Kinetics and mechanism of base hydrolysis of (dimethyl sulphoxide)penta-amminecobalt(III) ions

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Kinetics and Mechanism of Base Hydrolysis of (Dimethyl Sulphoxide)Penta-Amminecobalt(III) Ions*

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Data are presented showing that at constant 0.02 M OH$^-$ the rate of the base hydrolysis of the $(NH_3)_5 Co(DMSO)^{3+}$ ion increases with an increase in the nonaqueous component in aqueous-organic mixtures containing methanol, ethanol, DMSO (= dimethyl sulphoxide), acetone or dioxane. The enhancement in the rate, which amounts to more than 100 fold in organic component-rich mixtures, is discussed in terms of an increase of the basicity of the mixed solvents due to the decreasing solvation of OH$^-$. The base hydrolysis of the DMSO-complex ion in the presence of 1 M anion Y and 0.125 M OH$^-$ yields 12.8, 9.9, 7.8, 1.8, and 3.7 mol $^0/_0$ $(NH_3)_5$ CoY from $(NH_3)_5$ CoX for the competing anions N_3^-, SCN$^-$, NO$_2^-$, OAc$^-$, and SO$_4^{2-}$, respectively. The mechanistic implications of these results are discussed in terms of S_N1CB and I_d mechanisms.

Evidence has appeared[1] supporting the earlier contention[2] that the base hydrolyses of $Co(NH_3)_5X^{2+}$ ions (X$^-$ = Cl$^-$, Br$^-$, NO$_3^-$) took place by an S_N1CB mechanism. It has been shown that base hydrolyses of pentaammine — complex ions in the presence of anions Y$^-$ led to competition ratios

$$[Co(NH_3)_5Y^{2+}]/[Co(NH_3)_5OH^{2+}] [Y^-]$$

which showed little dependence on the nature of the leaving group, suggesting a common intermediate of reduced coordination number. However, as already pointed out for acid hydrolysis,[3,4] the product ratios can be explained by an I_d mechanism involving ion pairs such as $Co(NH_3)_4NH_2X^+,Y^-$ which will probably form to approximately the same extent[5] because of the constant charge of the complex when the leaving group is[1] Cl$^-$, Br$^-$, I$^-$ or NO$_3^-$.

In order to examine this possibility we determined the competition ratios for base hydrolysis of $Co(NH_3)_5(DMSO)^{3+}$ (DMSO = dimethyl sulphoxide) with Y$^-$ = N_3^-, NCS$^-$, NO$_2^-$, AcO$^-$, and SO$_4^{2-}$. If a common pentacoordinated intermediate is formed for DMSO, Cl$^-$, Br$^-$, I$^-$ and NO$_3^-$ leaving groups, the competition ratios should remain constant for a given Y$^-$. However, if an I_d mechanism within ion pairs is operating the competition ratios when X$^-$ =

= DMSO should be different from those ratios determined when X⁻ = anion, since the DMSO-complex ion is triply positively charged while, when X⁻ = = anion, the complex ion is doubly positively charged.

Further support for the conjugate base mechanism is also presented by showing that the rate of the base hydrolysis of the DMSO-complex increases with an increase in the non-aqueous component in aqueous — organic solvent mixtures due to the decreasing solvation of OH⁻ in the resulting solvent mixtures.

RESULTS AND DISCUSSION

The S_N1CB mechanism given in equations (1) to (3) inclusive accounts for the major features of the base hydrolysis of the DMSO-complex.

$$Co(NH_3)_5 (DMSO)^{3+} + OH^- \overset{fast}{\rightleftharpoons} Co(NH_3)_4(NH_2) (DMSO)^{2+} + H_2O \tag{1}$$

$$Co(NH_3)_4 (NH_2) ((DMSO)^{2+} \overset{slow}{\longrightarrow} Co(NH_3)_4 (NH_2)^{2+} + DMSO \tag{2}$$

$$Co(NH_3)_4 (NH_2)^{2+} + H_2O \overset{fast}{\longrightarrow} Co(NH_3)_5OH^{2+} \tag{3}$$
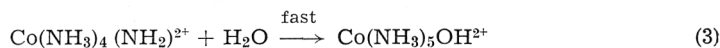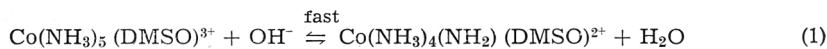
The kinetics of the base hydrolysis were followed spectrophotometrically using the difference in the molar extinction coefficients at 300 nm of the DMSO-complex (800) and of the hydroxo-complex (200 cm⁻¹ mol⁻¹ l). Most of the kinetic runs were too fast for conventional spectrophotometry and a stopped-flow technique was used. Table I contains the second-order rate constants for the base hydrolysis and the first-order rate constants of the acid hydrolysis of the DMSO-complex, together with literature values of rate constants for iodide and chloride as leaving ligands.

