and D. E. Rogers, *Inorg. Chim. Acta*, 1975, **13**, 35.

the rate of reaction of any *cis*-bromohydroxo-complex that might have been formed is also sufficiently fast, compared with that of the dibromo-complex, for its reaction not to interfere. In contrast, the reaction of the *trans*-hydroxo-iodo-complex is slower[4] that that of the *trans*-di-iodo-complex. This does not complicate the study of the reaction of the latter which involves a much greater absorbance decrease at *ca.* 340 nm, and this is also close to an isosbestic point for the reaction of the hydroxoiodo-complex.[4] The final absorbance at this wavelength in the reaction of the di-iodo-complex is, therefore, both low and virtually unaffected by the subsequent reaction, and excellent rate plots were obtained. Groups of up to five reactions were followed simultaneously in 10-mm cells contained in thermostatted cell holders in a Cary 16K or Perkin-Elmer 402 spectrophotometer. Temperatures of reacting solutions were measured directly with a calibrated thermistor (Cary 16K) or precision thermometer with emergent stem corrections (Perkin-Elmer 402), the former being more precise.

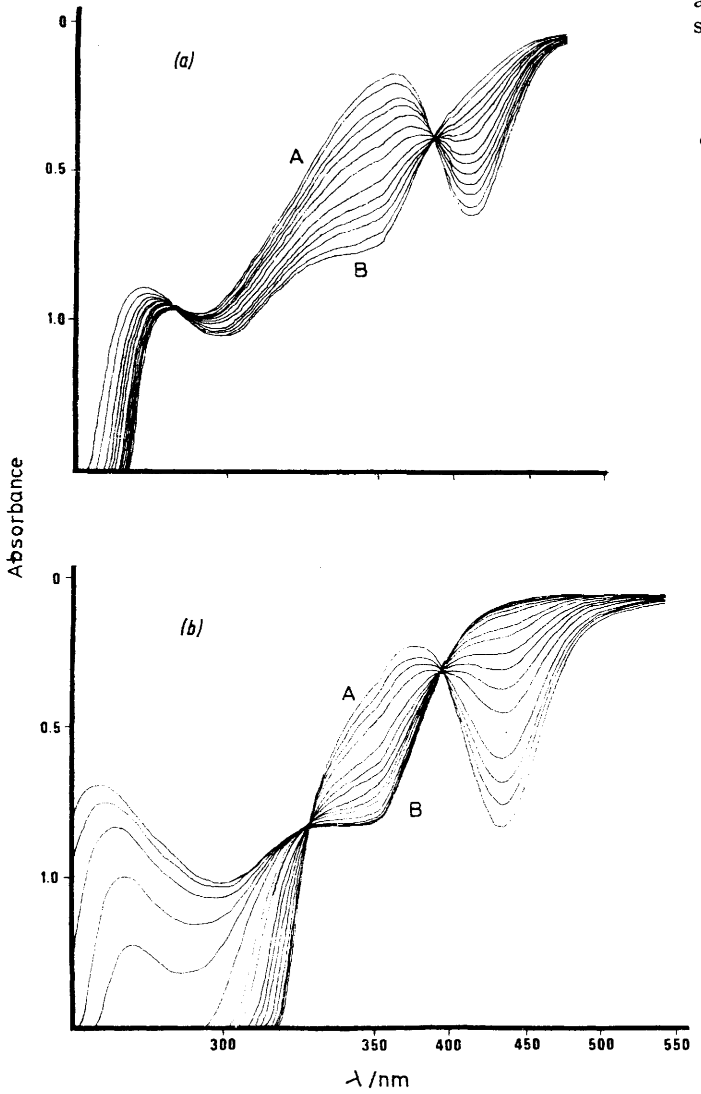

FIGURE 1 Spectroscopic changes (A ⟶ B) occurring during the reaction of 0.1 mol dm^{-3} hydroxide with *trans*-[Rh(en)$_2$X$_2$]$^+$ at 80 °C: X = Cl (*a*) and Br (*b*)

Solutions attained a constant temperature after 10 min. Observed pseudo-first-order rate constants are given in Table 1 and in each case there is a significant dependence on [OH$^-$], the ionic strength being kept constant with sodium perchlorate. Some reactions of the dichloro-complex with 0.01 mol dm^{-3} hydroxide were also followed at zero, 0.302, 0.604, and 0.906 mol dm^{-3} sodium perchlorate at 80.4 °C, and the values of $10^5 k_{obs.}$ were 4.17, 4.20, 4.21, and 4.07 s^{-1}, respectively.

