dissociation than those for N-bonded complexes.

Further studies using thiol ligands, where the reactivity of both RSH and RS^- species may be investigated in the high-pH range, are in progress.

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Registry No. $Fe(CN)_5OH_2^{3-}$, 18497-51-3; TU, 62-56-6; ATU, 109-57-9; DMTU, 534-13-4.

Contribution from the Departments of Chemistry, Faculty of Science, University of Sarajevo, Sarajevo, Yugoslavia,
and University of Minnesota, Minneapolis, Minnesota 55455

Solvent Interchange of Pentaamminecobalt(III) Ions in Water–Acetonitrile and in Dimethyl Sulfoxide–Acetonitrile Media

MIRA GLAVAŠ, MOHEB SEIF EL-NASR,[1] and WARREN L. REYNOLDS*

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Solvent-interchange reaction rates have been determined for $[CO(NH_3)_5(NCCH_3)](ClO_4)_3$ in acetonitrile–water and in acetonitrile–dimethyl sulfoxide solvent mixtures. Ratios of reactants and products in equilibrium mixtures and first-order rate constants are reported. The rate constants k_A and k'_A for reaction of acetonitrile with the aquo and dimethyl sulfoxide complexes were strongly dependent on the mole fraction of acetonitrile in the solvent. The rate constants for the reverse reactions for loss of acetonitrile from the acetonitrile complex were only slightly dependent on the mole fraction of acetonitrile. One interpretation of the results is that the $Co(NH_3)_5^{3+}$ group in the activated complex of the I_d mechanism for solvent interchange does not undergo any significant real rotation or pseudorotation within its solvent cage. The activation enthalpy for water reacting with the acetonitrile complex was 26.5 ± 0.5 kcal mol^{-1}, that for acetonitrile reacting with the aquo complex was 28.7 ± 0.4 kcal mol^{-1}, that for acetonitrile reacting with the dimethyl sulfoxide complex was 27.0 ± 0.5 kcal mol^{-1}, and that for dimethyl sulfoxide reacting with the acetonitrile complex was 27.8 ± 0.5 kcal mol^{-1}.

The I_d (interchange with dissociative character) model has been accepted[2-5] for the mechanism of substitution reactions of $Co(NH_3)_5S^{3+}$ such as shown in reaction 1, where S is a

$$Co(NH_3)_5S^{3+} + Y \rightleftarrows Co(NH_3)_5Y^{3+} + S \qquad (1)$$

solvent molecule and Y is an anion, an uncharged ligand, or another solvent molecule. In this mechanism $Co(NH_3)_5S^{3+}$ first forms an encounter complex with Y, and then the encounter complex becomes activated, breaking the Co(III)–S bond and moving S to the solvent cage[4] around the five-coordinate $Co(NH_3)_5^{3+}$ group. The nucleophile Y must also be in this solvent cage if it is to be interchanged for S because $Co(NH_3)_5^{3+}$ does not exist sufficiently long to diffuse from this solvent cage and react with nucleophiles outside of the solvent cage; Langford[3] has appropriately described this reaction as "accidentally bimolecular". When Y is another S molecule (solvent exchange), the potential energy barrier can be qualitatively described as in Figure 1. The barrier top is essentially flat, as assumed in absolute rate theory, within the energy uncertainty arising from the short lifetime of the transition state. At the configuration designated by X_1^* the Co(III)–S bond has been broken, at X_2^* the leaving and entering S molecules are equivalent as required by the principle of microscopic reversibility, and at X_3^* the Co(III)–*S bond has been broken in the reverse reaction. (Langford[4] has pointed out the lack of bonding in this mechanism between Co(III) and the entering group.) If the $Co(NH_3)_5^{3+}$ group can rotate or pseudorotate freely within its solvent cage before it is deactivated, it can fill the vacant first-coordination-shell site more or less statistically from among the properly oriented nucleophiles (all S molecules in solvent exchange) in the solvent cage. In this case, there will be many orientations of $Co(NH_3)_5^{3+}$ within the solvent cage, all with equal energies within the energy uncertainty, and there will be a barrier like that shown in Figure 1 for each orientation through which the system passes from breaking of the Co(III)–S bond to forming of the Co(III)–*S bond.

