Thiourea and Pyridine Derivatives as Entering and Leaving Groups in Reversible Chelate Ring-opening and Ring-closure Substitution Reactions of *trans*-Dichlorobis(*O*-dimethylaminophenyldimethylarsine-*NAs*)-rhodium(III) Complexes

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The kinetics of the reversible reaction (i) have been studied in methanol [X = thiourea, *NN'*-diphenylthiourea,

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

pyridine (py), 3Me-py, 3Cl-py, 3CN-py, 4CN-py, 2Me-py, 2,4Me_2-py, or 2,4,6Me_3-py; L and L' = *o*-dimethylaminophenyldimethylarsine-*NAs* and -*As* respectively]. The system obeys rate law (ii). The rate constant of the

$$-d[Rh(L)_2Cl_2^+]/dt = k_{(t\rightarrow m)}[Rh(L)_2Cl_2^+][X] - k_{(m\rightarrow t)}[Rh(L)(L')Cl_2X^+] \qquad (ii)$$

forward reaction is hardly affected by the nature of the entering group, apart from *ortho*-substituted pyridines which exhibit comparatively low reactivity. The rate constant of the reverse reaction is strongly dependent on the leaving group X. A linear relation between log $k_{(m\rightarrow t)}$ and pK_a of the pyridines which are not *ortho*-substituted indicates that the rate of the *mer* ⟶ *trans* conversion is largely governed by Rh–X bond rupture. A linear free-energy relation of type (iii) with a value of α of 1.2 correlates the free energy of activation of this conversion with the

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

standard free energy of the reaction. This result is taken as an indication that there is little interaction between Rh^{III} and X in the transition state.

IN previous papers [1,2] we have found that the octahedral complex *trans*-dichlorobis(*o*-dimethylaminophenyldimethylarsine-*NAs*)rhodium(III), *trans*-$[Rh(L)_2Cl_2]^+$, undergoes reversible nucleophilic substitution by chloride, bromide, iodide, and thiocyanate ions, where the leaving group of the forward reaction is the NMe_2 group of one of the chelate ligands [equation (1); L' = *o*-dimethylaminophenyldimethylarsine-*As*]. We now report the results of a series of kinetic investigations of system (1) in methanol with different entering groups, X^{n-}, namely the uncharged groups thiourea (tu), *NN'*-diphenylthiourea (dptu), pyridine (py), and substituted pyridine (see Table).

$$trans\text{-}[Rh(L)_2Cl_2]^+ + X^{n-} \underset{k_{(m\rightarrow t)}}{\overset{k_{(t\rightarrow m)}}{\rightleftharpoons}} mer\text{-}[Rh(L)(L')Cl_2X]^{1-n} \qquad (1)$$

EXPERIMENTAL

Materials.—The complex *trans*-$[Rh(L)_2Cl_2][NO_3]$ was prepared as described elsewhere.[3] Reagent-grade pyridines were purified either by distillation over K[OH] pellets or by sublimation (3CN- and 4CN-py). Thiourea and *NN'*-diphenylthiourea (dptu) were used without further purification. Methanol was dried over magnesium methoxide and used immediately.

Stoicheiometry of the Reactions, Preparation of the Reaction Mixtures, and Evaluation of the Reaction Rates and Equilibria.—Preliminary spectrophotometric measurements carried out over the range 280—360 nm showed that *trans*-$[Rh(L)_2Cl_2]^+$ reacts with each of the entering groups tested, with the exception of 2Me-py. Moreover, the overall absorption change occurring from the beginning to the end of the reaction, $|A_0 - A_{eq}|$, increased, at constant rhodium(III) concentration, on increasing the entering-group concentration (*e.g.* Figure 1) up to a maximum value which may be attained in some cases. These results can be regarded as indicative of the reversibility of the reactions examined. The stoicheiometry of the reaction was fully established only for X = py and tu. Thus, the reaction product was precipitated as the tetraphenylborate salt by addition of $Na[BPh_4]$ to a reaction mixture, at the end of the reaction, initially containing *trans*-$[Rh(L)_2Cl_2][NO_3]$ (5×10^{-3} mol dm^{-3}) and a suitable excess of the entering ligand. The analytical data for the products recovered were consistent with the formula $[Rh(L)(L')Cl_2X][BPh_4]$

