Kinetics of Solvolysis of the *trans*-Dichlorotetrapyridinecobalt(III) Ion in Water and in Water + Methanol

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Rates for the first-order solvolysis of the *trans*-dichlorotetrapyridinecobalt(III) ion have been measured in water and in mixtures of water and methanol for a range of temperatures. A non-linear dependence of log (rate constant) with reciprocal of dielectric constant suggests that the effects of solvent structure are important and this is confirmed by the comparison of the variation with solvent composition of the transition-state parameters with the variation with solvent composition of a range of physical properties of the solvent mixture. The application of a free-energy cycle relating the process initial state→transition state in water to that in water + methanol shows that changes in solvation of the transition state have a dominant effect on the rate.

In a survey of the kinetics of S_N1-type solvolysis reactions of octahedral complexes in mixtures of water + co-solvent, the variation of rate with respect to dielectric properties and solvent structure was investigated.[1] By applying a free-energy cycle to the long stretching of the metal–ligand bond it is possible to determine whether changes in solvation with solvent composition in the initial or in the transition state have a dominant effect on the rate of reaction. A high degree of unanimity was found for a large number of complexes for a range of co-solvents: changes in solvation in the transition state have a dominant effect on the rate. It is therefore of interest to explore the variation of rate with solvent composition for other complexes. Although the *trans*-dichlorotetrapyridinecobalt(III) ion was one of the complexes used to show that basic hydrolysis requires a mechanism different from hydrolysis under acidic or neutral conditions,[2] little further kinetic work has been done with it. It has been shown that, at high concentrations of OH^- and for the addition of other bases like azide or acetate ions, the loss of pyridine from the complex occurs,[3] contrary to the results in acidic solutions and in a borate buffer of pH 9.18 where only a chloride ion is lost. The effect of changes in dielectric constant on the rate of solvolysis has also been investigated by adding sucrose to the reaction mixture.[4]

EXPERIMENTAL

Materials.—General purpose reagent $CoCl_2 \cdot 6H_2O$ and laboratory grade pyridine, nitric acid, and hydrochloric acid were used in the preparation of *trans*-dichlorotetrapyridinecobalt(III) nitrate. The method used was based on that proposed by Werner and Feenstra [5] involving oxidation by chlorine gas. However, our observations during the preparation differed from those of Werner and Feenstra at one point. A considerable number of experiments was performed in order to achieve the optimum conditions for this preparation. When the chlorine was passed through the mixture used previously [5] (20 g of $CoCl_2$ in 30 g of water and 30 g of pyridine) a pink solid was formed and not a blue solution as previously reported, with a low yield of product due to poor contact between the solid and the chlorine gas. Addition of a large excess of pyridine (py) to dissolve this pink solid caused the subsequent absorption of greater than molar proportions of chlorine and no $[Co(py)_4Cl_2]Cl$ was precipitated. The addition of an excess of water to dissolve the pink precipitate resulted in only a small yield of the product. A combination of a slightly higher temperature with small volumes of water was found to give optimum yields of the product. The following final conditions were employed: pyridine (30 g) was added to a solution containing cobalt(II) chloride (20 g) dissolved in water (40 g), and the precipitate formed redissolved at 35 °C. After passing chlorine gas through the solution, it was cooled and allowed to stand for a few hours. The precipitate was then filtered off and washed successively with small volumes of ice–water, ethanol, and diethyl ether. The *trans*-dichlorotetrapyridinecobalt(III) chloride was purified by re-precipitation from an aqueous solution by adding HCl: this process was repeated. To prepare the nitrate, the chloride was dissolved in water at 45 °C and nitric acid added. The nitrate was purified by re-precipitation with added HNO_3, followed by repeated washings as described above for the chloride. The nitrate was then dried in air, producing very fine, green crystals. Large green needles were obtained after recrystallization from water containing a little acetic acid. The dry, crystalline nitrate showed no sign of decomposition or loss of pyridine when stored for several months. For the kinetic work, the very fine crystals were used to obtain rapid dissolution.

