Kinetic Studies on the Interconversion of *mer*-Trichloro(*o*-dimethylaminophenyldimethylarsine-*As*)(*o*-dimethylaminophenyldimethylarsine-*NAs*)rhodium(III) and *trans*-Dichlorobis(*o*-dimethylaminophenyldimethylarsine-*NAs*)rhodium(III) Chloride

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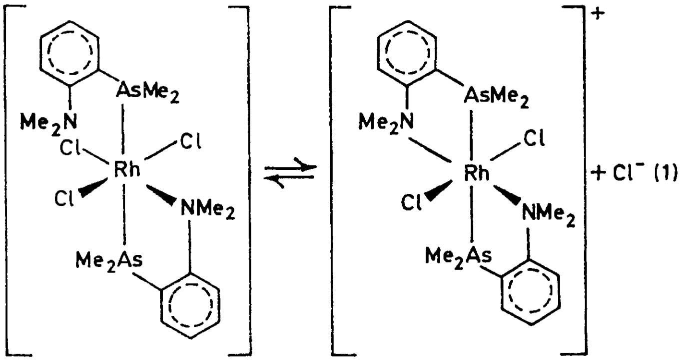
The kinetics of the interconversion (i) have been studied in hydroxylic solvents (L and L′ = *o*-dimethylaminophenyldimethylarsine-*NAs* and -*As* respectively).

$$mer\text{-}[Rh(L)(L')Cl_3] \rightleftharpoons trans\text{-}[Rh(L)_2Cl_2]^+ + Cl^- \qquad (i)$$

The rate of the forward reaction depends on the concentration of electrolytes in solution ($NaClO_4$, NEt_4ClO_4, or $LiNO_3$), according to the rate law, rate = $(k_{(m\rightarrow t)1} + k_{(m\rightarrow t)2}[\text{Salt}])[mer\text{-}Rh(nas)_2Cl_3]$, and increases sharply with the polarity of the solvents. A dissociative mechanism involving extensive Rh–Cl bond rupture in the activated complex is proposed. Such a mechanism is supported by the activation parameters. The rate of the reverse reaction shows a linear dependence on LiCl when the total amount of lithium salts is kept constant by addition of $LiNO_3$, while a square-root dependence on LiCl is observed in the absence of added $LiNO_3$. An S_N1(IP) mechanism is proposed for this reaction, involving a precursor ion-pair of the *trans*-complex with a free chloride ion. A very small solvent effect is observed in this case and is interpreted as the consequence of opposing effects of the polarity of the solvent both on the dissociation of LiCl and on the formation constant of the precursor ion-pair.

RELATIVELY little work has been done so far on the kinetics and mechanisms of substitution reactions of rhodium(III) complexes. The most interesting feature in this system is the wide variety of mechanisms apparently involved in nucleophilic substitution.[1-10]



(I) (II)

The rhodium(III) complex of stoicheiometric formula $[Rh(nas)_2Cl_3]$ (nas = *o*-dimethylaminophenyldimethylarsine) exhibits an interesting example of ionization isomerism.[11,12] Both isomers, (I) and (II), are indefinitely stable in the solid state, whereas they undergo interconversion in solution according to equation (1). In this paper the results of a kinetic investigation of this interconversion in hydroxylic solvents are reported.

EXPERIMENTAL

The complexes *mer*-$[Rh(L)(L')Cl_3]$ and *trans*-$[Rh(L)_2Cl_2]NO_3$ (L and L′ = *o*-dimethylaminophenyldimethylarsine-*NAs* and -*As*) were prepared according to the literature.[11] Reagent grade NEt_4ClO_4, $NaClO_4$, LiCl, and $LiNO_3$ were dried before use. Methanol, ethanol, propan-1-ol, and propan-2-ol were purified and dried by standard methods.[13]