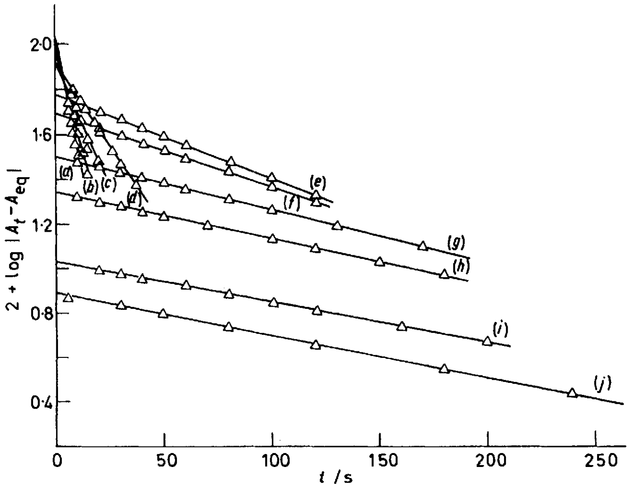

FIGURE 1 Plots of log $|A_t - A_{eq}|$ against time for reactions of *trans*-$[Rh(L)_2Cl_2][NO_3]$ (1.70×10^{-4} mol dm^{-3}) with 3Cl-py in methanol at 25.0 °C (λ 295 nm). [py] = 9.14×10^{-1} (*a*), 6.09×10^{-1} (*b*), 3.04×10^{-1} (*c*), 1.83×10^{-1} (*d*), 9.14×10^{-2} (*e*), 6.09×10^{-2} (*f*), 3.04×10^{-2} (*g*), 1.83×10^{-2} (*h*), 9.14×10^{-3} (*i*), and 6.9×10^{-3} mol dm^{-3} (*j*)

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

[2] A. Peloso and L. Volponi, *J.C.S. Dalton*, 1976, 923.

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

(Found: C, 56.5; H, 5.30; Cl, 6.90; N, 4.05. Calc. for X = py: C, 57.55; H, 5.60; Cl, 6.95; N, 4.10. Found: C, 52.4; H, 5.65; Cl, 6.75; N, 5.30; S, 2.95. Calc. for X = tu: C, 53.0; H, 5.55; Cl, 6.95; N, 5.50; S, 3.15%). Moreover, conductance measurements carried out with an LKB type 3216 B conductivity bridge showed that the conductivity of the reaction mixture does not change significantly in the course of the reaction. {For example, the conductivity of a freshly prepared (1 min) solution of *trans*-$[Rh(L)_2Cl_2][NO_3]$ (1.00×10^{-3} mol dm^{-3}) is 9.26×10^{-5} S cm^{-1} at 25.0 °C, and 9.49×10^{-5} S cm^{-1} after 7 380 s. In the same time interval the conductivity changes only from 9.24×10^{-5} to 9.63×10^{-5} S cm^{-1} when tu (4.00×10^{-3} mol dm^{-3}) is also present in the solution. However, in the latter case a reaction is occurring between the starting complex and tu with an half-time of 1 880 s.} This behaviour implies that the reaction does not involve the release of co-ordinated chloride ions. These are thought to retain their mutual *trans* position also in the reaction product.* From a study of the i.r. spectra of the isolated products in the 140—500 cm^{-1} region, only one Rh–Cl stretching frequency could be located, as a strong band at 350 cm^{-1} for X = tu and at 348 cm^{-1} for X = py {350 cm^{-1} for *trans*-$[Rh(L)_2Cl_2][NO_3]$}, in the region characteristic of the asymmetric stretching frequency for a *trans*-Cl–Rh–Cl unit (340—360 cm^{-1}).[4] In our opinion, the foregoing results are satisfactory evidence that the reactions with py and tu obey stoicheiometry (1). The kinetic and spectrophotometric behaviour displayed by the reactions with the other entering groups, together with the analytical expression holding for the related equilibrium constants (see below), strongly support stoicheiometry (1) also for the other reactions reported.

