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Anation of (Dimethyl sulfoxide)pentaamminecobalt(III) in Dimethyl Sulfoxide Solutions by N_3^-, Cl^-, and NCS^-

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The rates of anation of (dimethyl sulfoxide)pentaamminecobalt(III) in dimethyl sulfoxide (Me_2SO) solvent by N_3^-, Cl^-, and NCS^- have been determined at 45.2 ± 0.1 °C. The value of k_i, the first-order rate constant for interchange of leaving Me_2SO and entering anion within the ion pair, was found to be essentially independent of ionic strength (μ) and was approximately 15×10^{-5} s^{-1} for N_3^- at $\mu = 0.25$ M, 28×10^{-5} s^{-1} for Cl^- at $\mu = 0.10$ M, and 3.0×10^{-5} s^{-1} for NCS^- at $\mu = 0.10$ M. The ion-pair formation constants, K_0, determined kinetically in these three media were 5.8 ± 1.1, 21.6 ± 2.4, and 7.2 ± 1.7 M^{-1}, respectively. These values tended to decrease somewhat with increasing concentration of *p*-toluenesulfonic acid (PTSA) or with increasing ionic strength. Values of K_0 for N_3^- determined by an independent spectrophotometric method were in good agreement with the kinetic values. Solvent-exchange studies showed that the loss of coordinated Me_2SO-h_6 from the first coordination shell of $Co(NH_3)_5(Me_2SO\text{-}h_6)^{3+}$ in Me_2SO-d_6 media resulted from solvent exchange by the free cation, from anation by N_3^- within the ion pair, and from some solvent exchange within the ion pair. The rate constant k_i for N_3^- was markedly larger than k_{ex}', the rate constant for solvent exchange within the ion pair, so that most ion pairs yield $Co(NH_3)_5N_3^{2+}$ rather than $Co(NH_3)_5(Me_2SO\text{-}d_6)^{3+}$. The values of k_i and k_{ex}' showed that cobalt(III)–Me_2SO bond fission occurred somewhat faster in the ion pairs than it did in the free cation $Co(NH_3)_5(Me_2SO\text{-}h_6)^{3+}$. Also the value of k_i for Cl^- showed that cobalt(III)–Me_2SO bond fission was faster in the ion pairs than it was in the free cation. However, the small value of k_i for NCS^- did not require faster bond fission in $Co(NH_3)_5(Me_2SO)^{3+},NCS^-$ ion pair than in the free cation. Unfortunately, experimental difficulties prevented meaningful solvent-exchange studies being made for the Cl^- and NCS^- ion pairs.

Introduction

The observed pseudo-first-order rate constant for anation of a cationic metal complex ion via an I_d[2] ion-pair mechanism is given by

$$k_{an} = k_iK_0[Y^{n-}]/(1 + K_0[Y^{n-}]) \qquad (1)$$

where K_0 is the conditional formation constant of the precursor complex (ion pair in this case), Y^{n-} is the anion involved in the substitution reaction of the complex ion, and k_i is the rate constant for interchange of Y^{n-} and the departing ligand (solvent, S, in the case of $Co(NH_3)_5S^{3+}$ substitutions) within the ion pair. It has been assumed that k_i values could not exceed the value of the solvent-exchange rate constant, k_{ex}. However, it has recently been pointed out[3] that it is possible for k_i to be greater than k_{ex} if a relatively small Y^{n-} can prevent some, or all, of the internal return taking place with a relatively large S molecule. It has been rather convincingly demonstrated that in an I_d reaction the leaving solvent molecule is displaced to the solvation shell of the reactant complex and that there is, for practical purposes, zero bond formation between Co(III) and the departing S molecule and between Co(III) and the entering Y^{n-}. Thus Tong, Krouse, and Swaddle[4] have found that the volume of activation, $\Delta V^{\ddagger}$, for aquo exchange in *trans*-$Co(en)_2(OH_2)_2^{3+}$ indicates transfer of the water ligand to the solvation shell with no signficant change in solvation. Similar results have been obtained from $\Delta V^{\ddagger}$ measurements by Stranks and Vanderhoeck[5] for anation of *cis*-$Co(en)_2(OH_2)^{3+}$ by $H_2C_2O_4$ and $HC_2O_4^-$. And it is well-known that anation rate constants of $Co(NH_3)_5OH_2^{3+}$ are essentially independent of the nature of the incoming Y^{n-} so that a plot of log k_{aq} against –log K_f, where K_f is the formation constant of $Co(NH_3)_5Y^{2+}$, is linear with a slope of unity. Furthermore, competition product ratios $[Co(NH_3)_5N_3^{2+}]/[Co(NH_3)_5OH_2^{3+}]$ formed in base hydrolyses of $Co(NH_3)_5X^{(3-n)+}$ ($X^{n-} = Cl^-$, Br^-, NO_3^-, dimethyl sulfoxide (Me_2SO)), which proceed wholly, or in part, by I_d substitution reactions of the conjugate base,[6] are independent of temperature, indicating strongly that no significant bond formation occurs between the Co(III) center and any of the leaving or entering ligands.

