Kinetics of Reversible Chelate Ring-opening and Ring-closure Substitution Reactions of Rhodium(III)–*o*-Dimethylaminophenyldimethylarsine Complexes in Acidic Methanolic Solutions

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The effect of acidity on the rate of reversible interconversions (i) has been investigated in methanol (X = Cl, Br, or I; L and L' = *o*-dimethylaminophenyldimethylarsine-*NAs* and -*As* respectively). The forward reactions are acid

$$trans\text{-}[RhL_2Cl_2]^+ + X^- \rightleftharpoons mer\text{-}[RhL(L')XCl_2] \quad (i)$$

catalysed. The catalytic efficiency of acidity is found to increase in the order I < Br < Cl. The reverse reactions are inhibited by the presence of acid, with an inhibition efficiency of acidity increasing in the order I < Br < Cl. The kinetic results are interpreted in terms of a slow forward step involving a chelate-ring opening through a dissociative mechanism and formation of a highly reactive intermediate whose basic end NMe_2, made available by dechelation, undergoes fast reversible protonation. This step is followed by nucleophilic attack of the entering X^- on both the protonated and unprotonated intermediates.

THE kinetic behaviour of the reversible reactions (1),† where the chelate ring-opening occurring in the forward reaction involves the replacement of the NMe_2 group by

$$trans\text{-}[RhL_2Cl_2]^+ + X^{n-} \rightleftharpoons mer\text{-}[RhL(L')XCl_2]^{1-n} \quad (1)$$

X^{n-}, has been previously extensively studied (L and L' =*o*-dimethylaminophenyldimethylarsine-*NAs* and -*As*, respectively; X = Cl, Br, I, SCN, or amines).[1-4] Systematic kinetic investigations carried out using several X^{n-} groups led to the proposal of a dissociative mode of activation for such reactions. Unfortunately, it has not been possible to carry out competition studies in order to establish unambiguously the stoicheiometric mechanism since one of the labile groups is one end of a ligand which is already co-ordinated to the rhodium(III) reaction centre.[3]

In this paper the effect of acidity on the rate of the interconversions (1) (X = Cl, Br, or I) has been investigated in methanol. The aim of this research was to identify the reaction steps of such processes by taking advantage of the fact that acids would be likely to trap the basic reactive NMe_2 group of the chelating ligand.

EXPERIMENTAL

Materials.—The complexes *trans*-$[RhL_2Cl_2][NO_3]$ and *mer*-$[RhL(L')Cl_3]$ were prepared according to the literature.[5] The new *mer*-$[RhL(L')BrCl_2]$ and *mer*-$[RhL(L')ICl_2]$ complexes were prepared at room temperature from a concentrated methanolic solution of *trans*-$[RhL_2Cl_2][NO_3]$ (*ca.* 30—40 g dm^{-3}) and an excess of the appropriate sodium halide. The required complexes slowly separated from the stirred reacting mixture (Found: C, 34.0; H, 4.60; Br, 11.4; Cl, 9.90; N, 3.90. Calc. for X = Br: C, 34.1; H, 4.60; Br, 11.3; Cl, 10.1; N, 4.00. Found: C, 31.7; H, 4.20; Cl, 9.30; I, 17.3; N, 3.65. Calc. for X = I: C, 32.0; H, 4.30; Cl, 9.45; I, 16.9; N, 3.75%). The *mer* configuration has been previously postulated for these complexes.[2,‡]

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

Sodium chloride, bromide, iodide and toluene-*p*-sulphonate, and toluene-*p*-sulphonic acid (Hpts) were reagent grade. Dried methanol was cautiously distilled in the presence of small amounts of Hpts before use.

