Aquation of Penta-ammine(dimethyl sulphoxide)cobalt(III) Perchlorate in Water–Non-aqueous Solvent Mixtures

By **Warren L. Reynolds,* Mladen Biruš,** and **Smiljko Ašperger,** Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb and Institute 'Rudjer Bosković,' Zagreb, Croatia, Yugoslavia

The aquation rate constant of penta-ammine(dimethyl sulphoxide)cobalt(III) ion in various aqueous and aqueous–non-aqueous solvent mixtures has been determined. The rate constant does not correlate well with water activity, the Grunwald–Winstein solvating-power *Y* parameter, or the heat of mixing of dimethyl sulphoxide with the solvent components. The data support an I_d mechanism more readily than a *D* mechanism. The activation enthalpy and entropy are 23·9 ± 0·7 kcal mol^{-1} and 0·36 ± 2·29 cal K^{-1} mol^{-1}, respectively.

MECHANISMS of spontaneous and induced aquations of $[Co(NH_3)_5X]^{2+}$ complexes differ.[1-3] It has been postulated that induced aquations proceed[1,3] through intermediate $[Co(NH_3)_5]^{3+}$ formation and that spontaneous aquation of the ion $[Co(NH_3)_5Cl]^{2+}$ proceeds[4] by an interchange (I_d) mechanism. However, it is possible that the opposite assignment of these mechanisms should be made. Induced aquation may proceed by an interchange mechanism in which the competing ligands H_2O and Y^- enter as the X^- ligand is transformed and departs from the first co-ordination shell of $[Co(NH_3)_5X]^{2+}$ ions or of $[Co(NH_3)_5X]^{2+},Y^-$ ion-pairs, and spontaneous aquation may proceed by a *D* mechanism. In the work reported here we have attempted to obtain additional evidence supporting either the *D* or I_d mechanism for spontaneous aquation of penta-amminecobalt(III) complexes.

EXPERIMENTAL

Sodium perchlorate was prepared by recrystallization of Merck (*pro analysi*) reagent or from sodium carbonate and perchloric acid followed by recrystallization; both preparations gave the same results. Aluminium perchlorate was recrystallized as described[5] in the literature. Dimethyl sulphoxide (dmso) was distilled at *ca.* 90 °C under reduced pressure from potassium carbonate[6] and a central portion collected. The penta-ammine(dimethyl sulphoxide)-cobalt(III) complex was prepared as $[Co(NH_3)_5(dmso)](ClO_4)_3,2H_2O$,[7] a crystalline solid, and in solution by dissolving penta-ammineaquocobalt(III) perchlorate in liquid dmso and warming to 45 °C for 24 h. A 0·10M-solution of the dmso complex in dmso was stable over a period of 4 months when stored at room temperature in the dark. The two sources of the dmso complex gave the same

---

[1] A. Haim and H. Taube, *Inorg. Chem.*, 1963, **2**, 1199.

[2] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, 1964, **3**, 1334.

[3] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, 1967, **6**, 1027.

[4] C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, 1967, **89**, 3141.

[5] Gmelin, Handbuch der Anorganischen Chemie, 1933—54, Nachdruk 1953, Teil B, p. 217.

[6] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.

[7] C. R. P. Mac-Coll and L. Beyer, *Inorg. Chem.*, 1973, **12**, 7.

observed rate constant, except when the water content of the solvent mixture was so small that the back reaction in reaction mixtures containing the dmso complex from the solution source became observable as a result of the larger dmso concentrations. All other chemicals were *pro analysi* grade and were used without further purification. Distilled water was redistilled from potassium permanganate and sodium hydroxide in all-glass apparatus. The specific conductivity of the resulting water was (1—1·4) × 10^{-6} Ω^{-1} cm^{-1}; this water gave the same kinetic results as the initial distilled water.

