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

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The aquation rate constant for penta-ammine(dimethyl sulphoxide)cobalt(III) perchlorate has been determined in 71 different solvent media and at three different temperatures for each medium. The average enthalpy and entropy of activation, their standard deviations, and ranges are 24.6 ± 0.4 and 23.6—25.6 kcal mol^{-1} and 1.1 ± 1.2 and −2.4 to 4.4 cal K^{-1} mol^{-1}, respectively, without noticeable trends. The aquation rate constant is independent of ionic strength at constant perchlorate-ion concentration, but shows a specific perchlorate-ion effect. These results are discussed in terms of the I_d and Bennetto–Caldin mechanisms. It is concluded that there is, at most, only a very small solvent contribution to the activation parameters.

It is generally accepted that substitution reactions of many octahedral complexes of transition-metal ions proceed by dissociative modes.[1-3] In the case of substitution reactions of penta-ammineanionocobalt(III) complexes in particular the dissociative mode strongly indicated [4-11] is the I_d mechanism [12] proceeding *via* ion pairs rather than the D mechanism. For the I_d mechanism the experimental data indicate that there is no significant bond formation between the central metal ion and the entering ligand Y^{y-} in the transition state because k_Y, the first-order rate constant for interchange of the leaving and entering ligands, has only a small dependence on the nature of the entering group and this small dependence can be attributed to statistical factors rather than to bond formation.[2] As a result of this independence, a plot [13] of the logarithms of the aquation rate constants against the logarithms of the complex-formation constants for a number of ligands of 1— charge is linear with gradient equal to —1, indicating strongly that the state of Y^{y-} in the transition state is very similar to that in the products of the aquation reaction. Furthermore, the lack of any significant bond formation between Co^{III} and water is strongly indicated by the following two facts. The quotient k_Y/k_{ex}, where k_{ex} is the first-order water-exchange rate constant, is equal to 0.24, 0.21, 0.16, and 0.13 for the ligands [2] $[SO_4]^{2-}$, Cl^-, $[NCS]^-$, and $[H_2PO_4]^-$, respectively, and probably reflects differences between statistical factors for entry of Y^- and H_2O rather than significant Co^{III}–OH_2 bond formation. Also, k_Y/k_{ex} approaches unity [14] when the incoming ligand completely displaces water from the second co-ordination shell of $[Co(NH_3)_5(OH_2)]^{3+}$. Therefore the leaving and entering groups in solvent exchange, aquation, and anation reactions can be visualized as occupying positions outside of the first co-ordination shell of the metal ion in the transition state.

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The comparable picture in the Bennetto–Caldin [3,15,16] mechanism for substitution reactions is the transition state attained after solvent reorganization and after moving the leaving group from ordered region A [equivalent to the first co-ordination shell in cobalt(III) complexes] to disordered region B (outside the first co-ordination shell). The solvent reorganization requires an enthalpy contribution $\Delta H_{st}'$ and the breaking of the metal–leaving-group bond requires an enthalpy contribution ΔH_{MS} to the enthalpy of activation, $\Delta H^\ddagger$. In both the Bennetto–Caldin (BC) and I_dIP mechanisms the incoming and leaving groups are not significantly bonded to the central metal ion. In the BC mechanism solvent reorganization is explicitly considered. In the I_dIP mechanism solvent reorganization is implicitly taken into account, in part, when the leaving group changes its state of solvation from that which it has when occupying a first co-ordination shell to that which it has in the transition state (and which strongly resembles that in the product state). Solvent reorganization is also implicitly taken into account, in part, in the formation of the ion pair since the free energy of formation of the latter from separated components will depend on the solvent and solvent structure as is well known from ion-pairing studies in different solvents and at different ionic strengths.[17]

Substitution reactions of bivalent cations were treated by Bennetto and Caldin [16] on the basis of their model. The contribution $\Delta H_{st}'$ was found to be from -9 to 9 kcal mol^{-1}.* Since the BC model of the transition state for bivalent cationic complexes is so similar to the model adopted for substitution reactions of penta-ammineanionocobalt(III) complexes, it is possible that similar contributions from solvent reorganization may be found for the latter reactions, if indeed solvent reorganization is responsible for such large contributions to $\Delta H^\ddagger$.