Preparation of the Reaction Mixtures and Evaluation of the Reaction Rates.—The reactions were performed at an ionic strength $I = 5.14 \times 10^{-2}$ mol dm^{-3}, using sodium toluene-*p*-sulphonate as supporting electrolyte. Stock methanolic solutions of the reagents were prepared by weight. The solutions of Hpts were standardized by titration. Since the *mer* ⟶ *trans* conversions begin just after dissolution of the *mer* complexes, the related solutions were prepared by dissolving the complexes directly in 5.14×10^{-2} mol dm^{-3} sodium toluene-*p*-sulphonate thermostatted at the reaction temperature, and used immediately. When the reactions were carried out in an acidic medium the *mer* complexes were dissolved in acidic methanol where the *mer* ⟶ *trans* conversions were found to be very slow. The reactions were started by mixing appropriate volumes of thermostatted stock solutions of the reactants directly in 1-cm silica cells maintained in the thermostatted cell compartment of an Optica CF4R spectrophotometer. At suitable time intervals the spectrum of the reacting mixture was recorded in the 250—360 nm region, where the reaction causes large absorbance changes and, for X = Cl, also an isosbestic point (see below). Fast reactions were followed by recording the absorbance against time at a selected wavelength (285 or 290 nm). Some difficulties were met with the reactions of the *trans* complex with sodium iodide in relatively strongly acidic solutions owing to small amounts of iodine formed before the addition of the complex to the reacting mixture. In these cases, the substrate was added to the reacting mixture after the absorption spectrum had stabilized. By this procedure, smooth reactions were observed. The reactions were repeated and their course followed in the 400—450 nm region, using a higher concentration of *trans* complex (*ca.* 4×10^{-4} mol dm^{-3}). The relevant data were not very accurate, so that only a limited range of Hpts concentration could be carefully explored.

Apart from the above case, the starting concentration of the complexes examined was maintained in the range 1×10^{-5}—1×10^{-4} mol dm^{-3}. The ranges of concentr-

‡ Infrared spectral measurements, still in progress, appear to confirm the assigned configuration.[6]

TABLE 1

Rate constants, activation parameters, and K_1 values (see text) for *mer*-$[RhL(L')XCl_2] \longrightarrow$ *trans*-$[RhL_2Cl_2]^+ + X^-$ conversions

X	θ_c / °C	$k_{(m\rightarrow t)}^{Na}$ / s^{-1}	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}	K_1 / dm^3 mol^{-1}	ΔH_1 / kJ mol^{-1}	ΔS_1 / J K^{-1} mol^{-1}
Cl	25.0	2.86×10^{-3}			4.78×10^4		
	45.0	1.75×10^{-2}	69	−63	2.15×10^4	−31	−16
Br	25.0	4.43×10^{-3}			2.04×10^4		
	45.0	3.05×10^{-2}	73	−44	1.12×10^4	−24	3
I	25.0	6.10×10^{-3}			3.64×10^3		
	45.0	3.80×10^{-2}	70	−54	2.05×10^3	−23	−8

Errors (standard deviations): $k_{(m\rightarrow t)}^{Na} \pm 3\%$, $\Delta H^\ddagger \pm 3$ kJ mol^{-1}, $\Delta S^\ddagger \pm 9$ J K^{-1} mol^{-1}, $K_1 \pm 5\%$, $\Delta H_1 \pm 5$ kJ mol^{-1}, and $\Delta S_1 \pm 15$ J K^{-1} mol^{-1}.

ation explored for sodium halide and Hpts in the reactions of *trans*-$[RhL_2Cl_2][NO_3]$ were 8.57×10^{-3}—4.28×10^{-2} and 0.00—3.43×10^{-2} (1.38×10^{-2} for X = I) mol dm^{-3} respectively. In the case of the reactions of *mer*-$[RhL(L')XCl_2]$ the ranges explored were: (*i*) X = Cl, NaCl 0.00—4.28×10^{-2}; Hpts 0.00—6.47×10^{-4}; (*ii*) X = Br, NaBr 0.00—4.28×10^{-2}, Hpts 0.00—6.17×10^{-4}; (*iii*) X = I, NaI absent, Hpts 0.00—5.14×10^{-3}.*

Observed rate constants of the approach to equilibrium, $k_{obs.}$, and equilibrium constants of the reactions, K_c, were determined as described previously.[3] At least six different concentrations of acid were employed for each reaction. Reactions in the presence of sodium halide were studied by carrying out at least four kinetic runs for each concentration of acid examined, using different concentrations of sodium halide (for the reactions at the highest concentration of acid only three runs were carried out). The temperatures used are listed in the Tables.