For the kinetic investigation, A.R. nitric acid was used. Laboratory grade NaCl and K[OH] were used. A buffer solution of pH 8 was prepared by mixing 25 cm^3 of 0.2 mol dm^{-3} $Na[H_2PO_4]$ (A.R.) with 46.8 cm^3 of 0.2 mol dm^{-3} K[OH] and the resulting solution diluted to 100 cm^3 with distilled water. A.R. methanol was used and water was distilled once in an all-glass still.

Procedure.—The solvolysis kinetics were followed in the thermostatted cell compartments of various spectrophotometers: a Unicam SP800 with scale expansion unit and a millivolt recorder; a Unicam SP500 series 2 spectrophotometer equipped with SP505 programmed controller to allow the recording of optical densities at pre-set time intervals on a flat bed recorder; and a manually operated Unicam SP500 spectrophotometer. 5 mm and 10 mm stoppered cells were used, and the results obtained from these several spectrophotometers agreed well amongst themselves.

RESULTS AND DISCUSSION

Both the chloride and nitrate showed a peak absorption at 295 nm which disappeared completely when the solvolysis was finished. Addition of methanol to aqueous solutions produced no spectral shifts in this peak. All the kinetic results were obtained using the nitrate at 295 nm with an initial concentration *ca.* 8×10^{-5} mol dm^{-3}. The decay of optical density was measured in the following conditions at the same temperature: 5×10^{-3} mol dm^{-3} NaCl; 5×10^{-3} and 5×10^{-4} mol dm^{-3} HNO_3; 1×10^{-4} mol dm^{-3} K[OH]; pH 8 phosphate buffer and pH 8 borate buffer. The plots of log (optical density) against time for pure water and the NaCl solution gave straight lines with the same slope. For the solutions containing HNO_3, the plot of log (optical density) against time for 5×10^{-3} mol dm^{-3} was curved whereas that for 5×10^{-4} mol dm^{-3} was linear with a slope equal to that for pure water and the NaCl solution. The plots of log (optical density) against time for the K[OH] solution and the buffer solutions were curved. The detailed solvolysis kinetics were therefore followed in pure water and in the mixtures water + methanol without any adjustment of the pH or the ionic strength: this absence of an effect of acidity confirms the earlier observation.[2]

TABLE 1

First-order rate constants for the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in pure water

θ_c/°C	10^5k/s^{-1}	θ_c/°C	10^5k/s^{-1}
30.00	0.92	45.05	9.3
30.00	1.18	45.00	9.5
30.15	1.57	45.00	8.0
35.00	2.03	45.00	9.0
35.00	2.07	48.65	11.2
40.00	4.00	48.85	12.3
40.00	4.48	48.65	11.5
39.95	3.92	48.70	15.7
42.50	5.7	48.65	13.8
42.50	5.7	48.65	12.2
42.45	5.8	48.70	11.8
45.05	9.5		

Variation of Rate with Temperature in Pure Water.—The rates were followed for very long periods at 30, 35, 40, 42.5, 45, and 49 °C. Good linear plots for log (optical density) against time were always obtained. First-order rate constants k derived from the slopes of these plots are given in Table 1. A plot of log k against reciprocal of absolute temperature was linear; values for the enthalpy $\Delta H^\ddagger$ and entropy $\Delta S^\ddagger$ of activation obtained by the application of the least-squares procedure are given in Table 3.

Variation of Rate with Temperature in Water + Methanol.—Rates were measured in 5, 10, 20, 30, 40, 50, 66.7, 80, and 93.7% v/v methanol for temperatures 35, 40, 45, and 50 °C. Values for the first-order rate constants obtained from the slopes of the plots of log (optical density) against time are collected in Table 2. In addition, values of k obtained in pure methanol are

