

Kinetics and Equilibria of Reversible Chelate Ring-opening Nucleophilic Substitution Reactions of [(*o*-Dimethylaminophenyl)dimethylarsine]-rhodium(III) Complexes

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The kinetics and equilibria of the reversible reactions $trans\text{-}[\text{RhL}_2\text{Cl}_2]^+ + \text{X}^{n-} \rightleftharpoons mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2\text{X}]^{1-n}$ have been studied in methanol [$\text{X}^{n-} = \text{SCN}^-$, SeCN^- , NO_2^- , N_3^- , or pyridine; L and L' = (*o*-dimethylaminophenyl)-dimethylarsine-*NAs* and -*As* respectively]. The second-order rate constants of the forward reactions are scarcely affected by the nature of the entering group, whereas the first-order rate constants of the reverse reactions are strongly influenced by the leaving group involved. A linear free-energy relationship of the type $\Delta G_{(m \rightarrow t)}^\ddagger = \alpha \Delta G_{(m \rightarrow t)}^\ominus + \beta$ with a value of α of 0.75 exists for the activation and standard free energies of $mer \rightarrow trans$ reactions where a dissociative mechanism is considered to be operative. When X^{n-} is SCN^- , N_3^- , or NO_2^- , the $mer \rightarrow trans$ reactions are acid-catalyzed, through protonation of the leaving group.

In previous papers¹⁻⁵ a series of kinetic studies of reversible systems (1)* in hydroxylic solvents were described [L and L' = (*o*-dimethylaminophenyl)-dimethylarsine-*NAs* and -*As* respectively; $\text{X}^{n-} = \text{Cl}^-$, Br^- , I^- , thiourea, primary aliphatic amines, or substituted pyridines]. It was found that the rates of the



forward reactions, which involve opening of a chelate ring at the NMe_2 end, were little affected by the nature of the entering X^{n-} , whereas those of the reverse reactions strongly depend on the leaving group, at least when this is a primary aliphatic amine or a substituted pyridine. In these cases, the $mer \rightarrow trans$ reactions obey linear relationships of type (2), with values of α [1.2 (substituted pyridines),³ 0.84 (primary aliphatic amines)⁴] which are

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

consistent with extensive Rh-X bond rupture in the transition state. Although the solvent effect also suggests extensive Rh-X bond breaking for anionic leaving groups, linear relationships of type (2) were not obtained in these cases since only small changes in both $k_{(m \rightarrow t)}$ and K_{eq} , occur on going from $\text{X}^{n-} = \text{Cl}^-$ to Br^- and I^- .⁵ Some further indications as to the mechanism were obtained from the effect of acidity on the rates of the forward and reverse reactions (1) ($\text{X}^{n-} = \text{Cl}^-$, Br^- , or I^-), the former being acid-catalyzed and the latter acid-inhibited.⁵ It has been argued that reversible protonation of the NMe_2 group of L' in both the mer complex and the five-co-ordinate reaction intermediate, $[\text{RhL}(\text{L}')\text{Cl}_2]^+$, is responsible for the observed acidity effect.⁵

This paper concerns an investigation of the rates and equilibria of systems (1) with $\text{X}^{n-} = \text{SCN}^-$, SeCN^- , NO_2^- , or N_3^- , together with the effect of acidity on the $mer \rightarrow trans$ reactions, including that of $mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2(\text{py})]^+$ (py = pyridine). The above anionic ligands were chosen in order to (i) obtain a series of re-

actions of type (1), with anions as reactive groups, with sufficiently large differences between their standard free energies to allow detection of the influence of ΔG^\ominus on the reaction rates, and (ii) investigate the effect of acidity on the rates of the substitution reactions of complexes bearing leaving group ligands which exhibit a residual basic character even when co-ordinated.⁶

EXPERIMENTAL

Materials.—The complex $trans\text{-}[\text{RhL}_2\text{Cl}_2][\text{ClO}_4]$ was prepared from a concentrated methanolic suspension of $mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2]$ (0.5 g), prepared by literature methods,⁷ which was held at 40 °C for 30 min. The resulting clear yellow solution was then stirred with $\text{Na}[\text{ClO}_4]$ (2 g) followed by the addition of small quantities of water.