Rate constants, activation parameters, and equilibrium constants in methanol for the reaction:
trans-$[Rh(L)_2Cl_2]^+ + X \rightleftharpoons$ *mer*-$[Rh(L)(L')Cl_2X]^+$

X	θ_c °C	$k_{(m\to t)}$ s^{-1}	$\Delta H_{(m\to t)}^\ddagger$ kJ mol^{-1}	$\Delta S_{(m\to t)}^\ddagger$ J K^{-1} mol^{-1}	$k_{(t\to m)}$ dm^3 mol^{-1} s^{-1}	$\Delta H_{(t\to m)}^\ddagger$ kJ mol^{-1}	$\Delta S_{(t\to m)}^\ddagger$ J K^{-1} mol^{-1}	$k_{(t\to m)}/k_{(m\to t)}$ [a] dm^3 mol^{-1}	K dm^3 mol^{-1}
3Me-py	25.0	1.73×10^{-4}	97.0	8	2.05×10^{-2}	70	−42	118	147
	35.0	6.17×10^{-4}			5.21×10^{-2}			84	104
	45.0	2.16×10^{-3}			1.29×10^{-1}			60	68
py	25.0	2.58×10^{-4}	92.7	−3	2.34×10^{-2}	65	−59	91	95
	35.0	9.45×10^{-4}			5.70×10^{-2}			60	71
	45.0	2.90×10^{-3}			1.29×10^{-1}			45	54
3Cl-py	25.0	4.02×10^{-3}	83.9	−9	4.57×10^{-2}	63	−60	11	12
	35.0	1.22×10^{-2}			1.08×10^{-1}			8.9	10
	45.0	3.60×10^{-2}			2.40×10^{-1}			6.7	7
4CN-py [b]	18.0	3.8×10^{-3}			2.4×10^{-2}			6.3	5
	25.0	1.0×10^{-2}			4.0×10^{-2}			4.0	4
	33.0	2.5×10^{-2}			8.0×10^{-2}			3.2	3
3CN-py [c]	18.0	1.26×10^{-2}	77.9	−13	2.4×10^{-2}			2	3
	25.0	2.80×10^{-2}			4.5×10^{-2}			1.6	2
	33.0	6.40×10^{-2}			6.0×10^{-2}			1	
2,4,6Me_3-py	25.0	8.90×10^{-5}	92.9	−11	2.50×10^{-3}	67	−69	28	25
	35.0	2.95×10^{-4}			6.37×10^{-3}			22	22
	45.0	1.00×10^{-3}			1.47×10^{-2}			15	16
2,4Me_2-py	25.0	9.55×10^{-5}	94.9	−4	2.67×10^{-4}	67	−87	2.8	2.5
	35.0	3.20×10^{-4}			6.88×10^{-4}			2.1	2.0
	45.0	1.10×10^{-3}			1.58×10^{-3}			1.4	1.5
2Me-py	25.0 [d]								
tu	25.0	$<0.8 \times 10^{-4}$			9.22×10^{-2}	65	−48		
	35.0	$<1.5 \times 10^{-4}$			2.24×10^{-1}				
	45.0	$<8 \times 10^{-4}$			5.05×10^{-1}				
dptu [e]	25.0	8.7×10^{-5}			6.60×10^{-2}	71	−30	7.8×10^2	9×10^2
	35.0	3.3×10^{-4}			1.74×10^{-1}				
	45.0	7.0×10^{-4}			4.35×10^{-1}				

Errors: $k \pm 3\%$; $\Delta H^\ddagger \pm 4$ kJ mol^{-1}; $\Delta S^\ddagger \pm 13$ J K^{-1} mol^{-1}; $K \pm 10\%$.

[a] k_2/k_1 (see text). [b] $k \pm 15\%$. [c] $k_{(t\to m)} \pm 15\%$. [d] No reaction. [e] $k_{(m\to t)} \pm 10\%$.

The reactions were started by mixing directly appropriate volumes of thermostatted stock solutions of the reactants in 1-cm silica cells maintained in the thermostatted cell compartment of an Optica CF4R recording spectrophotometer. At suitable time intervals the spectrum of the reacting mixture was scanned in the 280—360 nm region (350—390 nm for dptu), where significant changes of absorbance were observed during the reaction, together with some isosbestic points (at 317 nm for py, 3Me-py, 2,4Me_2-py, and 2,4,6Me_3-py; at 320 nm for 3Cl-py, and at 347 and 333 nm for tu; the small extent of the reactions with 3CN- and 4CN-py prevented an accurate evaluation of the wavelength of the isosbestic points). Fast reactions were followed by recording the change of absorbance at a constant wavelength (310 nm for tu, 295 nm for substituted pyridines).

