Solvent Effects on Rates and Equilibria of Chelate Ring-closure $\rightleftharpoons$ Ring-opening Nucleophilic Substitution Reactions of Octahedral Rhodium(III) Complexes

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The solvent effects on rates and equilibria of reversible reactions (i) have been studied [X^{n-} = SCN^-,

$$mer\text{-}[RhL(L')Cl_2X]^{1-n} \rightleftharpoons trans\text{-}[RhL_2Cl_2]^+ + X^{n-} \quad \text{(i)}$$

$SeCN^-$, N_3^-, NO_2^-, or pyridine; L and L′ = (*o*-dimethylaminophenyl)dimethylarsine-*NAs* and -*As* respectively]. When X^{n-} is pyridine the reactions are both kinetically and thermodynamically independent of the nature of the solvent. When X^{n-} is anionic the equilibria and the rates of ring closure [forward reactions (i)] are strongly affected by the solvent as well as by the leaving group. Linear free-energy relationships of type (ii) exist for the activation and standard free energies of

$$\Delta G_{(m\rightarrow t)}{}^{\ddagger} = \alpha \Delta G_{(m\rightarrow t)}{}^{\ominus} + \beta \quad \text{(ii)}$$

either reactions of different *mer* complexes carried out in a given solvent or reactions of a given *mer* complex carried out in different solvents. An analysis of the solvent effect through Grunwald–Winstein or Kamlet–Taft relationships enables the observed results to be interpreted in terms of a dissociative mechanism for forward reactions (i).

In a previous paper [1] the rates and equilibria of the reversible reactions (1) * in methanol ($I = 5.14 \times 10^{-2}$ mol dm^{-3}) were described [X^{n-} = SCN^-, $SeCN^-$, N_3^-, or NO_2^-; L and L′ = (*o*-dimethylaminophenyl)dimethylarsine-*NAs* and -*As* respectively]. It was found that the equilibrium constants and the rates of the forward (ring-closure) reactions (1) were significantly dependent on the nature of the leaving ligand, with activation and standard free energies which obey relationship (2) (α = 0.75). On the other hand, the second-order rate constants of the reverse (ring-opening) reactions (1) were scarcely affected by the nature of X^{n-}, which acts in this case as the entering group.

$$mer\text{-}[RhL(L')Cl_2X]^{1-n} \underset{k_{(t\rightarrow m)}}{\overset{k_{(m\rightarrow t)}}{\rightleftharpoons}} trans\text{-}[RhL_2Cl_2]^+ + X^{n-} \quad (1)$$

$$\Delta G_{(m\rightarrow t)}{}^{\ddagger} = \alpha \Delta G_{(m\rightarrow t)}{}^{\ominus} + \beta \qquad (2)$$

The present paper concerns the investigation of the rates and equilibria of reactions (1) [X^{n-} as above and also pyridine (py)] in hydroxylic solvents.

Experimental

Materials.—The complexes *mer*-[RhL(L′)Cl_2X] (X^- = SCN^-, $SeCN^-$, N_3^-, or NO_2^-), *mer*-[RhL(L′)Cl_2(py)][ClO_4], and *trans*-[RhL_2Cl_2][ClO_4] were prepared as described previously.[1] Pyridine was purified by distillation over K[OH] pellets.

The solvents were commercial materials of reagent grade. Ethanol and 2-methylpropan-2-ol (Bu^{t}OH) were used without further purification. Dried methanol was cautiously distilled in the presence of small amounts of toluene-*p*-sulphonic acid. Ethane-1,2-diol was treated with anhydrous sodium sulphate, decanted, and fractionally distilled under vacuum. Propan-1-ol (1-PrOH), propan-2-ol (2-PrOH), and 2-methoxyethanol ($MeOC_2H_4OH$) were fractionally distilled.

Preparation and Analysis of the Reaction Mixtures.—The reactions were followed spectrophotometrically, taking advantage of the high differences between the absorbances of the *mer* complexes and *trans*-[RhL_2Cl_2]$^+$ in the 250—360 nm region.[1] As a rule, the reactions were carried out using the *mer* complexes as starting compounds and were followed either by scanning the absorption spectra of the reacting mixtures in the range 250—350 nm at suitable time intervals or by recording the absorbance at a selected wavelength against time. Stock solutions of *mer* complexes were prepared by dissolution of weighed quantities of complexes at 0 °C, where the conversion to the *trans* form was usually negligible over 2—3 h. Sometimes [*e.g.* when $C_2H_4(OH)_2$ or 2-PrOH was used] filtration of the solutions was required to eliminate some undissolved material. In these cases the initial concentrations of the complexes were evaluated spectrophotometrically from the molar absorbances of solutions prepared by dissolving weighed quantities of *mer* complexes in the presence of an excess of X^-.