The complexes $mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2\text{X}]$ ($\text{X}^- = \text{SCN}^-$, SeCN^- , NO_2^- , or N_3^-) and $mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2(\text{py})][\text{ClO}_4]$ were prepared by treating a concentrated methanolic solution of $trans\text{-}[\text{RhL}_2\text{Cl}_2][\text{ClO}_4]$ at 30 °C with an excess of entering group. The complex containing py was isolated as the perchlorate salt, as described above for $trans\text{-}[\text{RhL}_2\text{Cl}_2][\text{ClO}_4]$, while the other complexes spontaneously separated from the solution within 5–40 min as yellow crystals. The products were filtered off, washed with cold methanol, and dried under vacuum (Table 1). Their i.r. spectra (Nujol

TABLE 1
Analytical data for $mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2\text{X}]$,
 $mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2(\text{py})][\text{ClO}_4]$ and $trans\text{-}[\text{RhL}_2\text{Cl}_2][\text{ClO}_4]$

Complex	Analysis/% †			
	C	N	H	Cl
$mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2\text{X}]$				
	X = NO_2	35.8 (35.85)	6.20 (6.25)	4.70 (4.80)
SeCN	34.6 (34.6)	5.70 (5.75)	4.25 (4.40)	9.90 (9.70)
	SCN	37.0 (36.95)	6.15 (6.15)	4.65 (4.75)
N_3	36.1 (36.05)	10.6 (10.5)	4.80 (4.85)	10.6 (10.65)
	$mer\text{-}[\text{RhL}(\text{L}')\text{Cl}_2(\text{py})]\text{-}[\text{ClO}_4]$	37.2 (37.4)	5.25 (5.25)	4.60 (4.65)
$trans\text{-}[\text{RhL}_2\text{Cl}_2][\text{ClO}_4]$	33.5 (33.4)	3.85 (3.90)	4.55 (4.50)	14.8 (14.8)

† Calculated values are given in parentheses.

* The *mer* designation is appropriate only for $\text{X}^{n-} = \text{Cl}^-$. In the other cases it is intended to emphasize that X^{n-} and the *trans*-chlorides lie in the same meridional plane.

mulls) showed a single strong band at 350 cm^{-1} (likewise for *trans*-[RhL₂Cl₂][ClO₄]) attributable to the asymmetric stretching of a *trans* Cl-Rh-Cl unit.^{8,9} This suggests that the Xⁿ⁻ group occupies the meridional position, located between the two *trans* chlorides, vacated by the outgoing labile NMe₂ group of a chelate ligand of *trans*-[RhL₂Cl₂][ClO₄].

The complex *mer*-[RhL(L')Cl₂(NO₂)] exhibits a $\nu_{\text{asym.}}(\text{NO}_2)$ stretching frequency at $1\,323\text{ cm}^{-1}$ but no $\nu_{\text{sym.}}(\text{NO}_2)$ bands at frequencies lower than that of the free ion ($1\,261\text{ cm}^{-1}$), suggesting the presence of a nitro- rather than a nitrito-group.¹⁰ The assignments of M-N or M-S and M-Se bands for the complexes containing SCN⁻ and SeCN⁻ were only tentative. Therefore, it is not yet possible to specify which atom is bonded to rhodium(III), a point which is certainly important, but which is believed not to be essential for the purposes of this paper.

Potassium selenocyanate, sodium thiocyanate, nitrite, azide, toluene-*p*-sulphonate, and toluene-*p*-sulphonic acid (Hpts) were reagent grade. Dried methanol was carefully distilled in the presence of small amounts of Hpts before use.

