The Relative Nucleophilic Efficiency of Water and Dimethyl Sulphoxide in the Aqueous Substitution of Aquapentacyanocobaltate(III) and Chloropentacyanocobaltate(III)

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The kinetics of substitution of $[Co(CN)_5Cl]^{3-}$ by water and by dimethyl sulphoxide (dmso) may be quantitatively interpreted by the mechanism in equations (i)—(iii). High-performance liquid chromatographic analysis confirms the direct formation of a single, probably sulphur-bonded, isomer of $[Co(CN)_5(dmso)]^{2-}$ from $[Co(CN)_5Cl]^{3-}$ as well as *via* $[Co(CN)_5(OH_2)]^{2-}$. The kinetics suggests the participation of the dissociatively formed intermediate $[Co(CN)_5]^{2-}$, but charged nucleophiles (NCS^- or N_3^-) react more slowly with $[Co(CN)_5]^{2-}$ than do the uncharged nucleophiles (dmso and water) when the leaving group is Cl^- compared to the case when the leaving group is OH_2. These results support the view that the substitution occurs by an I_d interchange mechanism.

$$[Co(CN)_5Cl]^{3-} + H_2O \xrightarrow{k_9} [Co(CN)_5(OH_2)]^{2-} + Cl^- \qquad (i)$$

$$[Co(CN)_5Cl]^{3-} + dmso \xrightarrow{k_{10}} [Co(CN)_5(dmso)]^{2-} + Cl^- \qquad (ii)$$

$$[Co(CN)_5(OH_2)]^{2-} + dmso \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(CN)_5(dmso)]^{2-} + H_2O \qquad (iii)$$

In a previous paper[1] we presented a preliminary account of the evidence which indicated that the substitution of the pentacyanocobaltate(III) series of complexes should properly be classed as I_d despite their continued description[2] as *D*-type. In this paper we present an account of the kinetics of substitution of both $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5Cl]^{3-}$ by dimethyl sulphoxide (dmso) in aqueous solution. The interest in this work lies in the fact that dmso is the first uncharged nucleophile to be studied in competition with water both in the anation of $[Co(CN)_5(OH_2)]^{2-}$ and also during the hydrolysis of $[Co(CN)_5Cl]^{3-}$. The emphasis in mechanistic substitution studies has moved in recent years to the study of mainly cationic systems. Currently work is appearing on the base-catalysed substitution of penta-aminecobalt(III) cations where it seems[3,4] that electrostatic and ion-pairing interactions are of less importance than the purely kinetic efficiency of the incoming nucleophile. In complete contrast, in the pentacyanocobaltate(III) systems there is a marked effect due to charge interaction even though the complication of reactant ion association has been removed by the common anionic nature of the reactants. The reported values for the competition ratios between reactions (1) and (2) change by approximately an order of magnitude[5] when the charge on the ion forming $[Co(CN)_5]^{2-}$ changes from 2− to 3−. The present work has shown that the competition ratio for dimethyl sulphoxide compared to water is slightly dependent on the leaving group which forms the intermediate $[Co(CN)_5]^{2-}$. The result may also be used to show that the relative nucleophilic efficiency of dmso and either NCS^- or N_3^- increases by at least a factor of 30 when the leaving group Cl^- is replaced by H_2O. These results suggest that a change of leaving group affects the relative efficiencies of even neutral ligands and that electrostatic repulsion markedly reduces the nucleophilic efficiency of anions. The existence of these interactions is evidence that the departing ligand is still adjacent to the co-ordination sphere of the complex when the incoming nucleophile arrives and they imply that the substitution is I_d in character. By definition, the *D* mechanism requires that the fully formed and equilibrated intermediate $[Co(CN)_5]^{2-}$ should have lost all memory of the charge of the system from which it is formed.

$$[Co(CN)_5]^{2-} + X^- \longrightarrow [Co(CN)_5X]^{3-} \qquad (1)$$

$$[Co(CN)_5]^{2-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} \qquad (2)$$

The measurement of the nucleophilic efficiency ratio of dmso and water from the kinetics of substitution of $[Co(CN)_5(OH_2)]^{2-}$ was only possible when a correction for the variation of dmso activity with concentration was applied. The experiments closely resemble those with pyridine[6] where activity variation probably concealed a small kinetic effect. This problem highlights the advantage of the direct measurement of nucleophile competition where the desired ratio is measured in a single experiment rather than from a series of experiments under varying conditions.