TABLE 2

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

	Mole fraction of methanol									
θ_c/°C	0.023	0.047	0.100	0.160	0.229	0.308	0.471	0.641	0.870	1.000
34.95				4.30						
35.00		3.30	3.77	4.27	5.0	5.2		7.6	8.8	10.5
35.00		3.30	3.72	4.18	4.60	5.1		7.7	8.8	
35.00		3.22	3.72	4.45		5.9		8.3		
35.00		3.57				6.4		8.1		
35.00						5.6				
35.05	3.12	3.69					6.6	7.9		10.2
35.05	3.15	3.77					6.9	8.0		
35.10					4.83	5.6		10.3		
35.15						6.8				
35.55	3.38									
39.80					10.3					
40.00	7.3	7.7	8.1			12.3	15.2	18.3		
40.00		7.8	8.3			13.3	15.5			
40.00			8.5							
40.05	7.4	7.6	8.7	9.5	11.0	13.0		16.8	20.7	
40.05			8.5	9.5					21.5	
40.10					11.00			18.8		
44.80						26.2		32.7		
44.85							29.2			
44.90						27.7			40.3	
44.95									37.2	
45.00	12.0			21.5	24.2		28.0			
45.00				19.2						
45.05	18.5	16.8	19.7	21.8	25.3					
45.05				21.2	26.2					
45.10		16.5	19.2					33.0		
48.50					40.0		41.0			
48.60	22.7	25.3			36.8	28.8	44.2	55		
48.60								53		
48.65	22.7					46.5				
48.70				35.3						
48.75		27.7		35.0	41.5					
48.85			33.0							
48.85			33.5							
48.90			31.5							
49.0									64	
49.1									71	

TABLE 3

Values of the enthalpy and entropy of activation at 25 °C for the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in water + methanol

Mole fraction of methanol	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
0	101 ± 11	−3 ± 21
0.023	121 ± 7	64 ± 24
0.047	124 ± 4	74 ± 12
0.100	128 ± 5	88 ± 15
0.160	125 ± 2	81 ± 4
0.229	128 ± 6	88 ± 19
0.308	125 ± 8	83 ± 25
0.471	116 ± 8	51 ± 26
0.641	115 ± 7	51 ± 29
0.870	115 ± 7	54 ± 19

also included in Table 2. Linear plots of log k against $1/T$ K were obtained for all solvent compositions and values for $\Delta H^‡$ and $\Delta S^‡$ obtained by the application of the least-squares procedure to these plots are given in Table 3.

The Effect of Solvent Composition on the Solvolysis.—Tables 1 and 2 show that the rate constant tends to increase smoothly with increasing methanol content of the mixture. Extrapolation of the data in Table 3 to 25 °C for pure water produces $k = 5.8 \times 10^{-5}$ s^{-1} which compares reasonably well with the value reported [2] for this temperature, $k = 8.2 \times 10^{-5}$ s^{-1}. Figure 1 shows that a plot of log k against the Grunwald–Winstein [6] Y values is linear, which shows that the reaction is of an S_N1 type with considerable extension of the Co–Cl bond in the transition state: Y-values were interpolated from the collection of Wells.[7] However, $m = -0.13$ obtained from the slope of Figure 1 is considerably different from $m = 0.18$—0.35 obtained [8] from similar complexes with ammonia or 1,2-diaminoethane as complexing ligands instead of pyridine in water + methanol.

The relationship between log k and dielectric constant D for the solvolysis of a complex C^{Z_C} involving the extension of a $M^{Z_M} \cdots X^{Z_M-}$ is expressed [1] by equation (1),

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

where subscripts w and s indicate pure water and mixed solvent respectively, Z represents charge, r = radius, e = electronic charge, G is related to dipole moment, N = Avogadro's number, and $\Delta G_t^{\ominus}(i)_n$ includes all changes in free energy resulting from structural changes in the solvents when species i is transferred from water into the mixture. A linear plot for log k_s against D_s^{-1} can only be obtained if equation (2) holds. However,

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

Figure 2 shows that a plot of log k against D_s^{-1} is curved with a positive slope: values for D_s were interpolated from the data of Åkerlof [9] and of Martin and Brown.[10] The curvature is accentuated when points at mole fractions of methanol >0.31 are included.