Another reason for studying solvent participation in cobalt(III) substitution reactions is that the variation of the rate of aquation of a cobalt(III) complex has been used as a probe of variation of solvent structure.[18] This method assumes that solvent structure, through solvent-reorganization requirements, makes a contribution to the activation parameters of the substitution reaction. Obviously the probe will not be useful if the solvent contributions to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are very small. Furthermore, even if there was a very considerable solvent contribution to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ the aquation rate constant determined at one temperature would probably be rather insensitive to change of solvent structure because of the compensating nature of the $\Delta H_{st}'$ and $\Delta S_{st}'$ contributions.[16]

Here we report the rate of aquation of penta-ammine-(dimethyl sulphoxide)cobalt(III) ion, $[Co(NH_3)_5(dmso)]^{3+}$, in dioxan–, acetonitrile–, and methanol–water mixtures with various concentrations of different perchlorates.

EXPERIMENTAL

The cobalt(III) complex was prepared and the rate measurements were made as described elsewhere.[19] However, a different spectrophotometer was used to the Unicam SP 500.

RESULTS AND DISCUSSION

The solvent media used and the values of the aquation rate constant, k_{aq}, found are listed in the Table. It is noted that, for equal perchlorate-ion concentrations, k_{aq} is independent of ionic strength, I, within the experimental error and that, at constant ionic strength, k_{aq} decreases with increasing $[ClO_4^-]$. The specific perchlorate-ion effect is more readily explained in terms of aquation proceeding through, at least in part, formation of outer-sphere complexes such as $[Co(NH_3)_5(dmso)]^{3+},ClO_4^-$ with a corresponding decrease in the statistical availability of water in the solvation shell of $[Co(NH_3)_5(dmso)]^{3+}$ rather than in terms of changes of solvent contributions arising from changes of solvent structure. An analogous explanation has been given previously [2,7] to explain the fact that several anation rate constants are only one eighth to one quarter as large as the water-exchange rate constant of $[Co(NH_3)_5(OH_2)]^{3+}$.

Evidence is now available concerning another very important aspect of the theory of substitution reactions. Langford and Parris [2] pointed out that once the outer-sphere complex, say $[Co(NH_3)_5(OH_2)]^{3+},Y^-$, is formed all the replacements of H_2O by Y^- should proceed with essentially the same rate constant k_{-H_2O}'. If it is true that the only essential difference between k_{-H_2O} (for loss of water in the water-exchange reaction) and k_{-H_2O}' is the statistical factor for entry of Y^- rather than H_2O, then the rate of displacement of H_2O from first- to second-co-ordination shell sites in forming the transition state is independent of the presence or absence of Y^-. The same argument can be made concerning the replacement of dmso by dmso, H_2O, or Y^- in $[Co(NH_3)_5(dmso)]^{3+}$. The anation rate constant for replacement of dmso by $[NO_3]^-$ was approximately one ninth of the rate constant for dmso self-exchange.[14] Also the observed rate constant for replacement of dmso by H_2O increased with increasing water concentration in dmso–water and finally equalled [14] the rate constant for dmso self-exchange when water completely replaced dmso in the solvation shell of $[Co(NH_3)_5(dmso)]^{3+}$. The values of k_{aq} given in the Table are consistent with the viewpoint that k_{aq} decreases when $[ClO_4]^-$ replaces H_2O in the solvation shell of $[Co(NH_3)_5(dmso)]^{3+}$ because of a decrease of the statistical factor for water entry. Hence the experimental data are all consistent with the rate of displacement of dmso from first- to second-co-ordination shell sites in formation of the transition state being independent of the composition of the solvation shell of $[Co(NH_3)_5(dmso)]^{3+}$. That the available evidence is consistent with the view that