Kinetics.—Either the solid or liquid source of the dmso complex was added to *ca.* 90 cm^3 of reaction mixture at 45·0 ± 0·05 °C suspended in a water-bath, dissolved or mixed, and the solution brought to 100 cm^3 by addition of reaction mixture at the same temperature. Aliquot portions were removed at various times, their absorbances measured in a thermostatted cell compartment of a Cary 16 K spectrophotometer, and then discarded. Plots of log $(A - A_\infty)$ against time, where A and A_∞ are absorbances measured at times t and after 10 half-lives, were always linear over at least three half-lives. The absorbances were determined at 290 nm where the dmso complex has an intense, and the aquo-complex a very weak, absorption, except in the case of acetone–water mixtures where 530 nm was used. Aquation of the dmso complex was complete as judged by the spectrum of the final product.

RESULTS AND DISCUSSION

Values of the rate constant for the aquation reaction, k_{aq}, in various aqueous media are listed in Table 1. In water containing only 0·001M-$[Co(NH_3)_5(dmso)](ClO_4)_3$ and no added acid, a small correction for the absorbance of the ion $[Co(NH_3)_5OH]^{2+}$ resulting from acid dissociation of $[Co(NH_3)_5H_2O]^{3+}$ was made for each absorbance measurement; the pK_a value used for $[Co(NH_3)_5H_2O]^{3+}$ was[8] 6·21. The value of k_{aq} in water was not significantly different from that in 0·001M-$HClO_4$, nor from the value of the rate constant for self-exchange of dmso between $[Co(NH_3)_5(dmso)]^{3+}$ and bulk dmso[9] at 45 °C. The values of k_{aq} showed no trend with increasing charge of the cation in $NaNO_3$, $Al(NO_3)_3$, and $Th(NO_3)_4$ media. Values of k_{aq} decreased with increasing perchlorate-ion concentration; this effect is a specific-ion effect and not an ionic-strength effect because variation of the ionic strength, I, at constant perchlorate-ion concentration did not measurably affect k_{aq} whereas variation of perchlorate-concentration at constant I markedly affected k_{aq}. Likewise Jones *et al.*[10] have observed that perchlorate ion decreased anation and aquation rate constants in aqueous penta-amineanionochromium(III) solutions.

TABLE 1

Values of k_{aq} in various aqueous media at 45·00 ± 0·05 °C and 0·0010M total Co^{III}

Medium	$[HClO_4]$/M	$[z]$ [a]/M	I [b]/M	$10^4k_{aq}/s^{-1}$
Water		0·003	0·006	2·78 ± 0·03
0·001M-$HClO_4$	0·0010	0·004	0·007	2·83 ± 0·03
0·250M-$NaNO_3$	0·0010	0·250	0·257	2·95 ± 0·03
0·0833M-$Al(NO_3)_3$	0·010	0·250	0·516	2·88 ± 0·03
0·0625M-$Th(NO_3)_4$	0·010	0·250	0·641	2·98 ± 0·03
0·250M-$NaClO_4$	0·0010	0·254	0·257	2·47 ± 0·02
0·767M-$Al(ClO_4)_3$	0·020	0·253	0·486	2·44 ± 0·02
0·500M-$NaClO_4$	0·010	0·513	0·516	2·14 ± 0·02
0·166M-$Al(ClO_4)_3$	0·050	0·551	1·076	2·18 ± 0·02
0·250M-$Mg(ClO_4)_2$	0·010	0·513	0·765	2·22 ± 0·02
1·000M-$NaClO_4$	0·0010	1·004	1·007	1·86 ± 0·02
0·500M-$Mg(ClO_4)_2$	0·010	1·013	1·516	1·88 ± 0·02
2·000M-$NaClO_4$	0·010	2·013	2·016	1·41 ± 0·02
1·000M-$Mg(ClO_4)_2$	0·010	2·013	3·016	1·41 ± 0·02

[a] $[z]$ = the concentration of the major anion. [b] I = ionic strength.