TABLE I

Base and acid hydrolysis of $(NH_3)_5$ *CoX at 25 °C*

X	$k_{OH^-}/mol^{-1} l\, s^{-1}$	$10^6 k_{H_2O} /s^{-1}$	k_{OH^-}/k_{H_2O}
DMSO	36	20	1.9×10^6
I⁻	23[a]	8.3[b]	2.7×10^6
Cl⁻	0.85[a]	1.7[b]	0.5×10^6

[a] Data from Reference 6.
[b] Data from Reference 7.

It was found that DMSO leaves the complex slightly faster than the anions in both acid and base hydrolysis and that the charge effect was small. Moreover, the value of k_{OH^-}/k_{H_2O} for the DMSO-complex was between those of the iodide- and chloride-complexes suggesting that the high rates of base hydrolyses are caused primarily by a π-bonding effect of the amido-group of the conjugate base and that the charge difference between the complex and its conjugate base is of minor importance. If not so, one would expect the k_{OH^-}/k_{H_2O} value for DMSO as leaving ligand to be different from the ratios for the negatively charged leaving ligands, which was not the case.

The dependence of the rate of base hydrolysis of the DMSO-complex on temperature is given in Table II.

TABLE II.

Base hydrolysis of 0.0015 M Co(NH$_3$)$_5$(DMSO)$^{+3}$ *in* 0.0125 M NaOH

T/K	k/s^{-1} mol^{-1} l
295.2	26.4
298.4	37.0
300.8	46.2
307.0	102.6
311.3	178.9
313.7	299.8

Data from Table II gave a good Arrhenius plot. The least squares values of the energy and entropy of activation were: $E_A = 23.1 \pm 1.2$ kcal mol^{-1}, $\Delta S^{+} = 28.3 \pm 4.5$ cal K^{-1} mol^{-1}*, (uncertainties are standard deviations of the mean). The analogous parameters for acid hydrolysis of the DMSO-complex were[4]: $E_A = 24.5 \pm 0.7$ kcal mol^{-1}, $\Delta S^{+} = 0.36 \pm 2.29$ cal K^{-1} mol^{-1}. An interchange dissociation (I$_d$) mechanism has been proposed for acid hydrolysis[4]. An entropy of activation near zero is expected for a reaction which follows an I$_d$ mechanism, since breaking the bond to the leaving group involves an enthalpy change mainly and the leaving group does not gain a high-entropy free state[8]. The high positive value of entropy of activation in the base hydrolysis of the DMSO-complex supports the contention[1,2] that this process takes place by a S$_N$1CB mechanism.

Rates of Base Hydrolysis of the [(NH$_3$)$_5$Co(DMSO)]$^{3+}$ Complex in Aqueous Organic Mixtures

At constant 0.02 M OH$^-$ the rate of base hydrolysis of the DMSO-complex increased steadily with increase in the non-aqueous component in aqueous--organic mixtures containing DMSO, acetone, dioxane, ethanol, and methanol, as shown in Table III. The rate accelaration in aprotic solvents was high, *e. g.* in 80% acetone the rate was approximately 300 times higher than in aqueous solution. Rate acceleration was also observed in water-DMSO solutions (Table III). The hydroxo complex is about five orders of magnitude more stable than the DMSO-complex[9], and the reverse reaction forming DMSO-complex from the hydroxo-complex was negligible. At approximately equal mol fractions of the non-aqueous component the rate acceleration was approximately equal for the aprotic solvents DMSO, acetone and dioxane. When methanol or ethanol was the non-aqueous solvent component the rate acceleration was much smaller (Table III). The rate acceleration in organic component-rich mixtures can be explained in terms of the conjugate base mechanism (reactions 1 to 3) as being due to the increase of basicity of OH$^-$ in the mixed solvents because of the decreasing solvation of OH$^-$ [9,10]. When the non-aqueous component in the solvent mixtures was ethanol or methanol the change in solvation of OH$^-$ was smaller and the rate acceleration was much less than in aqueous--aprotic solvent mixtures (Table III). The reaction scheme 1—3 requires a

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* 1 cal = 4.184 J

TABLE III.