In a mixture of two solvents S and Y both of which can form bonds to Co(III) the solvated complex $Co(NH_3)_5S^{3+}\cdot S_s\cdot Y_y$, containing *s* S molecules and *y* Y molecules in the solvation shell, is the encounter complex. (There probably is a range of *s* and *y* values for any given bulk mole fraction of Y.) Activation of this complex and breaking of the bond between Co(III) and the inner-sphere S can occur. If there is free rotation or pseudorotation of $Co(NH_3)_5^{3+}$ within its solvent cage the vacant coordination site can be repositioned with respect to the solvent cage. When deactivation occurs, $Co(NH_3)_5^{3+}$ may combine (1) with the original S molecule (internal return), (2) with a different S molecule (solvent exchange) by passage through a configuration analogous to X_3^* in Figure 1, or (3) with a Y molecule and pass through a configuration X_4^* (not shown in Figure 1) on an unsymmetrical barrier for formation of $Co(NH_3)_5Y^{3+}$ from $Co(NH_3)_5S^{3+}$. Here we present some results consistent with the absence of such free rotation of $Co(NH_3)_5^{3+}$ with respect to the solvent cage in which it was formed.

Experimental Section

Materials. The compounds $[Co(NH_3)_5OH_2](ClO_4)_3$,[6] $[Co(NH_3)_5OSMe_2](ClO_4)_3\cdot 2H_2O$,[7] and $[Co(NH_3)_5(NCCH_3)](ClO_4)_3$[8] were prepared as described previously in the literature. The *p*-toluenesulfonic acid (PTSA) was obtained from Eastman Kodak Co. and was purified by recrystallization from ethanol. Dimethyl sulfoxide, Me_2SO, was obtained from Aldrich Chemical Co. and was purified by distillation under reduced pressure with the middle two-thirds fraction collected. Acetonitrile was obtained from Eastman Kodak Co. and was purified by distillation with the middle two-thirds fraction

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* To whom correspondence should be addressed at the University of Minnesota.

(1) Abstracted in part from a thesis submitted to the Unversity of Minnesota by M. Seif El-Nasr in partial fulfillment of the requirements for the Ph.D. degree.

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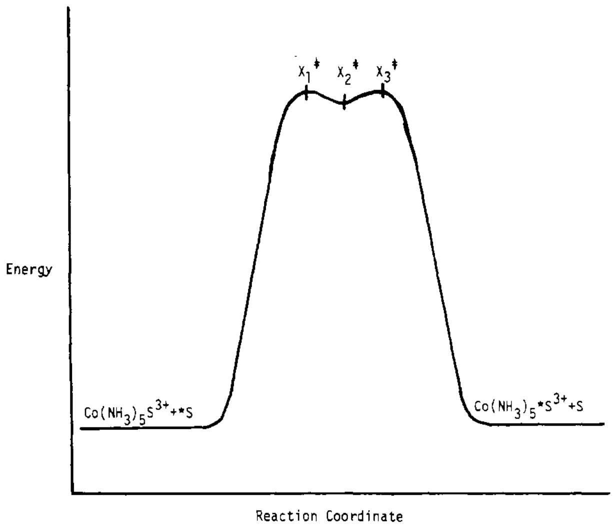

Figure 1. Qualitative representation of a potential energy barrier for a solvent-exchange reaction of a pentaamminecobalt(III) complex.

Table I. Water–Acetonitrile Solvent Interchange for the $Co(NH_3)_5(OH_2)^{3+}$ and $Co(NH_3)_5(NCCH_3)^{3+}$ Complexes in Water–Acetonitrile Mixtures at Different Temperatures[a]

X_A[b]	t, °C	Q[c]	10^5k_{obsd}, s^{-1}	10^5k_W, s^{-1}	10^5k_A, s^{-1}
0.0	35.0		0.219	0.219	
0.1		0.683	0.301	0.179	0.122
0.2		1.176	0.365	0.168	0.197
0.3		1.684	0.435	0.162	0.273
0.4		2.255	0.509	0.156	0.352
0.5		2.956	0.601	0.152	0.449
0.6		3.687	0.663	0.142	0.521
0.7		4.627	0.717	0.128	0.590
0.8		6.275	0.794	0.109	0.685
0.9		8.325	0.880	0.094_5	0.786
0.0	45.0		0.850	0.850	
0.1		0.911	1.37_5	0.722	0.658
0.2		1.587	1.61_5	0.624	0.991
0.3		2.141	1.84	0.586	1.25
0.4		2.707	2.10	0.567	1.54
0.5		3.467	2.45	0.548	1.90
0.6		4.134	2.61	0.509	2.10
0.7		5.134	2.87	0.469	2.41
0.8		6.753	3.12	0.402	2.72
0.9		9.529	3.39	0.322	3.07
0.0	55.0		3.69	3.69	
0.1		0.845	5.12	2.78	2.34
0.2		1.59	6.49	2.51	3.98
0.3		2.07	7.47	2.43	5.04
0.4		2.97	9.02	2.27	6.75
0.5		3.71	10.23	2.12	8.11
0.6		4.74	11.55	2.02	9.53
0.7		5.81	12.67	1.86	10.81
0.8		7.99	14.05	1.56	12.49
0.9		9.97	15.35	1.40	13.95