Values of k_{aq} in several different water–dioxan mixtures are listed in Table 2. These values do not parallel the bulk-water activity as reflected by partial vapour pressures of water, since the latter pass through a maximum[11] at *ca.* 0·1 mol fraction dioxan whereas k_{aq} decreased markedly and continuously with increasing dioxan content. Values of k_{aq} as a function of the Grunwald–Winstein solvating power parameter Y are listed in Table 3 and shown in Figure 1. Although many points satisfy a linear log k_{aq} against Y relation over the range $-1·13 \leqslant Y \leqslant 3·49$ there are some serious discrepancies. For example, k_{aq} is *ca.* (2·03—2·18) × 10^{-4} s^{-1} for Y equal to 1·00, −0·71, and −1·13 for the solvent systems used. Furthermore, the values of

TABLE 2

Values of k_{aq} for various dioxan–water mixtures at 45·00 ± 0·05 °C, 0·0010M-$HClO_4$, and 0·0010M total Co^{III}

x_d [a]	p_{H_2O}/Torr	$10^4k_{aq}/s^{-1}$
0·00	24·0	2·83
0·10	26·0	2·66
0·50	19·2	2·10
0·75	15·5	1·85
0·90	10·4	1·14

[a] x_d = Mol fraction of dioxan.

TABLE 3

Values of k_{aq} as a function of the Grunwald–Winstein Y parameter at 45·0 °C, 0·0010M-$HClO_4$, and 0·001M total Co^{III}

Solvent system	Y	10^4k_{aq} [a]$/s^{-1}$
Water	3·49	2·83
31·0 v/v % Methanol	2·72	2·60
31·0 v/v % Methanol	2·72	2·54 [b]
34·4 v/v % Dioxan	2·23	2·66
50·0 v/v % Ethanol	1·66	2·55
69·3 v/v % Methanol	1·00	2·17
76·5 v/v % Ethanol	0·21	2·40
80·0 v/v % Ethanol	0·00	2·30
80·3 v/v % Acetone	−0·71	2·14 [c]
80·3 v/v % Acetone	−0·71	2·18 [b,c]
90·7 v/v % Ethanol	−0·83	1·58 [b]
82·5 v/v % Dioxan	−1·13	2·03
82·5 v/v % Dioxan	−1·13	2·10 [b]
95·0 v/v % Ethanol	−1·29	1·20
95·0 v/v % Ethanol	−1·29	1·20 [b]

[a] Rate constants have *ca.* 2% standard deviation. [b] $[Co(NH_3)_5(dmso)](ClO_4)_3,2H_2O$ was used as the source of the complex ion. All other experiments used the complex prepared in dmso solution. [c] 0·010M total Co^{III}.

---

[8] R. G. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, 1968, **7**, 901.

[9] W. L. Reynolds, E. S. Barber, and R. Crandall, *Internat. J. Chem. Kinetics*, in the press.

[10] T. J. Jones, W. E. Harris, and W. J. Wallace, *Canad. J. Chem.*, 1961, **39**, 2371.

[11] F. Hovorka, R. A. Schaefer, and D. Dreisbach, *J. Amer. Chem. Soc.*, 1930, **52**, 2266.

1·58 × 10^{-4} and 1·20 × 10^{-4} s^{-1} for k_{aq} for Y equal to −0·83 and −1·29, respectively, are much less than those expected on the basis of the linear relation. Because of these serious discrepancies in the correlation between log k_{aq} and Y it is concluded that the solvent Y value is not the major factor controlling the value of k_{aq}.

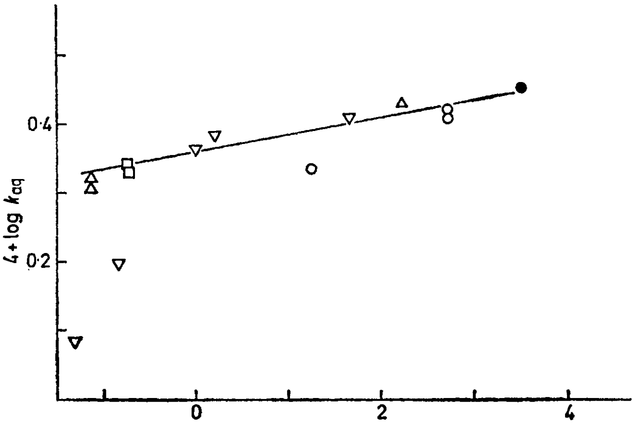

FIGURE 1 Plot of log k_{aq} against Y, the Grunwald–Winstein solvating-power parameter, for aquation of $[Co(NH_3)_5(dmso)]^{3+}$ ion: (●), water; (○), methanol; (△), dioxan; (▽), ethanol; and (□), acetone

Values of k_{aq} as a function of the heat of mixing of dmso with the solvent components, for 0·500 mol fraction non-aqueous component, are listed in Table 4.