Preparation of the Reaction Mixtures and Evaluation of the Reaction Rates.—Stock solutions of the salts and complexes were prepared by weight. Solutions of the complex *trans*-$[Rh(L)_2Cl_2]NO_3$, which were stable in the absence of free chloride ion, were used within 2—3 h of preparation. Solutions of the complex *mer*-$[Rh(L)(L')Cl_3]$ were prepared by adding the solid complex to the solvent, which had been previously thermostatted at the reaction temperature, and used immediately since the *mer* ⟶ *trans* conversion starts as soon as the *mer*-complex dissolves. The reactions

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

[12] G. Bombieri, R. Graziani, C. Panattoni, L. Volponi, R. J. H. Clark, and G. Natile, *J. Chem. Soc.* (*A*), 1970, 14.

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

were initiated by mixing appropriate volumes of thermostatted stock solutions of the reactants directly in 1 cm cells maintained in the thermostatted cell compartment of a Beckman DK 2A recording spectrophotometer. At suitable times the spectrum of the reacting mixture was scanned over the range 360—240 nm, where the *trans*- and *mer*-complexes exhibit very different spectra with two isosbestic points at 313 and 250 nm in each of the solvents used. Fast reactions were followed by recording the change of absorbance at 285 nm with time.

Observed rate constants, k_{obs}, were determined from gradients of plots of log $|A_t - A_\infty|$ against time, where A_t and A_∞ are the absorbances of the reacting mixture at time t and at the end of the reaction. Initial concentrations of the complexes were in the range $1{\cdot}0 \times 10^{-4}$—$5{\cdot}0 \times 10^{-4}$M. The concentration of LiCl for the *trans* ⟶ *mer* conversion was varied within the range $1{\cdot}07 \times 10^{-2}$—$1{\cdot}67 \times 10^{-1}$M. In some runs $LiNO_3$ was added to the reactants to keep the total concentration of lithium salts constant. The *mer* ⟶ *trans* conversion was carried out in the presence of $LiNO_3$ and, in methanol only, also in the presence of NEt_4ClO_4 or $NaClO_4$. Ranges of concentrations explored in methanol were 0—$1{\cdot}67 \times 10^{-1}$M for $LiNO_3$ and $NaClO_4$ and 0—$8{\cdot}35 \times 10^{-2}$M for NEt_4ClO_4. The concentration of $LiNO_3$ in the other solvents was varied from $1{\cdot}20 \times 10^{-2}$ to $1{\cdot}67 \times 10^{-1}$M. At least seven kinetic runs were carried out at any given temperature for each solvent and concentration of lithium salts (for the *trans* ⟶ *mer* conversion) or for each electrolyte (for the *mer* ⟶ *trans* conversion).

RESULTS

Reaction (1) is reversible in the solvents used so that the observed rate constant for the approach to equilibrium, in pseudo-first-order conditions, k_{obs}, is as shown in (2),[14] where $k_{(m\rightarrow t)obs}$ and $k_{(t\rightarrow m)obs}$ are observed rate constants for

$$k_{obs} = k_{(m\rightarrow t)obs} + k_{(t\rightarrow m)obs} \qquad (2)$$

the forward and the reverse reaction in the same experimental conditions. k_{obs} Becomes equal to $k_{(m\rightarrow t)obs}$ when the disappearance of the complex *mer*-$[Rh(L)(L')Cl_3]$ is carried out in the presence of $LiNO_3$, equilibrium (1) being quantitatively shifted to the right. This also occurs in methanol even in the absence of added salt or in the presence of $NaClO_4$ or NEt_4ClO_4. Under these conditions the observed rate constants obey equation (3). Values of

$$k_{(m\rightarrow t)obs} = k_{(m\rightarrow t)1} + k_{(m\rightarrow t)2}[\mathrm{Salt}]_{added} \qquad (3)$$

of $k_{(m\rightarrow t)1}$ are listed in Table 1 together with the related activation parameters and values of $k_{(m\rightarrow t)2}$.