[a] Total Co(III) concentration = 0.005 mol/dm^3 (0.010 mol/dm^3 $HClO_4$). [b] Calculated on the basis of the solvents only. [c] Q is defined by eq 2.

collected. All other chemicals were reagent grade and were used without further purification.

Chromatographic Separations. An AG50W-X4, 100–200 mesh, hydrogen form resin was used to separate the $Co(NH_3)_5(OH_2)^{3+}$ and $Co(NH_3)_5(NCCH_3)^{3+}$ complexes present at equilibrium in a water–acetonitrile reaction medium. The former complex was eluted from a 1 × 20 cm column of the resin with 2.5 M aqueous H_2SO_4 and the latter complex with 4.0 M aqueous H_2SO_4. The complexes in their respective eluants were determined spectrophotometrically at 490 nm for the aquo complex and at 465 nm for the acetonitrile complex. The latter did not aquate measurably in the time required for separation. Recovery was 98% or better.

Kinetic Measurements. The solvent-interchange reactions in H_2O + CH_3CN media were followed spectrophotometrically at 450 nm with a Unicam SP500, Series 2, spectrophotometer having a cell compartment thermostated to ±0.05 °C. After 10 half-lives the infinite-time absorbance, A_∞, was determined and an aliquot of the equilibrium reaction mixture was absorbed on a cation-exchange chromatographic column, and the products were separated, eluted, and determined as described in the previous paragraph in order to determine the values of Q defined by eq 2, where $M^{3+} = Co(NH_3)_5{}^{3+}$.

$$Q = \frac{[M(NCCH_3)^{3+}]_e}{[M(OH_2)^{3+}]_e} = \frac{k_A}{k_W} \qquad (2)$$

In this equation, the subscripts e refer to equilibrium concentrations, k_A is the first-order rate constant for reaction of acetonitrile with the aquo complex, and k_W is the first-order rate constant for reaction of water with the acetonitrile complex. The absorbance (A)–time data obeyed integrated first-order rate laws such as the one given in eq 3 to at least 3 half-lives.

$$\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - k_{obsd}t \qquad (3)$$

In this equation k_{obsd} is the observed first-order rate constant for approach to equilibrium and is equal to the sum (k_A + k_W). For each solvent medium the value of Q was used to separate k_{obsd} into k_A and k_W values.

The solvent-interchange reactions in Me_2SO–CH_3CN mixed-solvent media were followed spectrophotometrically at 555 nm with a Beckman DU having a cell compartment thermostated at 45.1 ± 0.1 °C. A_∞ values were determined after 10 half-lives and again after a further 24 h; the values were the same within the experimental error of an absorbance measurement. The A–t data obeyed the rate law given in eq 3 for at least 3 half-lives. All reaction media contained PTSA to prevent reduction of Co(III) to Co(II);[9] the presence of Co(II) could be easily detected as $CoCl_4{}^{2-}$ at 683 nm.[9] Equilibrium concentrations of the acetonitrile and dimethyl sulfoxide complexes in the reaction media were determined spectrophotometrically at 473 and 555 nm. The dimethyl sulfoxide complex has equimolar extinction coefficients at these two wavelengths whereas the acetonitrile complex absorbs very little at 555 nm and much more than the dimethyl sulfoxide complex at 473 nm. Subtraction of A^{555}, the measured absorbance at 555 nm, from A^{473}, the measured absorbance at 473 nm, gave a very good first approximation for the $M(NCCH_3)^{3+}$ concentration. Correction of A^{555} for the small absorbance of $M(NCCH_3)^{3+}$ at 555 nm gave a new value for the absorbance of $M(OSMe_2)^{3+}$ at 555 nm. Since this was equal to the absorbance of $M(OSMe_2)^{3+}$ at 473 nm, this value was subtracted from A^{473} to give a second approximation for the $M(NCCH_3)^{3+}$ concentration. Further approximations could be made in the same manner. Constant concentrations were obtained by the third approximation. This method was checked and found valid, by chromatographic separation on a cold (ca 7–8 °C) cation-exchange column and spectrophotometric determination of the separated complexes. Consequently, the easier, faster spectrophotometric determination of the final $M(NCCH_3)^{3+}$ and $M(OSMe_2)^{3+}$ concentrations was used almost exclusively. The equilibrium concentrations were used in eq 4 to calculate Q' values. In turn Q' values were used to

