Kinetics of Solvolysis of the *trans*-Dichlorotetrapyridinecobalt(III) Ion in Water + Isopropyl Alcohol

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To investigate the effect of solvent structure on the first-order solvolysis of the *trans*-dichlorotetrapyridinecobalt(III) ion, rates have been measured in mixtures of water with isopropyl alcohol as the physical properties of these mixtures show that the addition of isopropyl alcohol to water in water-rich conditions is very effective in inducing the formation of structure in the solvent. A linear plot of log-(rate constant) against the Grunwald–Winstein *Y* factor confirms that the solvolysis is an S_N1-type process with considerable extension of the metal-chloride bond in the transition state. A non-linear plot of log (rate constant) against reciprocal of the dielectric constant shows that changes in solvent structure with composition are important in determining the variation of rate constant and this is confirmed by the observation of a maximum in the variation of both the enthalpy and entropy of activation in the region where the physical properties of the mixture indicate a maximum in the structure formation. The application of a free-energy cycle shows that the effect of structure is greater in the transition state than in the initial state.

Following the observation [1] that log(rate constant) for the solvolysis of the cation *trans*-$[Co(py)_4Cl_2]^+$ (py = pyridine) in water + methanol and in water + sucrose, in common with the solvolysis of many other complexes in water + co-solvent mixtures,[2] does not obey the linear relationship with the reciprocal of dielectric constant predicted [3–5] for reactants as point charges in a dielectric continuum, but that the enthalpy and entropy of activation in water + methanol both show [1] a maximum in the region of composition where the formation of structure in the mixed solvent has a maximum, we have extended this kinetic investigation to mixtures of water with a co-solvent which has a greater effect on the solvent structure than methanol. Thus, although the variation of the excess enthalpy of mixing with composition in water + co-solvent deviates little for methanol [6–8] from the symmetry about mole fraction of co-solvent $x_2 \sim 0.5$ expected for no or little induced interaction between solvent molecules and deviates a little farther for ethanol,[6–8] isopropyl alcohol (Pr^iOH) added to water produces [7] twin extrema, a minimum at $x_2 \sim 0.10$ and a maximum at $x_2 \sim 0.75$. The small minimum [9,10] in the decrease in the partial molar volume of methanol in water + co-solvent, $\bar{V}_2 - V_2^\circ$, at $x_2 \sim 0.1$—0.15 increases [10] by more than a factor of 2.5 for Pr^iOH and occurs in more dilute solutions at $x_2 \sim 0.01$.[10] Water + Pr^iOH shows [11] a pronounced maximum in its ultrasonic absorption at $x_2 \sim 0.15$, whereas for water + methanol the ultrasonic absorption increases steadily from pure water to pure methanol.[11] Moreover, the structural contribution to the temperature of maximum density shows [12] that Pr^iOH induces more structure than methanol in the water-rich region of the water + co-solvent mixtures.

Experimental

trans-$[Co(py)_4Cl_2][NO_3]$ was prepared as described previously,[1] based on the method of Werner and Feenstra.[13] AnalaR Pr^iOH was used and other materials were as previously described.[1] The rates of solvolysis were followed using the method as described [1] for pure water and water + methanol mixtures.

Results and Discussion

Variation of Rate with Temperature in $H_2O + Pr^iOH$.—Good linear plots were always found for log(optical density) against time in these mixtures covering at least 85% reaction for the temperatures 35, 40, 45, and 50 °C for a range of solvent compositions up to 66.67% v/v. Values for the first-order rate constant *k* calculated using the slopes of these linear plots are collected in Table 1. The temperature was measured for each determination resulting in groups of determinations around each of the above temperatures rather than exact repeats; the temperature of each individual run is recorded in Table 1. Plots of log *k* against $1/T$ K were linear for each solvent composition. Values for the enthalpy, $\Delta H^\ddagger$, and entropy, $\Delta S^\ddagger$, of activation were determined using all the individual data in Table 1 by the least-squares procedure. These values are collected in Table 2.