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TABLE 1

Values of k_{aq}, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ for $[Co(NH_3)_5(dmso)]^{3+}$ in non-aqueous solvent–water–perchlorate-ion systems

Salt	[Salt]/mol dm^{-3}	$[HClO_4]$/mol dm^{-3}	I [a]/mol dm^{-3}	θ_c [b]/°C	$10^5 k_{aq}$ [c]/s^{-1}	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
(*a*) Water							
		0.001	0.001	45.0	28.3	24.5 ± 0.7	0.4 ± 2.3
		0.26	0.26	45.0	23.2		
(*b*) Dioxan–water (1 : 3) [d]							
		0.252	0.25	35.0	6.28	24.6	2.0
				45.0	23.4		
				55.0	77.4		
$Na[ClO_4]$	0.250	0.01	0.26	35.0	6.31	24.6	2.1
				45.0	23.4		
				55.0	77.8		
$Al[ClO_4]_3$	0.077	0.02	0.48	35.0	6.33	24.5	1.8
				45.0	23.7		
				55.0	77.6		
$Na[ClO_4]$	0.500	0.01	0.51	35.0	5.51	24.6	1.9
				45.0	20.2		
				55.0	68.3		
$Al[ClO_4]_3$	0.167	0.05	1.05	35.0	5.50	24.6	1.8
				45.0	20.3		
				55.0	67.9		
		0.501	0.50	35.0	5.47	24.6	1.9
				45.0	19.9		
				55.0	67.8		
$Mg[ClO_4]_2$	0.250	0.01	0.76	35.0	5.51	24.6	1.7
				45.0	20.2		
				55.0	67.8		
		0.995	1.00	35.0	4.25	25.0	2.7
				45.0	15.6		
				55.0	54.8		
$Mg[ClO_4]_2$	0.500	0.01	1.51	35.0	4.21	25.1	2.8
				45.0	15.3		
				55.0	54.5		
		1.95	1.95	35.0	2.72	24.9	1.4
				45.0	10.4		
				55.0	34.5		
$Mg[ClO_4]_2$	1.00	0.01	3.01	35.0	2.69	24.9	1.4
				45.0	10.2		
				55.0	34.2		
(*c*) Dioxan–water (1 : 1)							
		0.250	0.25	35.0	4.41	24.5	1.2
				45.0	15.7		
				55.0	54.2		
$Na[ClO_4]$	0.250	0.01	0.26	35.0	4.38	24.6	1.4
				45.0	16.1		
				55.0	53.9		
$Al[ClO_4]_3$	0.077	0.02	0.48	35.0	4.42	24.5	0.3
				45.0	15.9		
				55.0	54.2		
		0.500	0.50	35.0	3.71	24.7	0.4
				45.0	13.7		
				55.0	46.4		
$Mg[ClO_4]_2$	0.250	0.01	0.76	35.0	3.74	24.6	1.0
				45.0	13.8		
				55.0	46.1		
$Al[ClO_4]_3$	0.167	0.05	1.05	35.0	3.70	24.8	1.5
				45.0	13.6		
				55.0	46.4		
		1.00	1.00	35.0	2.51	24.7	0.7
				45.0	9.33		
				55.0	31.3		
$Mg[ClO_4]_2$	0.500	0.01	1.51	35.0	2.48	24.7	0.7
				45.0	9.30		
				55.0	31.0		
		1.95	1.95	35.0	1.26	24.7	−0.9
				45.0	4.61		
				55.0	15.7		
(*d*) Dioxan–water (3 : 1)							
		0.251	0.25	35.0	2.63	24.7	0.7
				45.0	9.76		
				55.0	32.8		
$Al[ClO_4]_3$	0.077	0.02	0.48	35.0	2.60	24.7	0.8
				45.0	9.75		
				55.0	32.5		
		0.50	0.50	35.0	1.79	24.9	0.5
				45.0	6.71		
				55.0	22.7		

TABLE 1 (*Continued*)