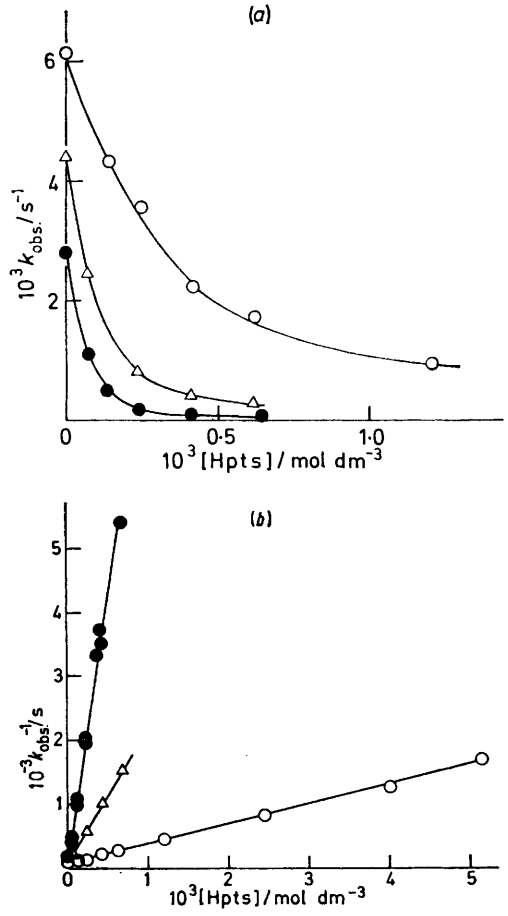

FIGURE 1 Effects of acidity on the *mer* ⟶ *trans* conversion of *mer*-$[RhL(L')Cl_3]$ (●), *mer*-$[RhL(L')BrCl_2]$ (△), and *mer*-$[RhL(L')ICl_2]$ (○) at 25.0 °C: (*a*) dependence of $k_{obs.}$ on [Hpts]; (*b*) same data plotted according to equation (3)

RESULTS

The *mer* ⟶ *trans* conversions go to completion when sodium halide is not added to the starting reaction mixture. Under these conditions the reactions obey a first-order rate law. When acid is added to the reacting mixture the rate of conversion is strongly decreased [Figure 1(*a*)], according to a dependence of $k_{obs.}$ on the concentration of Hpts described by relationship (2) [Figure 1(*b*)], where $k_{(m\rightarrow t)}^{Na}$ is the rate

$$k_{obs.} = k_{(m\rightarrow t)} = \frac{k_{(m\rightarrow t)}^{Na}}{1 + K_1[Hpts]} \quad (2)$$

$$\frac{1}{k_{obs.}} = \frac{1}{k_{(m\rightarrow t)}^{Na}} + \frac{K_1[Hpts]}{k_{(m\rightarrow t)}^{Na}} \quad (3)$$

constant of the *mer* ⟶ *trans* conversion carried out in the presence of only sodium toluene-*p*-sulphonate. The rate constants $k_{(m\rightarrow t)}^{Na}$ are collected in Table 1 together with the activation parameters and K_1 values. The values reported for $k_{(m\rightarrow t)}^{Na}$ are arithmetic means from five kinetic runs carried out in neutral solutions.

The reactions of *trans*-$[RhL_2Cl_2]^+$ with X^- do not go to completion in neutral solutions and the rate of approach to equilibrium obeys rate law (4), as previously found for this kind of reaction.[1,2] In an acidic medium the forward

$$-d[trans]/dt = k_{(t\rightarrow m)}[X^-][trans] - k_{(m\rightarrow t)}[mer] \quad (4)$$