TABLE 1

Observed pseudo-first-order rate constants for the reaction of *trans*-[Rh(en)$_2$X$_2$]$^+$ with hydroxide at I = 1.0 mol dm^{-3}

(*a*) X = Cl, [Complex] = 5.5 × 10^{-4} mol dm^{-3}

[OH$^-$]/mol dm^{-3} \ θ_c/°C	0.0100	0.250	0.500	0.750	1.00
	$10^6 k_{obs.}$/s^{-1}				
62.21	5.55	6.11	7.04	8.25	9.46
64.33	8.08	8.74	9.73	11.7	13.4
64.86	7.36	8.18	9.61	11.0	13.3
67.96	11.9	13.7	15.5	18.6	22.5
71.74	17.0	19.3	23.2	29.4	34.2
74.62	23.9	29.2	36.7	41.8	50.1
77.70	33.1	39.6 [a]	51.6 [b]	62.2 [c]	76.2

(*b*) X = Br, [Complex] = 1.2 × 10^{-4} mol dm^{-3}

θ_c/°C \ [OH$^-$]/mol dm^{-3}	60.4	64.8	70.0	75.2	80.2
	$10^5 k_{obs.}$/s^{-1}				
0.0100	1.83	3.12	5.86	9.86	18.3
	1.84	3.24			17.3
					17.9
0.100	1.97	3.31	6.08	10.9	19.7
0.200	2.08	3.55	6.84	12.0	22.6
0.300	2.32	3.80	7.53	13.1	26.0
0.400	2.46	4.06	8.15	15.0	27.2
0.500	2.52	4.48	8.72	16.4	30.8
0.600	2.77	4.89	9.52	17.8	35.1
0.700	3.03	5.24	10.5	20.2	37.1
0.800	3.09	5.55	11.3	21.9	40.8
0.900	3.48	6.24	12.4	23.9	47.1
1.00	3.48	6.67	13.1	27.0	51.4

(*c*) X = I, [Complex] = 6 × 10^{-5} mol dm^{-3}

[OH$^-$]/mol dm^{-3} \ θ_c/°C	0.0100	0.250	0.500	0.750	1.00
	$10^5 k_{obs.}$/s^{-1}				
36.35	2.10	2.22	2.30	2.43	2.42
41.10	4.08	4.29	4.49	4.71	5.07
45.96	7.52	8.07	8.38	9.27	9.75
50.18	12.8	13.7	14.7	15.8	17.1
55.07	22.7	24.3	26.3	28.8	31.7
59.60	39.1	42.4	47.2	52.0	57.0
65.06	67.1	71.3	80.3	89.0	101

[a] 0.200 mol dm^{-3} [OH$^-$]. [b] 0.550 mol dm^{-3} [OH$^-$]. [c] 0.800 mol dm^{-3} [OH$^-$].

Since perchlorate does not affect the rate, the data at constant ionic strength were analysed according to the rate equation $k_{obs.} = k_1 + k_2[OH^-]$ by a weighted linear least-squares analysis in which all the rate constants for a given reaction were assumed to have the same standard deviation. Previous studies on similar systems[3,4] had shown that $\sigma(k_{obs.})$ was not significantly dependent on temperature, and pooling the residuals from each group of measurements increased the number of degrees of freedom so that only small corrections had to be applied to the estimated standard deviations to give those characteristic of an infinite number of degrees of freedom. Activation parameters were obtained by a suitably weighted linear least-squares analysis of the dependence of $\log(k_1/T)$ or $\log(k_2/T)$ on $1/T$ and are shown in Table 2. The values of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ are close to, but not identical with, those obtained for aquation,[7] the values of $\Delta(\Delta H^\ddagger)/\sigma[\Delta(\Delta H^\ddagger)]$ * being *ca.* 2, 1, and 3 for X = Cl, Br, and I, respectively. This could be due to small but significant systematic differences caused by different ionic strengths or to the neglect of ion-association effects in the concentrated halide solutions used to determine the earlier values.[7] Ion association measurably increases the rates of substitution of these complexes.[3b]