Salt	[Salt] / mol dm^{-3}	[HClO$_4$] / mol dm^{-3}	I [a] / mol dm^{-3}	θ_c [b] / °C	$10^5\,k_{aq}$ [c] / s^{-1}	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal K^{-1} mol^{-1}
Al[ClO$_4$]$_3$	0.167	0.05	1.05	35.0	1.77	24.9	0.7
				45.0	6.69		
				55.0	22.6		
(*e*) Acetonitrile–water (1 : 3)							
Na[ClO$_4$]	0.250	0.01	0.26	35.0	7.71	23.7	−0.6
				45.0	26.6		
				55.0	86.7		
Al[ClO$_4$]$_3$	0.077	0.02	0.48	35.0	7.72	23.6	−0.7
				45.0	27.0		
				55.0	86.6		
Na[ClO$_4$]	0.500	0.01	0.51	35.0	6.22	24.2	0.8
				45.0	22.5		
				55.0	73.8		
Mg[ClO$_4$]$_2$	0.250	0.01	0.76	35.0	6.25	24.1	0.6
				45.0	22.2		
				55.0	73.8		
Al[ClO$_4$]$_3$	0.167	0.05	1.05	35.0	6.23	24.2	0.8
				45.0	22.3		
				55.0	74.0		
Na[ClO$_4$]	1.00	0.01	1.01	35.0	5.22	24.1	0.0
				45.0	18.8		
				55.0	61.1		
Mg[ClO$_4$]$_2$	0.500	0.01	1.51	35.0	5.24	24.1	0.0
				45.0	18.7		
				55.0	61.3		
Na[ClO$_4$]	2.00	0.01	2.01	35.0	3.44		
				45.0	12.5	24.7	1.3
				55.0	43.1		
Mg[ClO$_4$]$_2$	1.00	0.01	3.01	35.0	3.46	24.7	1.2
				45.0	12.4		
				55.0	43.1		
(*f*) Acetonitrile–water (1 : 1)							
Na[ClO$_4$]	0.250	0.01	0.26	35.0	6.84	24.0	0.3
				45.0	24.0		
				55.0	79.7		
Al[ClO$_4$]$_3$	0.077	0.02	0.48	35.0	6.80	24.2	0.8
				45.0	23.9		
				55.0	81.0		
Na[ClO$_4$]	0.500	0.01	0.51	35.0	5.21	24.5	1.3
				45.0	18.9		
				55.0	63.5		
Mg[ClO$_4$]$_2$	0.250	0.01	0.76	35.0	5.23	24.4	1.0
				45.0	18.8		
				55.0	63.3		
Al[ClO$_4$]$_3$	0.166	0.05	1.05	35.0	5.17	24.5	1.5
				45.0	19.1		
				55.0	63.5		
Na[ClO$_4$]	1.00	0.01	1.01	35.0	4.07	24.5	0.9
				45.0	14.6		
				55.0	49.9		
Mg[ClO$_4$]$_2$	0.500	0.01	1.51	35.0	4.11	24.5	0.7
				45.0	14.5		
				55.0	50.0		
Na[ClO$_4$]	2.00	0.01	2.01	35.0	2.48	23.8	−2.3
				45.0	8.69		
				55.0	28.3		
Mg[ClO$_4$]$_2$	1.00	0.01	3.01	35.0	2.47	23.8	−2.4
				45.0	8.88		
				55.0	28.1		
(*g*) Acetonitrile–water (3 : 1)							
Na[ClO$_4$]	0.250	0.01	0.26	35.0	4.30	24.6	1.3
				45.0	15.7		
				55.0	53.0		
Al[ClO$_4$]$_3$	0.077	0.02	0.48	35.0	4.32	24.6	1.1
				45.0	15.4		
				55.0	53.1		
Na[ClO$_4$]	0.500	0.01	0.51	35.0	3.20	24.7	0.9
				45.0	11.6		
				55.0	39.7		
Mg[ClO$_4$]$_2$	0.250	0.01	0.76	35.0	3.18	24.7	1.1
				45.0	11.7		
				55.0	39.6		
Al[ClO$_4$]$_3$	0.166	0.05	1.05	35.0	3.16	24.7	1.2
				45.0	11.9		
				55.0	39.6		
Na[ClO$_4$]	1.00	0.01	1.01	35.0	2.34	24.6	0.3
				45.0	8.74		
				55.0	29.0		

