Reversible Chelate Ring-opening and Ring-closure Substitution Reactions of *trans*-Dichlorobis(*o*-dimethylaminophenyldimethylarsine-*NAs*)-rhodium(III) Ions. A Kinetic Study in Hydroxylic Solvents

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The kinetics of the interconversion (i) have been studied in hydroxylic solvents (X = Cl, Br, I, and occasionally

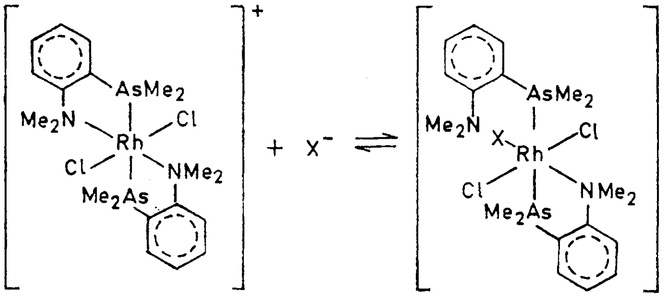
$$trans\text{-}[\mathrm{Rh(L)_2Cl_2}]^+ + \mathrm{X}^- \rightleftharpoons mer\text{-}[\mathrm{Rh(L)(L')Cl_2X}] \qquad \text{(i)}$$

SCN; L and L′ = *o*-dimethylaminophenyldimethylarsine-*NAs* and -*As* respectively). The system obeys rate law

$$-\,\mathrm{d}[\mathrm{Rh(L)_2Cl_2}^+]/\mathrm{d}t = k_{(t\rightarrow m)}{}^0\gamma_{\pm}{}^2[\mathrm{Rh(L)_2Cl_2}^+][\mathrm{X}^-] - k_{(m\rightarrow t)}[\mathrm{Rh(L)(L')Cl_2X}] \qquad \text{(ii)}$$

(ii). The rate of the forward reaction increases with decreasing polarity of the solvent, as expected for reactions between ions of opposite charge. The reactivity of the *trans* complex changes with the entering group, an order SCN > I > Br > Cl being observed in methanol, and is explained by the occurrence of some Rh–X bond making during formation of the transition state. The rate of the reverse reaction is also affected both by the solvent and by the nature of the X group. The solvent effect is rationalized in terms of the Grunwald–Winstein relation $\log k_{(t\rightarrow m)}{}^0 = mY + \text{constant}$. The high values of m obtained [1.24 (X = Cl), 1.19 (Br), and 0.95 (I)] are considered to indicate extensive Rh–X bond rupture in the activated complex of the *mer* ⟶ *trans* conversion. The reactivity order with respect to the leaving group, SCN < Cl < Br < I, is interpreted in terms of the energy required to break the Rh–X bond in order to attain the configuration of the activated complex.

We recently reported a kinetic investigation on the *trans* ⇌ *mer* interconversion between *trans*-dichlorobis(*o*-dimethylaminophenyldimethylarsine-*NAs*)rhodium(III) chloride, *trans*-$[\mathrm{Rh(L)_2Cl_2}]\mathrm{Cl}$, and *mer*-trichloro(*o*-dimethylaminophenyldimethylarsine-*As*)(*o*-dimethylaminophenyldimethylarsine-*NAs*)rhodium(III), *mer*-$[\mathrm{Rh(L)(L')Cl_3}]$ [equation (1); X = Cl], in methanol, ethanol, propan-1-ol, and propan-2-ol.[1] A dissociative-interchange mechanism, involving the formation of a precursor ion pair between the *trans* complex and the chloride ion, followed by a slow Rh–N bond rupture, has been proposed for the forward reaction. The reverse reaction is thought to imply a dissociative mechanism with extensive Rh–Cl bond rupture in the activated complex.



(1)

(I) *trans*-$[\mathrm{Rh(L)_2Cl_2}]^+$

(II) *mer*-$[\mathrm{Rh(L)(L')Cl_2X}]$

This paper reports the results of a kinetic study of system (1) with X = Br, I, and occasionally SCN in the solvents previously used. The investigation was made in order to achieve a more accurate description of the reaction mechanism on the grounds of either the solvent effects or the kinetic effects of X on both the forward and the reverse reactions. The reaction with chloride, previously studied by using LiCl as chloride source, has been reinvestigated by using $[\mathrm{NMe_4}]\mathrm{Cl}$, whose association constant is known in the solvents considered.