The starting concentration of rhodium(III) complex was kept in the range 7.0×10^{-5}—3.5×10^{-4} mol dm^{-3}; the ranges of concentration for the entering groups were 2.09×10^{-3}—1.04×10^{-1} py, 3.50×10^{-2}—2.18 2Me-py, 1.77×10^{-3}—8.83×10^{-2} 3Me-py, 1.75×10^{-1}—1.46 2,4Me_2-py, 2.58×10^{-2}—8.61×10^{-1} 2,4,6Me_3-py, 3.00×10^{-2}—4.15×10^{-1} 3CN-py, 6.26×10^{-3}—4.22×10^{-1} 4CN-py, 6.09×10^{-3}—9.14×10^{-1} 3Cl-py, 1.59×10^{-4}—2.98×10^{-2} tu, and 5.77×10^{-4}—1.73×10^{-2} mol dm^{-3} dptu. At least five kinetic runs were carried out at each temperature for each entering group. The temperatures explored are listed in the Table.

Observed rate constants of the approach to equilibrium, $k_{obs.}$, were determined from gradients of plots of

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* *mer* Symbolism for the reaction product has been adopted in order to point out its similarity with *mer*-$[Rh(L)(L')Cl_3]$, which is the reaction product when chloride is the entering group.

[4] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1847.

log $|A_t - A_{eq}|$ against time, where A_t and A_{eq} are the absorbances of the reacting mixture at time t and at the end of the reaction (*e.g.* Figure 1). The equilibrium constants of the reactions, K, were given by the ratios of the intercept and gradient of the straight lines obtained by plotting $1/(A_{eq} - A_0)$ against $1/[X]$ at constant rhodium(III) concentration (*e.g.* Figure 2). The equilibrium constants are related to these quantities by relation (2), where A_∞

$$\frac{1}{(A_{eq} - A_0)} = \frac{1}{K[X](A_\infty - A_0)} + \frac{1}{(A_\infty - A_0)} \quad (2)$$

is the absorbance expected when the reaction goes to completion. The values of $|A_{eq} - A_0|$ were obtained by extrapolating to $t = 0$ the straight lines (*e.g.* Figure 1) obtained by plotting $\log|A_t - A_{eq}|$ against time.

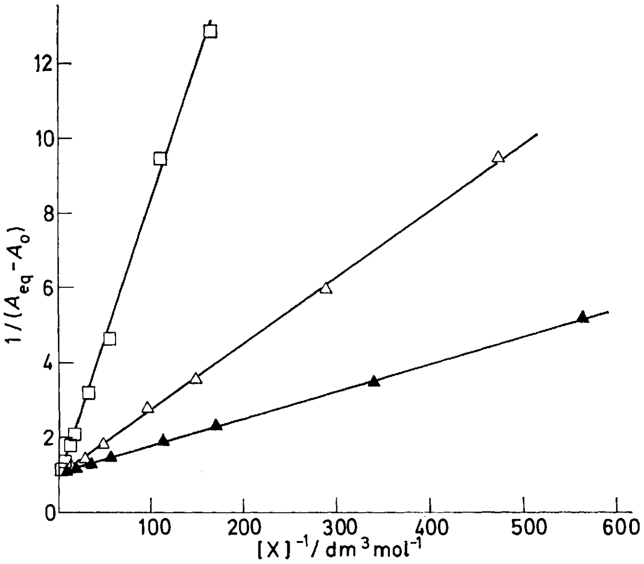

FIGURE 2 Examples of plots of $1/(A_{eq} - A_0)$ against $1/[X]$ for reactions in methanol at 25.0 °C: X = (□) 3Cl-py (λ 300 nm, $[Rh^{III}]_T$ 1.70 × 10^{-4} mol dm^{-3}), (△) py (λ 295 nm, $[Rh^{III}]_T$ 1.41 × 10^{-4} mol dm^{-3}), and (▲) 3Me-py (λ 295 nm, $[Rh^{III}]_T$ 1.41 × 10^{-4} mol dm^{-3})

RESULTS

The reactions, carried out in the presence of a large excess of X, always obeyed a pseudo-first-order rate law with an observed rate constant, $k_{obs.}$, which increased linearly with increasing ligand concentration according to relation (3). In individual cases the value of k_2/k_1 was