Preparation of the Reaction Mixtures.—The reactions were carried out in methanol ($I = 5.14 \times 10^{-2}\text{ mol dm}^{-3}$) with sodium toluene-*p*-sulphonate as supporting electrolyte. Stock solutions of the reactants were prepared by weight or by titration (Hpts).*

The reactions were initiated by mixing appropriate volumes of thermostatted stock solutions of the reactants in 1-cm silica cells maintained in the thermostatically controlled cell compartment of an Optica CF4R spectrophotometer. The initial concentrations of the complexes in the reaction mixtures were varied over the range 1.6×10^{-5} – $5.4 \times 10^{-5}\text{ mol dm}^{-3}$. The ranges of concentration of the entering groups in the reactions of the *trans* complexes were (i) 2.57×10^{-3} – 4.28×10^{-2} (SCN⁻), (ii) 3.43×10^{-4} – 5.14×10^{-3} (SeCN⁻), (iii) 5.14×10^{-4} – 5.14×10^{-2} (N₃⁻), and (iv) 3.43×10^{-3} – $5.14 \times 10^{-2}\text{ mol dm}^{-3}$ (NO₂⁻). The reactions with the *mer* complexes were performed in the absence of added Xⁿ⁻ and the ranges of Hpts concentration used in studying the effect of acidity were (i) 1.37×10^{-4} – 2.23×10^{-2} (SCN⁻, py), (ii) 2.57×10^{-3} – 1.54×10^{-2} (SeCN⁻), and (iii) 1.54×10^{-4} – $2.57 \times 10^{-3}\text{ mol dm}^{-3}$ (N₃⁻, NO₂⁻).

The reactions were clean and exhibited the expected isobestic points (Figure 1) over the entire course of the reaction [$\lambda_{\text{iso.}} = 262$ (SeCN⁻ and N₃⁻); 256 (NO₂⁻); $262, 332,$ and 345 nm (SCN⁻) †, ‡]. The final absorption spectrum for reactions which went to completion was quantitatively consistent with that of the expected product. Moreover, addition of Xⁿ⁻ to exhausted non-acidic solutions of the *mer* complexes restored the starting complex.

The progress of the reaction was followed by scanning the absorption spectrum of the reacting mixture in the range 290 – 360 nm at suitable time intervals. Fast reactions were followed by recording absorbance against time at a selected wavelength by conventional or stopped-flow techniques. Series of at least seven runs with different concentrations of entering group were performed for the reactions of the *trans*

* Solutions of *mer* complexes were prepared and maintained at 0°C , at which temperature *mer* \rightarrow *trans* conversions were usually negligible for 2–3 h. They were rapidly heated (15–20 s) to the required temperature before introduction into the reaction vessel.

† $\lambda_{\text{iso.}}$ changes with the acidity (*e.g.* from 332 to 325 nm).

‡ Data below 290 nm were obtained using Na[ClO₄] as supporting electrolyte.

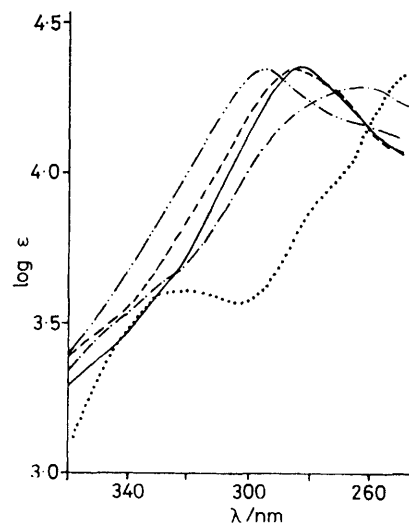


FIGURE 1 U.V. absorption spectra of *trans*-[RhL₂Cl₂][ClO₄] (···), *mer*-[RhL(L')Cl₂(SCN)] (—), *mer*-[RhL(L')Cl₂(SeCN)] (— · — ·), *mer*-[RhL(L')Cl₂(N₃)] (— — —), and *mer*-[RhL(L')Cl₂(NO₂)] (— · — ·) in methanol at 25°C . Data for the last compound are semiquantitative

complex, whereas in the reactions of *mer* complexes at least four different concentrations of the complexes were employed. Six or more different concentrations of Hpts were used in studying the effect of acidity on the *mer* \rightarrow *trans* reactions. The temperatures of reaction are listed in the Tables.