$$k_{obs.} = k_{(t\rightarrow m)}[X^-] + k_{(m\rightarrow t)} \quad (5)$$

reaction is more enhanced and the observed rate constant, $k_{obs.}$, as expressed by equation (5), is a function also of the concentration of Hpts. The overall kinetic effect rises from a specific effect of acidity on both the forward [$k_{(t\rightarrow m)}$ rate term] and the reverse reaction [$k_{(m\rightarrow t)}$ rate term]. In fact, both the slope and the intercept of the straight lines obtained by plotting $k_{obs.}$ against halide concentration (Figure 2) change with the acid concentration. The dependence of the intercept on [Hpts] is quantitatively consistent with relationship (2), thus showing that it represents the value of the rate constant of the reverse reaction (1) (*i.e.* the *mer* ⟶ *trans* conversion). The $k_{(t\rightarrow m)}$ of rate law (4) increases with the acid concentration according to relationship (6) (Figure 3), where $k_{(t\rightarrow m)}^{Na}$ is the rate constant of the *trans* ⟶ *mer* conversion carried out in the presence of only sodium toluene-

$$k_{(t\rightarrow m)} = k_{(t\rightarrow m)}^{Na} + k_{(t\rightarrow m)}^{H}[Hpts] \quad (6)$$

* In each case the highest concentration of sodium halide did not exceed the value (5.14×10^{-2} − [Hpts]) mol dm^{-3}.

TABLE 2

Rate constants and activation parameters for *trans* ⟶ *mer* conversions and equilibrium constants, K_c, for the interconversions (1)

X	θ_c / °C	$k_{(m\rightarrow t)}^{Na}$ / dm³ mol⁻¹ s⁻¹	$\Delta H^{\ddagger}_{Na}$ / kJ mol⁻¹	$\Delta S^{\ddagger}_{Na}$ / J K⁻¹ mol⁻¹	$k_{(m\rightarrow t)}^{H}$ / dm⁶ mol⁻² s⁻¹	$\Delta H^{\ddagger}_{H}$ / kJ mol⁻¹	$\Delta S^{\ddagger}_{H}$ / J K⁻¹ mol⁻¹	K_c / dm³ mol⁻¹
Cl	25.0	1.80×10^{-2}			8.40			6
	35.0	5.35×10^{-2}	81	−5	16.5	52	−53	
	45.0	1.51×10^{-1}			33.3			
Br	25.0	3.45×10^{-2}			4.17			8
	35.0	9.30×10^{-2}	75	−21	8.34	51	−63	
	45.0	2.45×10^{-1}			16.0			
I *	25.0	7.03×10^{-2}			1.5			13
	35.0	1.91×10^{-1}	79	−3	3.7	63	−29	
	45.0	5.52×10^{-1}			8.0			

Errors (standard deviations): k ±3%, $\Delta H^{\ddagger}$ ±3 kJ mol⁻¹, $\Delta S^{\ddagger}$ ±9 J K⁻¹ mol⁻¹, K_c ±10%.
* $k_{(t\rightarrow m)}^{H}$ ±10%, $\Delta H^{\ddagger}_{H}$ ±8 kJ mol⁻¹, $\Delta S^{\ddagger}_{H}$ ±24 J K⁻¹ mol⁻¹.

p-sulphonate. The absorption spectrum of *trans*-$[RhL_2Cl_2][NO_3]$ is not affected by the acidity of the medium, whereas the spectra of *mer* complexes probably change with the acid content. This statement is supported by the fact that the wavelength of the isosbestic point occurring in the interconversion for X = Cl changes from 314 nm in neutral solutions to a limiting value of 300 nm in acid concentrations higher than 4×10^{-4} mol dm⁻³. In Table 2 are listed the values of $k_{(t\rightarrow m)}^{Na}$ and $k_{(t\rightarrow m)}^{H}$, together with the activation parameters. The equilibrium constants, K, of the interconversions carried out in neutral solutions are also reported.