TABLE 2

Kinetic parameters for base hydrolysis of *trans*-$[Rh(en)_2X_2]^+$

X	Cl	Br	I
$\Delta H_1^\ddagger$/kJ mol^{-1}	109.0 ± 2.6	107.9 ± 1.4	102.0 ± 0.5
$\Delta H_1^{\ddagger\,a}$/kJ mol^{-1}	103 ± 1	105 ± 1	105 ± 1
$\Delta S_1^\ddagger$/J K^{-1} mol^{-1}	−21.5 ± 7.7	−13.4 ± 4.0	−5.6 ± 1.6
$\Delta S_1^{\ddagger\,a}$/J K^{-1} mol^{-1}	−38 ± 4	−21 ± 4	4 ± 4
$10^6k_1/s^{-1}$ (θ_c/°C)	5.33 ± 0.21 (62.21)	17.9 ± 0.4 (60.4)	384 ± 6 (59.60)
$\Delta H_2^\ddagger$/kJ mol^{-1}	146.7 ± 5.9	140 ± 2.7	130.5 ± 3.0
$\Delta S_2^\ddagger$/J K^{-1} mol^{-1}	87.9 ± 17.3	84.8 ± 7.7	73.9 ± 9.0
10^6k_2/dm^3 mol^{-1} s^{-1} (θ_c/°C)	3.85 ± 0.43 (62.21)	16.8 ± 0.9 (60.4)	181 ± 11 (59.60)
$\sigma(k_{obs.})$/%	4.6	4.0	1.8

[a] Aquation parameters from ref. 7.

trans ⟶ cis *Isomerisation*.—The dependence of the spectroscopic changes during base hydrolysis of these dihalogeno-complexes on the concentration of hydroxide can be ascribed to the formation of *cis*-dihydroxo-products. *trans* ⟶ *cis* Isomerisation of rhodium(III) complexes has previously been observed only in the base hydrolysis of *trans*-$[RhCl(en)_2(py)]^{2+}$ under conditions where the $[OH^-]$-independent path is negligible compared to the $[OH^-]$-dependent one.[2] Apart from slow *cis* ⟶ *trans* isomerisation of *cis*-$[RhI_2(en)_2]^+$,[6a] no stereochemical changes have been observed for acid hydrolysis [5,7] or anation [8] reactions of these or similar rhodium(III) complexes. Little or no stereochemical change accompanies base hydrolysis of *trans*-$[Rh(en)_2(OH)X]^+$ (X = Cl, Br, or I) [3,4] and *cis*-$[RhCl(en)_2(OH)]^+$,[2] so the stereochemistry of the product of the overall reaction (2) reflects the stereochemical

$$trans\text{-}[Rh(en)_2X_2]^+ + 2OH^- \longrightarrow [Rh(en)_2(OH)_2]^+ + 2X^- \quad (2)$$

changes occurring during reaction (3). Furthermore, the

$$trans\text{-}[Rh(en)_2X_2]^+ + OH^- \longrightarrow [Rh(en)_2(OH)X]^+ + X^- \quad (3)$$

spectrum of a solution of *trans*-$[Rh(en)_2(OH)_2]^+$ {prepared from an isolated [9] sample of *trans*-$[Rh(en)_2(OH)(OH_2)][ClO_4]_2$} in 1.0 mol dm^{-3} hydroxide was unaffected after 7 h at 81 °C. The reasonably good agreement between the values of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ in Table 2 and the corresponding activation parameters for aquation shows that the $[OH^-]$-independent process also corresponds to aquation, the presence of hydroxide being necessary only to drive the reaction to completion. It appears, therefore, that the different spectra of the products of reaction at high concentrations of hydroxide can reasonably be ascribed to *trans* ⟶ *cis* isomerisation that occurs only during the $[OH^-]$-dependent path for reaction (3). The extent of isomerisation was estimated as follows.