RESULTS

The reactions of *trans*-[RhL₂Cl₂][ClO₄] go to completion only when high concentrations of entering group are used; complete reaction was never achieved with NO₂⁻. The observed rate constants for the approach to equilibrium, k_{obs} , accord with equation (3), which is that usually found for this

$$k_{\text{obs.}} = k_f + k_r = k_{(t \rightarrow m)}[X^{n-}] + k_{(m \rightarrow t)} \quad (3)$$

compound.¹⁻⁵ The $k_{(m \rightarrow t)}$ term was determined independently from reaction mixtures initially containing the *mer* complexes without added Xⁿ⁻. In the concentration ranges explored, the reactions of *mer* complexes containing NO₂⁻ and SCN⁻ as leaving groups went to completion following a first-order rate law, with rate constant $k_{(m \rightarrow t)}$. When N₃⁻ or SeCN⁻ were the leaving groups, the reactions progressed only partially with the equilibrium being increasingly displaced towards the products as the concentration of the *mer* starting complex was decreased. In agreement with equation (3) these reactions follow rate law (4), which leads to the integrated form (5) for [X⁻] = [*trans*].¹¹ The values of $k_{(m \rightarrow t)}$ observed (Table 2) were consistent with those obtained

$$-d[\text{mer}]/dt = d[\text{trans}]/dt = \frac{k_{(m \rightarrow t)}[\text{mer}] - k_{(t \rightarrow m)}[X^-][\text{trans}]}{\ln \left\{ \frac{[\text{mer}]_0^2 - [\text{mer}][\text{mer}]_{\text{eq}}}{[\text{mer}]_0([\text{mer}] - [\text{mer}]_{\text{eq}})} \right\}} = \frac{k_{(m \rightarrow t)} \left\{ \frac{[\text{mer}]_0 + [\text{mer}]_{\text{eq.}}}{[\text{mer}]_0 - [\text{mer}]_{\text{eq.}}} \right\} t}{\quad} \quad (5)$$

from extrapolation of (3) to [X⁻] = 0.

The equilibrium constants of reactions (1) were obtained from equation (6) when *trans*-[RhL₂Cl₂]⁺ was the starting

TABLE 2

Equilibrium and rate constants and activation parameters^a for reactions (1) in methanol ($I = 5.14 \times 10^{-2} \text{ mol dm}^{-3}$)

X^{n-}	$\theta_c / ^\circ\text{C}$	$k_{(m \rightarrow t)}$ s^{-1}	$\Delta H_{(m \rightarrow t)}^\ddagger$ $\Delta S_{(m \rightarrow t)}^\ddagger$		$k_{(t \rightarrow m)}$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta S_{(t \rightarrow m)}^\ddagger$		$k_{(t \rightarrow m)}/k_{(m \rightarrow t)}$ $\text{dm}^3 \text{ mol}^{-1}$	$K_{\text{eq.}}$ $\text{dm}^3 \text{ mol}^{-1}$	$\Delta H_{(t \rightarrow m)}^{\text{ob}}$ $\Delta S_{(t \rightarrow m)}^{\text{ob}}$	
			kJ mol^{-1}	$\text{J K}^{-1} \text{ mol}^{-1}$		$\text{J K}^{-1} \text{ mol}^{-1}$	$\text{J K}^{-1} \text{ mol}^{-1}$			kJ mol^{-1}	$\text{J K}^{-1} \text{ mol}^{-1}$
N_3^-	25.0	1.95×10^{-6}	83	-57	7.94×10^{-2}	69	-35	4.1×10^3	4.5×10^3	-14	22
	45.0	1.70×10^{-4}			4.92×10^{-1}			2.9×10^3	4.0×10^3		
SeCN^-	25.0	6.40×10^{-5}	89	-27	3.42×10^{-1}	69	-22	5.3×10^3	5.0×10^3	-20	5
	45.0	6.48×10^{-4}			2.10			3.2×10^3	3.1×10^3		
SCN^-	25.0	3.08×10^{-4}	82	-36	2.26×10^{-1}	68	-29	734	798	-14	7
	45.0	2.65×10^{-3}			1.37			517	445		
NO_2^-	25.0	4.81×10^{-4}	83	-30	2.74×10^{-2}	79	-10	57	70	-4	20
	45.0	4.15×10^{-3}			2.17×10^{-1}			52	60		
py	25.0	2.68×10^{-4}	94	1	2.34×10^{-2} ^c	65 ^c	-59 ^c	87	95 ^c	-29	-60
	45.0	3.08×10^{-3}			1.29×10^{-1} ^c			42	54 ^c		
Cl^- ^d	25.0	2.86×10^{-3}	69	-63	1.80×10^{-2}	81	-5	6.3	6	12	58
Br^- ^d	25.0	4.43×10^{-3}	73	-44	3.45×10^{-2}	75	-21	7.8	8	2	23
I^- ^d	25.0	6.10×10^{-3}	70	-54	7.03×10^{-2}	79	-3	11.5	12	9	51