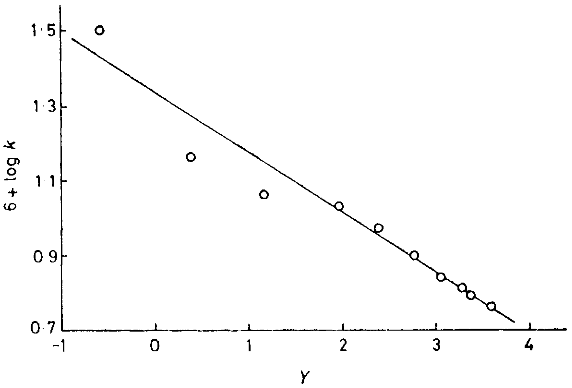

FIGURE 1 Plot of log k at 25 °C in water + methanol against Y values

Figure 2 also shows a plot of log k_s and D_s^{-1} for the solvolysis in H_2O + sucrose: [4] values for D_s were interpolated from the data of Åkerlof [9] and Malmberg and Maryott.[11] This is also a curve, contrary to the figure shown in the original reference,[4] where rate data for pure water are not given; but it has a negative slope and that in water + methanol has a positive slope. For a solvolysis like this where $Z_C = +1$, $Z_M = +2$, $Z_X = -1$, and $r_M \sim r_C$, plots of log k_s against D_s^{-1} should have a negative slope if the term in G in equation (1) can be ignored and if equation (2) holds. The non-linearity of the plots in Figure 2 combined with the diversity of the slope suggests that equation (2) does not hold since it is not expected that the term in G will vary greatly between mixtures with different co-solvents. It therefore seems likely that structural changes induced in the mixture by the addition of the co-solvent are important.

The effect of solvent structure on the rate is shown more clearly in Figure 3, where plots of $\Delta H^‡$ and $\Delta S^‡$ show extrema at a mole fraction of methanol *ca.* 0.2—0.3: the errors, which are not abnormal, are given in Table 3 and Figure 3 and show that the extrema are real. Properties of water + methanol mixtures, such as the excess thermodynamic functions of mixing,[12,13] decrease in the partial molar volume of methanol,[14,15] increase in the structural contribution to the change in the temperature of maximum density,[16] and viscosity [17] show that the addition of methanol to water first

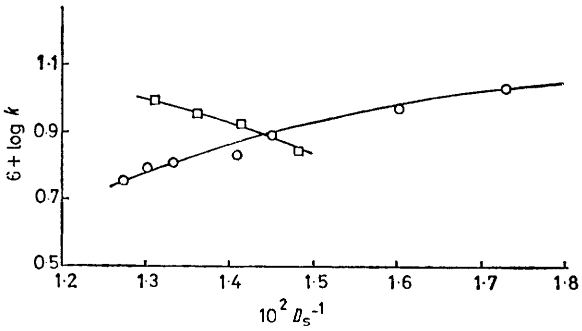

FIGURE 2 Plots of log k at 25 °C against reciprocal of dielectric constant for water + methanol ( ) and water [illegible] ( )

increases the structure in solution. The comparison of these properties with those of other water + alcohol mixtures shows that, compared with other alcohols, methanol has only a small structural effect. Thus, the deviation of the minimum in the excess enthalpy of mixing from mole fraction = 0.5 is small for methanol compared with the other alcohols, particularly those with a branched carbon chain;[12,13,18] the decrease in the partial molar volume of methanol, $\bar{V}_2 - V_2^\ominus$, is only small compared with the decrease found for other alcohols;[14,15] methanol produces no real elevation of the absorption of ultrasonic waves, unlike the high absorption found with branched chain alcohols.[19] However, the maximum of the effect on $\bar{V}_2 - V_2^\ominus$ [14,15] and viscosity[17] in water + methanol occurs in the same region of composition as that found for the extrema in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Figure 3.

Application of the free-energy cycle,[1] referred to earlier, concerning the process initial state→transition state in water and in water + alcohol to this present system produces the scheme shown, where subscript w

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

and s refer to water and water + methanol, respectively, and $\Delta G_t^\ominus(i)$ is the free energy of transfer of species i from water into water + methanol. Equation (3) can be deduced[1] from this.