EXPERIMENTAL

The complexes *mer*-$[\mathrm{Rh(L)(L')Cl_3}]$ and *trans*-$[\mathrm{Rh(L)_2Cl_2}][\mathrm{NO_3}]$ were prepared as described elsewhere.[2] The new complexes *mer*-$[\mathrm{Rh(L)(L')Cl_2X}]$ (X = Br, I, or SCN) were identified in solution (see below). Reagent grade $[\mathrm{NMe_4}]\mathrm{Cl}$, $[\mathrm{NBu_4}]\mathrm{Br}$, $[\mathrm{NBu_4}]\mathrm{I}$, $[\mathrm{NBu_4}][\mathrm{ClO_4}]$, Na[SCN], and $\mathrm{Na[ClO_4]}$ were dried before use. Methanol, ethanol, propan-1-ol, and propan-2-ol were purified by standard methods.[3]

Stoicheiometry of the Reactions, Preparation of the Reaction Mixtures, and Evaluation of the Reaction Rates.—Reactions of the *trans*-dichloro-complex with chloride are already known to obey stoicheiometry (1).[1] The identification of the stoicheiometry of the reactions with bromide and iodide was not straightforward. Thus, when bromide or iodide

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[1] A. Peloso and L. Volponi, *J.C.S. Dalton*, 1974, 278.

[2] L. Volponi, C. Panattoni, R. Graziani, and G. Bombieri, *Gazzetta*, 1966, **96**, 1158.

[3] A. Weissberger, E. S. Praskasuer, J. A. Reddick, and E. E. Toops, jun., 'Technique of Organic Chemistry,' vol. 7, 'Organic Solvents,' 2nd edn., Interscience, New York, 1955, pp. 333, 337, 343, 344.

were treated with *trans*-[Rh(L)$_2$Cl$_2$][NO$_3$] in boiling methanol products of formula *mer*-[Rh(L)(L′)X$_3$] were isolated.[4] These complexes are not, however, the reaction products formed in the kinetic conditions. Thus, for instance, *mer*-[Rh(L)(L′)Br$_3$] exhibits an absorption maximum at 297 nm compared with the value of 275 nm (Figure 1) shown by the reaction products formed under kinetic conditions. Stoicheiometry (1) was found to hold for X = Br and I by indirect evidence. Solutions of *trans*-[Rh(L)$_2$Cl$_2$][NO$_3$] (*ca.* 3.3×10^{-5} mol dm^{-3}) were treated with [NBu$_4$]Br (*ca.* 10^{-2} mol dm^{-3}) or [NBu$_4$]I (*ca.* 10^{-2} mol dm^{-3}) in methanol at 25 °C. The course of the reaction was followed spectrophotometrically in the 350—250 nm region until equilibrium was attained. Subsequent addition of a large amount of Na[ClO$_4$] to the solution caused almost quantitative disappearance of the reaction product and the reappearance of the starting rhodium(III) complex. The process could be repeated by further addition of halide followed by Na[ClO$_4$]. This behaviour was observed also in the other alcohols, as well as in the case of the chloride reaction of known stoicheiometry. The reappearance of the starting dichloro-complex merely by increasing the ionic strength implies that both the chloride ions are firmly bonded to Rh^{III} even when the incoming ligand X co-ordinates to the central metal atom, and is fully consistent with the expectation of a reversible reaction of type (1). In our opinion, these results substantiate stoicheiometry (1). We were not able to isolate the complexes [Rh(L)(L′)Cl$_2$X] (X = Br or I). Their non-ionic nature prevented use of an appropriate counter ion as precipitating agent. On the other hand, precipitation by addition of a suitable solvent also resulted in separation of the salts present in solution which were not easily removed without concomitant transformation of the complex to the starting *trans* isomer. Therefore no precise information is available on the mutual position of the halides. However, structure (II) is proposed for such complexes in view of their kinetic behaviour which is very similar to that of *mer*-[Rh(L)(L′)Cl$_3$]. A similar *mer* complex is also formed in the reaction with thiocyanate.