Experimental

Reagents.—G.P. dimethyl sulphoxide was used as received. The complex $[Co(CN)_5(dmso)]^{2-}$ was synthesized in solution from $[Co(CN)_5(OH_2)]^{2-}$ prepared photolytically[7] by reaction with 10 mol dm^{-3} dmso at 40 °C. A single product was shown to be formed stoicheiometrically by high-performance liquid chromatography (h.p.l.c.) and u.v. spectroscopy. The preparation and sources of the remaining chemicals have been described previously.[5] The solutions of $[Co(CN)_5(OH_2)]^{2-}$ required for the substitution reactions were usually prepared by the hydrolysis of $[Co(CN)_5Cl]^{3-}$ for 2 h at 40 °C. The h.p.l.c. experiments used photolytically prepared $[Co(CN)_5(OH_2)]^{2-}$

Apparatus.—The reactions were carried out in a thermostatted 1-cm cell held at 40.0 ± 0.1 °C using a Perkin-Elmer 402 spectrophotometer. They were started by the injection of a *ca.* 1 mol dm^{-3} solution (0.01 cm^3) of either $[Co(CN)_5Cl]^{3-}$ or $[Co(CN)_5(OH_2)]^{2-}$ into a solution (2.5 cm^3) containing the remaining components.

The h.p.l.c. apparatus has been described previously[8,9] although in this application Whatman cartridge columns were employed. The eluting medium was water containing 0.1 mol dm^{-3} tetraethylammonium chloride and between 0 and 10% methanol, depending on the age of the column. In this, as in previous analyses, the retention characteristics of the columns varied with use.[8] The reactions were started by the addition and rapid solution of the calculated weight of $[Co(CN)_5Cl]^{3-}$ in a solution (25 cm^3) of the remaining reactants held in a stoppered conical flask thermostatted at 40.0 ± 0.2 °C. The samples for h.p.l.c. were immediately diluted five-fold with water and frozen in liquid nitrogen. If the analysis could not be performed immediately they were stored at −30 °C. This technique prevented any detectable changes occurring after sampling.

Results

Reactant and Product Analysis.—The anion $[Co(CN)_5(dmso)]^{2-}$, formed by reaction of dmso with $[Co(CN)_5Cl]^{3-}$ or $[Co(CN)_5(OH_2)]^{2-}$, gives a single chromatographic peak having a retention volume roughly twice that of $[Co(CN)_5Cl]^{3-}$ in spite of the lower charge of $[Co(CN)_5(dmso)]^{2-}$. The solid product isolated by precipitation from reaction mixtures was microchemically impure but the i.r. spectrum showed the presence of sulphur-bonded dmso and the n.m.r. spectrum of the methyl protons in D_2O consisted of a single peak shifted downfield by 0.68 p.p.m. from that of free dmso. The same peak appeared during the reaction of $[Co(CN)_5Cl]^{3-}$ and dmso in D_2O. The h.p.l.c. detector was calibrated using $[Co(CN)_5(dmso)]^{2-}$ prepared in solution. The agreement between the u.v. spectroscopic and the h.p.l.c. analyses is satisfactory when the reactant and products are present in comparable concentrations, but the agreement is less satisfactory at very low concentrations of the products.

Table 1. Equilibrium spectroscopic data for reaction (3) at 40 °C and unit ionic strength ($NaClO_4$)

[dmso]/ mol dm^{-3}	A_∞/A_0					
	385 nm		346 nm		298 nm	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0.1	0.626	0.639	1.26	1.27	1.34	1.37
	0.629	0.639	1.36	1.27	1.47	1.37
	0.662[a]	0.639	1.28[a]	1.27	1.41[a]	1.37
0.2	0.500	0.507	1.43	1.37	1.61	1.52
	0.528[a]	0.507	1.33[a]	1.37	1.57[a]	1.52
0.3	0.450[a]	0.440	1.42[a]	1.42	1.51[a]	1.59
	0.456	0.440	1.46	1.42	1.62	1.59
	0.433	0.440	1.46	1.42	1.62	1.59
0.4	0.413	0.397	1.44	1.45	1.70	1.63
	0.378	0.397	1.47	1.45	1.61	1.63
	0.385	0.397	1.50	1.45	1.69	1.63
0.5	0.359	0.368	1.46	1.47	1.58	1.66
	0.348	0.368	1.45	1.47	1.53	1.66
	0.329	0.368	1.41	1.47	1.60	1.66
0.8	0.320	0.322	1.32	1.50	1.48	1.71
	0.335[a]	0.322	1.54[a]	1.50	1.92[a]	1.71
2.0	0.281	0.266	1.43	1.55	1.70	1.77
	0.269[a]	0.266	1.55[a]	1.55	1.68	1.77
5.0	0.231[b]	0.243	1.55	1.56	1.73	1.79
	0.278[a]	0.243	1.50[a]	1.56	1.83[a]	1.79

[a] Equilibrium data from the reaction of dmso and $[Co(CN)_5Cl]^{3-}$ [b] The fast initial absorbance changes due to the dmso and $[Co(CN)_5(OH_2)]^{2-}$ reaction made the extrapolation to find A_0 inaccurate.