Variation of Rate with Solvent Composition.—Figure 1 shows that a plot of log *k* against reciprocal of dielectric constant, D_s^{-1}, gives a curve whose curvature is much more pronounced than that found in water + methanol. The values of *k* at 25 °C were calculated using the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Table 2; *k* determined previously for pure water is included in Figure 1. The values of D_s were interpolated from the data of Åkerlöf.[14]

Values for the Grunwald–Winstein function [15] have been calculated [16] for water + Pr^iOH from two sets of data [17,18] on the rates of solvolysis of t-butyl chloride in these mixtures. Figure 2 shows plots of log *k* at 25 °C for the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ against *Y* in water + Pr^iOH. The plot using the *Y* values derived from the rate data of Akhtar and Begum [18] is linear whilst that using the *Y* values derived from Robertson and Sugamori [17] is a curve; this result is comparable with that found [16] for the rates of solvolysis of the *trans*-dichloro(1,2-diaminoethane)cobalt(III) ion in water + Pr^iOH. The values of *k* at 25 °C used in Figure 2 were calculated from the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Table 2. The slope of the linear plot in Figure 2 is obtained using the *Y* values derived from the rate data of Akhtar and Begum which gives $m = -0.14$ which compares well with $m = -0.13$ found [1] for a similar plot for this complex in water + methanol where *Y* values were derived from a different source. This linear plot confirms [16] that the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in these mixed aqueous solvents is an S_N1-type reaction with the Co–Cl bond considerably extended in the transition state approximating to complete fission.[1] This is supported by the conclusions derived for complexes of this type for cobalt(III) from volumes of activation for solvolysis and comparison with overall volume changes [19,20] which suggest a *D*-type mechanism.

Table 1. First-order rate constants ($10^5 k/s^{-1}$) for the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in H_2O + Pr^iOH

	Mole fraction of Pr^iOH					
θ_c/°C	0.025	0.055	0.104	0.134	0.189	0.317
35.00	3.30		4.65		5.4	6.1
35.00						6.1
35.05	3.33	3.88	4.53	4.95	5.2	
36.10				5.1		
35.15					5.8	
35.20		3.68				
35.30					5.7	
39.95		8.7				
40.00	6.6	8.5	10.7			14.0
40.00	7.4					
40.05			11.8			
40.05			11.5			
40.10					13.3	
40.15				10.2		
40.20					12.5	
40.30						12.5
40.35					9.7	
40.50			10.3			
40.75	8.3					
44.30		14.5				
44.55	13.2					
44.65	13.2					
44.75			20.3			
44.80						25.7
44.90				21.8		
44.95			20.7			
45.05					24.2	
45.20		17.0		21.2		
45.25					25.0	
46.05						30.3
47.90						34.5
48.10				34.2		
48.20	21.5				38.3	
48.30						41.5
48.50	18.3				33.0	
48.50	27.7					
48.60			36.0		37.2	
48.80			37.8	37.2		
48.80				37.2		
48.85					40.0	
49.00		31.5				
49.00		27.7				

Table 2. Values of the enthalpy and entropy of activation at 25 °C for the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in H_2O + Pr^iOH

Mole fraction of Pr^iOH	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
0 *	101 ± 11	−3 ± 21
0.025	113 ± 3	39 ± 7
0.055	119 ± 4	54 ± 11
0.104	122 ± 4	67 ± 12
0.134	118 ± 2	54 ± 6
0.189	116 ± 4	53 ± 11
0.317	114 ± 7	44 ± 9

* Values taken from ref. 1.

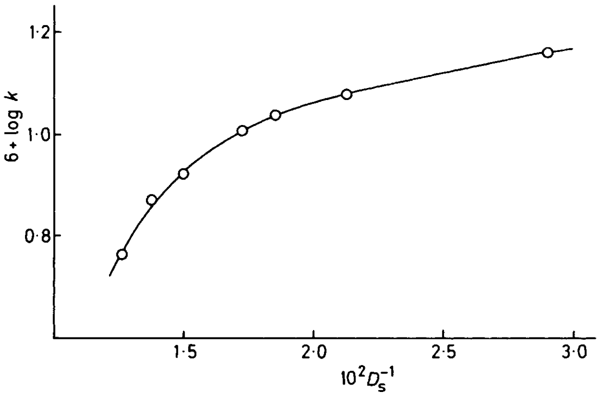

Figure 1. Plot of log *k* at 25 °C in H_2O + Pr^iOH against the reciprocal of the dielectric constant.