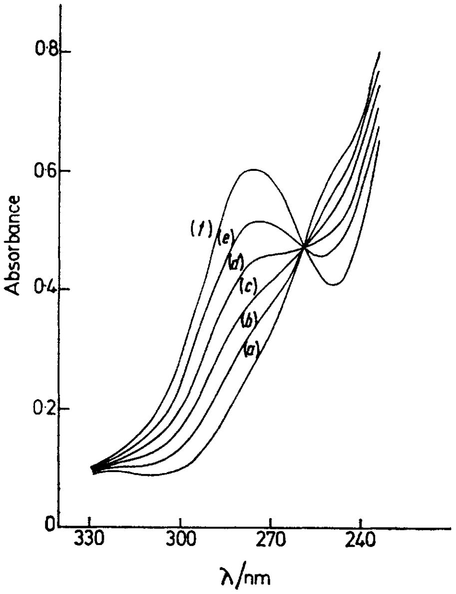

FIGURE 1 Spectra of a solution originally containing *trans*-[Rh(L)$_2$Cl$_2$][NO$_3$] (*ca.* 3.3×10^{-5} mol dm^{-3}), [NBu$_4$]Br (5.0×10^{-2} mol dm^{-3}), and [NBu$_4$][ClO$_4$] (1.67×10^{-2} mol dm^{-3}) in propan-2-ol at 25 °C: after 15 (*a*), 120 (*b*), 240 (*c*), 420 (*d*), 720 (*e*), and 4 500 s (*f*)

The reactions were started by mixing appropriate volumes of thermostatted stock solutions of the reagents, prepared by weight, in a 1 cm silica cell maintained in the thermostatted cell compartment of either a Beckman DK2A or an Optica CF4R recording spectrophotometer. At suitable times the spectrum of the reacting mixture was scanned in the range 350—250 nm, where large changes in absorbance were observed during the reaction, together with the occurrence of isosbestic points [at 313 and 250 (X = Cl), at 259 (Br), at 262 (I), and at 345, 332, and 262 nm (SCN)]. Faster reactions were followed by recording the changes in absorbance with time at a suitable wavelength [285 (X = Cl), 280 nm (Br and I)]. The reactions were clean, as shown from the spectrophotometric behaviour of the reacting mixtures, the isosbestic points being maintained over the course of the reaction (*e.g.* Figure 1). The initial concentration of *trans*-[Rh(L)$_2$Cl$_2$][NO$_3$] was in the range 1×10^{-5}—5×10^{-5} mol dm^{-3}. The concentrations of the other reagents were varied as follows: [NMe$_4$]Cl, 1.33×10^{-2}—8.68×10^{-2}; [NBu$_4$]Br and [NBu$_4$]I, 3.33×10^{-3}—6.67×10^{-2} mol dm^{-3}. The reactions with bromide and iodide were made at four different concentrations of [NBu$_4$]X + [NBu$_4$][ClO$_4$], *i.e.* 6.67×10^{-2}, 3.32×10^{-2}, 1.67×10^{-2}, and 8.33×10^{-3} mol dm^{-3}. In each series the concentration of [NBu$_4$]X was varied at least five times. The temperatures explored are listed in Table 1. A single series of kinetic runs was made in methanol at 25 °C with X = SCN, using a constant concentration of Na[SCN] + Na[ClO$_4$] (3.56×10^{-2} mol dm^{-3}). The concentration of Na[SCN] was varied in the range 7.13×10^{-4}—3.56×10^{-2} mol dm^{-3}.

TABLE 1

Comparison between the equilibrium constants, K_{eq}, of system (1), derived from the absorbances of the reaction mixtures at equilibrium at 25 °C, and the quotients k_2/k_1

Solvent	X	[Salt] [a] / mol dm^{-3}	$10^2 I$ / mol dm^{-3}	K_{eq} [b] / dm^3 mol^{-1}	k_2/k_1 [b] / dm^3 mol^{-1}
Ethanol	Br	6.67×10^{-2}	3.5	90	112
		1.67×10^{-2}	1.2	210	180
	I	6.67×10^{-2}	2.9	165	152
		1.67×10^{-2}	1.0	260	212
Propan-1-ol	Br	6.67×10^{-2}	2.3	350	495
		1.67×10^{-2}	0.86	580	680
	I	6.67×10^{-2}	1.9	470	560
		1.67×10^{-2}	0.73	800	820

[a] [NBu$_4$X] + [NBu$_4$ClO$_4$]. [b] ±10%.

The observed rate constants, $k_{obs.}$, were determined from the gradients of plots of $\log|D_t - D_\infty|$ against time, where D_t and D_∞ are the absorbances of the reaction mixture at time t and at the end of the reaction. The gradients of the plots were independent of the particular wavelength considered.