TABLE 4

Values of k_{aq} as a function of heat of mixing, ΔH_m, of dmso with various solvent components at 45·00 ± 0·05 °C and 0·0010M-$HClO_4$

Solvent component [a]	ΔH_m [b]/cal mol^{-1}	$10^4k_{aq}/s^{-1}$
Water	−715	2·83
Methanol	−85	2·17
Acetone	−80	2·14
Ethanol	+85	2·40
n-Propanol	+125	2·60

[a] All solutions had 1 : 1 mol ratios of solvent components.
[b] W. L. Reynolds in *Progr. Inorg. Chem.*, 1970, **12**, 1—99.

Except for water, which has the most exothermic heat of mixing and the largest rate constant, the rate constants do not correlate with the heat of mixing. Values of k_{aq} as a function of water mol fraction are listed in Table 5.

If the D mechanism, shown in reactions (1) and (2), is

$$[Co(NH_3)_5(dmso)]^{3+} \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} [Co(NH_3)_5]^{3+} + dmso \quad (1)$$

$$[Co(NH_3)_5]^{3+} + H_2O \underset{k_{-w}}{\overset{k_w}{\rightleftharpoons}} [Co(NH_3)_5H_2O]^{3+} \quad (2)$$

operative then the rate law for aquation is given by equation (3) and the equilibrium quotient by (4) (where a_i are activities of dmso and of water as indicated by the subscripts). At 45 °C k_{-w} is equal[12] to 9·3 × 10^{-5} s^{-1} and k_{-d} can be taken as 2·83 × 10^{-4} s^{-1}, the limiting aquation rate constant in purely aqueous media, which is also equal to the dmso self-exchange rate constant of the ion $[Co(NH_3)_5(dmso)]^{3+}$ in liquid dmso.[9] When there is no appreciable back reaction (less than 1%) producing the ion $[Co(NH_3)_5(dmso)]^{3+}$ the following inequality must hold: $(k_da_d/k_wa_w) \leqslant 0{\cdot}03$. In this case the rate law reduces to (5) and k_{-d} is equal to the observed

$$R_{aq} = \frac{k_{-d}k_wa_w}{k_wa_w + k_da_d}[Co(NH_3)_5(dmso)^{3+}] \quad (3)$$

$$\frac{[Co(NH_3)_5(dmso)^{3+}]}{[Co(NH_3)_5H_2O^{3+}]} = \frac{k_{-w}k_da_d}{k_{-d}k_wa_w} \quad (4)$$

$$R_{aq} = k_{-d}[Co(NH_3)_5(dmso)^{3+}] \quad (5)$$

aquation rate constant, k_{aq}. Although k_{aq} does not depend explicitly on water activity or on water mol fraction it should be sensitive to those properties of the solvent (which surrounds the activated complex) which affect removal of dmso from the complex. We have shown that changes in k_{aq} definitely do not parallel changes in solvent properties (heats of mixing of dmso with the solvent components and solvating power of the solvent) which would be expected to most influence loss of dmso in the activated complex, and hence k_{-d}, in the D mechanism. The specific-ion effect, rather than a general ionic-strength effect, on k_{aq} is also difficult to explain on the basis of equation (5).

TABLE 5

Dependence of k_{aq} on water mol fraction in various solvent mixtures at 45·00 ± 0·05 °C and 0·0010M-$HClO_4$

Non-aqueous component	x_{H_2O}	$10^4k_{aq}/s^{-1}$
None	1·000	2·83
Dioxan	0·900	2·66
Dioxan	0·500	2·03
Dioxan	0·500	2·10 [a]
Dioxan	0·250	1·85 [a]
Dioxan	0·100	1·14
Ethanol	0·764	2·55
Ethanol	0·500	2·40
Ethanol	0·440	2·30
Ethanol	0·250	1·58
Ethanol	0·146	1·20
Ethanol	0·146	1·19 [a]
Acetonitrile	0·850	2·99
Acetonitrile	0·667	3·12
Acetonitrile	0·500	3·04
Acetonitrile	0·250	2·36
Acetonitrile	0·180	1·83
Acetonitrile	0·120	1·34
Acetonitrile	0·091	1·09
n-Propanol	0·667	2·85 [a]
n-Propanol	0·500	2·60 [a]
n-Propanol	0·323	2·10
Methanol	0·833	2·60
Methanol	0·833	2·54 [a]
Methanol	0·500	2·17
Acetone	0·500	2·14
Acetone	0·500	2·18 [a]