^a $k \pm 3\%$, $\Delta H^\ddagger \pm 4 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$, $K_{\text{eq.}} \pm 10\%$. ^b Values obtained from $K_{\text{eq.}} = k_{(t \rightarrow m)}/k_{(m \rightarrow t)}$. Errors: $\Delta H_{(t \rightarrow m)}^{\text{ob}} \pm 6 \text{ kJ mol}^{-1}$, $\Delta S_{(t \rightarrow m)}^{\text{ob}} \pm 18 \text{ J K}^{-1} \text{ mol}^{-1}$. ^c Values taken from ref. 3. ^d Values taken from ref. 5.

complex, and from equation (7) when $\text{mer} \cdot [\text{RhL}(\text{L}')\text{Cl}_2\text{X}]$ ($X^- = \text{N}_3^-$ or SeCN^-) was the starting material. The values obtained (Table 2) agree satisfactorily with $k_{(t \rightarrow m)}/k_{(m \rightarrow t)}$.

$$\frac{1}{(A_0 - A_{\text{eq.}})} = \frac{1}{K_{\text{eq.}}[\text{X}^-](A_0 - A_\infty)} + \frac{1}{(A_0 - A_\infty)} \quad (6)$$

$$K_{\text{eq.}} = \frac{[\text{mer}]_{\text{eq.}}}{[\text{trans}]_{\text{eq.}}[\text{X}^-]_{\text{eq.}}} = \frac{[(A_0 - A_\infty)/(A_0 - A_{\text{eq.}})][(A_0 - A_\infty)/(A_0 - A_{\text{eq.}}) - 1]}{[\text{mer}]_0} \quad (7)$$

The reaction of each *mer* complex ($X^{n-} = \text{SCN}^-$, SeCN^- , NO_2^- , N_3^- , or py) in acidified methanol goes to completion following a first-order rate law.* The dependence of the rate on acidity is a function of the leaving group involved. The observed rate constant, $k_{\text{obs.}}$, of *mer* \rightarrow *trans* reactions of $\text{mer} \cdot [\text{RhL}(\text{L}')\text{Cl}_2(\text{SCN})]$ increases with increasing Hpts concentration (Figure 2) and approaches a limiting value according to equation (8), where $k_{(m \rightarrow t)}^{\text{H}}$ corresponds to k_6 [see equation (13)]. The addition of acid also has a

$$k_{\text{obs.}} = (k_{(m \rightarrow t)} + k_{(m \rightarrow t)}^{\text{H}}K_1[\text{Hpts}]) / (1 + K_1[\text{Hpts}]) \quad (8)$$

catalytic effect on the *mer* \rightarrow *trans* reactions of nitro- and azido-complexes as shown (Tables 2 and 3) by the

TABLE 3

Rate constants and values of K_1 (see text) for reactions (1) in acidic methanol^a