RESULTS

The observed rate constants, $k_{obs.}$, for the reactions with bromide and iodide increased linearly with the concentration of [NBu$_4$]X provided a constant salt concentration ([NBu$_4$]X + [NBu$_4$][ClO$_4$]) was used. However, an adequate

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[4] L. Volponi, C. Panattoni, and B. Zarli, *Proc. Annual Meeting Chim. Inorg.*, Padova, 1967, p. 25.

description of the dependence of $k_{obs.}$ on $[X^-]$ requires the knowledge of the effective concentration of X^- in solution. This was obtained from the association constants, K, of the salts used at 25 °C, referred to the particular ionic strength in the reacting mixture according to the relation $K = K_0\gamma_\pm^2$, where K_0 is the association constant at zero ionic strength.[5-7] The mean ionic activity coefficient, $\gamma_\pm$, was calculated from the extended Debye–Huckel expression (2),

$$\log \gamma_\pm = \frac{1.826 \times 10^6 z_+z_-(dI)^{\frac{1}{2}}}{(DT)^{\frac{3}{2}}[1 + 50.29(DT)^{\frac{1}{2}}r(dI)^{\frac{1}{2}}]} \qquad (2)$$

where d is the density of the solvent, D its dielectric constant, and I the ionic strength.[8] The Bjerrum critical distance for 1 : 1 electrolytes (equal to $e^2/2DkT$) was used as a value of r in equation (2) in place of the ion-size parameter, according to recent practice.[7,9,10] The association constants of $[NBu_4]X$ were assumed to be negligibly affected by the temperature in the range of temperature explored.[7] Figure 2 gives an example of a plot of $k_{obs.}$ against $[X^-]$.

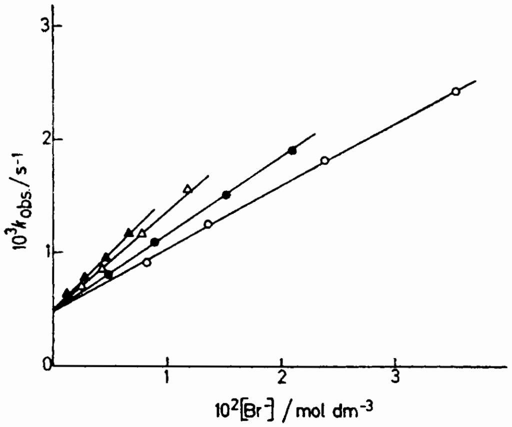

FIGURE 2 Observed rate constants, $k_{obs.}$, for the reaction of *trans*-$[Rh(L)_2Cl_2][NO_3]$ with $[NBu_4]Br$ in ethanol at 25 °C as a function of the concentration of bromide ions. Salt concentrations ($[NBu_4]Br$ + $[NBu_4][ClO_4]$): 6.67 × 10^{-2} (○), 3.34 × 10^{-2} (●), 1.67 × 10^{-2} (△), and 8.33 × 10^{-3} mol dm^{-3}(▲)

Thus, the observed rate constant appears to be governed by equation (3). System (1) is reversible, the concentration

$$k_{obs.} = k_1 + k_2[X^-] \qquad (3)$$

of *mer*-$[Rh(L)(L')Cl_2X]$ at equilibrium increasing to a limiting value either by increasing the concentration of X^- or by decreasing the ionic strength. From the dependence of the absorbances of the reaction mixtures at equilibrium on the concentration of X^-, it was possible to derive the equilibrium constants, K_{eq}, of system (1) for X = Br and I at any ionic strength. Some typical values are collected in Table 1. For first-order or pseudo-first-order reversible reactions,[1,11] k_1 in equation (3) may be identified with $k_{(m\rightarrow t)}$ and k_2 with $k_{(t\rightarrow m)}$ referred to the particular ionic strength in solution. This is confirmed by the fact that the quotients k_2/k_1 from equation (3) are fairly similar to the measured equilibrium constants (Table 1).