The reactions were initiated by introducing 0.50 cm^3 of a stock solution of the *mer* complex, rapidly (15—20 s) brought to the required temperature, into a 1-cm silica cell containing 3.00 cm^3 of solvent maintained in the thermostatically controlled cell compartment of an Optica CF4R spectrophotometer. The time of mixing was taken as the starting time of the reaction. By this procedure the progress of the reactions during preliminary handling was small enough to be ignored. The reactions with X^{n-} = py were followed also using *trans*-[RhL_2Cl_2]$^+$ as starting complex, and were initiated by mixing appropriate volumes of thermostatted stock solutions of both *trans*-[RhL_2Cl_2][ClO_4] and pyridine in the silica cell.

All the reactions exhibited the expected isosbestic points over their entire courses. The final spectra of mixtures for which the reactions had gone to completion were as expected

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* The *mer* designation indicates that X^{n-} and the *trans* chlorides lie in the same meridional plane.

Table 1. Rate and equilibrium constants and activation parameters [a] for reactions (1) of *mer*-$[RhL(L')Cl_2(py)][ClO_4]$ in hydroxylic solvents

Solvent	$\frac{\theta_c}{°C}$	$\frac{k_{(m\rightarrow t)}}{s^{-1}}$	$\frac{\Delta H_{(m\rightarrow t)}{}^{\ddagger}}{kJ\ mol^{-1}}$	$\frac{\Delta S_{(m\rightarrow t)}{}^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$	$\frac{k_{(t\rightarrow m)}}{dm^3\ mol^{-1}\ s^{-1}}$	$\frac{\Delta H_{(t\rightarrow m)}{}^{\ddagger}}{kJ\ mol^{-1}}$	$\frac{\Delta S_{(t\rightarrow m)}{}^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$	$\frac{K_{eq.}}{mol\ dm^{-3}}$
MeOH [b]	30.0	5.15×10^{-4}	94	1	3.64×10^{-2}	65	−53	
EtOH	30.0	4.54×10^{-4}			7.70×10^{-2}			6.25×10^{-3}
	50.0	4.44×10^{-3}	90	−11	4.10×10^{-1}	66	−50	1.05×10^{-2}
$MeOC_2H_4OH$	30.0	4.42×10^{-4}			3.87×10^{-2}			1.25×10^{-2}
	50.0	4.72×10^{-3}	94	0	2.17×10^{-1}	68	−49	2.33×10^{-2}
1-PrOH	30.0	3.79×10^{-4}			8.67×10^{-2}			5.55×10^{-3}
	50.0	4.07×10^{-3}	95	2	4.20×10^{-1}	62	−62	9.52×10^{-3}
2-PrOH	30.0	3.58×10^{-4}			1.20×10^{-1}			2.94×10^{-3}
	50.0	3.77×10^{-3}	93	−3	5.50×10^{-1}	59	−68	6.25×10^{-3}
Bu^{t}OH	30.0	4.52×10^{-4}			1.12×10^{-1}			5.55×10^{-3}

[a] $k_{(m\rightarrow t)}$ and $k_{(t\rightarrow m)}$ ± 3%; $\Delta H^{\ddagger}$ ± 4 kJ mol^{-1}; $\Delta S^{\ddagger}$ ± 12 J K^{-1} mol^{-1}; $K_{eq.}$ ± 10%; activation parameters evaluated assuming linearity of log k/T *vs.* $1/T$. [b] Values taken from ref. 1.

Table 2. Rate and equilibrium constants and activation parameters [a] for reactions (1) of *mer*-$[RhL(L')Cl_2(N_3)]$ in hydroxylic solvents