[a] $[Co(NH_3)_5(dmso)](ClO_4)_3,2H_2O$ was used as the source of the complex ion. All other results were obtained using $[Co(NH_3)_5(dmso)]^{3+}$ prepared in liquid dmso.

In the I_d mechanism there is an interchange of water for dmso in the activated complex and the process is 'accidentally bimolecular;' there must be a water molecule in the second co-ordination shell of the dmso

---

[12] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.

complex when it becomes activated or interchange cannot occur. Availability of water in the second co-ordination shell of the complex ion will probably depend on two factors, namely mol fraction of water in the bulk solvent and specific solvation of the complex by one of the solvent components, in this case, probably water. When there is no specific solvation of the reactant complex by either solvent component, the mol fraction of water in the solvent of the second co-ordination shell will be equal to the bulk-water mol fraction and k_{aq} will decrease linearly with water mol fraction. Specific solvation of the complex by water could increase the water content of the second co-ordination shell above that for the solution as a whole and cause the dependence of k_{aq} on water mol fraction to be non-linear as observed for ethanol, n-propanol, and acetonitrile. In the latter case an increase in k_{aq} was actually observed for decreasing mol fraction of water between 1·0 and 0·5; perhaps acetonitrile has the effect of breaking water structure sufficiently so that it is easier to position a water molecule in the activated complex from the second co-ordination shell than in the case of the other solvents used.

The specific-ion effect of ClO_4^- can be explained by formation of $[Co(NH_3)_5(dmso)]^{3+},ClO_4^-$ ion-pairs in which ClO_4^- displaces water from the second co-ordination shell of the complex and there is less water available for the interchange reaction with dmso. The absence of a decrease in k_{aq} in the presence of NO_3^-, even though NO_3^- should also form ion-pairs with the ion $[Co(NH_3)_5(dmso)]^{3+}$, could be explained if NO_3^- formed solvent-separated ion-pairs so that water was not displaced from the second co-ordination shell of $[Co(NH_3)_5(dmso)]^{3+}$.

Values of k_{aq} were obtained at six temperatures in the range 25·4—55·4 °C for 0·0010M-aqueous $HClO_4$. A plot of log k_{aq} against $10^3K/T$ is shown in Figure 2.

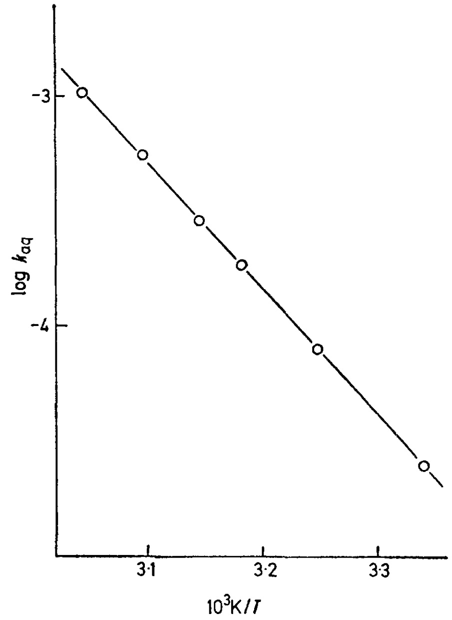

FIGURE 2 Plot of log k_{aq} against $10^3K/T$ for aquation of $[Co(NH_3)_5(dmso)]^{3+}$ ion in 0·0010M-$HClO_4$

The enthalpy and entropy of activation were 23·9 ± 0·7 kcal mol^{-1} and 0·36 ± 2·29 cal K^{-1} mol^{-1},* respectively, at 25 °C.

[3/1535 *Received, 23rd July,* 1973]

* 1 cal = 4·184 J.