X	θ_c $^\circ\text{C}$	$k_{(m \rightarrow t)}^{\text{H}}$ s^{-1}	$\Delta H_{\text{H}^\ddagger}$ kJ mol^{-1}	$\Delta S_{\text{H}^\ddagger}$ $\text{J K}^{-1} \text{ mol}^{-1}$	K_1 $\text{dm}^3 \text{ mol}^{-1}$
SCN^- ^b	25.0	2.8×10^{-3}			75
	45.0	2.1×10^{-2}			80
N_3^-	20.0	7.10×10^{-2}	77	-6	$> 10^4$
	25.0	1.22×10^{-1}			$> 10^4$
	30.0	2.10×10^{-1}			$> 10^4$
NO_2^-	20.0	4.44×10^{-2}	81	6	$> 10^4$
	25.0	7.74×10^{-2}			$> 10^4$
	30.0	1.33×10^{-1}			$> 10^4$

^a $k_{(m \rightarrow t)}^{\text{H}} \pm 3\%$; $\Delta H_{\text{H}^\ddagger} \pm 4 \text{ kJ mol}^{-1}$; $\Delta S_{\text{H}^\ddagger} \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$.

^b $k_{(m \rightarrow t)}^{\text{H}}$ and $K_1 \pm 10\%$.

marked increase in the observed rate constant (by factors of ca. 1.6×10^2 for NO_2^- and 6×10^3 for N_3^-) on going from

* Completion of the reaction of the azido-complex is probably due to protonation of the leaving N_3^- , whereas decomposition of SeCN^- in acidic solution could account for the irreversibility of the reaction of the selenocyanato-complex.¹² Such decomposition was found to be very fast in methanol.

neutral to Hpts ($10^{-3} \text{ mol dm}^{-3}$) solutions. If equation (8) is assumed to hold in these cases too, it can be concluded that $k_{\text{obs.}}$ has already reached its limiting value at the above Hpts concentration since the rate is little affected by further increases in acid concentration. Thus, the value of K_1 must

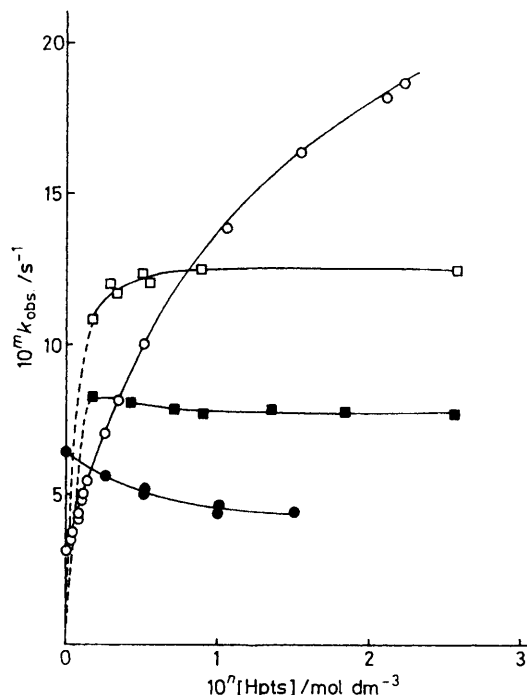


FIGURE 2 Effects of acidity on the *mer* \rightarrow *trans* reactions of $\text{mer} \cdot [\text{RhL}(\text{L}')\text{Cl}_2\text{X}]$ in methanol ($I = 5.14 \times 10^{-2} \text{ mol dm}^{-3}$) at 25°C . $X = \text{SCN}^-$ (\circ , $m = 4$, $n = 2$), SeCN^- (\bullet , $m = 5$, $n = 2$), N_3^- (\square , $m = 2$, $n = 3$), or NO_2^- (\blacksquare , $m = 2$, $n = 3$)

be greater than $10^4 \text{ dm}^3 \text{ mol}^{-1}$ and $k_{\text{obs.}}$ coincident with $k_{(m \rightarrow t)}^{\text{H}}$. In order to obtain more information on the course of these reactions, some runs have been carried out in acidic solutions in the presence of chloride ions. It was found that the final product, $\text{mer} \cdot [\text{RhL}(\text{L}')\text{Cl}_3]$, is never formed directly, $\text{trans} \cdot [\text{RhL}_2\text{Cl}_2]^+$ always being the first reaction product. The values of $k_{(m \rightarrow t)}^{\text{H}}$ and K_1 from equation (8) are given in Table 3.