Solvent	Range of substrate concentration explored / mol dm^{-3}	$\frac{\theta_c}{°C}$	$\frac{k_{(m\rightarrow t)}}{s^{-1}}$	$\frac{\Delta H_{(m\rightarrow t)}{}^{\ddagger}}{kJ\ mol^{-1}}$	$\frac{\Delta S_{(m\rightarrow t)}{}^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$	$\frac{K_{eq.}}{mol\ dm^{-3}}$	$\frac{k_{(t\rightarrow m)}{}^{b}}{dm^3\ mol^{-1}\ s^{-1}}$
$C_2H_4(OH)_2$	9.2×10^{-6}—4.3×10^{-5}	30.0	7.50×10^{-5}	84	−46	*ca.* 2.5×10^{-4}	*ca.* 0.2
		40.0	2.06×10^{-4}				
		50.0	5.95×10^{-4}			*ca.* 3.3×10^{-4}	*ca.* 1
MeOH	1.4×10^{-5}—7.7×10^{-5}	30.0	2.73×10^{-5}	85	−50	4.3×10^{-5}	0.63
		40.0	8.75×10^{-5}			5.5×10^{-5}	1.6
		50.0	2.38×10^{-4}			4.5×10^{-5}	5.3
EtOH [c]	2.1×10^{-5}—3.9×10^{-5}	50.0	4.0×10^{-5}			8.3×10^{-6}	4.8
$MeOC_2H_4OH$ [c]	1.4×10^{-5}—4.9×10^{-5}	50.0	1.1×10^{-5}			9.1×10^{-7}	12
1-PrOH [c]	6.6×10^{-6}—2.1×10^{-5}	50.0	2.0×10^{-5}			2.8×10^{-6}	7

[a] $k_{(m\rightarrow t)}$ ± 3%; $K_{eq.}$ ± 10%; $\Delta H_{(m\rightarrow t)}{}^{\ddagger}$ ± 4 kJ mol^{-1}; $\Delta S_{(m\rightarrow t)}{}^{\ddagger}$ ± 12 J K^{-1} mol^{-1}; activation parameters evaluated assuming linearity of log k/T *vs.* $1/T$. [b] Values obtained from equation (7). [c] $k_{(m\rightarrow t)}$ ± 6%; $K_{eq.}$ ± 20%.

Table 3. Rate and equilibrium constants and activation parameters [a] for reactions (1) of *mer*-$[RhL(L')Cl_2(SCN)]$ in hydroxylic solvents

Solvent	Range of substrate concentration explored / mol dm^{-3}	$\frac{\theta_c}{°C}$	$\frac{k_{(m\rightarrow t)}}{s^{-1}}$	$\frac{\Delta H_{(m\rightarrow t)}{}^{\ddagger}}{kJ\ mol^{-1}}$	$\frac{\Delta S_{(m\rightarrow t)}{}^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$	$\frac{K_{eq.}}{mol\ dm^{-3}}$	$\frac{k_{(t\rightarrow m)}{}^{b}}{dm^3\ mol^{-1}\ s^{-1}}$
$C_2H_4(OH)_2$	8.2×10^{-6}—7.3×10^{-5}	30.0	1.02×10^{-3}	79	—42	$>10^{-2}$	
		40.0	2.78×10^{-3}				
		50.0	7.40×10^{-3}			$>10^{-2}$	
MeOH	1.9×10^{-5}—7.4×10^{-5}	30.0	4.19×10^{-4}	86	—25	3.6×10^{-4}	1.2
		40.0	1.23×10^{-3}			3.3×10^{-4}	3.7
		50.0	3.56×10^{-3}			4.8×10^{-4}	7.4
EtOH	1.6×10^{-5}—5.8×10^{-5}	30.0	6.73×10^{-5}	88	−35	3.4×10^{-5}	2.0
		40.0	2.05×10^{-4}			4.8×10^{-5}	4.3
		50.0	6.35×10^{-4}			5.9×10^{-5}	11
$MeOC_2H_4OH$	1.0×10^{-5}—5.1×10^{-5}	30.0	6.91×10^{-5}	80	—59	4.5×10^{-5}	1.5
		40.0	1.86×10^{-4}			4.3×10^{-5}	4.3
		50.0	5.15×10^{-4}			3.7×10^{-5}	14
1-PrOH [c]	1.1×10^{-5}—3.9×10^{-5}	50.0	2.95×10^{-4}			2.0×10^{-5}	15
2-PrOH [c]	5.6×10^{-6}—5.1×10^{-5}	50.0	1.1×10^{-4}			3.3×10^{-6}	33

[a] $k_{(m\rightarrow t)}$ ± 3%; $K_{eq.}$ ± 10%; $\Delta H_{(m\rightarrow t)}{}^{\ddagger}$ ± 4 kJ mol^{-1}; $\Delta S_{(m\rightarrow t)}{}^{\ddagger}$ ± 12 J K^{-1} mol^{-1}; activation parameters evaluated assuming linearity of log k/T *vs.* $1/T$. [b] Values obtained from equation (7). [c] $k_{(m\rightarrow t)}$ ± 6%; $K_{eq.}$ ± 20%.

for systems (1). On the other hand, reactions which went to an equilibrium gave final spectra fully consistent with those of appropriate mixtures of *mer* and *trans* complexes.