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

Values for $\Delta G_t^\ominus(Cl^-)$ are available[20,21] for mole fractions of methanol up to *ca.* 0.35 at 25 °C and values for k_w and k_s at 25 °C can be calculated from the transition-state parameters in Table 3. In general, for water + co-solvent mixtures, $\Delta G_t^\ominus(i)$ for i = a cation are negative,[20-22] except for some unipositive alkali metals with small positive values in water + methanol,[20] and $\Delta G_t^\ominus(i)$ for i = bipositive cation M^{2+} are always negative with $\Delta G_t^\ominus(M^{2+})$ more negative than $\Delta G_t^\ominus(M^+)$. Therefore, if the left-hand side of equation (3) is negative, changes in solvation on the bipositive transition state have a dominant effect on the rate; alternatively, if the left-hand side of equation (3) is positive, changes of solvation on the unipositive initial state have a dominant effect. Figure 4 shows that a plot of the left-hand side of equation (3) for *trans*-$[Co(py)_4Cl_2]^+$ at 25 °C in water + methanol is negative; and therefore, changes in solvation on the transition state have a dominant effect on the rate. This is comparable with the conclusions reached from the application of a cycle of the above type to the solvation of a range of transition-metal complexes in water + co-solvent with a variety of co-solvents.

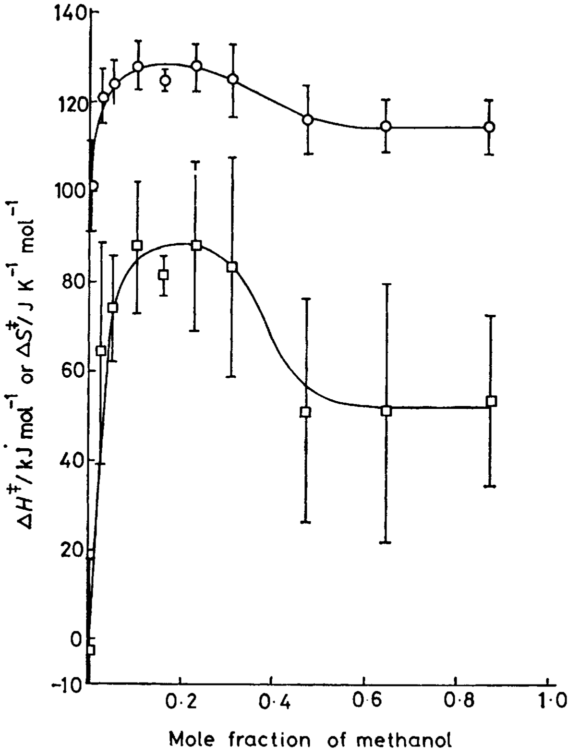

FIGURE 3 Plots of $\Delta H^\ddagger$ (kJ mol^{-1}) (○) and $\Delta S^\ddagger$ (J K^{-1} mol^{-1}) (□) for 25 °C against solvent composition for water + methanol

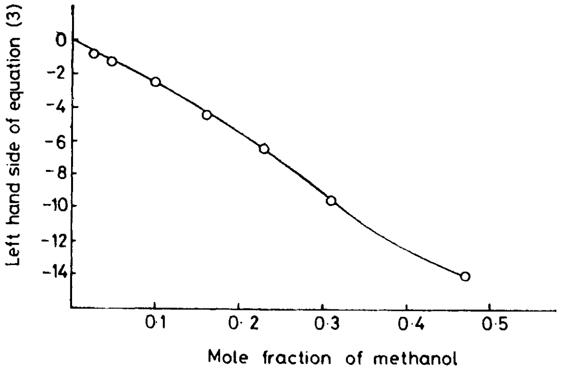

FIGURE 4 Plot of the left-hand side of equation (3) for 25 °C against solvent composition in water + methanol: the value of $\Delta G_t^\ominus$ (Cl$^-$) for mole fraction = 0.471 is extrapolated from the experimental data in ref. 20

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