Equilibrium Measurements.—The reactant $[Co(CN)_5Cl]^{3-}$ decomposed to $[Co(CN)_5(OH_2)]^{2-}$ in the absence of added chloride ions but the latter complex was not completely converted into $[Co(CN)_5(dmso)]^{2-}$ at dmso concentrations of 5 mol dm^{-3} or less. The position of the equilibrium (3) was the

$$[Co(CN)_5(OH_2)]^{2-} + dmso \rightleftharpoons [Co(CN)_5(dmso)]^{2-} + H_2O \quad (3)$$

same whether the reactant was $[Co(CN)_5Cl]^{3-}$ or $[Co(CN)_5(OH_2)]^{2-}$, Table 1.

Dimethyl sulphoxide is strongly non-ideal in aqueous solution so that the equilibrium constants measured in dmso–water mixtures must be corrected to the corresponding values in pure water. The activity coefficients are not available for 1 mol dm^{-3} $NaClO_4$ but the data given in Table 2, calculated from parameters determined at zero ionic strength[10] and corrected to molar concentration units, should be satisfactory since salt effects on the activity of neutral molecules are usually small.[11] This theoretical expectation has been confirmed although over only a narrow range of conditions.[12] The molar concentrations of dmso and water are multiplied by the respective ratios of their activity coefficients in the mixture to the corresponding values in pure water, R_{dmso} and R_{water}. The equilibrium constants calculated in this way are each estimates of the theoretical value in pure water, K_3^0. An activity correction is apparently also required for the complex ions $[Co(CN)_5(dmso)]^{2-}$ and $[Co(CN)_5(OH_2)]^{2-}$. Fortunately the similarity of these ions means that, as the composition of the solvent changes, their activity coefficients will both vary in the same way.[11] Therefore their effects on the equilibrium compensate and no correction is required.

The absorbance data were analysed using equation (4) in

$$\frac{A_\infty}{A_0} = \frac{A_{dmso}}{A_0} - \frac{(A_\infty/A_0 - 1)R_{water}[H_2O]}{K_3^0 R_{dmso}[dmso])} \quad (4)$$

which A_∞ is the absorbance at equilibrium and A_{dmso} is the absorbance if the reactant were fully converted into $[Co(CN)_5(dmso)]^{2-}$. The absorbance A_0 is either that

Table 2. Activity corrections[a] and equilibrium constants[b] for the substitution of dmso in $[Co(CN)_5(OH_2)]^{2-}$, reaction (3)

[dmso]/mol dm^{-3}	$[H_2O]$[c]/mol dm^{-3}	R_{dmso}	R_{water}	K_3
0.05	54.8	1.012	1.000	487
0.10	54.6	1.018	1.000	490
0.20	54.2	1.026	1.000	494
0.30	53.8	1.036	1.000	499
0.40	53.3	1.045	1.000	503
0.50	52.9	1.055	1.000	508
0.80	51.6	1.083	1.000	521
2.00	46.7	1.225	0.995	586
5.00	35.3	1.803	0.961	833

[a] Calculated in molar units at 40 °C and zero ionic strength from ref. 10. [b] Calculated from K_3^0 using $K_3 = R_{dmso}K_3^0/R_{water}$. [c] Calculated from densities at 40 °C intrapolated from J. J. Lindberg and R. Lauren, *Finska Kemistsamfundets Medd.*, 1962, **71**, 37 and R. K. Wolford, *J. Phys. Chem.*, 1964, **68**, 3392.

measured initially if the reactant is $[Co(CN)_5(OH_2)]^{2-}$ or, if the reactant is $[Co(CN)_5Cl]^{3-}$, it is calculated from the initial absorbance using the absorption coefficients shown in Table 3. At each wavelength the equilibrium constant K_3^0 is calculated from the slope of a plot of A_∞/A_0 *versus* $(A_\infty/A_0 - 1)R_{water}[H_2O]/R_{dmso}[dmso]$, while the absorption coefficient of $[Co(CN)_5(dmso)]^{2-}$ is found from the intercept A_{dmso}/A_0. The three wavelengths used were all analysed in the same way but the relatively large absorbance change at 385 nm allowed a very much more reliable measurement of K_3^0, 481 ± 23. The results at the other two wavelengths were not significantly different from that quoted but both have a ten-fold larger standard deviation. The agreement between the observed and calculated absorbances in Table 1 shows that the quoted constant satisfies the data at all three wavelengths. The equilibrium constants expressed in concentrations without any activity corrections are shown in Table 2 and illustrate the importance of such corrections when the concentration exceeds 1 mol dm^{-3}. Independent measurements by h.p.l.c. gave $K_3 = 470$ at 0.5 mol dm^{-3}, which does not significantly differ from the spectroscopic value of 508 (Table 2).