TABLE 1 (*Continued*)

Salt	[Salt] mol dm^{-3}	[HClO$_4$] mol dm^{-3}	I [a] mol dm^{-3}	θ_c [b] °C	$10^5 k_{aq}$ [c] s^{-1}	$\Delta H^\ddagger$ kcal mol^{-1}	$\Delta S^\ddagger$ cal K^{-1} mol^{-1}
Na[ClO$_4$]	2.00	0.01	2.01	35.0	1.21	24.8	−0.5
				45.0	4.47		
				55.0	15.3		
(*h*) Methanol–water (1 : 3)							
		0.01	0.01	35.0	7.81	24.3	1.5
				45.0	27.4		
				55.0	93.6		
Na[ClO$_4$]	0.250	0.01	0.26	35.0	6.35	24.5	1.8
				45.0	22.9		
				55.0	77.6		
Na[ClO$_4$]	0.500	0.01	0.51	35.0	5.56	24.7	2.2
				45.0	21.3		
				55.0	69.4		
Mg[ClO$_4$]$_2$	0.250	0.01	0.76	45.0	21.4		
Na[ClO$_4$]	1.00	0.01	1.01	35.0	4.74	24.7	1.9
				45.0	18.0		
				55.0	59.1		
Mg[ClO$_4$]$_2$	0.500	0.01	1.51	35.0	4.78	24.6	1.7
				45.0	18.0		
				55.0	59.3		
Na[ClO$_4$]	2.00	0.01	2.01	35.0	3.47	25.2	3.0
				45.0	13.1		
				55.0	45.7		
		1.95	1.95	35.0	3.54	25.0	2.4
				45.0	13.1		
				55.0	45.7		
(*i*) Methanol–water (1 : 1)							
		0.01	0.01	35.0	6.77	24.2	0.8
				45.0	24.2		
				55.0	80.1		
Na[ClO$_4$]	0.250	0.01	0.26	35.0	5.49	24.7	2.2
				45.0	20.4		
				55.0	68.7		
Na[ClO$_4$]	0.500	0.01	0.51	35.0	4.86	24.7	1.8
				45.0	18.2		
				55.0	60.4		
Mg[ClO$_4$]$_2$	0.250	0.01	0.76	45.0	18.4		
Na[ClO$_4$]	1.00	0.01	1.01	35.0	4.14	24.2	0.0
				45.0	14.9		
				55.0	49.2		
Mg[ClO$_4$]$_2$	0.500	0.01	1.51	45.0	15.0		
Na[ClO$_4$]	2.00	0.01	2.01	35.0	2.76	25.4	1.7
				45.0	10.3		
				55.0	35.4		
Mg[ClO$_4$]$_2$	1.00	0.01	3.01	35.0	2.78	24.9	1.5
				45.0	10.4		
				55.0	35.5		
		1.95	1.95	35.0	2.77	24.8	1.2
				45.0	10.2		
				55.0	35.0		
(*j*) Methanol–water (3 : 1)							
		0.01	0.01	35.0	4.92	25.4	4.3
				45.0	18.7		
				55.0	66.1		
Na[ClO$_4$]	0.250	0.01	0.26	35.0	4.04	25.6	4.4
				45.0	15.2		
				55.0	55.0		
Na[ClO$_4$]	0.500	0.01	0.51	35.0	3.58	25.4	3.5
				45.0	13.7		
				55.0	47.8		
Mg[ClO$_4$]$_2$	0.250	0.01	0.76	45.0	13.6		
Na[ClO$_4$]	1.00	0.01	1.01	35.0	2.80	25.2	2.5
				45.0	10.7		
				55.0	36.7		
Mg[ClO$_4$]$_2$	0.500	0.01	1.51	35.0	2.85	25.2	2.6
				45.0	10.9		
				55.0	37.4		
Na[ClO$_4$]	2.00	0.01	2.01	35.0	1.98	24.9	0.8
				45.0	7.19		
				55.0	25.2		
Mg[ClO$_4$]$_2$	1.00	0.01	3.01	35.0	2.01	24.8	0.4
				45.0	7.24		
				55.0	25.2		
		1.95	1.95	35.0	2.01	24.7	0.3
				45.0	7.21		
				55.0	25.2		