The specific rate of Co^{III}–*S (*S = labeled solvent molecule) bond breaking in forming nuclear configurations within the activated-complex region of the reaction coordinate is greater than the specific rate of solvent exchange. If the $Co(NH_3)_5^{3+}$ moiety formed by the breaking of the Co^{III}–*S bond is sufficiently long-lived to allow it to rotate within its solvation shell so that *S becomes equivalent to the rest of the S molecules in the solvation shell, then the probability of internal return would be $1/n$ where n is the number of equivalent solvent molecules in the first solvation shell of the five-coordinate $Co(NH_3)_5^{3+}$ moiety. In this case the specific rate of bond breaking would be equal to $(n/(n-1))k_{ex}$, only slightly larger than k_{ex}. On the other hand, if $Co(NH_3)_5^{3+}$ is too unstable to make a rotation equalizing solvent molecules in its solvation shell, the maximum value expected for the specific rate of bond breaking would be $2k_{ex}$ for two equivalent solvent molecules in the activated complex. In solvent exchange there is no overall reaction so the principle of microscopic reversibility requires that the energy barrier be symmetric with respect to its midpoint and that leaving and entering S molecules be equivalent in the activated complex. Hence, the probabilities of internal return and solvent exchange are each equal to one-half. If the specific rate of bond breaking in the I_d mechanism is not affected by ion-pair formation, then k_i for S–Y^{n-} interchange should not exceed $2k_{ex}$. If k_i for a specific ligand does exceed $2k_{ex}$, then that ligand is increasing the specific rate of Co^{III}–S bond breaking by its presence. Here we report on the measurement of k_i values for Cl^-, N_3^-, and NCS^- anation of $Co(NH_3)_5(Me_2SO)^{3+}$ in Me_2SO solutions.

Experimental Section

Materials. The compounds $[Co(NH_3)_5(Me_2SO)](ClO_4)_3\cdot 2H_2O$,[7] $[Co(NH_3)_5Cl](ClO_4)_2$,[8] and $[Co(NH_3)_5N_3](ClO_4)_2$[9] were prepared by literature methods. The tetraethylammonium chloride and perchlorate salts and *p*-toluenesulfonic acid (PTSA) were obtained from Eastman Kodak Co. and were purified by recrystallization from ethanol. Dimethyl sulfoxide (Me_2SO) from Aldrich Chemical Co., Inc., was distilled under reduced pressure and the middle two-thirds fraction collected. Me_2SO-d_6 (99.5 atom %) from Stohler Isotope Chemicals was used without further purification. Other chemicals were reagent grade and were also used without further purification.

Kinetic Measurements. The ion-pair formation constant, K_0, of $Co(NH_3)_5(Me_2SO)^{3+},N_3^-$ was determined spectrophotometrically in Me_2SO solvent at 315 nm. The analogous Cl^- and NCS^- ion pairs did not sufficiently enhance the UV absorption to give reliable differences, $\bar{\epsilon} - \epsilon_0$, between the observed molar extinction coefficients in the presence and absence of anion and thus reliable K_0 values.