Base Hydrolysis of 0.0015 M $(NH_3)_5Co$ $(DMSO^{3+}$ in Aqueous-Organic Mixture at 0.02 M OH^- and 25.3 °C (ac = Acetone, di = dioxane)

DMSO			Acetone			Dioxane			Ethanol			Methanol		
V/V% DMSO	X_{DMSO}[a]	k/k_0[b]	V/V% ac	X_{ac}[a]	k/k_0[b]	V/V% di	X_{di}[a]	k/k_0[b]	V/V% EtOH	X_{EtOH}[a]	k/k_0[b]	V/V% MeOH	X_{MeOH}[a]	k/k_0[b]
0	0	1	0	0	1	0	0	1	0	0	1	0	0	1
19	0.036	2.04	10	0.027	1.55	10	0.023	1.92	10	0.033	1.37	10	0.046	1.11
38	0.133	7.86	20	0.058	2.29	20	0.049	3.71	20	0.072	1.91	20	0.100	1.31
58	0.258	59.50	30	0.095	5.67	30	0.082	7.36	30	0.117	2.92	30	0.160	1.59
			40	0.134	11.0	40	0.124	14.7	40	0.170	4.50	40	0.229	1.93
			50	0.198	26.2	50	0.174	25.0	50	0.236	6.27	50	0.306	2.47
			60	0.268	52.4	60	0.240	41.7	60	0.315	11.2	60	0.401	3.72
			70	0.363	71.9	70	0.327	62.5	70	0.418	17.2	70	0.508	4.68
			75	0.425	141	80	0.457	125	80	0.570	32.5	80	0.629	6.85
			80	0.495	306				90	0.736	62.7	90	0.797	11.9
		0.759	90	0.687					95	0.852	146			

[a] X = mole fraction of the non-aqueous component

[b] $k_0 = 0.682 \pm 0.061$ s⁻¹ (Uncertainty is standard deviations of the mean).

water molecule for the formation of the hydroxo-complex and it is to be expected that the rate of formation of the hydroxo-complex must decrease with increasing non-aqueous component in solvent mixtures containing more than a certain limit of non-aqueous component because reaction 3 will become rate determining at sufficiently low water activities. Indeed such a rate decrease was observed in 90 V/V % acetone, but the reduction in rate is too drastic to be explained by decrease in water concentration only. The effect is under further investigation.

Table IV shows that there is no correlation between the reaction rate acceleration and the heat of mixing of the DMSO ligand with the solvent components. E. g. water-MeOH and water-acetone solvent mixtures (1 : 1 mole ratios of the solvent components) have almost equal heats of mixing with DMSO but k/k_o is 5 and 300, respectively. This observation excludes the interaction between DMSO and solvent components as a possible explanation for the observed rate acceleration. The base hydrolysis rate acceleration in aqueous-non-aqueous solvent mixtures is not specific for the DMSO leaving ligand. Table V shows that the rate acceleration for the NO_3^- leaving ligand is approximately that observed for the DMSO leaving ligand. $((NH_3)_5CoNO_3^{2+}$ is practically insoluble in solvent compositions rich in non-aqueous component, such as were used in the base hydrolysis of the DMSO-complex.)

TABLE IV.

Base Hydrolysis of 0.0015 M $(NH_3)_5Co(DMSO)^{3+}$ in Water-non-Aqueous Mixture with 1 : 1 Mole Ratios at 0.02 M OH^- and 25.3 °C. ΔH = Heat of Mixing of DMSO with various Solvents (Water, MeOH, Acetone, and EtOH, respectively)

Solvent	k/k_o[a]	ΔH/cal mol^{-1}
Water	1	— 715
Water-MeOH	5	— 85
Water-acetone	300	— 80
Water-EtOH	25	85

[a] $k_o = 0.682 \pm 0.061$ s^{-1}

TABLE V.

Base Hydrolysis of 0.0015 M $(NH_3)_5CoNO_3^{2+}$ in Water-non-Aqueous Solvent Mixtures at 0.02 M OH^- and 25.3 °C

V/V %	Non-aqueous component	k/k_o[a]
0		1
10	MeOH	1.06
50	MeOH	1.72
10	Acetone	1.83
50	Acetone	20.0

[a] $k_o = 0.326$ s^{-1}

Base Hydrolysis of $(NH_3)_5Co(DMSO)^{3+}$ *in Presence of Competing Nucleophiles*

Table VI contains the competition ratios of $(NH_3)_5Co(DMSO)^{3+}$ for competing nucleophiles $Y^- = N_3^-$, NCS^-, NO_2^-, AcO^-, and SO_4^{2-} using the same base hydrolysis conditions as used by Buckingham *et al*[1]. for leaving ligands I^-, Br^-, Cl^- and NO_3^-. We repeated the results of Buckingham *et al.* for leaving ligands Cl^- and NO_3^-, the entering ligand being N_3^-, and obtained good agreement, as seen from Table VI. Table VI also includes the competition ratios of Buckingham *et al.* The latter authors concluded that the comparatively constant competition ratios for the chloro-, bromo-, iodo-, and nitrato-penta-ammine ions with each entering anion suggested a common intermediate. The data now presented for leaving ligand DMSO reveal that

TABLE VI.