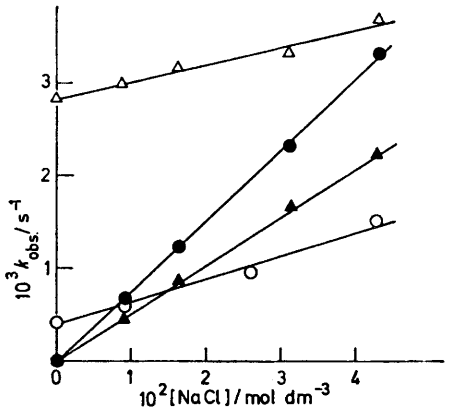

FIGURE 2 Effect of acidity on the pseudo-first-order rate constant of the approach to equilibrium, $k_{obs.}$ of the interconversion *trans*-$[RhL_2Cl_2]^+ + Cl^- \rightleftharpoons$ *mer*-$[RhL(L')Cl_3]$ at 25.0 °C. [Hpts] = absent (△), 1.20×10^{-4} (○), 3.43×10^{-3} (▲), and 6.00×10^{-3} mol dm⁻³ (●). The data at [NaCl] = 0 are the $k_{obs.}$ values related to the *mer* ⟶ *trans* conversion; see equation (5)

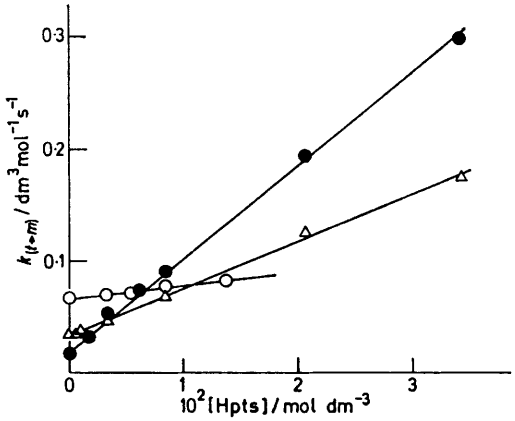

FIGURE 3 Effect of the acidity on $k_{(t\rightarrow m)}$ for the conversion *trans*-$[RhL_2Cl_2]^+ + X^- \rightleftharpoons$ *mer*-$[RhL(L')XCl_2]$ at 25.0 °C. X = Cl (●), Br (△), or I (○)

DISCUSSION

According to the experimental results the interconversions described by equation (1) follow rate law (7), when carried out in neutral or acidic solutions. Therefore, the forward ring-opening substitution reaction is acid catalysed. Acid-catalysed ring-opening substitution reactions are rather common for both octahedral and square-planar complexes.[7,8] The catalysis often arises from protonation of some basic site available on the co-ordinated chelate ligand. However, such a reaction path cannot be expected to operate in the cases under discussion since the chelation of L in *trans*-$[RhL_2Cl_2]^+$ engages all the electron pairs available on the chelating ligand. The acid catalysis could be explained by invoking an attack of the proton on the complex which should then bind the proton by means of the non-bonding electrons of the d^6 central atom, as formerly suggested to account for the acid catalysis which takes place in the hydrolysis of ruthenium(II) amine complexes.[9] However, the catalytic reaction path is plainly explained on the basis of the mechanism originally proposed for the acid hydrolysis of $[Fe(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridyl),[10] and afterward proposed for acid-catalysed reactions of many other octahedral and square-planar complexes containing polydentate ligands.[7,8,11] The mechanism which better explains the results for the *trans* ⟶ *mer* conversion implies, as a first reaction step, the opening of the chelate ring through a dissociative mechanism and possible formation of a five-co-ordinate intermediate [equation (8)],* whose basic end NMe_2 made available by dechelation undergoes fast reversible protonation [equation (9)]. The following

$$-\frac{d[trans]}{dt} = \frac{d[mer]}{dt} = \{k_{(t\rightarrow m)}^{Na} + k_{(t\rightarrow m)}^{H}[Hpts]\}[X^-][trans] - \frac{k_{(m\rightarrow t)}^{Na}[mer]}{1 + K_1[Hpts]} \quad (7)$$

* However, a solvent complex intermediate cannot be ruled out.

steps are nucleophilic attack of the entering X^- on both the unprotonated and protonated intermediates [equations (10) and (11)]. The reversibility of each step accounts also for the experimental results on the *mer* ⟶ *trans* conversion.