Only the specific rate constant of the forward reaction is

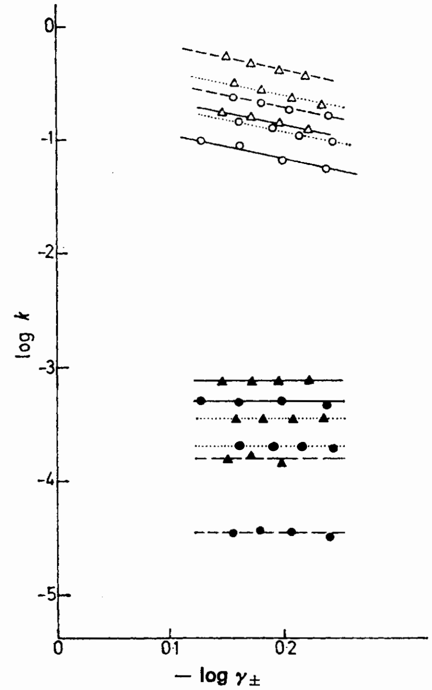

FIGURE 3 Effect of ionic strength at 25 °C, expressed in terms of the mean ionic activity coefficient, $\gamma_\pm$, on $k_{(t\rightarrow m)}$ (open symbols) and on $k_{(m\rightarrow t)}$ (closed symbols) for the reactions with $[NBu_4]Br$ (circles) and $[NBu_4]I$ (triangles) in ethanol (—), propan-1-ol (· · ·), and propan-2-ol (– – –)

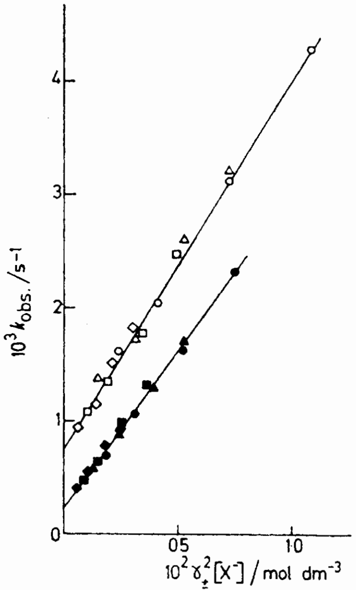

FIGURE 4 Observed rate constants, $k_{obs.}$, for the reactions of *trans*-$[Rh(L)_2Cl_2][NO_3]$ with $[NBu_4]Br$ in propan-1-ol (closed symbols) and with $[NBu_4]I$ in ethanol (open symbols) at 25 °C as a function of $\gamma_\pm^2[X^-]$. Salt concentrations ($[NBu_4]X$ + $[NBu_4][ClO_4]$): 6.67 × 10^{-2} (○, ●); 3.34 × 10^{-2} (△, ▲); 1.67 × 10^{-2} (□, ■); 8.33 × 10^{-3} mol dm^{-3} (◇, ♦)

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[5] R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, 1965, **69**, 4208.

[6] D. F. Evans and P. Gardan, *J. Phys. Chem.*, 1968, **72**, 3281.

[7] M. A. Matesich, J. A. Nadas, and D. F. Evans, *J. Phys. Chem.*, 1970, **74**, 4568.

[8] 'The Chemistry of Non-aqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York, 1966, vol. 1, p. 102.

[9] J. C. Justice, R. Bury, and C. Treiner, *J. Chim. phys.*, 1968, **65**, 1708.

[10] J. C. Justice, *J. Chim. phys.*, 1969, **66**, 1193.

[11] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1962, p. 185.

affected by variations in the ionic strength (Figures 2 and 3), in such a way that relation (4) is obeyed, where $k_{(t\rightarrow m)}{}^0$ is the specific rate constant of the forward reaction at zero

$$k_{\text{obs.}} = k_{(m\rightarrow t)} + k_{(t\rightarrow m)}{}^0\gamma_{\pm}{}^2[\mathrm{X}^-] \qquad (4)$$

ionic strength. Plots of $k_{\text{obs.}}$ against $\gamma_{\pm}{}^2[\mathrm{X}^-]$ (*e.g.* in Figure 4) gave the same straight line regardless of the salt concentration used. The values of $k_{(m\rightarrow t)}$ and $k_{(t\rightarrow m)}{}^0$ obtained are listed in Table 2 together with the related activation parameters. Equation (4) held also for the reactions with Na[SCN] and [NMe$_4$]Cl. In the first case the data reported in Table 2 were derived with the assumption that Na[SCN] is essentially fully dissociated in methanol, which appears to be a reasonable approximation in view of the general behaviour of sodium halides and pseudo-halides in this solvent.[12,13] The values of $k_{(t\rightarrow m)}{}^0$ for the reactions with [NMe$_4$]Cl were obtained from gradients of plots of $k_{\text{obs.}}$ against $\gamma_{\pm}{}^2[\mathrm{Cl}^-]$, the association constant of [NMe$_4$]Cl being known in the solvents used.[5-7] As expected, the intercepts of these plots were close (within an error of $\pm 6\%$) to the values of $k_{(m\rightarrow t)}$ previously obtained [1] from the direct conversion *mer* ⟶ *trans*.