The initial concentrations of *mer*-$[RhL(L')Cl_2X]$ in the reaction mixtures were varied over the range reported in Tables 2—5. At least four runs with different initial concentrations of the *mer* complexes were performed for each complex at each temperature and in each solvent. The initial concentration of *trans*-$[RhL_2Cl_2][ClO_4]$ in the reactions with pyridine was in the range 3×10^{-5}—2×10^{-4} mol dm^{-3},* and that of pyridine was varied in the ranges 2.13×10^{-3}—1.06×10^{-1} (EtOH, 2-PrOH, $MeOC_2H_4OH$), 2.11×10^{-3}—8.87×10^{-2} (Bu^{t}OH), or 2.48×10^{-3}—1.24×10^{-1} mol dm^{-3} (1-PrOH). At least seven runs with different concentrations of pyridine

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* Lower concentrations were used in Bu^{t}OH where the complex is sparingly soluble.

Table 4. Rate and equilibrium constants and activation parameters[a] for reactions (1) of *mer*-[RhL(L′)Cl$_2$(SeCN)] in hydroxylic solvents

Solvent	Range of substrate concentration explored / mol dm^{-3}	θ_c / °C	$k_{(m \rightarrow t)}$ / s^{-1}	$\Delta H_{(m \rightarrow t)}^{\ddagger}$ / kJ mol^{-1}	$\Delta S_{(m \rightarrow t)}^{\ddagger}$ / J K^{-1} mol^{-1}	$K_{eq.}$ / mol dm^{-3}	$k_{(t \rightarrow m)}$[b] / dm^3 mol^{-1} s^{-1}
$C_2H_4(OH)_2$	6.2×10^{-6}—3.6×10^{-5}	30.0	2.00×10^{-4}	89	−19	$>10^{-2}$	
		40.0	9.10×10^{-4}				
		50.0	2.72×10^{-3}			$>10^{-2}$	
MeOH	9.9×10^{-6}—7.4×10^{-5}	30.0	1.06×10^{-4}	88	−32	6.2×10^{-5}	1.7
		40.0	3.13×10^{-4}			7.7×10^{-5}	4.1
		50.0	9.87×10^{-4}			10×10^{-5}	9.9
EtOH	1.4×10^{-5}—6.7×10^{-5}	30.0	2.00×10^{-5}	85	−56	4.5×10^{-6}	4.4
		40.0	6.21×10^{-5}			7.1×10^{-6}	8.7
		50.0	1.69×10^{-4}			8.3×10^{-6}	20
$MeOC_2H_4OH$	8.0×10^{-6}—1.2×10^{-5}	30.0	1.97×10^{-5}	85	−55	1.0×10^{-5}	2.0
		40.0	6.03×10^{-5}			1.3×10^{-5}	4.6
		50.0	1.65×10^{-4}			1.1×10^{-5}	15
1-PrOH[c]	9.6×10^{-6}—5.0×10^{-5}	50.0	7.0×10^{-5}			2×10^{-6}	35

[a] $k_{(m \rightarrow t)} \pm 3\%$; $K_{eq.} \pm 10\%$; $\Delta H_{(m \rightarrow t)}^{\ddagger} \pm 4$ kJ mol^{-1}; $\Delta S_{(m \rightarrow t)}^{\ddagger} \pm 12$ J K^{-1} mol^{-1}; activation parameters evaluated assuming linearity of log k/T *vs.* $1/T$. [b] Values obtained from equation (7). [c] $k_{(m \rightarrow t)} \pm 6\%$; $K_{eq.} \pm 20\%$.

Table 5. Rate and equilibrium constants and activation parameters[a] for reactions (1) of *mer*-[RhL(L′)Cl$_2$(NO$_2$)] in hydroxylic solvents