A known weight of *trans*-dichloro- or *trans*-dibromo-complex was heated under reflux with an excess of 1 mol dm^{-3} hydroxide for *ca.* 30 reaction half-lives. The product was then heated with an excess of HCl or HBr in a foil-wrapped flask until no further change in the spectrum was observed. (During the reaction with HBr, nitrogen was bubbled through the solution to prevent oxidation of the HBr.) The product solutions were then transferred quantitatively to a column of Dowex 50W cation-exchange resin and eluted first with 0.1 and then with 1.0 mol dm^{-3} $Na[ClO_4]$, the separation of two distinct complexes being confirmed by measuring the spectra of the eluates. The spectra of the first group of eluates corresponded exactly to those of the *trans*-dihalogeno-complexes and the total amount of *trans* product was obtained from a knowledge of the total absorbances of all the fractions and the appropriate molar absorption coefficients. The total amount of product from the second group of eluates was obtained by difference and the absorption coefficients obtained from this and the sums of the absorbances of all the fractions. These eluates had absorption maxima at 356 and 296 nm (X = Cl; ε 192 and 188 dm^3 mol^{-1} cm^{-1}) and 372 and 276 nm (X = Br; ε 220 and 943 dm^3 mol^{-1} cm^{-1}). These are in excellent agreement with the spectrum obtained by Klabunde [2] for the *cis*-dichloro-complex, *viz.* 352 and 294 nm (ε 190 and 190 dm^3 mol^{-1} cm^{-1}) and in quite good agreement with the spectrum obtained [6a] for the *cis*-dibromo-complex, *viz.* 362 and 276 nm (ε 210 and 900 dm^3 mol^{-1} cm^{-1}). Since isomerisation occurs only during the $[OH^-]$-dependent path, and knowing the proportion of the base hydrolysis that occurs by this path, the percentage rearrangement calculated from the separated *cis*- and *trans*-dihalogeno-complexes produced by the anation of the *cis*- and *trans*-dihydroxo-products of the base hydrolysis is 23 (X = Cl) and 51% (X = Br).

However, since the spectra of the *cis*- and *trans*-dihalogeno-complexes are both known, the mole fraction x_c of *cis* complex can also be calculated from unseparated mixtures of the two dihalogeno-complexes, produced by base hydrolysis followed by anation, by using the equation $\varepsilon_{obs.} = \varepsilon_t(1 - x_c) + \varepsilon_c x_c$ where ε_t and ε_c are the absorption coefficients of the *trans* and *cis* complexes, respectively, at a given wavelength. At 80 °C, x_c is 0.6 (X = Cl) and 0.7 (X = Br) with an uncertainty of *ca.* 0.1 in each case. These values both correspond to *ca.* 100% rearrangement during $[OH^-]$-dependent base hydrolysis. This value is much higher than those calculated from the separated *cis* and

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* That is, the value of the difference in $\Delta H_1^\ddagger$ values divided by the standard deviation of this difference.

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

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

[9] A. J. Poë and K. Shaw, *J. Chem. Soc.* (*A*), 1970, 393.

trans complexes. The higher value is almost certainly more reliable since the solutions were not shielded from light during chromatography whereas experiments involving unseparated mixtures were carried out in thermostatted cells in a spectrophotometer exactly in the way that the kinetics were observed. Photoisomerisation of *cis*-$[RhCl_2(en)_2]^+$ has been recently reported [10] and this would have decreased the estimated *trans* ⟶ *cis* rearrangement. It would not, of course, have affected the calculations of the spectra of the *cis*-dihalogeno-complexes. The spectrum of the *cis*-dihydroxo-complex was calculated from the known values of x_c, the spectra of the *trans* products of base hydrolysis of the *trans*-halogenohydroxo-complexes with low $[OH^-]$, and the spectra of the *cis–trans* mixtures produced from the reaction of *trans*-$[Rh(en)_2X_2]^+$ ($X = Cl$ or Br) with 1.0 mol dm^{-3} hydroxide. The complex has absorption maxima at 332 and 284 nm (ε 170 and 164 $dm^3\ mol^{-1}\ cm^{-1}$).

The percentage rearrangement during the $[OH^-]$-dependent base hydrolysis of the *trans*-di-iodo-complex with 1.0 mol dm^{-3} hydroxide was then estimated to be *ca.* 50 from the known spectra of the *cis*- and *trans*-dihydroxo-complexes and the measured spectrum of the mixed *cis–trans* product, substantially less than that for the dichloro- and dibromo-complexes.