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

very close to that of the equilibrium constant, K, evaluated from spectrophotometric measurements (see Table). Therefore, the second-order rate term of relation (3), k_2, can be regarded as the rate constant of the forward reaction (1), $k_{(t\rightarrow m)}$, and the first-order rate term, k_1, as the rate constant of the reverse of reaction (1), $k_{(m\rightarrow t)}$, *i.e.* we obtain equation (4). Relations of this kind have been previously found

$$k_{obs.} = k_{(m\rightarrow t)} + k_{(t\rightarrow m)}[X] \quad (4)$$

also for anionic entering groups.[1,2] The values of $k_{(m\rightarrow t)}$ and $k_{(t\rightarrow m)}$ obtained in each case are listed in the Table together with the related activation parameters. The values of the equilibrium constants, K, are also quoted in the Table.

DISCUSSION

The results obtained indicate that all the reactions studied obey the rate law (5), which is typical of a reversible process involving a second-order forward reaction and a first-order reverse reaction. The knowledge of both the $k_{(t\rightarrow m)}$ and $k_{(m\rightarrow t)}$ rate terms allows one to point out the part played by X as either the entering or leaving group in determining the rates of the ring-opening and ring-closure nucleophilic substitutions, respectively, as described by the forward and reverse reactions of (1).

$$-d[Rh(L)_2Cl_2^+]/dt = k_{(t\rightarrow m)}[Rh(L)_2Cl_2^+][X] - k_{(m\rightarrow t)}[Rh(L)(L')Cl_2X^+] \quad (5)$$

The results listed in the Table show that the rate constants of the forward reaction (*trans* ⟶ *mer*) are usually slightly affected by the entering group. Thus, the greatest decrease (4.5 times) is observed in going from tu to 3Me-py. However, the reactions with *ortho*-substituted pyridines are particularly slow, *i.e.* the rate constants for 2,4,6Me$_3$-py and 2,4Me$_2$-py are 37 and 345 times less than those with tu. The importance of the nature of the entering group is better shown when the uninegative entering groups previously reported[1,3] are also considered. Thus the following order is obtained for the rate constants at 25 °C: $[SCN]^-(10.7) > I^-(2.7) > tu(1.6) \sim Br^-(1.6) > dptu\ (1.2) > Cl^-\ (1.00) > 3Cl\text{-}py(0.81) \sim 3CN\text{-}py(0.8) \sim 4CN\text{-}py(0.7) > py(0.42) \sim 3Me\text{-}py(0.37)$; $2,4,6Me_3\text{-}py(0.04) > 2,4Me_2\text{-}py(0.005)$. The whole sequence seems to indicate that the extent of bond making in the activated complex of the forward reaction is very low. This hypothesis is also consistent with the fact that a significant change in the properties of the entering group [either in terms of basicity of the pyridines (see Figure 3) or in terms of the nature of the donor atom (N of substituted py or S of dptu)] results in

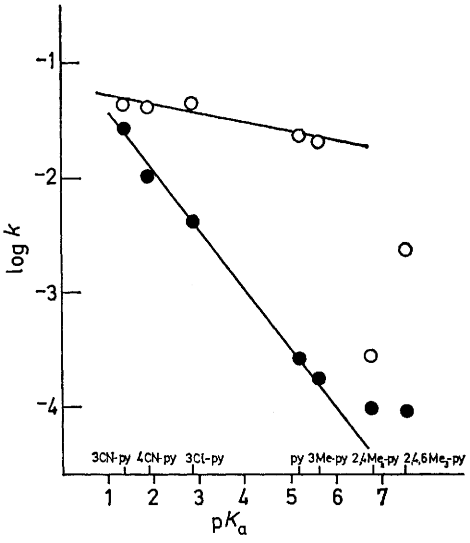

FIGURE 3 Plots of log k against pK_a for substituted pyridines, X, for the reaction *trans*-$[Rh(L)_2Cl_2]^+ + X \rightleftharpoons$ *mer*-$[Rh(L)(L')Cl_2X]^+$ in methanol at 25.0 °C: (○) $k_{(t\rightarrow m)}$; (●) $k_{(m\rightarrow t)}$

only small changes in the free energy of activation, whereas much higher changes in the standard free energy of the related reactions are observed. For instance, the free energy of activation decreases only by *ca.* 1 kJ mol^{-1} on going from 3CN-py to dptu, compared with a decrease of *ca.* 15 kJ mol^{-1} in the standard free energy of the related reactions.