The *mer* \rightarrow *trans* reaction rate for $\text{mer} \cdot [\text{RhL}(\text{L}')\text{Cl}_2(\text{SeCN})]$ is slightly suppressed by Hpts, a decrease in the rate

$$k_{\text{obs.}} = k_t + k_r = \left(\frac{k_1 k_3}{k_2} + \frac{k_1 k_5 K[\text{H}^+]}{k_2} \right) [\text{X}^-] + \left(\frac{k_4 + k_6 K_1 [\text{H}^+]}{1 + K_1 [\text{H}^+]} \right) \quad (15)$$

$$k_t = k_{(t \rightarrow m)} = k_1 k_3 / k_2; \quad k_r = k_{(m \rightarrow t)} = k_4 \quad (16)$$

mechanism, extensive Rh-X bond rupture occurring in the transition state of the $k_4 = k_{(m \rightarrow t)}$ reaction step accounts for the effect of the leaving group on *mer* \rightarrow *trans* reaction rate, whereas the slight dependence of $k_{(t \rightarrow m)}$ on the nature of the incoming X^- group can be ascribed to the associative nature of the activation process in reaction step k_3 [equation (16)].

The above mechanism also accounts satisfactorily for the kinetic behaviour displayed in acidic solutions by the *mer* complexes [equation (8)], with $k_{(m \rightarrow t)}^{\text{H}} = k_6$. According to this mechanism, the observed lack of direct formation of *mer*-[RhL(L')Cl₃], when *mer*-[RhL(L')Cl₂X] ($\text{X}^- = \text{NO}_2^-$ or N_3^-) reacts in acidic solutions in the presence of chloride ions, implies that the five-coordinate intermediate undergoes ring closure (k_2 reaction step) much more readily than associative attack by chloride ion (k_3 and k_5 reaction steps). The proton in the *mer*-H⁺ form [equation (14)] of complexes previously studied with $\text{X}^- = \text{halide}$ is probably linked to the basic NMe₂ group of L',⁵ so that K_1 in these cases is mainly a measure of the basicity of co-ordinated L'. The value of K_1 for the *mer* complexes examined in this paper sharply increases with the basicity of bonded X^- (Table 3) so that it is reasonable to assume that protonation involves this group in some way. Protonation of co-ordinated SCN^- , N_3^- , and NO_2^- is widely documented, e.g. in aquation reactions of several co-ordination complexes.^{6,17} However, since the basic NMe₂ group of L' is always close to the reactive X^- , it is possible that the proton interacts with both NMe₂ and X^- . Also, the reactivity of protonated *mer* complexes, measured by $k_{(m \rightarrow t)}^{\text{H}} = k_6$, increases with the basicity of X^- , i.e. Cl^- , Br^- , I^- (rate term absent)⁵ \ll SeCN^- (ca. 4×10^{-5}) \ll SCN^- (2.8×10^{-3}) \ll NO_2^- (7.74×10^{-2}) $<$ N_3^- ($1.22 \times 10^{-1} \text{ s}^{-1}$) at 25 °C. This sequence does not parallel that

found for the reactions of unprotonated *mer* complexes [i.e. $k_{(m \rightarrow t)}$ at 25 °C; N_3^- (1.95×10^{-5}) $<$ SeCN^- (6.40×10^{-5}) $<$ SCN^- (3.08×10^{-4}) $<$ NO_2^- (4.81×10^{-4}) $<$ Cl^- ($2.86 \times 10^{-3} \text{ s}^{-1}$)] and can be ascribed to the increased importance of the interaction between the proton and the outgoing ligand as its basicity increases. This interaction promotes the release of X^- , stabilized as HX. Finally, the absence of a kinetic effect of acidity on the reaction rate of *mer*-[RhL(L')Cl₂(py)]⁺ is assignable to a very low value of K_1 [equation (14)], due to the fact that this complex is positively charged, and also indicates that the effect of acidity observed for basic leaving groups is not related to their basicity as unco-ordinated species.

[1/639 Received, 22nd April, 1981]

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