DISCUSSION

Base hydrolysis of these *trans*-dianiono-complexes has not been observed before because sufficiently high hydroxide concentrations were not used. The need for such high concentrations does raise the problem of whether, even at constant ionic strength, the activity coefficient of the hydroxide ion remains constant over the wide range of ionic composition so that the values of k_2 can be considered to be true second-order rate constants. There are no good grounds for being sure that this is the case, but one can take a simple empirical approach in considering the data. Since $Na[ClO_4]$ has no effect on the rate of aquation, at least of the dichloro-, di-iodo-,[3b] and hydroxoiodo-complexes,[4] it will also probably have no effect when hydroxide is present and the rate enhancement in the presence of hydroxide must be due to the latter. Other workers [11] have found a linear dependence of $k_{obs.}$ on $[OH^-]$ for base hydrolysis of some cobalt(III) complexes in solutions of similar ionic composition to ours, and Burnett [12] has discussed the problems of medium effects in such solutions. Whatever the effect of large changes in reaction medium, the linear dependence of $k_{obs.}$ on $[OH^-]$ at all temperatures, and the good precision of the values of $\Delta H_2^‡$ and $\Delta S_2^‡$, imply that the temperature coefficients of the $[OH^-]$-dependent paths are independent of ionic composition, and the activation parameters should be useful for comparative purposes.

It has been pointed out [3,4] that when base hydrolysis of rhodium(III) complexes is pronounced the value of $\Delta H_2^‡$ is usually greater (by up to 25 kJ mol^{-1}) than $\Delta H_1^‡$. The unfavourable enthalpy is overcompensated by very positive values of $\Delta S_2^‡$.[1,2,5] The relative unimportance of the $[OH^-]$-dependent term in the rate law for the halogenohydroxo-complexes was caused by the much less positive values of $\Delta S_2^‡$, the values of $\Delta H_2^‡$ being approximately equal to $\Delta H_1^‡$.[3,4] The *trans*-dihalogeno-complexes differ from both the above cases. The values of $\Delta S_2^‡ - \Delta S_1^‡$ (80—100 J $K^{-1}\ mol^{-1}$) are comparable to those for rhodium(III) complexes that are very susceptible to base hydrolysis, but the values of $\Delta H_2^‡ - \Delta H_1^‡$ are even more unfavourable than for the latter. Moreover, the *trans*-dihalogeno-complexes are the only ones for which stereochemical rearrangement occurs during base hydrolysis.

The trends in the parameters are shown in Figure 2.

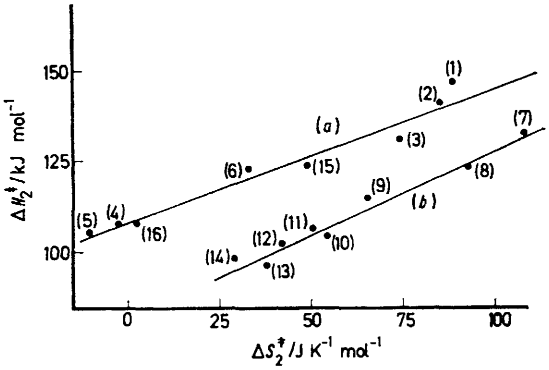

FIGURE 2 Isokinetic plots for base hydrolysis of rhodium(III) complexes (*a*) with no Rh–NH bond, and (*b*) with an Rh–NH group *trans* to the leaving group: (1), *trans*-$[RhCl_2(en)_2]^+$; (2), *trans*-$[RhBr_2(en)_2]^+$; (3), *trans*-$[RhI_2(en)_2]^+$; (4), *trans*-$[RhCl(en)_2(OH)]^+$;[3] (5), *trans*-$[RhBr(en)_2(OH)]^+$;[3] (6), *trans*-$[RhI(en)_2(OH)]^+$;[4] (7), $[RhCl(NH_3)_5]^{2+}$;[15] (8), $[RhBr(NH_3)_5]^{2+}$;[15] (9), $[RhI(NH_3)_5]^{2+}$;[15] (10), *cis*-$[RhCl(en)_2(OH)]^+$;[2] (11), *cis*-$[RhCl(en)_2(NO_2)]^+$;[2] (12), *cis*-$[RhCl_2(en)_2]^+$;[1] (13), *cis*-$[RhCl(en)_2(py)]^{2+}$;[2] (14), *cis*-$[RhCl(en)_2(NH_3)]^{2+}$;[2] (15) and (16), bimolecular reaction of *trans*-$[RhI_2(en)_2]^+$ with Cl^- and Br^-, respectively [3b]