The equilibrium spectroscopic data for reaction (3) were analysed with explicit allowance for variations in activity and water concentration. In fact, the value of the constant depends on measurements between 0.1 and 0.8 mol dm^{-3} dmso where the combined effect of these terms is only *ca.* 13%. The data are not sufficiently precise to detect such a small change but preliminary h.p.l.c. measurements have confirmed that the uncorrected constant K_3 does vary in the way shown in Table 2.

Kinetic Measurements.—$[Co(CN)_5(OH_2)]^{2-}$ *and dmso.* The substitution of the aqua ligand was monitored at the three wavelengths which were selected for the analysis of the $[Co(CN)_5Cl]^{3-}$–dmso system. Equation (5) was used to analyse

$$\ln(A_\infty - A_0)/(A - A_0) = k_{obs.}t \qquad (5)$$

the absorbance data since there was only a single product and the nucleophile concentration was always more than twenty times that of the reactant; A, A_0, and A_∞ are the absorbances measured at any time t, at zero time, and at equilibrium respectively. The equation has been derived[13] for the standard case of two opposed first-order reactions and the slope of the log absorbance plot, $k_{obs.}$, gave the forward and reverse rate constants *via* equations (6) and (7). The rate constants found did

$$k_3 = k_{obs.}K_3/([H_2O] + K_3[dmso]) \qquad (6)$$

$$k_{-3} = k_{obs.}/([H_2O] + K_3[dmso]) \qquad (7)$$

not depend on the wavelength used in their measurement but the quality of the data obtained at 298 nm was inferior to that at 346 and 385 nm. The observed rate constants quoted in Table 4 are therefore the means of the values found at the two latter wavelengths. A further experiment using h.p.l.c. and $[Co(CN)_5(OH_2)]^{2-}$ prepared photolytically from $[Co(CN)_6]^{3-}$ rather than hydrolytically from $[Co(CN)_5Cl]^{3-}$ confirmed the result at 0.8 mol dm^{-3} dmso.

Table 3. Mean absorption coefficients[a] from kinetic and equilibrium spectroscopic data for $[Co(CN)_5X]^{n-}$ (n = 2 or 3)

X	ε_{385}	ε_{346}	ε_{298}
OH_2	261	139	99
Cl	198	78	173
dmso[b]	61.8	218	178

[a] In units of $dm^3\ mol^{-1}\ cm^{-1}$. [b] Least-squares coefficient of variation of the quoted means *ca.* ±1%.

$[Co(CN)_5Cl]^{3-}$ *and dmso.* The numerical analysis used in this study is broadly similar to that used previously.[5] Two methods are employed.

(*i*) The absorbance data at the three wavelengths selected were used in three simultaneous equations which could be solved to give the concentrations of the reactant and the two products. This approach is superior to the earlier application of the same method since previously[5] the third simultaneous equation was based on the assumption that the total concentration of the complexes present was equal to the initial reactant concentration. In the present case the calculated total always remained constant to within the uncertainties of the measurements and thus independently confirmed the method's validity. This agreement is reassuring but, on the other hand, it should be remembered that the absorption coefficients used in any run are found from the initial and final measured absorbances of that same run. Therefore, the method itself ensures that the concentrations at the beginning and end of a reaction will be constant and the test only has value during the run.

The rate constant for the removal of $[Co(CN)_5Cl]^{3-}$ is now conveniently determined from equation (8) by plotting ln a

$$k'_{obs.} = -(1/a)[d(\ln a)/dt] \qquad (8)$$

versus t, where a denotes the concentration of $[Co(CN)_5Cl]^{3-}$. The results shown in Table 5 confirm that the rate of removal of $[Co(CN)_5Cl]^{3-}$ is unaffected by the concentration of dmso below 2 mol dm^{-3}. It is quite possible to test detailed mechanistic models of this reaction using the concentration data but we have found that the direct method given below is more reliable.

Table 4. Rate constants for the substitution[a] of $[Co(CN)_5(OH_2)]^{2-}$ by dmso, reaction (3)

		$10^4k_3/dm^3\ mol^{-1}\ s^{-1}$				$10^7k_{-3}/dm^3\ mol^{-1}\ s^{-1}$
[dmso]/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$	Exptl.	Calc.[b]	Calc.[c]	Calc.[d]	Exptl.
0.1	0.816	3.87	4.58	4.39	4.50	7.82
0.2	1.29	4.18	4.63	4.44	4.53	8.39
0.3	1.71	4.19	4.67	4.47	4.58	8.38
0.4	2.40	4.74	4.75	4.55	4.62	9.38
0.5	2.95	4.88	4.84	4.65	4.66	9.51
0.8	4.40	4.88	4.98	4.80	4.78	9.36
2.0	12.5	5.99	5.90	5.74	5.46	10.1
5.0	44.6	8.85	8.87	9.09	7.96	10.5

[a] At 40 °C and unit ionic strength ($NaClO_4$). [b] $k_{-2} = 1.37 \times 10^{-2}\ s^{-1}$, $k_{14}^0/k_2^0 = 1.80$. [c] $k_{-2} = 1.65 \times 10^{-2}\ s^{-1}$, $k_{14}^0/k_2^0 = 1.43$. [d] $k_3^0 = 4.42 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$.