Solvent	Range of substrate concentration explored / mol dm^{-3}	θ_c / °C	$k_{(m \rightarrow t)}$ / s^{-1}	$\Delta H_{(m \rightarrow t)}^{\ddagger}$ / kJ mol^{-1}	$\Delta S_{(m \rightarrow t)}^{\ddagger}$ / J K^{-1} mol^{-1}	$K_{eq.}$ / mol dm^{-3}	$k_{(t \rightarrow m)}$[b] / dm^3 mol^{-1} s^{-1}
MeOH	2.0×10^{-5}—1.4×10^{-4}	30.0	7.68×10^{-4}	82	−34	2.3×10^{-3}	0.33
		40.0	2.20×10^{-3}				
		50.0	6.16×10^{-3}			3.0×10^{-3}	2.0
EtOH	1.4×10^{-5}—9.4×10^{-5}	30.0	9.42×10^{-5}	89	−30	1.9×10^{-4}	0.50
		40.0	3.05×10^{-4}			3.3×10^{-4}	0.92
		50.0	8.95×10^{-4}			3.7×10^{-4}	2.4
$MeOC_2H_4OH$	1.6×10^{-5}—8.3×10^{-5}	30.0	4.52×10^{-5}	85	−47	5.6×10^{-5}	0.81
		40.0	1.41×10^{-4}			7.7×10^{-5}	1.8
		50.0	3.80×10^{-4}			9.1×10^{-5}	4.2
1-PrOH	1.0×10^{-5}—7.4×10^{-5}	30.0	5.31×10^{-5}	82	−56	4.8×10^{-5}	1.1
		40.0	1.55×10^{-4}			8.3×10^{-5}	1.9
		50.0	4.13×10^{-4}			1.1×10^{-4}	3.8
2-PrOH[c]	1.5×10^{-5}—4.2×10^{-5}	50.0	1.2×10^{-4}			1.2×10^{-5}	10

[a] $k_{(m \rightarrow t)} \pm 3\%$; $K_{eq.} \pm 10\%$; $\Delta H^{\ddagger}_{(m \rightarrow t)} \pm 4$ kJ mol^{-1}; $\Delta S_{(m \rightarrow t)}^{\ddagger} \pm 12$ J K^{-1} mol^{-1}; activation parameters evaluated assuming linearity of log k/T *vs.* $1/T$. [b] Values obtained from equation (7). [c] $k_{(m \rightarrow t)} \pm 8\%$; $K_{eq.} \pm 20\%$.

were performed at each temperature and in each solvent (Table 1).

Results

Reactions (1) with X^{n-} = pyridine were followed kinetically starting either from the *trans* or *mer* complexes. The forward reaction, carried out in the absence of added pyridine, went to completion in all the solvents used, following a first-order rate law, the values of the rate constant, $k_{(m \rightarrow t)}$, being collected in Table 1. The reverse (ring-opening) reactions (1), carried out in the presence of an excess of pyridine, progressed only partially, showing the same kinetic behaviour previously found in methanol.[2] In particular, the observed rate constant for the approach to equilibrium, $k_{obs.}$, exhibited form (3). The values of $k_{(t \rightarrow m)}$ derived from equation (3), and those of $K_{eq.}$

$$k_{obs.} = k_{(t \rightarrow m)}[py] + k_{(m \rightarrow t)} \tag{3}$$

obtained as previously described for such reactions in methanol,[2] are also collected in Table 1.

Reactions (1) with X^{n-} = SCN$^-$, SeCN$^-$, N$_3^-$, or NO$_2^-$ have been investigated only using pure *mer*-[RhL(L′)Cl$_2$X] as the starting rhodium(III) complex. The reactions of thiocyanato- or selenocyanato-complexes in ethane-1,2-diol were found to go to completion following a first-order rate law. The reactions of the nitro-complex were too fast to be followed in this solvent. On the other hand, the reactions of *mer*-[RhL(L′)Cl$_2$(N$_3$)] in ethane-1,2-diol, as well as those of all the *mer* complexes in the other solvents employed, progressed only partially, the equilibrium being increasingly displaced towards the products as the starting concentration of the *mer* complexes was decreased. These reactions were found to follow relationship (4) which is the integrated form of rate law (5). The equilibrium constants, $K_{eq.}$, were obtained from

$$\ln\left\{\frac{[mer]_0^2 - [mer][mer]_{eq.}}{[mer]_0([mer] - [mer]_{eq.})}\right\} = k_{(m \rightarrow t)}\left\{\frac{[mer]_0 + [mer]_{eq.}}{[mer]_0 - [mer]_{eq.}}\right\}t \tag{4}$$

$$-d[mer]/dt = k_{(m \rightarrow t)}[mer] - k_{(t \rightarrow m)}[trans][X^{n-}] \tag{5}$$

relationship (6). The values of $k_{(m \rightarrow t)}$ and $K_{eq.}$ obtained from equations (5) and (6) using different initial concentrations of *mer* complexes agreed within the experimental errors. The mean values are collected in Tables 2—5 together with the