Data for complexes without a co-ordinated N–H group *trans* to the leaving halide fall on a reasonably good isokinetic plot which is quite distinct from that for the complexes with a *trans*-NH group. The respective isokinetic temperatures are *ca.* 100 and 190 °C. For clarity, error bars have not been included in the Figure. However, because the kinetic measurements, at least of the *trans*-dianiono-complexes, were made at a mean temperature close to the isokinetic temperature, the main effect of the uncertainties is that the points lie within long narrow error contours, the major axes of which lie closely parallel to the isokinetic plots.[13] It has been shown [14] that an isokinetic relation exists for base hydrolysis of the complexes $[Rh(NH_3)_5X]^{2+}$ ($X =$ Cl, Br, and I) and the data [15] for these complexes at $I = 0.1$ mol dm^{-3} are included in Figure 2 and show that charge effects do not cause deviations.

Isokinetic plots are usually assumed to have mechan-

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[14] G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1206.

[15] S. C. Chan, *Austral. J. Chem.*, 1967, **20**, 61.

istic significance only when substituent effects are remote from the reactive site,[16] whereas these data include changes not only in ligands *cis* and *trans* to the leaving group but also in the leaving group itself. The effects of these changes can be compensated for by plotting values of $\Delta H_2^\ddagger - \Delta H_1^\ddagger$ against $\Delta S_2^\ddagger - \Delta S_1^\ddagger$ to give 'pseudo-isokinetic plots' (Figure 3). Data for complexes without a *trans*-NH group fall on an excellent straight line. There are fewer data for the other group (and one point shows a major deviation), but a similar trend is shown. The linearity for the *trans*-dianiono-complexes can be taken to imply a qualitative similarity of mechanism along the series, although there may be systematic changes of emphasis. The stereochemical rearrangement that occurs during the reactions of the *trans*-dihalogeno-complexes suggests that hydroxide is playing a profound role such as would be expected for the S_N1 CB mechanism now widely accepted [5,17] for amine complexes of Co^{III}. No detectable rearrangement occurs during reactions of the *trans*-halogeno-hydroxo-complexes of Rh^{III} so these may react by an S_N1 IP mechanism. However, the hydroxide ligand may take part in hydrogen bonding with the NH groups so that the *trans*-configuration is maintained, and the absence of isomerisation does not, therefore, rule out the possibility that all the base hydrolyses occur by the S_N1 CB mechanism. This rigidity of the *trans*-halogeno-hydroxo-complexes would prevent rearrangement in forming the transition state and result in a less positive value of $\Delta S_2^\ddagger$, but the value of $\Delta H_2^\ddagger$ would be smaller because the increase in enthalpy, caused by ligand-field effects during rearrangement, would be avoided. The distinction between the S_N1 IP and S_N1 CB mechanisms is not necessarily sharp in that an ion pair could be the intermediate in which the reactants are brought together but, as the Rh–X bond stretches to form the transition state, a simultaneous transfer of the proton from a co-ordinated nitrogen to the hydroxide could occur.[18] This transfer could be complete in the *trans*-halogeno-complexes but only partial in the *trans*-hydroxo-complexes. The fit to the isokinetic and pseudo-isokinetic plots of data [3b] for bimolecular reactions involving halides as attacking ligands, although it might be quite coincidental, could be taken as evidence for the operation of an S_N1 IP mechanism in the region of the plots where $\Delta H_2^\ddagger$ and $\Delta H_2^\ddagger - \Delta H_1^\ddagger$ are smaller since S_N1 CB reactions involving the much less basic halides are unlikely. The linear dependence of $k_{obs.}$ on $[OH^-]$ might imply that the concentration of any conjugate base formed is very small and proportional to $[OH^-]$. However, arguments based on this linearity and the relative size of conjugate-base and ion-pair formation constants are dubious because of the unknown effects of the large changes in the ionic medium.