Evaluation of the $k_{(t\rightarrow m)obs}$ term was made by carrying out the *trans* ⟶ *mer* conversion using solutions initially containing the *trans*-complex. When reacting mixtures initially contained only the *trans*-complex and lithium chloride, the reaction did not go to completion and the $k_{(t\rightarrow m)obs}$ term (equal to $k_{obs} - k_{(m\rightarrow t)obs}$) was linearly dependent on $[LiCl]^{\frac{1}{2}}$ in ethanol, propan-1-ol, and propan-2-ol, where such a dependence could be evaluated with good accuracy. However, when $LiNO_3$ was also added to keep constant the total concentration of lithium salts, this rate term became linearly dependent on [LiCl] according to equation (4) (Figure 1). Values of $k_{(t\rightarrow m)}$ obtained under various experimental conditions are collected in Table 2

$$k_{(t\rightarrow m)obs} = k_{(t\rightarrow m)}[\mathrm{LiCl}]_{added} \qquad (4)$$

together with the related activation parameters.

DISCUSSION

An interesting result is the solvent effect. It appears from Figure 2 that the rate constant for the reverse reaction in equilibrium (1), $k_{(t\rightarrow m)}$, is only slightly affected by the polarity of the solvent. Conversely, the rate of the *mer* ⟶ *trans* conversion is strongly dependent on the solvent and increases linearly with the polarity of the solvent expressed in terms of Kosower's Z values.[15] The rate of the conversion is also enhanced by the presence of salts [equation (3)].

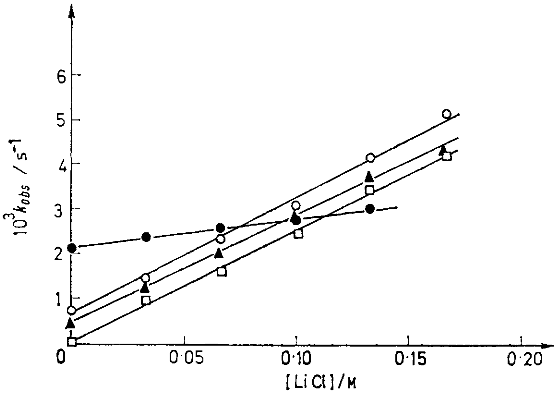

FIGURE 1 Dependence of the rate constant of approach to equilibrium, k_{obs}, on [LiCl] in the presence of added $LiNO_3$, in propan-2-ol (□), propan-1-ol (△), and ethanol (○) at 30 °C, and in methanol (●) at 20 °C. Initial concentration of *trans*-$[Rh(L)_2Cl_2]NO_3$ *ca.* 2×10^{-4}M; $[LiCl]_{added} + [LiNO_3]_{added} = 1{\cdot}67 \times 10^{-1}$M. The points at [LiCl] = 0 are referred to experimental values of k_{obs} for the *mer* → *trans* conversion at $[LiNO_3] = 1{\cdot}67 \times 10^{-1}$M [as expected from equation (2)]

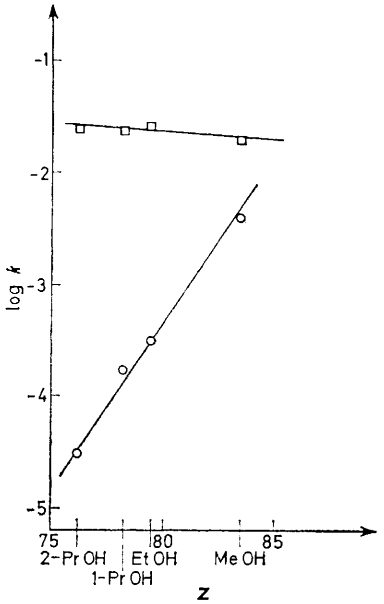

FIGURE 2 Dependence of $k_{(m\rightarrow t)1}$ (○) and $k_{(t\rightarrow m)}$ (□) on the polarity of the solvent at 30 °C and [Salt] = $1{\cdot}67 \times 10^{-1}$M