Table 5. Rate constants[a] for the reaction of $[Co(CN)_5Cl]^{3-}$ and dmso at 40 °C and unit ionic strength ($NaClO_4$)

[dmso]/mol dm^{-3}	$10^4k'_{obs.}$/s^{-1}	$10^4(k_a + k_b)$/s^{-1}	k_b/k_a	10^4k_c/s^{-1}	k^0_{14}/k^0_2
0	4.82	5.0			
0.05	5.24	4.2	0.04	0.21	(45)[b]
0.10	5.44	5.0	0	0.38	(0)
0.20	5.36	5.1	0.05	0.92	(14)[b]
0.40	5.08	5.0	0.07	1.9	9[c]
0.80	4.93	5.5	0.15	4.0	9[c]
2.00	4.46	4.3	0.15	9.8[d]	3[c]
5.00	8.18	7.5	2.0	44	8[c]

[a] Rate constants obtained by method (*i*) have a coefficient of variation of ±5%, but method (*ii*) suggests the error is *ca.* ±10%. [b] The accuracy of k_b/k_a is sufficient only to show that $k^0_{14}/k^0_2 > 0$. [c] ±30% estimated from fitting sensitivity. [d] k_c is significantly different from k_3[dmso], taken from Table 4, only for 2 mol dm^{-3} dmso where $k_3[\text{dmso}] = 12 \times 10^{-4}$ s^{-1}.

(*ii*) This approach has been described previously[5] for the substitution reactions of N_3^- and NCS^-, but in this case the decomposition of the product $[Co(CN)_5(dmso)]^{2-}$ cannot be neglected. The simplest scheme includes reactions (9), (10), and (3). Since water and dmso are always in excess, their concentrations are constant and the rates of the four bimolecular reactions (9), (10), and (3) can be calculated using

$$[Co(CN)_5Cl]^{3-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} + Cl^- \quad (9)$$

$$[Co(CN)_5Cl]^{3-} + \text{dmso} \longrightarrow [Co(CN)_5(\text{dmso})]^{2-} + Cl^- \quad (10)$$

$$[Co(CN)_5(OH_2)]^{2-} + \text{dmso} \rightleftharpoons [Co(CN)_5(\text{dmso})]^{2-} + H_2O \quad (3)$$

the pseudo-first-order constants, k_a, k_b, k_c, and k_d defined by the expressions:—$k_a = k_9[H_2O]$,$k_b = k_{10}[\text{dmso}]$,$k_c = k_3[\text{dmso}]$, and $k_d = k_{-3}[H_2O]$. The integrated solutions for this system of simultaneous differential equations are given in equations (11)—(13) in which the concentrations of $[Co(CN)_5Cl]^{3-}$,

$$a = a_0 \exp[-(k_a + k_b)t] \quad (11)$$

$$b = a_0\{A + B\exp[-(k_a + k_b)t] - (A + B)\exp[-(k_c + k_d)t]\} \quad (12)$$

$$c = a_0 - a - b \quad (13)$$

$[Co(CN)_5(OH_2)]^{2-}$, and $[Co(CN)_5(dmso)]^{2-}$ at time t are denoted by a, b, and c respectively and a_0 is the initial concentration of $[Co(CN)_5Cl]^{3-}$. The terms A and B are composite rate constants, in which $A = k_d/(k_c + k_d)$ and $B = (k_a - k_d)/(k_c + k_d - k_a - k_b)$. The calculated concentrations are then used to obtain the absorbances at any time during the reaction and the rate constants are adjusted to produce the best fit for all three wavelengths. The number of adjustable kinetic parameters was reduced to three by the equilibrium condition, $k_c/k_d = K_3[\text{dmso}]/[H_2O]$. The values of K_3 are taken from Table 2. The fitting procedure is illustrated in the Figure. The sensitivity of the fit to k_c is very low at 5 mol dm^{-3} but elsewhere the values of k_c agree with the observations in Table 4 for all experiments except that with 2 mol dm^{-3} dmso. The rate constants obtained are given in Table 5 and the error quoted is derived from the observed sensitivity-of-fit to the constants' numerical values. It is generally impossible to get a perfect fit for all three wavelengths over the full duration of an experiment and the results shown in the Figure are typical in this respect.