$$Q' = \frac{[M(OSMe_2)^{3+}]}{[M(NCCH_3)^{3+}]} = \frac{k_D}{k'_A} \qquad (4)$$

calculate k_D and k'_A values from the observed first-order rate constants for approach to equilibrium; k_D is the first-order rate constant for reaction of dimethyl sulfoxide with $M(NCCH_3)^{3+}$ and k'_A is the first-order rate constant for reaction of acetonitrile with $M(OSMe_2)^{3+}$.

Results

Water–Acetonitrile Solvent Interchange. Table I lists the results obtained for solvent interchange between the $M(OH_2)^{3+}$ and $M(NCCH_3)^{3+}$ complexes at various mole fractions, X_A, of acetonitrile in water–acetonitrile mixtures at three different temperatures; the first-order rate constants k_A and k_W are defined by the solvent-interchange reaction 5. All results given

$$M(OH_2)^{3+} + CH_3CN \underset{k_W}{\overset{k_A}{\rightleftharpoons}} M(NCCH_3)^{3+} + H_2O \qquad (5)$$

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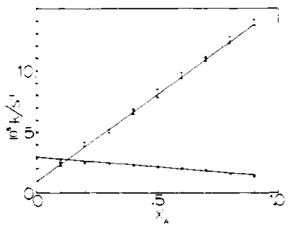

Figure 2. Plot of first-order rate constants for solvent interchange vs. mole fraction of acetonitrile at 55 °C. Solid circles are for k_W, and bars are for k_A.

Table II. Acetonitrile–Dimethyl Sulfoxide Solvent Interchange for $Co(NH_3)_5(NCCH_3)^{3+}$ and $Co(NH_3)_5(OSMe_2)^{3+}$ Complexes in Acetonitrile–Dimethyl Sulfoxide Mixtures[a]

X_A[b]	Q'[c]	$10^5 k_{obsd}$, s^{-1}	$10^5 k_A$, s^{-1}	$10^5 k_D$, s^{-1}
0.0		3.63		3.63
0.1	16.0	3.40	0.20	3.20
0.2	11.7	3.52	0.28	3.24
0.3	7.61	3.85	0.45	3.40
0.4	4.92	4.26	0.72	3.54
0.5	3.86	3.92	0.81	3.11
0.6	2.71	3.97	1.07	2.90
0.7	1.77	3.89	1.40	2.45
0.8	1.16	5.63	2.61	3.02
0.9	0.52	6.46	4.25	2.21
1.0		4.82	4.82	

[a] Total Co(III) concentration = mol/dm³ (0.001 mol/dm³ *p*-toluenesulfonic acid; 45.1 ± 0.1 °C). [b] Calculated on the basis of the solvents only. [c] Q' is defined by eq 4.

in Table I are averages of four separate experiments except for the purely aqueous media where three separate experiments were done. The standard deviation for a single measurement of Q was no more than ±2%. Use of the law for propagation of error for $k_W = k_{obsd}/(1 + Q)$ and for $k_A = k_W Q$ gave percentage errors of ±4.5% and ±5% for k_W and k_A, respectively.

The values of k_A and k_W at 55 °C are plotted as a function of X_A in Figure 2. It is seen that both k_A and k_W are linearly dependent on X_A, the mole fraction of acetonitrile in the bulk solvent over the range $0.1 \leq X_A \leq 0.9$. It is also seen that the absolute value of the slope of the plot for k_A is much larger than the absolute value of the slope of the plot for k_W. Therefore k_A increases much more rapidly than k_W decreases for a given change in the solvation shell produced by a given change in X_A at 55 °C. Plots (not shown) of k_A and k_W vs. X_A at 35 and 45 °C were also linear and showed the relatively large dependence of k_A on X_A as compared to the dependence of k_W on X_A.