[a] Calculated on the basis of the HClO$_4$ and salt concentrations. [b] Temperature variation was ±0.05 °C. [c] Average of two or more separate determinations; the standard deviation for an average value was $\leqslant 2\%$. [d] Calculated on the basis of non-aqueous solvent and water only.

displacement of dmso or H_2O from the first to second co-ordination shell during transition-state formation is independent of the composition of the solvation shell has important consequences on the study of $[Co(NH_3)_5]^{3+}$ substitution reactions. Reynolds and Barber[11] assumed that the rate of loss of water from $[Co(NH_3)_5(OH_2)]^{3+}$ was independent of the composition of the solvation shell of the complex ion and were able to show quantitatively that the experimental data for the anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by Cl^- in various media disproved the D mechanism but were consistent with the I_d mechanism.

Penta-ammineperchloratocobalt(III) ion has been found[20] as an intermediate in some assisted aquation reactions of $[Co(NH_3)_5(dmso)]^{3+}$ and was shown to be very labile. If this complex ion were formed in the unassisted aquation reactions studied by us by $[ClO_4]^-$ competing with water for vacated dmso sites it would aquate rapidly. All the dmso displaced from the first co-ordination shell would be replaced by water as in the absence of $[ClO_4]^-$ and k_{aq} would be virtually unaffected by a small concentration of perchlorato-complex intermediate.

The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values listed in the Table were calculated as described previously.[19] The $\Delta H^{\ddagger}$ values in particular show no trend outside of the experimental error of *ca.* 2%; the average of the 71 $\Delta H^{\ddagger}$ values and the standard deviation for a single value is 24.6 ± 0.4 in the range 23.6—25.6 kcal mol^{-1}. This value is equal within the experimental error to the value determined for purely aqueous media[21] and for ethanol–water–perchlorate-ion media.[19] The lack of significant dependence of $\Delta H^{\ddagger}$ on the solvent composition is consistent with the view that the energy requirement for completely breaking the metal–dmso bond in the transition state is independent of the composition of the solvation shell. Furthermore, it indicates that the solvent rearrangement contribution, $\Delta H_{st}'$, is negligible for the aquation reaction and media studied unless solvent participation and the extent of bond breaking effectively cancel. Such correlation of bond breaking and solvent participation does not seem likely because one expects that a greater extent of bond breaking requires more, rather than less, solvent rearrangement to accommodate the change. The lack of dependence of leaving groups such as water and dmso, when creating vacancies in the first co-ordination shell of the metal ion in the transition state, on the composition of the solvation shell may result from the uncharged nature of the leaving group. Studies of aquation rates of $[Co(NH_3)_5X]^{2+}$ complexes[22] have shown that the observed rates of aquation show a dependence on the composition of the solvation shell. However, in these cases it cannot be determined whether the effect arises from the energetics for the creation of a vacancy in the first co-ordination shell or from a decrease in the re-entry probability for the leaving group.

The $\Delta S^{\ddagger}$ values are very small as observed for other solvent systems.[19,21] An error contribution of 1.2 cal K^{-1} mol^{-1} arising from the 0.4 kcal mol^{-1} error in $\Delta H^{\ddagger}$ effectively obscures any trend in $\Delta S^{\ddagger}$ values with decreasing k_{aq} values. The best that can be said is that $\Delta S^{\ddagger}$ shows no significant trend outside of experimental error.

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