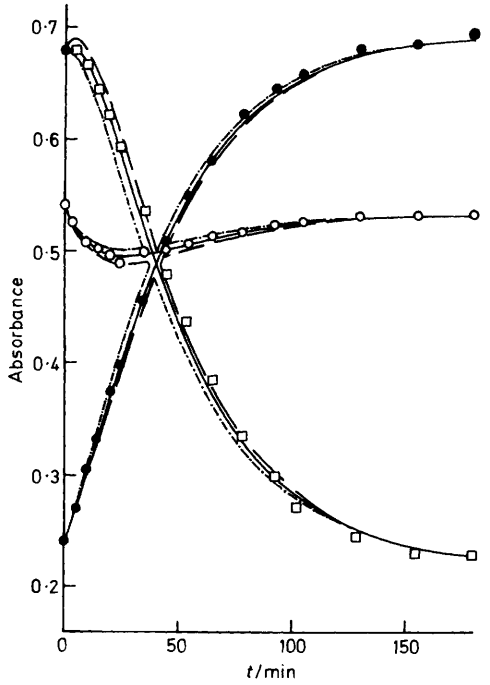

Figure. Absorbance–time curves for 3.2×10^{-3} mol dm^{-3} $[Co(CN)_5Cl]^{3-}$ reacting with 2 mol dm^{-3} dmso at 40 °C and unit ionic strength ($NaClO_4$). Observed absorbance at 346 (●), 298 (○), and 385 nm (□) calculated for $k_a + k_b = 4.5 \times 10^{-4}$ s^{-1} and $k_c = 9.8 \times 10^{-4}$ s^{-1}: k_b/k_a = 0 (– – –), 0.16 (——), or 0.37 (• – •)

Discussion

dmso and $[Co(CN)_5(OH_2)]^{2-}$.—The rate constants in Table 4 show a continuous increase with increasing concentration of dmso.

The expression for k_3 derived from the *D*-type dissociative scheme based on reactions (2) and (14), is given in equation (15).

$$[Co(CN)_5]^{2-} + H_2O \rightleftharpoons [Co(CN)_5(OH_2)]^{2-} \quad (2)$$

$$[Co(CN)_5]^{2-} + \text{dmso} \rightleftharpoons [Co(CN)_5(\text{dmso})]^{2-} \quad (14)$$

$$k_3 = k_{-2}k_{14}/(k_2[H_2O] + k_{14}[\text{dmso}]) \quad (15)$$

The results are apparently inconsistent with this expression but since the activity corrections for dmso shown in Table 2 change rapidly even at low concentrations this failure is not unexpected. However, it is possible by means of the transition-state formulation[13] to express the bimolecular rate constants for reactions (2) and (14) in terms of their values measured in pure water, k^0_2 and k^0_{14}, combined with the ratios $R_{\rm water}$ and $R_{\rm dmso}$ respectively. It also apparently requires the corresponding ratios for the reactant ion $[Co(CN)_5]^{2-}$ and the transition states formed with either dmso or water. However these species are all so similar that their activity changes will compensate and no overall correction is needed. Equation (16) is obtained from

$$k_3 = \frac{R_{\rm dmso}k_{-2}k^0_{14}}{R_{\rm water}k^0_2[H_2O] + R_{\rm dmso}k^0_{14}[\rm dmso]} \qquad (16)$$

(15) by substituting the transition-state expressions $k_{-2} = R_{\rm water}k^0_{-2}$ and $k_{14} = R_{\rm dmso}k^0_{14}$.

Equation (16) now fits the data above 0.4 mol dm^{-3} very well but there is a systematic discrepancy at the lower concentrations (column 4 of Table 4). It is possible that the approximations needed to obtain the activity corrections are responsible. The constants finally adopted give a better overall fit (column 5 of Table 4), but the deviations are not random. Work is in progress in an attempt to identify the source of this failure.

The transition-state treatment provides an alternative interpretation for the change of k_3 with solvent composition. If it is assumed that reaction (3) is a single-step I_d process then k_3 may be fitted by the expression $R_{\rm dmso}k^0_3$ where k^0_3 is the substitution constant in pure water. The result of this calculation is shown in column 6 of Table 4. The discrepancies between the observed and calculated constants are now very much worse than before but three factors prevent this being convincing evidence in favour of the dissociative mechanism. First there is now only one fitted constant rather than two, secondly the fitted limiting rate constant of dissociation, k_{-2}, is between five and ten times larger than any previous estimate,[7,14] and finally the low-concentration results fail consistently to follow the predictions of the theory. The safest conclusion is that the increase in the observed rate constant may be explicable as a solvent effect on an I_d reaction but that if the reaction were a *D*-type process, the competition ratio k^0_{14}/k^0_2 must be *ca.* 1.4.