Mol % $(NH_3)_5CoY$ from $(NH_3)_5CoX$ (0.05 M)[a] at 1 M Y^- and 0.125 M OH^- [b]

Y^-	— X					
	— DMSO	— Cl[c]	— Br[c]	— I[c]	— NO₃[c]	
N_3^-	12.8 ± 0.7[e]	8.5	8.4[d]	8.7	9.9	10.4	10.8[d]
SCN^-	9.9 ± 0.2	5.5		6.1	6.3	7.1	
NO_2^-	7.8 ± 1.0	4.2		5.0	4.5	5.1	
OAc^-	1.8 ± 0.6				4.8		
SO_4^{2-}	3.7				8.2		

[a] When $Y^- = N_3^-$, SCN^-, $(NH_3)_5CoX = 0.025$ M
[b] In experiments with SO_4^{2-}, [OH⁻] = 0.10 M
[c] Data from reference 1
[d] Our measurements
[e] Uncertainties are standard deviations of the mean

the competition ratios for this leaving ligand are about 50% higher than for the leaving ligand Cl^-, the competing ligands being N_3^-, SCN^-, and NO_2^-, respectively. This result is outside of experimental error and does not appear to be due to ion pairing since the competition ratios for the competing reagent NCS^- remained constant when the solvent composition was changed from aqueous solution (dielectric constant = 80) to 50 V/V % dioxan (d. c. $\simeq$ 40) (see Table VII).

TABLE VII.

Mol % $(NH_3)_5CoNCS^{2+}$ from 0.025 M $(NH_3)_5Co(DMSO)^{3+}$ in 1 M KSCN and 0.125 M NaOH at 25 °C

V/V % dioxane	% $(NH_3)_5CoNCS^{2+}$
0	9.9
15	9.3
30	9.1
50	9.5

It appears that the kinetic data are only in a rough agreement with the S_N1CB mechanism, since the intermediate appears to have some memory of the leaving group. Even the results of Buckingham *et al.* for leaving groups Cl^- and NO_3^- and entering groups N_3^- and NCS^- differ significantly. It might well be that the base hydrolysis of the ligandopentaamminecobalt(III) ions is on the border line between D and I_d mechanism, with more D than I_d character.

EXPERIMENTAL

Materials

Dimethyl sulphoxide was destilled at ca. 90 °C under reduced pressure from potassium carbonate[11] and a central portion collected. A Merck's chemical of analytical purity was also used and there were no difference in kinetics. Dioxane and acetone were purified according to literature[12]. All other chemicals were of Merck analytical purity. The pentaammine-(dimethyl sulphoxide)-cobalt(III) complex was prepared as $[Co(NH_3)_5 (DMSO)] (ClO_4)_3 \cdot 2 H_2O^{13}$, a crystalline solid.

Kinetic

The kinetics of base hydrolysis were followed at 300 nm where a minimum of absorption of hydroxopentaamminecobalt(III) ion ($\varepsilon \simeq 200$) occurs, while the absorption of the DMSO-complex is high ($\varepsilon \simeq 800 \ mol^{-1} \ cm^{-1} \ l$). The kinetics were followed by a stopped-flow technique. Water used was redistilled and CO_2 removed.

Competition experiments in presence of N_3^-, NCS^-, NO_2^-, AcO^-, and SO_4^{2-} were carried out as described by Buckingham *et al*[1]. The separation of the reaction products was carried out on the Dowex H^+ 50 W-X2, 200—400 Mesh ion exchange column, as described[1].

Spectrophotometry

Absorption spectra were recorded using Cary 16 K spectrophotometer, and for following fast reactions Durrum-D-110 (Durrum Instrument Co., Palo Alto, Calif.) was used.

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SAŽETAK

Kinetika i mehanizam bazne hidrolize (dimetil sulfoksid)pentaamminekobalt(III) iona

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Pri konstantnoj koncentraciji hidroksid-iona, 0,02 M, povećava se brzina bazne hidrolize $(NH_3)_5Co(DMSO)^{3+}$ s porastom organske komponente u vodenim otopinama organskih otapala kao što su metanol, etanol, DMSO (dimetil-sulfoksid), aceton i dioksan. Brzina hidrolize se povećava za više od 100 puta u smjesama otapala koje su bogate organskom komponentom. Povećanje brzine protumačeno je kao posljedica porasta bazičnosti miješanih otapala zbog umanjene solvatacije hidroksid-iona.

Kod bazne hidrolize DMSO-kompleksa u prisutnosti 0.125 M OH⁻ i 1 M aniona Y nastaje 12,8, 9,9, 7,8, 1,8 i 3,7 mol % $(NH_3)_5CoY$ gdje je Y = N_3^-, SCN^-, NO_2^-, OAc⁻ i SO_4^{2-}.

Dobiveni rezultati diskutiraju se na temelju S_N1CB i I_d mehanizma.

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