According to the reversibility of these reactions the above considerations strongly suggest that the activated complex of the rate-determining step of the reverse of reaction (1) (*i.e. mer* ⟶ *trans*) exhibits very extensive Rh–X bond rupture. This conclusion can also be inferred from an examination of the so-called enthalpies of transition, ΔH_T, of the *mer* ⟶ *trans* conversions, which are simply the enthalpies of activation of the reverse reaction, $\Delta H_{(t\rightarrow m)}^{\ddagger}$.[5-8] These values are essentially independent of X (see Table), implying a high degree of Rh–X bond breaking in the activated complex, and agree with the requirements of a dissociative mechanism for the *mer* ⟶ *trans* reaction. The rates of this conversion are strongly affected by the leaving group (see Table and Figure 3). In particular, it is found (Figure 3) that log $k_{(m\rightarrow t)}$ at 25 °C is linearly dependent on the pK_a of the leaving pyridines (apart from *ortho*-substituted py), according to relation (6). Such a relation implies that the reaction rate increases

$$\log k_{(m\rightarrow t)} = -0.52\mathrm{p}K_a - 0.90 \qquad (6)$$

with decreasing strength of the σ interaction between Rh^{III} and the co-ordinated heterocyclic amine. This is an indication that the rate is largely governed by the Rh–X bond rupture. The relatively higher rate found for leaving *ortho*-substituted pyridines, with respect to that expected from equation (6), is likely due to the existence of some steric strain about the Rh–X bond, caused by the steric hindrance of the *ortho* groups. On the other hand, the low rate observed for leaving tu and dptu is likely due to the higher affinity of Rh^{III} for the sulphur atom of thioureas rather than for the nitrogen of pyridines, as shown from the values of the equilibrium constants, *K*, of the related reactions (see Table). A more accurate evaluation of the extent of Rh–X bond breaking occurring in the activated complex can be obtained from an inspection of the linear relation (7) between $\Delta G_{(m\rightarrow t)}^{\ddagger}$ and $\Delta G_{(m\rightarrow t)}^{\ominus}$ found for the reactions with *ortho*-unsubstituted pyridines as leaving groups (see Figure 4). Here α is equal to 1.2 (*ca.* 1.0 if the data for

$$\Delta G_{(m\rightarrow t)}^{\ddagger} = \alpha\Delta G_{(m\rightarrow t)}^{\ominus} + \beta \qquad (7)$$

dptu are also included). A value of α = 1.0 is suggested to indicate that the leaving group is, at most, very weakly bound to the central metal atom in the transition state, where it would be present merely as a solvated unco-ordinated ligand.[8-10] The slightly higher value found in our case might arise from the inability of the leaving pyridine to give rise to hydrogen-bonding association with methanol in the transition state, because of the presence of the residual Rh–X bond. The standard free energy of hydrogen-bonding association of methanol with a series of amines, including some pyridines, in toluene decreases with increasing pK_a, being *ca.* 3.7 kJ mol^{-1} per 5 pK_a units.[11] Therefore, if there is no hydrogen bonding in the transition state, one would expect a relative extra destabilization of the activated complex in the order 3CN-py < 4CN-py < 3Cl-py < py < 3Me-py, the overall destabilization being *ca.* 3.2 kJ mol^{-1} in going from 3CN-py (pK_a 1.38) to 3Me-py (pK_a 5.68). Such a destabilization would imply an increase of *ca.* 0.3 in the value of α expected if the leaving group were fully solvated, and would satisfactorily explain the value experimentally found for α. Solvation requirements would also be adequate to explain the gradual decrease in the rate constants found in the *trans* ⟶ *mer* conversions on increasing the pK_a of the incoming pyridines (see Figure 3). In such a case, the free energy required to desolvate the incoming ligand in order for it to attain the transition-state configuration would increase with pK_a, thus causing an increase of *ca.* 3.2 kJ mol^{-1} in the overall free energy of activation in going from 3CN- to 3Me-py, which must be compared with the increase of 2 kJ mol^{-1} (Figure 4) experimentally found.