dmso and $[Co(CN)_5Cl]^{3-}$.—A primary aim of this work was the accurate measurement of k_b/k_a for $[Co(CN)_5Cl]^{3-}$ but unfortunately this has been frustrated by the unexpectedly small value of the ratio combined with the fundamental limitations of the spectroscopic method. The problem is superficially an ideal case for the application of a statistical fitting routine but, in our opinion, it is the systematic errors which are more important than the random errors. In the present case, three wavelengths were chosen so that each complex had one particular wavelength where its formation produced the largest change in absorbance. The absorption coefficients in Table 3 show that $[Co(CN)_5(dmso)]^{2-}$, $[Co(CN)_5Cl]^{3-}$, and $[Co(CN)_5(OH_2)]^{2-}$ respectively dominate at 385, 346, and 298 nm. Below 1 mol dm^{-3} dmso, the initial reaction profile was determined for 20 min by the values of k_b and k_a and for the final 200 min by k_c. At either end of the dmso concentration range the results were only slightly affected by the ratio of k_b and k_a. The ratio could be varied by 50% at either 5 or 0.05 mol dm^{-3} dmso while producing only 2—3% changes in the calculated absorbances. This gives the impression that the competition ratio can be measured to a similar low level of accuracy over the whole dmso concentration range. However this is quite misleading. The method depends substantially on the accuracy of the absorption coefficients in the calculation and in the high- or low-concentration cases quoted above the absorption–time plots are extremely sensitive to the values of the absorption coefficients. In fact the ideal situation is where large concentrations of $[Co(CN)_5(dmso)]^{2-}$ and $[Co(CN)_5(OH_2)]^{2-}$ are both produced at similar rates by direct substitution of $[Co(CN)_5Cl]^{3-}$. The preliminary analysis of the results in concentration terms immediately showed that this occurred only at 5 mol dm^{-3}. At this concentration however the rate of $[Co(CN)_5(OH_2)]^{2-}$ substitution, equation (3), was so fast that its concentration was largely determined by competition with reaction (9). This meant that the sensitivity of the data to k_b/k_a was much reduced. At 0.05 mol dm^{-3} dmso less than 5% of the product formed in the first 10 min was $[Co(CN)_5(dmso)]^{2-}$, while at 0.8 mol dm^{-3} dmso *ca.* 40% of the $[Co(CN)_5(dmso)]^{2-}$ formed was produced from $[Co(CN)_5(OH_2)]^{2-}$.

In the light of these considerations, it is obviously quite easy to produce a strongly biased result. In practice only the values of k_b/k_a from 0.4 up to and including 5.0 mol dm^{-3} dmso are usable. The illustration provided for 2 mol dm^{-3} dmso was deliberately chosen since it seems to be close to the optimum concentration for the measurement of k_b/k_a and yet even in this case the fit is relatively insensitive to the ratio.

It is of course necessary to correct the results at the higher dmso concentrations to the equivalent values in aqueous solution and the arguments already used to develop equation (16) are used to treat the hypothetical dissociative mechanism given by reactions (17), (2), and (14). The required ratio, k^0_{14}/k^0_2,

$$[Co(CN)_5Cl]^{3-} \longrightarrow [Co(CN)_5]^{2-} + Cl^- \qquad (17)$$

$$[Co(CN)_5]^{2-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} \qquad (2)$$

$$[Co(CN)_5]^{2-} + \rm dmso \longrightarrow [Co(CN)_5(dmso)]^{2-} \qquad (14)$$

may now be found from the fitted constants, k_a and k_b, defined earlier, as $k^0_{14}/k^0_2 = R_{\rm water}k_b[H_2O]/R_{\rm dmso}k_a[\rm dmso]$. The value favoured by our preliminary analysis,[1] 13, was calculated by a simpler procedure which depended heavily on the initial spectroscopic observations and in which no allowance was made for changes in water concentration or the activity coefficients. The mean of the results above and including 0.4 mol dm^{-3} dmso in Table 5 gives the final value, 7 ± 3, and this is supported by our preliminary h.p.l.c. measurements. The systematic error is impossible to estimate reliably but minor changes in the absorption coefficients could alter the result by a factor of two. Even h.p.l.c. does not completely avoid the fundamental difficulty of the system. The competition ratio has to be determined in the presence of a rapidly rising concentration of $[Co(CN)_5(dmso)]^{2-}$ formed indirectly from $[Co(CN)_5Cl]^{3-}$ by the substitution of $[Co(CN)_5(OH_2)]^{2-}$. The measurements must therefore depend heavily on the analysis of low concentrations of the products formed in the first few minutes of reaction. We are currently finding that trace impurities can dramatically affect such analyses and that the proportions of the products during the first 1 or 2% of the reaction can often be totally different from what is observed later. This is partly due to the presence of trace impurities in the reactant complex which are not detected by the conventional methods of microanalysis and spectroscopic characterisation but which interfere with the initial chromatograms. However it also appears that the practice of starting experiments by adding solid complex to a background solution can induce heterogeneous reactions during the solution process having very different rates from the corresponding homogeneous reactions. We have noticed before that the substitution reactions of this class of compounds are slightly surface sensitive.[8]

The Mechanism of $[Co(CN)_5X]^{n-}$ (*n* = 2 *or* 3) *Substitution.*—The status of these reactions is of peculiar and unexpected interest. Although they were originally investigated for their potential as examples of a limiting dissociative substitution,[14] they now apparently must be described as being interchange dissociative, I_d, in type. The present work provides two distinct lines of argument to support such a view.