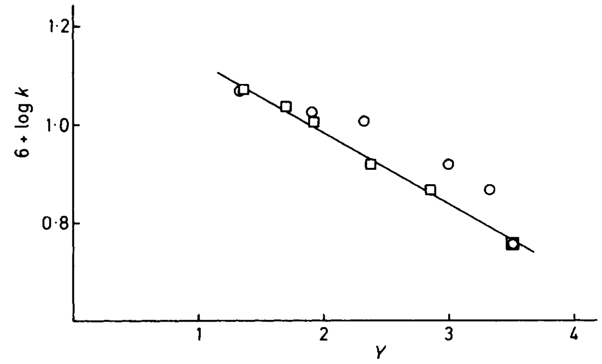

Figure 2. Plot of log *k* at 25 °C in H_2O + Pr^iOH against *Y* values; rate data used in calculation of *Y* values from ref. 17 (○) and ref. 18 (□)

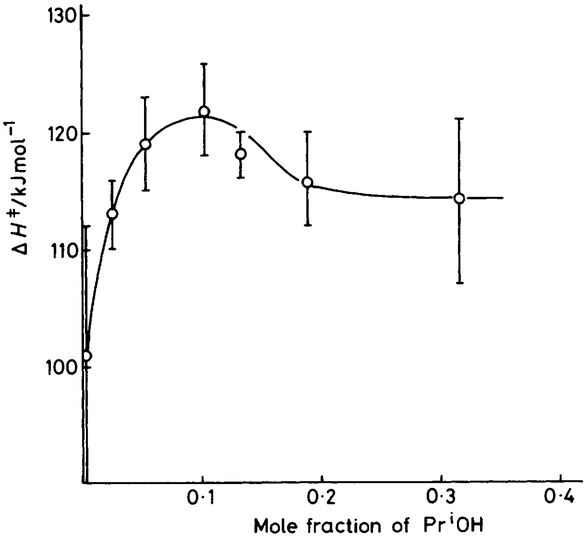

Figure 3. Plot of $\Delta H^\ddagger$ against solvent composition in H_2O + Pr^iOH

Variation of Transition State Parameters with Solvent Composition.—The errors quoted for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Table 2 are fairly normal, and plots of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ against solvent composition in Figures 3 and 4 show that each has a maximum in the composition range x_2 = 0.05—0.15. This is the composition region where changes[10,11] in $\bar{V}_2 - V_2^\circ$ and the ultrasonic absorption indicate a maximum in the structure formation in the solvent. This correlation can be compared with the variation of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in water + methanol both of which show a maximum of $x_2 \sim$ 0.2—0.03 where the physical properties of water + methanol show a maximum in the formation of

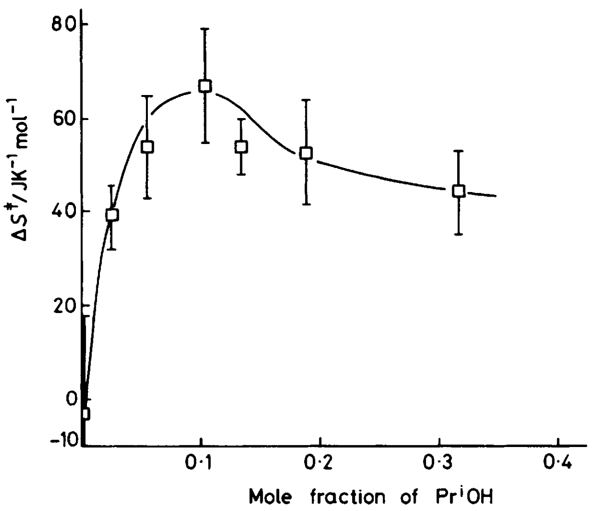

Figure 4. Plot of $\Delta S^\ddagger$ at 25 °C against solvent composition in H_2O + Pr^{i}OH

structure in the solvent.[10,11] The maxima in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for water + Pr^{i}OH have moved to lower mole fractions of co-solvent, corresponding to the shift of the maximum in structure formation to lower mole fractions from that for water + methanol. The effect of these maxima in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ tends to cancel out in $\Delta G^\ddagger$ as a plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ is linear.

The effect of change in solvent composition on the free-energy of activation [or on log (rate constant)] for such a solvolysis is represented [1,2] by an extension of the Laidler–Landskroener equation [3] which itself only represents the change of rate with change in the bulk dielectric constant [equation (1)]. This equation applies to the rate determining

$$2.303RT\log\left(\frac{k_w}{k_s}\right) = \frac{Ne^2}{2}\left(\frac{1}{D_s}-\frac{1}{D_w}\right)\left[\frac{Z_M^2}{r_M}+\frac{Z_X^2}{r_X}-\frac{Z_C^2}{r_C}+\frac{3}{2}\left(\frac{G_M}{r_M^3}+\frac{G_X}{r_X^3}-\frac{G_C}{r_C^3}\right)\right] + \Delta G^\ominus_t(M)_n + \Delta G^\ominus_t(X)_n - \Delta G^\ominus_t(C)_n \quad (1)$$