Table I. Anation of $[Co(NH_3)_5(Me_2SO)](ClO_4)_3$ in Me_2SO Solutions by $X^- = N_3^-$, Cl^-, and NCS^- (45.2 ± 0.1 °C)

$10^3[Co(III)]^a$/M	$[X^-]$/M	$10^3[PTSA]$/M	μ^b/M	$10^5 k_{an}{}^c$/s^{-1}
		NaN_3		
3.00	0.200	3.00	0.25	7.56
	0.150	3.00	0.25	6.73
	0.100	3.00	0.25	4.80
	0.070	3.00	0.25	4.46
	0.050	3.00	0.25	3.29
	0.040	3.00	0.25	2.70
	0.030	3.00	0.25	1.93
	0.200	30.0	0.25	6.39
	0.150	30.0	0.25	5.32
	0.120	30.0	0.25	4.30
	0.100	30.0	0.25	3.58
	0.090	30.0	0.25	3.23
	0.080	30.0	0.25	2.82
	0.070	30.0	0.25	2.47
	0.040	30.0	0.25	1.67
	0.602	3.00	1.00	8.78
	0.495	3.00	1.00	7.03
	0.390	3.00	1.00	5.42
	0.250	3.00	1.00	4.77
	0.185	3.00	1.00	3.40
	0.102	3.00	1.00	2.38
		$(C_2H_5)_4NCl$		
2.00	0.070	2.00	0.10	17.9
	0.050	2.00	0.10	15.3
	0.040	2.00	0.10	12.4
	0.025	2.00	0.10	10.3
	0.020	2.00	0.10	9.09
	0.012	2.00	0.10	5.39
	0.010	2.00	0.10	4.38
	0.006	2.00	0.10	2.30
	0.060	20.0	0.10	12.5
	0.050	20.0	0.10	10.9
	0.040	20.0	0.10	9.90
	0.030	20.0	0.10	7.33
	0.020	20.0	0.10	4.90
	0.012	20.0	0.10	3.45
	0.010	20.0	0.10	2.01
		NaNCS		
0.600	0.096	0.600	0.10	12.1
	0.080	0.600	0.10	10.9
	0.060	0.600	0.10	7.63
	0.045	0.600	0.10	6.04
	0.030	0.600	0.10	4.14
	0.018	0.600	0.10	3.00
	0.012	0.600	0.10	2.00
	0.090	6.00	0.10	10.5
	0.060	6.00	0.10	7.30
	0.030	6.00	0.10	3.85
	0.015	6.00	0.10	2.10
	0.010	6.00	0.10	1.37
	0.006	6.00	0.10	0.81

[a] Total cobalt(III) concentration. [b] Ionic strength maintained with $NaClO_4$ for N_3^- and NCS^- media and with $(C_2H_5)_4NClO_4$ for Cl^- media. [c] Averages of two or three separate rate experiments. Errors are about 4%.

However, K_0 values for all three anions were obtained from kinetic measurements because at least partial saturation with respect to ion-pair formation was observed in the dependence of the anation rate constants, k_{an}, on anion concentration.

The anation rates for Cl^-, N_3^-, and NCS^- were determined spectrophotometrically at 340, 515, and 318 nm, respectively, in a Beckman DU with thermostated cell compartment; all anations went to completion for practical purposes. All anations obeyed the integrated first-order rate law given in the equation

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

where the A's are the indicated absorbances. The A_∞ values were read after 10 half-lives and again 24 h later to determine whether further reaction(s) was (were) occurring. Within this time span the appearance of cobalt(II) was not detected in the presence of PTSA although it was in the absence of PTSA.[3]

Table II. Summary of Data from Plots of $1/k_{an}$ against $1/[X^-]$ for $X^- = N_3^-$, Cl^-, and NCS^- and from Spectrophotometric Determination of K_0 (45.2 ± 0.1 °C)

X^-	[PTSA]/[Co(III)]	$10^5 k_i{}^a$/s^{-1}	$(I/S)^b$/M	K_0/M	μ^c/M
N_3^-	1	14.7 ± 3.2	5.8 ± 1.1	5.9 ± 1.4	0.25
N_3^-	10	15.1 ± 4.8	3.2 ± 0.8	3.9 ± 1.2	0.25
N_3^-	1	13.4 ± 3.2	2.1 ± 0.4	2.6 ± 0.4	1.00
Cl^-	1	30.2 ± 3.5	21.6 ± 2.4		0.10
Cl^-	10	24.9 ± 7.0	15.5 ± 3.5		0.10
NCS^-	1	2.6 ± 0.8	7.2 ± 1.7		0.10
NCS^-	10	3.5 ± 0.7	4.3 ± 0.7		0.10

[a] Error from errors in the intercept, I, of the least-squares plot. [b] Error from errors in the intercept and slope using the law of propagation of error. [c] $NaClO_4$ used.