(*i*) The dissociation rate and equilibrium constants for $[Co(CN)_5(dmso)]^{2-}$, k_{-3} and $1/K_3$, fit exactly in the correlation of log k_{-3} *versus* $-\log K_3$ previously observed[7] for X = N_3^-, NCS^-, I^-, Br^-, Cl^-, and HN_3. This implies that the transition state for these reactions must be close to the structure of the products and that the mechaniam is therefore dissociative. It does not however imply that the reactions must necessarily involve any detectable effects due to a reduced co-ordination intermediate.

(*ii*) There is a strong leaving-group effect on the efficiency of both neutral and anionic nucleophiles. The effect can be illustrated by combining the results of the present work with those of our previous studies on the substitution of $[Co(CN)_5Cl]^{3-}$ by N_3^- or NCS^-. The dissociative mechanism for the substitution of $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5Cl]^{3-}$ is given by reactions (2), (17), (14), and (18). If this mechanism is

$$[Co(CN)_5Cl]^{3-} \longrightarrow [Co(CN)_5]^{2-} + Cl^- \quad (17)$$

$$[Co(CN)_5]^{2-} + H_2O \rightleftharpoons [Co(CN)_5(OH_2)]^{2-} \quad (2)$$

$$[Co(CN)_5]^{2-} + dmso \longrightarrow [Co(CN)_5(dmso)]^{2-} \quad (14)$$

$$[Co(CN)_5]^{2-} + N_3^- \longrightarrow [Co(CN)_5(N_3)]^{3-} \quad (18)$$

assumed to operate in the substitution of $[Co(CN)_5(OH_2)]^{2-}$ then the competition ratio k_{14}/k_2 must be *ca.* 1.4. When the leaving group is Cl^- the ratio becomes *ca.* 7. Although these ratios may be subject to systematic errors, it seems reasonably certain that a competition ratio above 2 is incompatible with the kinetics of the dmso–$[Co(CN)_5(OH_2)]^{2-}$ substitution but not necessarily with the kinetics of the chloride substitution. Thus there may be a slight leaving-group effect even in the absence of ionic interactions with the incoming nucleophiles.

A similar comparison may be made for either NCS^- or N_3^- and dmso. The anion N_3^- will be used as the example but these ions are so alike that the results would be similar for NCS^-. The observed second-order rate constant for substitution by low concentrations of dmso is given by equation (19), and for N_3^- by equation (20). Consequently the relative nucleophilic efficiency

$$k_{obs.}(dmso) = k_{-2}k_{14}/k_2[H_2O] \quad (19)$$

$$k_{obs.}(N_3^-) = k_{-2}k_{18}/k_2[H_2O] \quad (20)$$

of N_3^- and dmso may be calculated directly from the expression $k_{obs.}(N_3^-)/k_{obs.}(dmso)$ at the lower nucleophile concentrations. The same quantity may be calculated from our previous measurements of the competition ratio of N_3^- and water in the hydrolysis[5] of $[Co(CN)_5Cl]^{3-}$ when it is combined with the present result. The upper limit of the ratio, 0.06, is very much less than the value from $[Co(CN)_5(OH_2)]^{2-}$, 1.5, indicating that there is a strong leaving-group effect. The nucleophilic efficiency of NCS^- compared to water has previously[5] been found to increase by more than ten when the negative chloride-leaving group was replaced by HN_3. It seems very likely that electrostatic interactions of the entering and leaving groups play a considerable part in the nucleophilic efficiency changes.

The summary of the steps in the hypothetical dissociative mechanism of reactions (17), (2), (14), and (18) is only a convenience for the purpose of discussion. It cannot be regarded as a true stoicheiometric mechanism since the source of the key intermediate $[Co(CN)_5]^{2-}$ controls its reaction rate in steps (2), (14), and (18). Although the range of the data is not sufficient to prove the generality of the conclusions, it is sufficient to indicate a model for the reaction path. The hypothetical intermediate $[Co(CN)_5]^{2-}$ is formed in the primary step but it is removed before the solvation sphere can be fully equilibrated with the bulk of the solution. This simple picture immediately accommodates all the effects so far observed and suggests that unreactive solvents are essential in order to allow this potentially dissociative system to exhibit the appropriate kinetic characteristics.

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