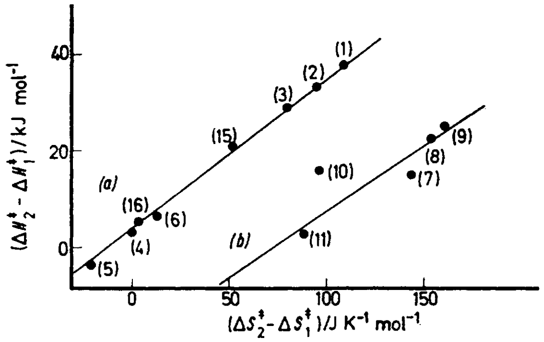

FIGURE 3 'Pseudo-isokinetic plots' for base hydrolysis of rhodium(III) complexes. See Figure 2 for key

The occurrence of rearrangement in the *trans*-dihalogeno-complexes can be rationalised as follows. The conjugate-base mechanism in rhodium(III) complexes is said to act through a strong σ *trans*-bond weakening effect (t.b.w.e.) due to the amido-group.[5a] When a Rh–N bond is *trans* to the Rh amido-group there will be a strong tendency for a trigonal-bipyramidal intermediate to be formed with the amido-group in the trigonal plane so that the strength of the $Rh–NH^-$ bond can be maximised without greatly weakening the other Rh–N bonds. When a $Rh–OH_2$ bond is subsequently formed the water molecule will find it easier to approach the intermediate in the segment *trans* to the amido-group since the $Rh \cdots OH_2$ bond in the transition state is weak. It will therefore suffer less from the t.b.w.e. because weak bonds have a lower susceptibility to t.b.w.e. (s.t.b.w.e.).[6b,19] Coincident with this, the Rh–N bond that was *trans* to the amido-group will move to become *trans* to the ligand L which has a lower t.b.w.e. and, therefore, a relatively small effect on the rather strong Rh–N bond. If the water molecule were to approach the segment in the trigonal plane opposite to the L ligand (so that the $Rh \cdots OH_2$ bond in the transition state was *trans* to L) it would not take as much advantage of the lower t.b.w.e. of L and a strong Rh–N bond would be forced into a position *trans* to the $Rh–NH^-$ bond where it would suffer a large t.b.w.e. The occurrence of *trans* ⟶ *cis* isomerism can, therefore, be understood in terms of a σ-bonding model. Evidently it is only when a ligand is present (such as an amido-group) with an exceptionally high t.b.w.e. that this can overcome the unfavourable ligand-field effects.

The isokinetic plots for reactions of penta-ammine-halogeno-rhodium(III) and -cobalt(III) complexes have been adduced [5c,14] as evidence for a similar mechanism in both sets of complexes. Although the activation enthalpies for the penta-amminehalogenocobalt(III) complexes cover a range of only *ca.* 5 kJ mol^{-1} (which is the same as the range of published values for base hydrolysis of the penta-amminechloro-complex itself [5d]), if data all obtained by one set of workers are considered a good isokinetic plot is obtained.[14] The values of $\Delta H_2^\ddagger$ for loss of halide from the *trans*-dianionobis(ethylenediamine)rhodium(III) complexes studied so far cover a

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[16] Ref. 13, ch. 9.

[17] 'Inorganic Reaction Mechanisms,' *Specialist Periodical Report*, The Chemical Society, London, 1972, vol. 2, pp. 171—173.

[18] S. C. Chan and O. W. Lau, *Austral. J. Chem.*, 1969, **22**, 1851.

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

range of over 40 kJ mol^{-1} whereas those for similar complexes of cobalt(III) [5d] cover a range of only 10 kJ mol^{-1}. The range of values of $\Delta S_2^{\ddagger}$ is about the same in both cases (*ca.* 100 J K^{-1} mol^{-1}) so the ordering of rates in the cobalt complexes is therefore almost entirely dependent on entropy factors.* The isokinetic temperatures show that the ordering of the *trans*-dianionorhodium complexes is determined almost equally by enthalpy and entropy factors, while that of the rhodium(III) complexes with *trans*-NH groups is more enthalpy-controlled. This is still not to say that there is necessarily any major difference of mechanism, but only that the relative contributions of the various factors in determining the activation parameters are different. Indeed Lalor and Carrington [20] have suggested that certain regularities in the kinetic and spectroscopic properties of the penta-amminehalogeno-complexes of trivalent chromium, cobalt, rhodium, and iridium imply that all these complexes undergo base hydrolysis by a similar mechanism.

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* This is illustrated quantitatively by the fact that the isokinetic temperature corresponding to the isokinetic plot for the penta-amminehalogencobalt(III) complexes is only *ca.* −60 °C.

[20] G. C. Lalor and T. Carrington, *J. Chem. Soc.* (*A*), 1969, 2509.