Acetonitrile–Dimethyl Sulfoxide Solvent Interchange. The results of the solvent interchange shown in reaction 6 are listed

$$M(AcN)^{3+} + Me_2SO \underset{k'_A}{\overset{k_D}{\rightleftharpoons}} M(OSMe_2)^{3+} + AcN \quad (6)$$

in Table II. Each set of Q', k_{obsd}, k_D, and k'_A values represents the averages for at least four separate experiments. The standard deviations for Q' and k_{obsd} where approximately ±8% and ±4%, respectivey; those calculated for k'_A and k_D by the law for propagation of error were approximately ±9%. It is seen from Table II that in the range $0 \leq X_A \leq 0.4$, k'_A increased approximately 350% whereas k_D remained essentially unchanged from an average value of 3.4×10^{-5} s^{-1}. Also, in the range $0.4 \leq X_A \leq 0.9$, k'_A increased approximately 600% whereas k_D decreased only about 30%. The dependence of k'_A and of k_D on X_A was not linear over the range $0.1 \leq X_A \leq 0.9$ as was the dependence of k_A and of k_W for the water–acetonitrile system, but there is no reason that the dependence of either k'_A or k_D should be linear with X_A. The important fact is that k'_A showed a very strong dependence on X_A whereas k_D did not.

Table III. Activation Parameters for the First-Order Rate Constants k_W and k_A in the Water–Acetonitrile Media

X_A	$\Delta H_W^{\ddagger}$, kcal/mol	$\Delta S_W^{\ddagger}$, cal/(mol K)	$\Delta H_A^{\ddagger}$, kcal/mol	$\Delta S_A^{\ddagger}$, cal/(mol K)
0.0	27.7 ± 0.9	+5.5 ± 0.6		
0.1	26.9 ± 1.0	+2.2 ± 0.3	29.1 ± 0.6	+8.7 ± 2.0
0.2	26.5 ± 0.3	+0.8 ± 0.9	29.5 ± 0.3	+11.2 ± 1.0
0.3	26.5 ± 0.4	+0.9 ± 1.3	28.6 ± 1.9	+8.8 ± 0.6
0.4	26.2 ± 0.4	−0.2 ± 1.1	29.0 ± 0.3	+10.5 ± 0.7
0.5	26.1 ± 0.4	−0.7 ± 1.1	28.4 ± 0.3	+9.0 ± 0.8
0.6	26.0 ± 0.4	−0.5 ± 1.1	28.5 ± 0.4	+9.7 ± 1.2
0.7	26.3 ± 0.4	−0.5 ± 1.0	28.5 ± 0.4	+10.0 ± 1.0
0.8	26.1 ± 0.3	−1.4 ± 0.9	28.5 ± 0.5	+10.1 ± 1.4
0.9	26.4 ± 0.6	−0.7 ± 1.9	28.2 ± 0.5	+9.5 ± 1.4

The enthalpies and entropies of activation for the water–acetonitrile systems are listed in Table III. Each set of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values was calculated from eq 7 with use of a linear

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta H^{\ddagger}}{10^3 R} \frac{10^3}{T} \quad (7)$$

least-squares computer program for 12 data points, four at each of the three different temperatures, except for $X_A = 0.0$ where nine data points were used, three at each of the three different temperatures. The temperature range (20 °C) was rather small, but the values of the activation parameters are not used for any critical decisions, and the values for each rate constant show reasonable agreement.