TABLE 2

Rate constants and activation parameters for the interconversion *trans*-[Rh(L)$_2$Cl$_2$]$^+$ + X$^-$ $\rightleftharpoons$ *mer*-[Rh(L)(L′)Cl$_2$X] at zero ionic strength

Solvent	X	θ_c/°C	$k_{(m\rightarrow t)}$/s^{-1}	$\Delta H_{(m\rightarrow t)}{}^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$k_{(t\rightarrow m)}{}^0$/dm^3 mol^{-1} s^{-1}	$\Delta H_{(t\rightarrow m)}{}^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Methanol	Cl	20	1.50×10^{-3} [a]			3.27×10^{-2} [b]		
		30	4.14×10^{-3} [a]	71 [a]	−54 [a]	9.65×10^{-2} [b]	72 [b]	−27 [b]
		40	1.04×10^{-2} [a]			2.33×10^{-1} [b]		
	Br	25	4.14×10^{-3}			9×10^{-2} [c]		
		40	1.67×10^{-2}	70	−55	7×10^{-1} [c]		
	I	25	6.35×10^{-3}			1.5×10^{-1} [c]		
		40	2.38×10^{-2}	66	−64	1.5 [c]		
	SCN	25	3.50×10^{-4}			5.95×10^{-1}		
Ethanol	Cl	30	3.20×10^{-4} [a]			2.55×10^{-1}		
		50	2.30×10^{-3} [a]	76 [a]	−58 [a]	1.52	70	−25
	Br	25	5.03×10^{-4}			1.76×10^{-1}		
		40	2.20×10^{-3}	73	−61	7.44	72	−17
	I	25	7.76×10^{-4}			3.44×10^{-1}		
		40	3.62×10^{-3}	77	−46	1.41	70	−18
Propan-1-ol	Cl	30	1.66×10^{-4} [a]			4.85×10^{-1}		
		50	1.20×10^{-3} [a]	78 [a]	−58 [a]	3.20	74	−6
	Br	25	2.01×10^{-4}			3.16×10^{-1}		
		40	1.05×10^{-3}	83	−35	1.31	71	−15
	I	25	3.65×10^{-4}			6.36×10^{-1}		
		40	1.87×10^{-3}	81	−38	2.60	70	−13
Propan-2-ol	Cl	30	2.90×10^{-5} [a]			8.10×10^{-1}		
		50	2.20×10^{-4} [a]	80 [a]	−71 [a]	5.30	74	+17
	Br	25	6×10^{-5} [c]			4.91×10^{-1}		
		40	4×10^{-4} [c]			2.16	74	−2
	I	25	1.7×10^{-4} [c]			1.09		
		40	6.0×10^{-4} [c]			5.10	77	+14

Errors: $k \pm 3\%$; $\Delta H^{\ddagger} \pm 4$ kJ mol^{-1}; $\Delta S^{\ddagger} \pm 10$ J K^{-1} mol^{-1}.

[a] Data taken from ref. 1. [b] $k \pm 5\%$; $\Delta H^{\ddagger} \pm 7$ kJ mol^{-1}; $\Delta S^{\ddagger} \pm 18$ J K^{-1} mol^{-1}. [c] $\pm 15\%$.

DISCUSSION

The dependence of $k_{\text{obs.}}$ on the concentration of X$^-$ [equation (4)] indicates that system (1) follows rate law (5). The results are better examined by considering separately the forward and the reverse reactions of system (1).

$$-\mathrm{d}[\mathrm{Rh(L)_2Cl_2}^+]/\mathrm{d}t = k_{(t\rightarrow m)}{}^0\gamma_{\pm}{}^2[\mathrm{Rh(L)_2Cl_2}^+][\mathrm{X}^-] - k_{(m\rightarrow t)}[\mathrm{Rh(L)(L')Cl_2X}] \qquad (5)$$