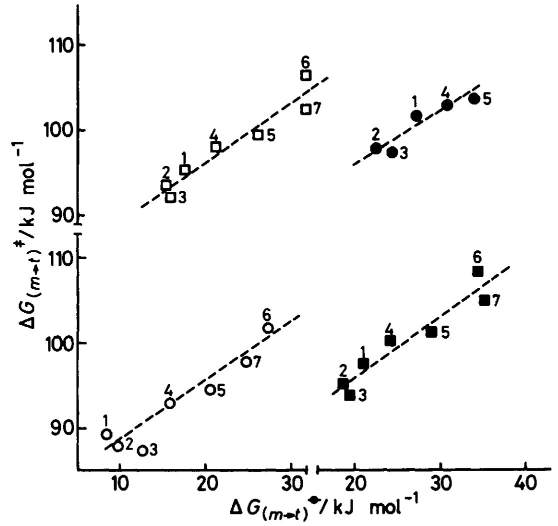

Figure 1. Relationships between the free energy of activation and the standard free energy of the *mer*-[RhL(L′)Cl$_2$X] ⟶ *trans*-[RhL$_2$Cl$_2$]$^+$ + X$^-$ reaction in methanol (○), ethanol (□), propan-1-ol (■), and propan-2-ol (●). X$^-$ = Cl$^-$ (1), Br$^-$ (2), I$^-$ (3), NO$_2^-$ (4), SCN$^-$ (5), N$_3^-$ (6), and SeCN$^-$ (7)

$$K_{eq.} = \frac{[trans]_{eq.}[X^{n-}]_{eq.}}{[mer]_{eq.}} = \frac{[mer]_0}{[(A_0 - A_\infty)/(A_0 - A_{eq.})][(A_0 - A_\infty)/(A_0 - A_{eq.}) - 1]} \qquad (6)$$

values of $k_{(t\rightarrow m)}$ derived from relationship (7) previously found

$$k_{(t\rightarrow m)} = k_{(m\rightarrow t)}/K_{eq.} \qquad (7)$$

to be valid for this type of reaction.[1–4]

Discussion

Both forward and reverse reactions (1) involving pyridine display activation parameters and equilibrium constants which are essentially independent of the nature of the solvent (Table 1). A very small solvent effect is expected for these reactions, where neutralization or separation of charges is not involved, provided that similar changes of solvation energies of the species involved are observed on changing the solvent.[5] In this connection it must be noted that the transfer free energy of uncharged ligands such as pyridine in non-aqueous solvents is generally relatively small [6] so that the transfer free energy of *mer*-[RhL(L′)Cl$_2$(py)]$^+$ must be close to that of *trans*-[RhL$_2$Cl$_2$]$^+$ since the standard free energy of the reaction under discussion is independent of the nature of the solvent.

A different kinetic and thermodynamic effect is displayed by reactions (1) with anionic X^{n-} groups. In these cases the second-order rate constants of the reverse (ring-opening) reactions (1) are still relatively little affected by the nature of the solvent, as well as by the entering ligand, although some trends may be discerned (Tables 2—5). Conversely, the forward (ring-closure) reactions (1) are both kinetically and thermodynamically strongly affected by the solvent and by the leaving X^{n-}. The effect of the leaving group is roughly the same in all the solvents used (N$_3^-$, SeCN$^-$ < SCN$^-$ < NO$_2^-$; Tables 2—5 and Figure 1). In these cases a linear relationship of type (2), which also fits the data available for X^{n-} = halide,[3] roughly correlates $\Delta G_{(m\rightarrow t)}^{\ddagger}$ to $\Delta G_{(m\rightarrow t)}^{\ominus}$ in each solvent, the values of α being nearly independent of the solvent considered [0.71 (MeOH), 0.70 (EtOH), 0.73 (1-PrOH), 0.62 (2-PrOH), and 0.84 (MeOC$_2$H$_4$OH) *]. Such values for α suggest that the driving forces which control the thermodynamics of the ring-closure processes under discussion are operative even in the activation process, implying the occurrence of an extensive separation of charges in the activated complex. The highly negative entropies of activation, $\Delta S_{(m\rightarrow t)}^{\ddagger}$, of these reactions can also be explained on this basis, since increasing solvation is expected on going from the complex in its ground state to the strongly dipolar activated complex. Although values of α lower than 1 are usually considered as indicative of a mechanism with an associative mode of activation,[7] arguments have been presented previously which account for such values by the occurrence of a dissociative mechanism, *D*, involving a long-lived five-co-ordinate intermediate [equations (8) † and (9)].