Solvent-exchange rates were determined by using previously described techniques.[10]

Results and Discussion

Anation Reactions. The observed first-order rate constants for anation of the Me_2SO complex by N_3^-, Cl^-, and NCS^- are given in Table I. For the I_d ion-pair mechanism the pseudo-first-order anation rate constant is given by eq 1, and a plot of $k_{an}{}^{-1}$ against $[Y^{n-}]^{-1}$ should be linear if the data are consistent with the mechanism. Each of the three anions N_3^-, Cl^-, and NCS^- gave linear least-squares plots. The intercepts of these plots gave k_i values and their standard deviations as listed in Table II; the ratios of intercept to slope (I/S) gave values for ion-pair formation constants and their standard deviations as also listed in Table II.

From Table II it is seen that there may be a tendency for the kinetically determined ion-pair formation constant $(=I/S)$ to decrease as the PTSA concentration is increased, possibly as a result of displacement of X^- by the PTSA anion. Since the absorbance of $Co(NH_3)_5(Me_2SO)^{3+}$ in the absence of X^- was not affected by addition of either PTSA or ClO_4^- at the wavelength used, ion-pair formation with the latter two anions could not be detected. However, the changes in (I/S) were less than three standard deviations and may not be significant. The same small trend was noted for the spectrophotometrically determined values, K_0, for N_3^-.

Spectrophotometric Determination of K_0. Plots of $(\bar{\epsilon} - \epsilon_0)/[N_3^-]$ against $\bar{\epsilon}$, where ϵ_0 is the molar extinction coefficient of the free Me_2SO complex and $\bar{\epsilon}$ is the measured corrected absorbance divided by the total cobalt(III) concentration in the presence of N_3^-, were linear. Ion-pair formation constants K_0 were obtained from the slopes of these plots at PTSA concentrations equal to 1 and to 10 times the cobalt(III) concentration. The K_0 values for N_3^- are in very good agreement with the kinetic values $(=I/S)$ and give one confidence in the correct assignment of mechanism. Reliable K_0 values for Cl^- and NCS^- could not be obtained spectrophotometrically for the reasons given in the Experimental Section.

The molar extinction coefficient of the ion pair at 315 nm was 2.0×10^3 M^{-1} cm^{-1} at both PTSA concentrations at μ = 0.25 M and 1.8×10^3 M^{-1} cm^{-1} at μ = 1.00 M at 25 °C.

Solvent Exchange. Solvent-exchange rate measurements for the Me_2SO complex could not be made for Cl^- and NCS^-. In the case of Cl^- the insolubility of the chloride salt of the complex prevented sufficient intensity in the ^1H NMR spectrum of the complex. In the case of NCS^- the reaction mixtures quickly yellowed and then formed copious quantities of a yellow precipitate at the high NCS^- concentrations needed to maintain a constant NCS^- concentration over the lifetime of the anation and solvent-exchange processes.

For N_3^- it was found that Me_2SO-h_6 was lost from the Me_2SO-complex by solvent exchange in the free cation, by

Table III. Solvent-Exchange Studies for $Co(NH_3)_5(Me_2SO)^{3+}$ in the Presence of N_3^- (0.050 M Cobalt(III), 0.050 M PTSA, $\mu = 1.00$ M ($NaClO_4$); 45.2 °C)

$[N_3^-]_0$/M	$[N_3^-]_f$/M	$10^5 k_{loss}$/s^{-1}	$10^5 k_{ex}'$/s^{-1}
0.000	0.000	6.33 ± 0.39	
0.490	0.452	12.0 ± 0.7	3.4
0.515	0.476	12.2 ± 0.2	3.6
0.631	0.591	12.3 ± 0.9	2.8
0.656	0.619	13.4 ± 0.3	4.5

anation within the ion pair, and by solvent exchange within the ion pair, according to reactions 2–5. In these reactions

$$Mh_6^{3+} + d_6 \xrightarrow{k_{ex}} Md_6^{3+} + h_6 \quad (2)$$

$$Mh_6^{3+} + N_3^- \overset{K_0}{\rightleftharpoons} Mh_6^{3+},N_3^- \quad (3)$$