Discussion

Consider, for example, $Co(NH_3)_5(OH_2)^{3+}$ dissolved in a binary solvent mixture such as a water–acetonitrile mixture. This relatively inert complex cation will find itself in contact with, on the average, a certain number of molecules of each component of the binary solvent. These solvent molecules will define the primary solvation shell surrounding the inert first coordination sphere. Average mole fractions, X'_W and X'_A, of water and acetonitrile, respectively, based on the total number of solvent molecules in the primary solvation sphere can be assigned for the fractions of each solvent in the primary solvation sphere at each bulk mole fraction, X_A, of acetonitrile. These mole fractions will be the same as the mole fractions X_W and X_A for the bulk solvent if there is no preferred solvation by one or the other of the solvent components, but they will be different if there is. Behrendt, Langford, and Frankel[10] have found that the total number of solvent molecules in the primary solvation sphere of $Cr(NCS)_6^{3-}$ remained essentially constant with increase of X_A in water–acetonitrile mixtures and that there was approximately one-for-one replacement of water molecules by acetonitrile molecules. However, for our purposes here it is not necessary that X'_W and X'_A be equal to X_W and X_A, respectively, that the total number of solvent molecules in the primary solvation sphere remain constant, or that there is a one-for-one replacement of water molecules by acetonitrite molecules in the primary solvation sphere when X_A is varied. These solvated complex cations are the encounter complexes E defined by Langford and co-workers.[11,12] When X_W and X_A in the bulk solvent are changed, the composition of the primary solvation sphere in E probably changes also. It is well-known, and King and co-workers have recently emphasized,[13] that the molar extinction coefficients and wave-

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lengths of absorption maxima of inert Cr(III) and Co(III) complexes show some dependence on mole ratios in mixed solvents, probably as a result of changes in the primary solvation sphere. Thus the rate of solvent exchange for a particular solvent composition will be given by eq 8 and that for

$$R(\text{exchange}) = \frac{k_{ex}\gamma_E}{\gamma_\ddagger}[E] \tag{8}$$

solvent interchange will be given by eq 9.

$$R(\text{interchange}) = \frac{k_i\gamma_E}{\gamma_\ddagger}[E] \tag{9}$$

Because the encounter complex and activated complex are so similar (except for the "hole" in the first coordination sphere left by the leaving solvent molecule), the activity coefficients γ_E and $\gamma_\ddagger$ can be expected to cancel to a large degree. Support for this assumption comes from many previous studies so that only a few need be mentioned. The first-order rate constants for aquation of $Co(NH_3)_5(OS(Me)_2)^{3+}$ in various water–nonaqueous solvent mixtures[14,15] did not depend on the ionic strength of the medium but upon the concentration of ClO_4^- in the medium presumably because ClO_4^- could displace water from the primary solvation sphere. The first-order rate constants for aquation of $Co(NH_3)_5(DMF)^{3+}$, where DMF = dimethylformamide, in purely aqueous perchlorate media[16] also did not depend on ionic strength but did depend somewhat on the ClO_4^- concentration, probably for the same reason. Even the first-order rate constant for aquation of $Co(NH_3)_5Cl^{2+}$ was remarkably free[17] of ionic strength effects, indicating cancellation of the activity coefficients for $Co(NH_3)_5Cl^{2+}$ and for the activated complex despite the separation of charge occurring in the activation step. Consequently, the observed values of k_{ex} and k_i should depend mainly on the composition and structure of the primary solvation sphere and not on the activity coefficients.

For the purpose of this discussion let us assume that rotation or pseudorotation of the $Co(NH_3)_5^{3+}$ group can occur freely within the solvent cage in which it was formed when the encounter complex gains sufficient potential energy to break the $Co(III)-OH_2$ bond and move the first-coordination-sphere water molecule to the solvent cage and thus vacate a first-coordination-sphere site. The vacant site can change its position with respect to the solvent cage in which $Co(NH_3)_5^{3+}$ was formed. Deactivation will occur before diffusional processes change the composition of the solvent cage allowing $Co(NH_3)_5^{3+}$ to react with nucleophiles outside the solvent cage in which it was formed; $Co(NH_3)_5^{3+}$ must combine with one of the possible ligands from the original solvent cage when it deactivates. Let deactivation occur a fraction f_{W1} times with water from this solvent cage and a fraction f_{A1} times with acetonitrile from this solvent cage when the bulk mole fraction of acetonitrile is X_{A1}. Similarly, deactivation occurs a fraction f_{W2} and a fraction f_{A2} times with water and acetonitrile, respectively, when the bulk mole fraction of acetonitrile is X_{A2}. Now

$$f_{W1} + f_{A1} = f_{W2} + f_{A2} = 1 \tag{10}$$

because all deactivations occur by combination with either water or acetonitrile from the original solvent cage of $Co(NH_3)_5^{3+}$. (It is not necessary that the ratios f_W/f_A be equal to the ratios of the mole fractions of water and acetonitrile in the solvent cage as they would be if there was a strictly statistical formation of aquo and acetonitrile complexes according to the composition of the solvent cage.) A change in the bulk mole fractions produces changes in the primary solvation sphere of $Co(NH_3)_kOH_2^{3+}$, in the compositions of the encounter complex and solvent cage of $Co(NH_3)_5^{3+}$, and in the fractions f_W and f_A. Thus