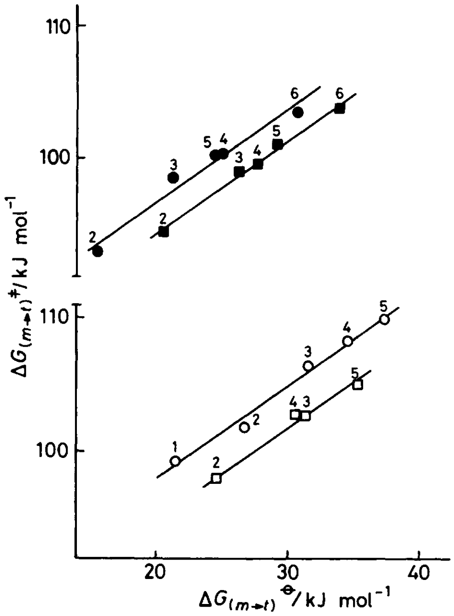

Figure 2. Relationships between the free energy of activation and the standard free energy of the *mer*-[RhL(L′)Cl$_2$X] ⟶ *trans*-[RhL$_2$Cl$_2$]$^+$ + X$^-$ reactions on changing the solvent. X$^-$ = SeCN$^-$ (□), N$_3^-$ (○), SCN$^-$ (■), or NO$_2^-$ (●). Solvent = C$_2$H$_4$(OH)$_2$ (1), MeOH (2), EtOH (3), MeOC$_2$H$_4$OH (4), 1-PrOH (5), and 2-PrOH (6)

$$\underset{(mer)}{\text{XRh–AsN}} \underset{k_3}{\overset{k_4}{\rightleftharpoons}} \underset{\text{(reactive intermediate)}}{\text{Rh–AsN}^+} + X^- \qquad (8)$$

$$\text{Rh–AsN}^+ \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \underset{(trans)}{\text{Rh(AsN)}^+} \qquad (9)$$

As far as the solvent effect is concerned, the forward (ring-closure) reactions (1) are invariably both kinetically and thermodynamically favoured by changing the solvent in the sequence 2-PrOH < 1-PrOH < MeOC$_2$H$_4$OH < EtOH < MeOH < C$_2$H$_4$(OH)$_2$, a relationship of type (2) (Figure 2) holding for each substrate [α = 0.70 (N$_3^-$ or SCN$^-$), 0.68 (SeCN$^-$), and 0.71 (NO$_2^-$)]. In these cases, changes of $\Delta G_{(m\rightarrow t)}^{\ominus}$ on changing the solvent are expected to stem only

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* Data for X^{n-} = halide are not available for this solvent.

† The slight dependence of $k_{(t\rightarrow m)}$ (*i.e.* k_1k_3/k_2) on the nature of the entering group can be explained by the associative nature of the k_3 rate step.

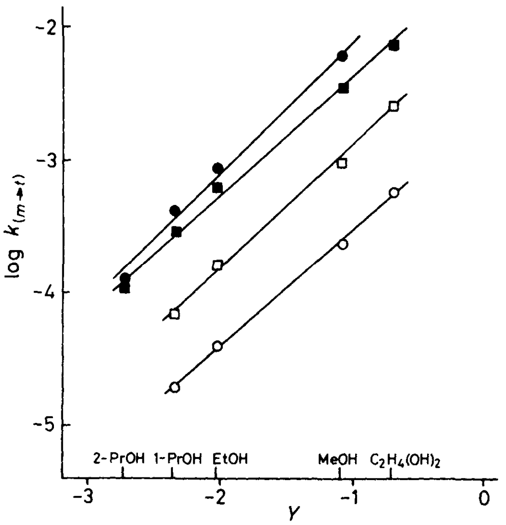

Figure 3. Dependence of log $k_{(m\rightarrow t)}$ at 50 °C on Y values for the reaction *mer*-[RhL(L')Cl_2X] $\longrightarrow$ *trans*-[RhL_2Cl_2]$^+$ + X^-. X^- = $SeCN^-$ (□), N_3^- (○), SCN^- (■), or NO_2^- (●)