$$Mh_6^{3+},N_3^- + d_6 \xrightarrow{k_{ex}'} Md_6^{3+},N_3^- + h_6 \quad (4)$$

$$Mh_6^{3+},N_3^- \xrightarrow{k_i} MN_3^{2+} + h_6 \quad (5)$$

M^{3+}, h_6, and d_6 are abbreviations for $Co(NH_3)_5^{3+}$, Me_2SO-h_6, and Me_2SO-d_6, respectively. The expression for the observed rate constant for h_6 loss from the first-coordination-shell site is given by eq 6 where k_{ex} is the pseudo-first-order solvent-

$$k_{loss} = \frac{k_{ex} + (k_{ex}' + k_i)K_0[N_3^-]}{1 + K_0[N_3^-]} \quad (6)$$

exchange rate constant for the free cation, k_{ex}' is the pseudo-first-order rate constant for solvent exchange within the ion pair, and k_i is as defined for eq 1. The values of k_{loss} and of the total N_3^- ion concentrations are listed in columns 3 and 1, respectively, of Table III. When each N_3^- ion concentration was corrected for ion-pair formation and for loss through anation and an average taken for each experiment, the values listed for $[N_3^-]_f$, the free N_3^- ion concentration, in column 2 of Table III, were found.

If one uses the values $k_i = 13.4 \times 10^{-5}$ s^{-1} and $K_0 = 2.6$ M^{-1} for N_3^- at $\mu = 1.00$ M in Table II along with the value of $k_{ex} = 6.3 \times 10^{-5}$ s^{-1} determined previously,[3,10] then one may calculate the values of k_{ex}' listed in column 4, Table III, from

$$k_{ex}' = \frac{k_{loss}(1 + K_0[N_3^-]) - (k_i K_0[N_3^-] + k_{ex})}{K_0[N_3^-]}$$

The values of k_{ex}' are not very precise because the numerator of this expression involves a difference between comparable terms. However, some solvent exchange did occur within the ion pair (average value of $k_{ex}' = 3.6 \times 10^{-5}$ s^{-1}). The value of k_i (13.4×10^{-5} s^{-1}) is much larger, and solvent exchange occurs only one-third to one-fourth as often as anation.

If there are just two equivalent Me_2SO molecules (Me_2SO-h_6 and Me_2SO-d_6) in the activated complex formed from an ion pair so that there is either internal return of Me_2SO-h_6, solvent exchange with Me_2SO-d_6, or anation by N_3^-, then the specific rate of Co(III)–Me_2SO bond fission in forming this activated complex is equal to $(2k_{ex}' + k_i) = 21 \times 10^{-5}$ s^{-1}, a little larger than the maximum value of 13×10^{-5} s^{-1} ($=2k_{ex}$) for the free ion $M(Me_2SO)^{3+}$. The value of 21×10^{-5} s^{-1} is a maximum specific rate; it would be smaller if there were a greater number of equivalent Me_2SO molecules in the activated complexes, thus reducing the frequency of internal return for Me_2SO-h_6.

The fact that k_i is much less than $2k_{ex}$ for NCS^- indicates that NCS^- does not compete well with Me_2SO for the vacated inner-sphere site. There should be much internal return and solvent exchange in the $M(Me_2SO)^{3+},NCS^-$ ion pair.

The fact that k_i for Cl^- is greater than the maximum value for the specific rate of bond fission in the $M(Me_2SO)^{3+},N_3^-$ ion pair indicates that the specific rate of bond fission in $M(Me_2SO)^{3+},Cl^-$ is at least somewhat greater than in the N_3^- ion pair.

In the case of Br^-[10] $k_i = 7 \times 10^{-5}$ s^{-1} and $k_{ex}' \simeq 2.5 \times 10^{-5}$ s^{-1}. The maximum specific rate of bond fission would be $\sim 12 \times 10^{-5}$ s^{-1}, in very good agreement with the value of $2k_{ex}$ for the free cation $M(Me_2SO)^{3+}$.

We can tentatively conclude that, in the ion pairs, Br^- has little, if any, effect on the specific rate of Co(III)–Me_2SO bond fission, N_3^- has some accelerating effect, and Cl^- has more.

We also conclude that values of k_i can exceed k_{ex} in I_d reactions as predicted by Swaddle and co-workers.[3]

Registry No. $Co(NH_3)_5(Me_2SO)^{3+}$, 44915-85-7; N_3^-, 14343-69-2; Cl^-, 16887-00-6; NCS^-, 302-04-5.

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