step of the solvolysis of a complex $C^{Z}{}_{C}$ involving the loss of a ligand $X^{Z}{}_{X}$ from the metal $M^{Z}{}_{M}$ with sufficient extension of the transition state that $M^{Z}{}_{M}$ and $X^{Z}{}_{X}$ can be regarded as separate solvated species. Subscripts w and s indicate pure water and the mixed solvent respectively, r = radius, Z represents charge, e = electronic charge, N = Avogadro's number, G is related to dipole moment, and $\Delta G_t^\ominus(i)_n$ represents all the contributions to the free energy of transfer of the species i except that due to Born charging effects. If the original Laidler–Landskroener equation is to apply,[3] the effect of the terms $\Delta G_t^\ominus(i)_n$ must cancel, as in equation (2).

$$\Delta G_t^\ominus(C)_n \sim \Delta G_t^\ominus(M)_n + \Delta G_t^\ominus(X)_n \quad (2)$$

The non-linearity of Figure 1 shows that this does not happen in water + Pr^{i}OH and the importance of structural contributions, represented by $\Delta G_t^\ominus(i)_n$, are shown in Figures 3 and 4. This absence of equality in equation (2) in this case can be pursued further by the application of a free-energy cycle to the process initial state→transition state in pure water and in the mixture shown below; these two processes are related by the total free energies of transfer, $\Delta G_t^\ominus(i)$, the values of which are known for Cl^-.[21]

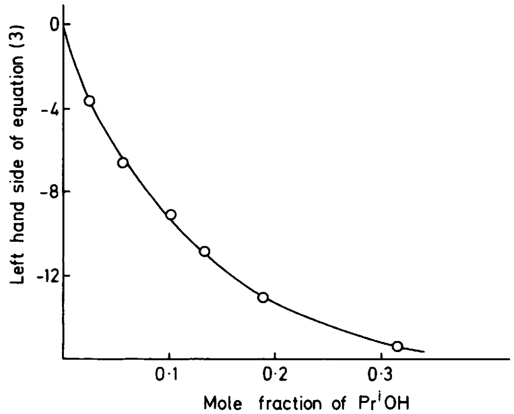

Figure 5. Plot of the left hand side of equation (3) at 25 °C against solvent composition in H_2O + Pr^{i}OH

$$\begin{tikzcd}
{[Co(py)_4Cl_2]^+{}_w} \arrow[r, "\Delta G_w^\ddagger"] & {[Co(py)_4Cl]^{2+}{}_w} \arrow[d, "\Delta G_t^\ominus\{[Co(py)_4Cl]^{2+}\}"] & + & {Cl^-{}_w} \arrow[d, "\Delta G_t^\ominus(Cl^-)"] \\
{[Co(py)_4Cl_2]^+{}_s} \arrow[u, "-\Delta G_t^\ominus\{[Co(py)_4Cl_2]^+\}"] \arrow[r, "\Delta G_s^\ddagger"] & {[Co(py)_4Cl]^{2+}{}_s} & + & {Cl^-{}_s}
\end{tikzcd}$$

Equation (3) follows [1,2] from this cycle.

$$2.303RT\log\frac{k_w}{k_s} - \Delta G^\ominus_t(Cl^-) = \Delta G^\ominus_t\{[Co(py)_4Cl]^{2+}\} - \Delta G_t^\ominus\{[Co(py)_4Cl_2]^+\} \quad (3)$$

Using the values of k_w in ref. 1 with those for k_s in Table 1 and the interpolated values [21] for $\Delta G_t^\ominus(Cl^-)$ in water + Pr^{i}OH, Figure 5 shows that a plot of the left hand side of equation (3) against solvent composition is always negative, as found also in water + methanol.[1] As $\Delta G_t^\ominus(i)$ for i = cation in water + alcohol mixtures are always negative (except for some unipositive ions in water + methanol), with $|\Delta G_t^\ominus(i)|$ for $i = M^{2+}$ greater than that with $i = M^+$,[21–23] Figure 5 shows that $|\Delta G_t^\ominus\{[Co(py)_4Cl]^{2+}\}| > |\Delta G_t^\ominus\{[Co(py)_4Cl_2]^+\}|$ and the effect of change in solvent structure with solvent composition is greater on the transition state than on the initial state.

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