The specific rate of the forward reaction (*trans* ⟶ *mer* conversion) at infinite dilution, $k_{(t\rightarrow m)}{}^0$, is affected by the solvent and the entering group X$^-$. This rate term increases with decreasing polarity of the solvent expressed in terms of both the Grunwald–Winstein parameters (Figure 5) * or the reciprocal of the dielectric constant, as expected for reactions involving an interaction between ions of opposite charge. An increase in the entropy of activation, $\Delta S_{(t\rightarrow m)}{}^{\ddagger}$, in going from methanol to the less polar propan-2-ol, appears to be mainly responsible for the observed solvent effect, and is in the order expected from theoretical considerations.[16]

Indirect evidence against the dissociative-interchange mechanism, I_d, previously proposed [1] is obtained when the solvent effect is examined in terms of the dielectric constants of the solvents used. Thus, radii of 6.5—7.5 Å can be derived for the possible precursor ion pair *trans*-[Rh(L)$_2$Cl$_2$]$^+$, X$^-$ from gradients of plots of log $k_{(t\rightarrow m)}{}^0$ against $1/D$.[17] Introducing these values into the Fuoss

* The value of *Y* for propan-1-ol has been derived by interpolation of the relation between the Kosower *Z* values with the *Y* values of alcohols.[14,15]

[12] J. Miller and A. J. Parker, *J. Chem. Soc.*, 1961, **117** and refs. therein.

[13] B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc.* (*B*), 1966, 152.

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[16] K. J. Laidler, 'Chemical Kinetics,' McGraw-Hill, New York, 1950, ch. 5.

[17] K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107.

equation,[18] the following values for the formation constant, K_{IP}, of the ion pair are obtained: 10 (methanol); 25 (ethanol); 50 (propan-1-ol); and 70 dm^3 mol^{-1} (propan-2-ol). These values are high enough to imply a non-linear dependence of $k_{obs.}$* on $\gamma_{\pm}^2[X^-]$. This expectation does not appear to be experimentally verified (*e.g.* Figure 4). The sensitivity of the reaction rate to the nature of the entering group is also good evidence against an I_d mechanism. The rate term, $k_{(t\rightarrow m)}^0$ changes with changing X^- (Table 2), a definite order SCN(10.7) > I(2.7) > Br(1.6) > Cl(1) being observed in methanol. Conversely, on the basis of an I_d mechanism such a rate term would be little affected by changes in the entering anion, provided that anions of constant charge are considered.[17] The sensitivity of the rates to the nature of X^- must be assigned to some bond making during formation of the transition state. An associative-interchange mechanism, I_a, appears to be adequate to account for the observed results. According to this mechanism some Rh–X bond formation would be involved before Rh–N bond breaking is complete. Although such a mechanism appears to be satisfactory in all respects, a pure dissociative mechanism, D, of type (6), cannot be ruled out. Such a mechanism is governed by rate law (7) † which is of the same form as that found

$$trans\text{-}[Rh(L)_2Cl_2]^+ + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Rh(L)(L')Cl_2]^+ + X^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} mer\text{-}[Rh(L)(L')Cl_2X] \quad (6)$$

$$\frac{-d[Rh(L)_2Cl_2^+]}{dt} = \frac{k_1k_3[Rh(L)_2Cl_2^+][X^-]}{k_2 + k_3[X^-]} - \frac{k_2k_4[Rh(L)(L')Cl_2X]}{k_2 + k_3[X^-]} \quad (7)$$

experimentally, provided that $k_2 \gg k_3[X^-]$. Such a condition would be expected for mechanism (6) because the five-co-ordinate intermediate, $[Rh(L)(L')Cl_2]^+$, has the outgoing group NMe_2 very near to the reaction site and would be very similar to the activated complex of the reaction step k_2. Although no information is yet available for a correct choice between the alternative mechanisms I_a and D, both mechanisms imply an I_a path for the attack of the entering group X^-.