$$\frac{df_A}{dX_A} = -\frac{df_W}{dX_A} \tag{11}$$

and the slope of the k_W vs. X_A plot *should be equal to the negative of the slope of the* k_A *vs.* X_A *plot at each different composition* X_A. This was not found experimentally. We conclude that free rotation or pseudorotation of $Co(NH_3)_5^{3+}$ with respect to its solvent cage containing different ratios of the two solvents for different bulk solvent compositions does not occur for either of the two systems studied.

However, if $Co(NH_3)_5^{3+}$ remains in a relatively fixed position with respect to its original solvent cage until deactivation occurs, then the dependencies of the rate constants on X_A can be readily explained. For example, preferred solvation of $Co(NH_3)_5(NCCH_3)^{3+}$ by water in solvation sphere sites adjacent to the leaving acetonitrile molecule (so that the water is there at all X_A values used) can explain the slow decrease of k_W even though other solvation sphere sites may be increasingly occupied by acetonitrile as X_A increases. The increase in k_A can occur as a result of the need for at least one acetonitrile molecule (this is the leaving acetonitrile molecule in the reverse reaction in reaction 5) to occupy a solvent cage site adjacent to the vacant first-coordination-sphere site. The occupancy of this site by acetonitrile in the forward reaction of reaction 5 increases with increasing X_A (but not necessarily linearly).

Similarly, preferred solvation of $Co(NH_3)_5(NCCH_3)^{3+}$ by Me_2SO in solvation sphere sites adjacent to the leaving acetonitrile molecules (so that the Me_2SO is there at all X_A values used) can explain the relatively small dependence of k_D on X_A in the forward reaction of reaction 6. The increase in k'_A for the reverse reaction in (6) can occur as a result of the need for at least one molecule of acetonitrile (the leaving acetonitrile molecule in the forward reaction) to occupy a solvent cage site adjacent to the vacant first-coordination-sphere site. The occupancy of this site by acetonitrile in the reverse reaction increases with X_A but not linearly.

There is some additional evidence indicating the solvent cage may break up before $Co(NH_3)_5^{3+}$ can undergo significant reorientation within it. The rotational correlation time for water at 20 °C is approximately 3–4 ps.[18] One may expect such motions of relatively small solvent molecules to break up the original solvent cage. On the other hand, rotational correlation times of $Co(NH_3)_6^{3+}$ and of $Co(en)_3^{3+}$ are approximately 30 ± 10 ps,[19] that is, approximately 10 times longer. Furthermore, Langford[4] has discussed the contribution to volumes of activation from the collapse of solvent in the solvation shell onto the contracted first coordination sphere of $Co(NH_3)_5^{3+}$. Hydrogen bonding between coordinated NH_3 molecules and solvent molecules in the solvent cage could provide the linkage between first coordination sphere and the surrounding solvent. Such hydrogen bonding would certainly tend to hold the orientation of $Co(NH_3)_5^{3+}$ fixed with respect to the solvent cage.

Preferred solvation of transition-metal complexes has been proposed previously. Langford and Tong[12] have suggested specific solvation sphere binding to explain the lack of dependence of the first-order solvent-exchange rate constant of $Cr(OSMe_2)_6^{3+}$ on the mole fraction of Me_2SO in dimethyl

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sulfoxide–nitromethane mixtures. Scott, Weeks, Bracken, and King[20] have suggested hydrogen bonding between coordinated water molecules in $Cr(OH_2)_6^{3+}$ and Me_2SO to explain the stabilization of this complex relative to $Cr(OH_2)_5(Me_2SO)^{3+}$. Johnson and King[13] have proposed that the dominant factor governing the outer-sphere interactions is hydrogen bonding between $Co(NH_3)_5(OH_2)^{3+}$ and Me_2SO. Glavaš and Reynolds[21] have suggested a specific interaction between coordinated and free dimethylformamide (DMF) for $Co(NH_3)_5(DMF)^{3+}$ in water–DMF mixed-solvent media to explain the dependence of the first-order aquation rate constant on the mole fraction of DMF.