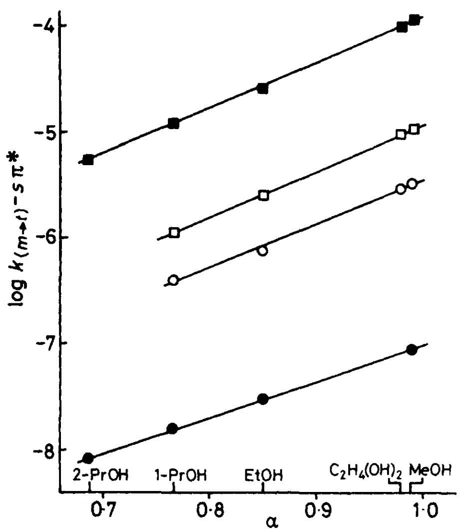

Figure 4. Variation of log $k_{(m\rightarrow t)} - s\pi^*$ at 50 °C with α of the solvents for *mer*-[RhL(L')Cl_2X] $\longrightarrow$ *trans*-[RhL_2Cl_2]$^+$ + X^- reactions. X^- = $SeCN^-$ (□), N_3^- (○), SCN^- (■), or NO_2^- (●)

from solute–solvent interactions, other factors (*e.g.* the Rh–X bond rupture) being unchanged. Therefore, the occurrence of relationship (2) suggests that the effect of the solvent on the reactivity is mainly governed by the same changes of solute–solvent interactions which control the thermodynamic behaviour of these reactions. This is in agreement with the above mechanism, where the transition state of the k_4 rate-determining step would resemble the reaction products at least as far as the leaving group and charge separation are concerned.

Further information on the intimate mechanism can be obtained by analysing the solvent effect with the aid of the several scales of solvent polarity now available.[8–10] Thus, the Grunwald–Winstein Y parameters have often been used to interpret the solvent effect in nucleophilic substitution reactions of octahedral complexes.[3,11] It is found here that the reactivity of each *mer* complex towards ring closure [log $k_{(m\rightarrow t)}$ at 50 °C] is linearly correlated to Y values by relationship (10) * (Figure 3), the values of m being close to 1.0, which is

$$\log k_{(m\rightarrow t)} = mY + C \qquad (10)$$

the standard value for the dissociative solvolysis of t-butyl chloride, and comparable with values previously found for *mer* complexes with X^{n-} = halide [m = 0.88 (N_3^- or SCN^-), 0.93 ($SeCN^-$), 1.02 (NO_2^-), 0.95 (I^- at 25 °C),[3] 1.19 (Br^- at 25 °C),[3] and 1.24 (Cl^- at 25 °C)[3]]. These values are much higher than those usually found (0.2—0.4) in dissociative nucleophilic substitution reactions of other octahedral complexes.[11,13] On the other hand, they are fully consistent with the occurrence of a dissociative mechanism D and strongly suggest that Rh–X bond rupture in the transition state of the k_4 rate-determining step is extensive, if not already complete.[3,11] A deeper knowledge of the specific role played by the solvent in affecting both rates and equilibria of the reactions under examination may be attained by analysing the observed solvent effects in terms of multiparametric equations.[9] The Kamlet and Taft equation (11)[14–16] is particularly suitable, since it refers to reactions not involving hydrogen bond donor acid

$$XYZ = XYZ_0 + s\pi^* + a\alpha' \qquad (11)$$

solutes, just as those examined in this paper [α' and π* measure the solvent ability to donate a proton and its polarization–polarizability, respectively]. It is found that the effects of the solvent on the rates and equilibria of the present ring-closure processes are quantified at 50 °C by equation (11) (*e.g.* Figure 4), with values of s and a always positive [s and a, for log $k_{(m\rightarrow t)}$: 3.191 and 4.091 (N_3^-), 2.590 and 4.254 (SCN^-), 3.372 and 4.344 ($SeCN^-$), and 8.259 and 3.422 (NO_2^-); for log $K_{eq.}$: 6.227 and 3.924 (N_3^-), 6.348 and 5.314 (SCN^-), and 7.234 and 5.833 (NO_2^-)].† A positive value of a reasonably reflects the contribution of the hydrogen bond donor acidity of the solvent in stabilizing the outgoing X^{n-}. Rather similar values of a are found for log $k_{(m\rightarrow t)}$ and log $K_{eq.}$, suggesting that solvation of the outgoing group, X^{n-}, in the activated complex has already reached a rather similar extent to that of a fully solvated anion. The positive values for s are attributable to increased stabilization of extensively dipolar transition states, or oppositely charged reaction products, on increasing the polarization–polarizability of the solvent. A tentative comparison of s values would suggest that the polarization–polarizability of the solvent is more effective in stabilizing the reaction products than the activated complex. This could be explained by taking into consideration that the charges are fully separated only in the reaction products.

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* Y values for propan-1-ol (−2.35) and ethane-1,2-diol (−0.70) have been derived by interpolation from the relationship existing between Kosower Z values and Y values for hydroxylic solvents,[8,12] and they fit very well the experimental results (Figure 3).

† Equation (11) gives a rather poor fit to log $K_{eq.}$ of the SCN and NO_2 complexes.

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