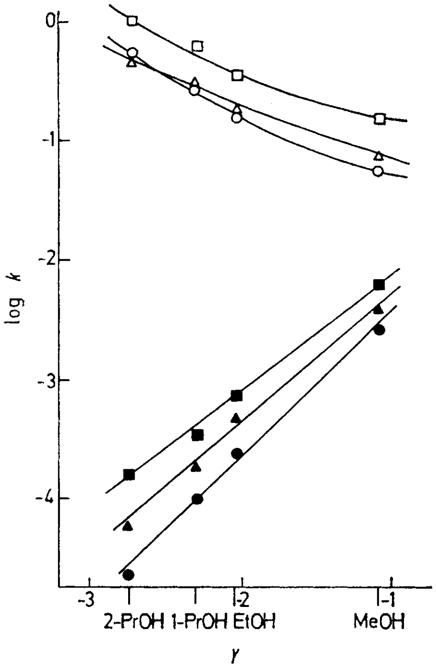

FIGURE 5 Dependence of $k_{(t\rightarrow m)}^0$ (open symbols) and $k_{(m\rightarrow t)}$ (closed symbols) on the polarity of the solvent at 25 °C for the reactions with $[NMe_4]Cl$ (○, ●), $[NBu_4]Br$ (△, ▲), and $[NBu_4]I$ (□, ■)

The tendency of *mer*-$[Rh(L)(L')Cl_2X]$ to convert into the *trans* isomer [reverse reaction of system (1)] increases in the order SCN < Cl < Br < I. The high negative values of the activation entropies are an indication of increasing solvation in going from the ground state to the activated complex, possibly due to significant charge separation caused by extensive Rh–X bond breaking during the formation of the transition state. The extent of Rh–X bond rupture in the activated complex related to the *mer* ⟶ *trans* conversion is best considered by examining the solvent effect. It is seen (Table 2) that $k_{(m\rightarrow t)}$ increases in the order propan-2-ol < propan-1-ol < ethanol < methanol. The effect of the solvent on the rates of substitutions of halide in octahedral complexes has been usually examined in terms of the Grunwald–Winstein Y parameters.[19-21] Satisfactory linear correlations between log $k_{(m\rightarrow t)}$ and Y are found in our cases (Figure 5), and the solvent effect can be rationalized in terms of the Grunwald–Winstein equation log $k_{(m\rightarrow t)} = mY +$ constant. The m values obtained are very high [1.24 ± 0.10 ($X = Cl$), 1.19 ± 0.13 (Br), and 0.95 ± 0.05 (I)] and can be taken as a positive indication of extended Rh–X bond rupture in the activated complex.[22,‡] In view of the fact that the activated complex for both the forward and the reverse reactions of system (1) is the same, this conclusion implies that there is little Rh–X bond formation in the transition state for the *trans* ⟶ *mer* conversion. This is possibly the reason why the effect of the entering group on the reactions of *trans*-$[Rh(L)_2Cl_2]^+$ is not as marked as in nucleophilic substitutions on other co-ordination

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* $k_{obs.}$ Would be equal to $\frac{k\,K_{IP}\,\gamma_{\pm}^2[X^-]}{1 + K_{IP}\,\gamma_{\pm}^2\,[X^-]} + k_{(m\rightarrow t)}$, where k is the first-order rate constant for 'isomerization' of the ion pair.

† The mean ionic activity coefficient, $\gamma_{\pm}$, is assumed to be unity.

‡ A specific solvation effect of the reactive NAs ligand may also contribute to the extraordinarily high values of m. We are grateful to one of the referees for this suggestion.

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compounds such as square-planar platinum(II) complexes. The *mer* ⟶ *trans* conversion has a reactivity sequence Cl < Br < I for the leaving halide, opposite to the sequence usually found in substitution reactions of rhodium(III) complexes in aqueous solution.[23-25] This peculiar behaviour is probably related to differences in the solvation energy of the outgoing halide ions in the activated complex in going from water to alcohols. In fact, the enthalpy of activation, which appears to be most important in determining the observed variation of reactivity with the solvent, depends significantly both on the contribution from the increased solvation of the leaving group in going from the ground state to the activated complex and on the energy required to break the Rh–X bond in order to attain the transition-state configuration. Another contribution in water would be given by the enthalpy of solvation of the outgoing halides, which is in the order Cl < Br < I for the free anions.[26] This would lead to a reactivity order I < Br < Cl. In the less solvating alcohols the energy required to break the Rh–X bond, which is expected to be in the order I < Br < Cl,[27] tends to be larger than the solvation contribution, thus causing the sequence of reactivity Cl < Br < I. The low reactivity observed for X = SCN is then regarded as a consequence of the strong affinity of Rh^{III} for sulphur. In agreement with the above considerations, a reactivity sequence I < Br < Cl is also expected in water (Y 3.49) for the *mer* ⟶ *trans* conversion, provided that the relation between log $k_{(m\rightarrow t)}$ and Y still holds for values of Y outside the range explored.

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