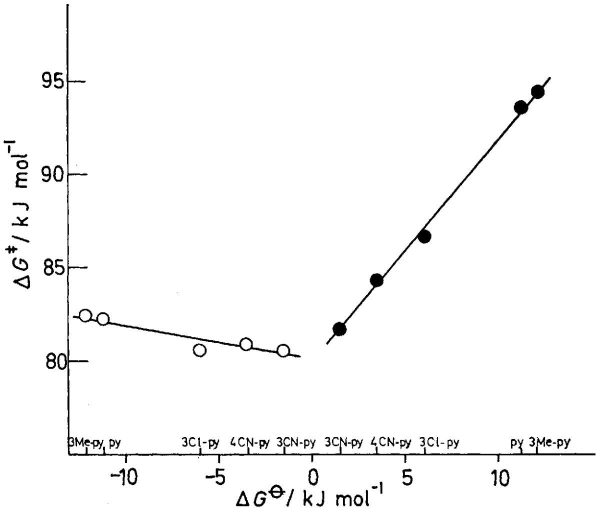

FIGURE 4 Relation between the free energy of activation and the standard free energy of the reactions *trans*-[Rh(L)$_2$Cl$_2$]$^+$ + X $\rightleftharpoons$ *mer*-[Rh(L)(L′)Cl$_2$X]$^+$ in methanol at 25.0 °C: (●) $\Delta G_{(m\rightarrow t)}^{\ddagger}$ and $\Delta G_{(m\rightarrow t)}^{\ominus}$; (○) $\Delta G_{(t\rightarrow m)}^{\ddagger}$ and $\Delta G_{(t\rightarrow m)}^{\ominus}$

Apart from the above considerations, the value found for α implies that the interaction between Rh^{III} and X in the activated complex of the *mer* ⟶ *trans* conversion, which is the same also for the reverse reaction, is very weak. This does not allow a definite choice between an I_d or a *D* mechanism. There are, however,

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[10] A. Haim, *Inorg. Chem.*, 1970, **9**, 426.

[11] A. Kolbe and H. Pracejus, *Ber. Bunsengesellschaft. Phys. Chem.*, 1966, **70**, 883.

some indications which appear to be against an I_d mechanism. First, according to such a mechanism the second-order rate constant for the forward reaction of (1), $k_{(t\rightarrow m)}$, ought to be roughly independent of the nature of entering ligands which bear the same charge, and to decrease on going from uninegative to uncharged ligands.[12] On the contrary, the reactivity observed is 10.7 times greater on going from Cl^- to SCN^-, and uncharged tu and dptu react as fast as Br^- and even faster than Cl^-. On the other hand, an I_d mechanism should hardly justify the strong decrease in the rates observed when one or two methyl groups occupy *ortho* positions in the entering ligand.[13] Unfortunately, the fact that the reaction involves as leaving or entering group one end of a ligand already bonded to Rh^{III} does not allow us to perform competition studies to establish unequivocally the stoicheiometric mechanism. However, a *D* mechanism (8) seems to be adequate to explain the value obtained for α in equation (7). The experimental rate law (5) requires that k_2 is much higher than $k_3[X]$. Therefore, the rate constant of the forward reaction, $k_{(t\rightarrow m)}$, is given by k_1k_3/k_2, and is shown to be also affected by the ability of the five-co-ordinate intermediate to react with the entering group, as measured by the term k_3. Thus, if such a mechanism is

$$\textit{trans}\text{-}[Rh(L)_2Cl_2]^+ + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\substack{\text{five-co-ordinate}\\ \text{intermediate}}}{[Rh(L)(L')Cl_2]^+} + X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \textit{mer}\text{-}[Rh(L)(L')Cl_2X]^+ \quad (8)$$

$$k_{\text{obs.}} = \frac{k_1k_3[X]}{k_2 + k_3[X]} + \frac{k_2k_4}{k_2 + k_3[X]} \quad (9)$$

operating, the minor role played by the entering group on the rate constant of the *trans* ⟶ *mer* conversion denotes a poor ability of the five-co-ordinate intermediate to discriminate between groups which are not sterically hindered, probably because of the previously mentioned low extent of Rh–X interaction exhibited in the transition state. The relatively lower reactivity exhibited by entering *ortho*-substituted pyridines can be ascribed to the fact that methyl groups adjacent to nitrogen hinder the approach of the nucleophilic centre to Rh^{III} in the five-co-ordinate intermediate.

[7/610 *Received*, 6*th April*, 1977]

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