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TABLE 1

Rate constants and activation parameters for the conversion

$$mer\text{-}[Rh(L)(L')Cl_3] \longrightarrow trans\text{-}[Rh(L)_2Cl_2]^+ + Cl^-$$

Solvent	Salt	$\frac{t}{^\circ C}$	$\frac{k_{(m\rightarrow t)1}}{s^{-1}}$	$\frac{\Delta H^\ddagger_{(m\rightarrow t)1}}{kJ\ mol^{-1}}$	$\frac{\Delta S^\ddagger_{(m\rightarrow t)1}}{J\ K^{-1}\ mol^{-1}}$	$\frac{k_{(m\rightarrow t)2}}{l\ mol^{-1}\ s^{-1}}$
Methanol	NEt_4ClO_4	40	$1{\cdot}04 \times 10^{-2}$	71	−54	$2{\cdot}3 \times 10^{-2}$
		30	$4{\cdot}14 \times 10^{-3}$			$1{\cdot}0 \times 10^{-2}$
		20	$1{\cdot}50 \times 10^{-3}$			$3{\cdot}0 \times 10^{-3}$
	$NaClO_4$	40	$1{\cdot}04 \times 10^{-2}$	73	−54	$3{\cdot}6 \times 10^{-2}$
		30	$4{\cdot}20 \times 10^{-3}$			$1{\cdot}6 \times 10^{-2}$
		20	$1{\cdot}45 \times 10^{-3}$			$6{\cdot}0 \times 10^{-3}$
	$LiNO_3$	40	$1{\cdot}01 \times 10^{-2}$	72	−54	$2{\cdot}4 \times 10^{-2}$
		30	$4{\cdot}10 \times 10^{-3}$			$9{\cdot}0 \times 10^{-3}$
		20	$1{\cdot}43 \times 10^{-3}$			$4{\cdot}1 \times 10^{-3}$
Ethanol	$LiNO_3$	50	$2{\cdot}30 \times 10^{-3}$	76	−58	$1{\cdot}5 \times 10^{-2}$
		30	$3{\cdot}20 \times 10^{-4}$			$2{\cdot}3 \times 10^{-3}$
Propan-1-ol	$LiNO_3$	50	$1{\cdot}20 \times 10^{-3}$	78	−58	$1{\cdot}2 \times 10^{-2}$
		30	$1{\cdot}66 \times 10^{-4}$			$1{\cdot}9 \times 10^{-3}$
Propan-2-ol	$LiNO_3$	50	$2{\cdot}20 \times 10^{-4}$	80	−71	$4{\cdot}3 \times 10^{-3}$
		30	$2{\cdot}90 \times 10^{-5}$			$7{\cdot}2 \times 10^{-4}$

Errors: $k_{(m\rightarrow t)1}$ ±3%; $k_{(m\rightarrow t)2}$ ±10%; $\Delta H^\ddagger_{(m\rightarrow t)1}$ ±4 kJ mol⁻¹; $\Delta S^\ddagger_{(m\rightarrow t)1}$ ±10 J K⁻¹ mol⁻¹.

TABLE 2

Rate constants and activation parameters for the conversion

$$trans\text{-}[Rh(L)_2Cl_2]^+ + \left\{\begin{array}{c} LiCl \\ \upharpoonleft\downharpoonright \\ Li^+ + Cl^- \end{array}\right\} \longrightarrow mer\text{-}[Rh(L)(L')Cl_3] + Li^+$$