$$\underset{(trans)}{Rh(AsN)^+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(reactive\ intermediate)}{Rh\text{–}AsN^+} \quad (8)$$

$$Rh\text{–}AsN^+ + H^+ \overset{K}{\rightleftharpoons} Rh\text{–}AsNH^{2+} \quad (9)$$

$$Rh\text{–}AsN^+ + X^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{(mer)}{XRh\text{–}AsN} \quad (10)$$

$$Rh\text{–}AsNH^{2+} + X^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \underset{(mer\text{-}H^+)}{XRh\text{–}AsNH^+} \quad (11)$$

$$\underset{(mer)}{XRh\text{–}AsN} + H^+ \overset{K_1}{\rightleftharpoons} \underset{(mer\text{-}H^+)}{XRh\text{–}AsNH^+} \quad (12)$$

The overall rate law for this reversible reaction mechanism is described by equation (13).* In order to explain the experimental results it is required that neither

$$-\frac{d[trans]}{dt} = \frac{k_1(k_3 + k_5K[H^+])[X^-][trans]}{k_2 + k_3[X^-] + k_5K[H^+][X^-]} - \frac{k_2(k_4 + k_6K_1[H^+])[mer]_t}{(1 + K_1[H^+])(k_2 + k_3[X^-] + k_5K[H^+][X^-])} \quad (13)$$

the concentration of halide nor that of hydrogen ions has an important part in the denominator of the first term on the right-hand side of the above expression. Therefore, relationships (14) must hold, so that expression (13) takes

$$k_2 \gg k_3[X^-];\ k_2 \gg k_5K[H^+][X^-] \quad (14)$$

the simplified form (15). This is consistent with the rate

$$-\frac{d[trans]}{dt} = \left(\frac{k_1k_3}{k_2} + \frac{k_1k_5K[H^+]}{k_2}\right)[X^-][trans] - \frac{(k_4 + k_6K_1[H^+])[mer]_t}{1 + K_1[H^+]} \quad (15)$$

law (7) ($[H^+] = [Hpts]$), provided relationships (16) are introduced.

$$k_{(t\to m)}^{Na} = k_1k_3/k_2;\ k_{(t\to m)}^{H} = k_1k_5K/k_2;\ k_{(m\to t)}^{Na} = k_4;\ k_6 \approx 0 \quad (16)$$

According to the proposed mechanism the reactivity of *trans*-$[RhL_2Cl_2]^+$ towards different entering groups both in neutral and acidic solutions may depend to some extent on the nature of the incoming ligand since this may affect the k_3 and k_7 rate terms. It is apparent from the data in Table 2 that the reactivity order found for the uncatalysed reaction path [$k_{(t\to m)}^{Na}$; Cl < Br < I] is opposite to that found for the acid-catalysed one [$k_{(t\to m)}^{H}$; Cl > Br > I]. It is hard to rationalise these results merely in terms of different Rh · · · X bond formations in the k_3 with respect to k_5 reaction steps, since one would expect a similar trend for both reaction pathways. It is probable that the inversion of reactivity in going from uncatalysed to acid-catalysed reactions comes from some degree of hydrogen-bond formation in the protonated activated complex between the incoming halide and the protonated free amine end of L′. The basicity order of halides would imply a hydrogen-bond interaction with X^- in the activated complex of step (11) increasing in the order I < Br < Cl, and as such to qualitatively account for the inversion of the reactivity order experimentally found. Also the order of K_1 values (Table 1; Cl > Br > I), which according to the proposed mechanism describe the protonation constants of the NMe_2 end of the *mer* complexes, can be explained in a similar way, *i.e.* by the occurrence of hydrogen-bonding interactions between the proton and the co-ordinated halide in *mer*-H^+ [equation (12)].

The proposed mechanism explains the acid inhibition of the *mer* ⟶ *trans* conversion in terms of withdrawal of the reactive free end of the monoco-ordinated chelating ligand L′ by protonation, thus preventing the conversion through the k_4 reaction path. A *mer* ⟶ *trans* conversion through the k_6 reaction step would be still possible in acidic solutions. However, at least with halides as leaving groups, such a reaction step must be of little importance since it has never been observed whatever the leaving halide involved.

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* If equation (9) is not regarded as a labile equilibrium, rate law (13) changes form, becoming somewhat more complicated, but the limiting relationships (15) and (16) are still valid.

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