An alternative explanation for the observed results is that the acetonitrile complex is preferentially completely solvated by water in the water–acetonitrile solvent systems and by Me_2SO in the Me_2SO–acetonitrile solvent systems. In case this were true, the data yield no information on the possible rotation of $Co(NH_3)_5^{3+}$ or the lack of it. However, complete preferential solvation by one solvent seems less likely than partial preferential solvation.

The $\Delta H^{\ddagger}$ values for both k_W and k_A in Table III do not show any significant trend with X_A; the values for $X_A = 0.1$ are equal to those for $X_A = 0.9$ within the experimental error. The values of $\Delta S_A^{\ddagger}$ for k_A are also constant over the same solvent range. The $\Delta S_W^{\ddagger}$ values for k_W may show a slight trend from small positive to small negative values with increasing X_A, but the trend is too small to have much significance. However, $\Delta S_A^{\ddagger}$ is positive relative to $\Delta S_W^{\ddagger}$ so that moving a water molecule from the first to the second coordination sphere in the reaction with acetonitrile seems to create more disorder than moving an acetonitrile molecule from first- to second-coordination-shell sites in the reaction with water. The $\Delta H_A^{\ddagger}$ values for acetonitrile replacing water are somewhat larger than the value (26.6 kcal mol^{-1})[22] for water replacing water and also somewhat larger than the value (25.4 ± 1.3 kcal mol^{-1})[13] for Me_2SO replacing water. In mixed water–DMF media the $\Delta H^{\ddagger}$ value[21] for DMF replacing water decreased slightly with increasing X_{DMF}, but at 0.1 mole fraction of DMF it was 29.4 ± kcal mol^{-1} in good agreement with the present values of $\Delta H_A^{\ddagger}$. The small differences in $\Delta H_A^{\ddagger}$ for water replacement could reflect differences in solvation energy changes in the different solvents when the leaving water molecule moves from a first- to a second-coordination-sphere site and when the entering solvent molecule (water, Me_2SO, DMF, or acetonitrile) is correctly positioned for entry to the vacated first-coordination-sphere site.

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Registry No. $Co(NH_3)_5(NCCH_3)^{3+}$, 44819-13-8; $Co(NH_3)_5(OH_2)^{3+}$, 14403-82-8; $Co(NH_3)_5(OSMe_2)^{3+}$, 44915-85-7; $NCCH_3$, 75-05-8; $OSMe_2$, 67-68-5.

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Contribution from the Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Victoria, Australia, and the Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds 3217, Victoria, Australia

Oxidation of Substituted Iron Carbonyl Complexes in Acetonitrile, Acetone, and Dichloromethane at Mercury and Platinum Electrodes

S. W. BLANCH,[1] A. M. BOND,*[2] and R. COLTON[1]

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The oxidative electrochemistry of the substituted iron carbonyl complexes $Fe(CO)_4L$ and $Fe(CO)_3L_2$, where L is a monodentate tertiary phosphine, arsine, or stibine ligand, has been studied in acetone, dichloromethane, and acetonitrile at both Hg and Pt electrodes. At platinum electrodes, for L = $AsPh_3$ or $SbPh_3$ the initially generated 17-electron cations $[Fe(CO)_4L]^+$ and $[Fe(CO)_3L_2]^+$ are unstable in all solvents while with phosphorus ligands the species $[Fe(CO)_3(PPh_3)_2]^+$ has some stability in dichloromethane. Reactions leading to decomposition are considered. In marked contrast, at mercury electrodes, the cations appear to be substantially more stable than at platinum, and chemically reversible behavior can be observed where the response is completely irreversible at platinum. The data are explained in terms of a chemically modified pathway at mercury electrodes giving rise to "mercury stabilized" cations.

Redox processes are often studied at mercury electrodes. However, organometallic carbonyl complexes are commonly involved in formation of mercury complexes[3] and therefore the possibility of observing an interaction between mercury and the complex at the electrode surface is likely.[4,5] In work from these laboratories concerning organometallic electrode processes, the apparently faster rate of electron transfer (heterogeneous charge transfer) at mercury electrodes than at platinum or carbon electrodes has been noted.[6,7] Furthermore, the occurrence of chemically modified behavior (homogeneous kinetics) at mercury electrodes for oxidation of molybdenum and tungsten complexes[8,9] as well as for other systems[7] has also been observed. The possibility that the above

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