Solvent	$\frac{[Salt]^a}{M}$	$\frac{t}{^\circ C}$	$\frac{k_{(t\rightarrow m)}}{l\ mol^{-1}\ s^{-1}}$	$\frac{\Delta H^\ddagger_{(t\rightarrow m)}}{kJ\ mol^{-1}}$	$\frac{\Delta S^\ddagger_{(t\rightarrow m)}}{J\ K^{-1}\ mol^{-1}}$
Methanol	$1{\cdot}67 \times 10^{-1}$	40	$5{\cdot}40 \times 10^{-2}$	80	−16
		20	$6{\cdot}19 \times 10^{-3}$		
Ethanol	$1{\cdot}67 \times 10^{-1}$	50	$1{\cdot}55 \times 10^{-1}$	70	−46
		30	$2{\cdot}60 \times 10^{-2}$		
	$1{\cdot}07 \times 10^{-1}$	50	$1{\cdot}70 \times 10^{-1}$	74	−33
		30	$2{\cdot}62 \times 10^{-2}$		
	$5{\cdot}35 \times 10^{-2}$	50	$2{\cdot}54 \times 10^{-1}$	75	−25
		30	$3{\cdot}74 \times 10^{-2}$		
	$2{\cdot}67 \times 10^{-2}$	50	$3{\cdot}65 \times 10^{-1}$	74	−25
		30	$5{\cdot}60 \times 10^{-2}$		
Propan-1-ol	$1{\cdot}67 \times 10^{-1}$	50	$1{\cdot}54 \times 10^{-1}$	72	−38
		30	$2{\cdot}45 \times 10^{-2}$		
	$1{\cdot}07 \times 10^{-1}$	50	$1{\cdot}80 \times 10^{-1}$	72	−38
		30	$2{\cdot}90 \times 10^{-2}$		
	$5{\cdot}35 \times 10^{-2}$	50	$2{\cdot}44 \times 10^{-1}$	72	−33
		30	$3{\cdot}90 \times 10^{-2}$		
	$2{\cdot}67 \times 10^{-2}$	50	$3{\cdot}85 \times 10^{-1}$	74	−25
		30	$5{\cdot}85 \times 10^{-2}$		
Propan-2-ol	$1{\cdot}67 \times 10^{-1}$	50	$1{\cdot}62 \times 10^{-1}$	73	−33
		30	$2{\cdot}55 \times 10^{-2}$		
	$1{\cdot}07 \times 10^{-1}$	50	$2{\cdot}19 \times 10^{-1}$	76	−21
		30	$3{\cdot}12 \times 10^{-2}$		
	$5{\cdot}35 \times 10^{-2}$	50	$2{\cdot}92 \times 10^{-1}$	79	−12
		30	$3{\cdot}92 \times 10^{-2}$		
	$2{\cdot}67 \times 10^{-2}$	50	$4{\cdot}05 \times 10^{-1}$	79	−8
		30	$5{\cdot}35 \times 10^{-2}$		

Errors: $k_{(t\rightarrow m)}$ ±3%; $\Delta H^\ddagger_{(t\rightarrow m)}$ ±4 kJ mol⁻¹; $\Delta S^\ddagger_{(t\rightarrow m)}$ ±10 J K⁻¹ mol⁻¹.

[a] $[Salt] = [LiCl]_{added} + [LiNO_3]_{added}$.

Both solvent and salt effects support mechanism (6)

$$[Rh(L)(L')Cl_3] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Rh(L)(L')Cl_2{}^+,Cl^-] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Rh(L)_2Cl_2{}^+,Cl^-] \underset{K_{IP}}{\rightleftharpoons} [Rh(L)_2Cl_2]^+ + Cl^- \quad (6)$$

in which slow Rh–Cl bond breaking followed by fast attack by the free end of the unidentate arsine ligand (L′) is involved in the forward reaction.* According to this mechanism the rate law for approach to equilibrium is as shown in (7), where K_{IP} is the equilibrium

$$-\frac{d[Rh(L)(L')Cl_3]}{dt} = \frac{d[Rh(L)_2Cl_2{}^+]}{dt} = \frac{k_1k_3[Rh(L)(L')Cl_3]}{k_2 + k_3} - \frac{k_2k_4K_{IP}[Rh(L)_2Cl_2{}^+][Cl^-]}{k_2 + k_3} \quad (7)$$

constant for formation of the ion-pair $[Rh(L)_2Cl_2{}^+,Cl^-]$ and $k_1k_3/(k_2 + k_3)$ is the $k_{(m\rightarrow t)obs}$ rate term (which becomes equal to $k_{(m\rightarrow t)1}$ when no salt is added to the reacting mixture). The increase in this rate term with

