Mechanism of Aquation of (Dimethyl sulphoxide)penta-amminecobalt(III) Perchlorate

By WARREN L. REYNOLDS,* SMILJKO AŠPERGER, and MLADEN BIRUŠ

(Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, and Institute "Rudjer Bošković", Zagreb, Croatia, Yugoslavia)

Summary Evidence is presented which shows that the reaction $Co(NH_3)_5(DMSO)^{3+} + H_2O \rightleftharpoons Co(NH_3)_5OH_2^{3+} +$ DMSO, over a range of solvents from aqueous to water-poor systems, probably proceeds by the I_d mechanism and not the D mechanism.

IF it is assumed that the rate constants k_e and k'_e, defined by Haim and Taube,[1] for displacement of H_2O from the first to the second co-ordination shell of cobalt(III) in MOH_2^{3+} and in MOH_2^{3+},X^-, $M^{3+} \equiv Co(NH_3)_5^{3+}$, are equal because anation rate constants are very insensitive to the nature of the incoming group, then the rate laws for anation and aquation in the D mechanism proposed[1] reduce to a form identical to those for the same processes in the I_d mechanism and distinguishing between these two mechanisms is very difficult. The assignment of an I_d mechanism to the aquation and anation reactions of penta-amminecobalt(III) complexes depends on the results of Pearson and Moore[2] and upon the assumption that the five-co-ordinate intermediate M^{3+} is formed in the reactions studied by Haim and Taube[1] and by Buckingham *et al.*[3] However, the product ratios obtained[1,3] in the latter reactions can be explained simply, without assuming M^{3+} formation, by elimination of first-co-ordination-shell N_3^- (or $NH_2CO_2^-$) by an I_d mechanism involving ion pairs such as MN_3^{2+},X^- (or $MNH_2CO_2^{2+},X^-$), which will probably form to the same extent,[4] as well as involving the free cations. Consequently, mechanisms can be assigned only tentatively to all these reactions at present.

Here we report that a study of the reaction $Co(NH_3)_5(DMSO)^{3+} + H_2O \rightleftharpoons Co(NH_3)_5OH_2^{3+} +$ DMSO has given evidence, over a wide range of solvent media from purely aqueous to water-poor systems, which strongly supports the I_d mechanism and which does not support the D mechanism. Some rate constants obtained are listed in the Table. We have studied the dependence of the firstorder aquation rate constant, k_{aq}, of $Co(NH_3)_5(DMSO)^{3+}$ (DMSO = dimethyl sulphoxide) on ionic strength, concentration of 'inert electrolyte', activity of water, solvent ionizing power, mole fraction of water, and the heat of mixing of DMSO with various organic solvents under conditions where the reverse reaction, namely, formation of $Co(NH_3)_5(DMSO)^{3+}$, is negligible and $k_{aq} = k'_{-y}$ for the *D* mechanism shown in equations (1) and (2) or $k_{aq} = k_{-y}$ for the I_d mechanism shown in equation (3). The rate

$$MOH_2^{3+} \underset{k_s}{\overset{k_{-s}}{\rightleftharpoons}} M^{3+} + H_2O \qquad (1)$$

$$M^{3+} + DMSO \underset{k'_{-y}}{\overset{k_y'}{\rightleftharpoons}} M(DMSO)^{3+} \qquad (2)$$

$$MOH_2^{3+} + DMSO \underset{k_{-y}}{\overset{k_y}{\rightleftharpoons}} M(DMSO)^{3+} + H_2O \qquad (3)$$

constant k'_y for the *D* mechanism should be insensitive to the mole fraction of water in the solvent medium because water does not explicitly enter the activated complex $[(M \cdots DMSO)^{3+}]^{\ddagger}$ by which the intermediate M^{3+} is formed, but k'_y should be sensitive to those properties of the solvent (which surrounds the activated complex and solvates it) which affect the removal of DMSO from the complex. We have shown that changes in k_{aq} do not parallel changes in the heats of mixing of DMSO with the solvent components and hence that the interaction between DMSO and solvent components is not the controlling factor in the change of k_{aq}. Furthermore we have shown that the dependence of k_{aq} on the Grunwald–Winstein *Y*-factor is very small and hence that changes in the water concentration do not affect the solvating power of the solvent for the activated complex as compared to the reactant complex. Therefore we have found experimentally that the properties of the solvent media which should affect the stability of $[(M \cdots DMSO)^{3+}]^{\ddagger}$, and which are affected by the change of water content, do not appear to be the properties which determine k_{aq}.

On the other hand, the rate constant k_{-y} for the I_d mechanism should be sensitive to the mole fraction of water in the solvent media if the change of mole fraction of water in the bulk solvent is reflected by changes in the amount of water in the solvation shell of $Co(NH_3)_5(DMSO)^{3+}$ when the activated complex is formed. This is so because water should be considered as entering explicitly into the activated complex ('accidental bimolecularity') because the M^{3+} unit cannot survive the activated complex to go in search of the water necessary for completion of the reaction. If the importance of the mole fraction in the solvation shell of $Co(NH_3)_5(DMSO)^{3+}$ over-rides the importance of changes of enthalpy of interaction of the departing DMSO with solvent components and the importance of the solvation energy difference between the ground state and the activated complex as determined by *Y*-values, then the aquation rate constant can show a marked dependence on the mole fraction of water as has been found experimentally.

TABLE

Aquation rate constants of $Co(NH_3)_5(DMSO)^{3+}$ *in aqueous–nonaqueous binary solvent mixtures,* 45·0 ± 0·1 °C, 0·001M-$HClO_4$

Nonaqueous component	$X(H_2O)$[a]	Y[b]	$10^4k_{aq}/s^{-1}$
None	1·000	3·49	2·83
Dioxan	0·900	2·23	2·66
MeOH	0·833	2·72	2·54[c]
MeOH	0·833	2·72	2·60
EtOH	0·764	1·66	2·55
Pr^nOH	0·667	—	2·85[c]
Pr^nOH	0·5 0	—	2·60[c]
Dioxan	0·500	−1·13	2·03
Dioxan	0·500	−1·13	2·10[c]
EtOH	0·500	2·08	2·40
Me_2CO	0·500	−0·71	2·14
Me_2CO	0·500	−0·71	2·18[c]
MeOH	0·500	1·00	2·17
EtOH	0· 40	0·00	2·30
Pr^nOH	0·323	—	2·10
EtOH	0·250	−0·95	1·58[c]
EtOH	0·146	−1·29	1·20
EtOH	0·146	−1·29	1·19[c]
Dioxan	0·100	—	1·14

[a] Mole fraction water. [b] Grunwald–Winstein *Y*-parameter. [c] $[Co(NH_3)_5OH_2](ClO_4)_3,2H_2O$ prepared by method of C. R. P. Mac-Coll and L. Beyer, *Inorg. Chem.*, 1973, **12**, 7 was used. All other results obtained with $[Co(NH_3)_5OH_2](ClO_4)_3$ dissolved in DMSO as source of $Co(NH_3)_5(DMSO)^{3+}$.

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[5] We use the symbolism given by C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965.