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* However, a salt-catalysed dissociative path could also explain the positive salt effect.

increasing polarity of the solvent is consistent with the occurrence of extensive breaking of the Rh–Cl bond in the activated complex.* Also the entropies of activation are consistent with such a mechanism.[16]

According to mechanism (6) an $S_N1(\mathrm{IP})$ process is postulated for the *trans* ⟶ *mer* conversion. On the basis of rate law (7), the rate term $k_{(t\rightarrow m)\mathrm{obs}}$ is equal to $k_2k_4K_{\mathrm{IP}}[\mathrm{Cl}^-]/(k_2 + k_3)$ and is expected to be linearly dependent on the concentration of free chloride ions. The dependence on $[\mathrm{LiCl}]^{\frac{1}{2}}$ observed when no $\mathrm{LiNO_3}$ is added to the reacting mixture may be explained on the basis of low dissociation of LiCl in ethanol, propan-1-ol, and propan-2-ol.†,[17,18] On the other hand, the first-order dependence on LiCl observed when $\mathrm{LiNO_3}$ is also added can be regarded as evidence that, under these conditions, the degree of dissociation of LiCl, α_{LiCl}, is at least nearly independent of [LiCl].‡ Thus, $k_{(t\rightarrow m)\mathrm{obs}}$ can be formulated as shown in equation (8), from which it appears that the $k_{(t\rightarrow m)}$ term should be strongly affected by the effect of the solvent on both K_{IP} and

$$k_{(t\rightarrow m)\mathrm{obs}} = \frac{k_2k_4K_{\mathrm{IP}}[\mathrm{Cl}^-]}{k_2 + k_3} = \frac{k_2k_4K_{\mathrm{IP}}\alpha_{\mathrm{LiCl}}[\mathrm{LiCl}]_{\mathrm{added}}}{k_2 + k_3} = k_{(t\rightarrow m)}[\mathrm{LiCl}]_{\mathrm{added}} \qquad (8)$$

α_{LiCl}. The very low overall solvent effect experimentally found for such a reaction path can be regarded as a consequence of the balance of the opposing effects caused by the solvent on α_{LiCl} and K_{IP}. In fact, α_{LiCl} is reported to increase with the polarity of the solvents employed in the present investigation,[18] whereas K_{IP} is expected to exhibit opposite behaviour.[19] On this basis the specific effect of the solvent on the $k_2k_4/(k_2 + k_3)$ rate term does not appear to be very significant, but its contribution cannot yet be fully appreciated.

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* However, the possibility of an internal S_N2 path, involving Rh–N bond formation as the rate-determining step, cannot be definitely ruled out.

† This would lead to the relation $[\mathrm{Cl}^-] = ([\mathrm{LiCl}]_{\mathrm{added}}/K_{\mathrm{LiCl}})^{\frac{1}{2}}$ provided that the solutions are not very dilute and no other lithium or chloride salts are present.

‡ Such behaviour is expected provided that the association constants of LiCl and $\mathrm{LiNO_3}$ have similar values. Data available in ethanol show that $K_{\mathrm{LiCl}}/K_{\mathrm{LiNO_3}}$ at 25 °C is *ca.* 2.[17]

[16] Ref. 14, p. 137.

[17] C. W. Davies, 'Ion Association,' Butterworths, London, 1962, p. 95.

[18] A. Z. Golik, G. Allanarazov, and P. F. Cholpai, *Izvest. Akad. Nauk Turm. S.S.R.*, 1969, 112 (*Chem. Abs.*, 1969, **71**, 95,609h).

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