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# Solvent Exchange and Anation of (Dimethyl sulfoxide)pentaamminecobalt(III) Perchlorate in Dimethyl Sulfoxide

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The limiting rate constant for Br⁻ anation of $Co(NH_3)_5(Me_2SO)^{3+}$ in dimethyl sulfoxide solutions by an I_d ion-pair mechanism at 45.3 °C was found to be $(6.7 \pm 0.4) \times 10^{-5}$ s⁻¹ and $(8.1 \pm 0.7) \times 10^{-5}$ s⁻¹ for two different *p*-toluenesulfonic acid (PTSA) concentrations and 0.4 M ionic strength and $(7.0 \pm 0.6) \times 10^{-5}$ s⁻¹ for 1.0 M ionic strength. The solvent-exchange rate constant between $Co(NH_3)_5(Me_2SO)^{3+}$ and Me_2SO solvent in the presence of PTSA and absence of Br⁻ at 45.3 °C and 1.0 M ionic strength was found to be $(6.33 \pm 0.39) \times 10^{-5}$ s⁻¹, in excellent agreement with a previously reported value. In the presence of Br⁻ solvent displacement from $Co(NH_3)_5(Me_2SO\text{-}h_6)^{3+}$ also occurred within the ion pairs $Co(NH_3)_5\text{-}(Me_2SO\text{-}h_6)^{3+},Br^-$ by both solvent exchange and anation reactions with the latter reaction predominating. Most ion pairs lost coordinated $Me_2SO\text{-}h_6$ by interchange with the Br⁻ ion rather than by solvent interchange.

Introduction

Unassisted anation reactions of $Co(NH_3)_5S^{3+}$ complexes, where S is a solvent molecule, as in reaction 1 are generally

$$Co(NH_3)_5S^{3+} + Y^- \underset{k_s}{\overset{k_{an}}{\rightleftharpoons}} Co(NH_3)_5Y^{2+} + S \qquad (1)$$
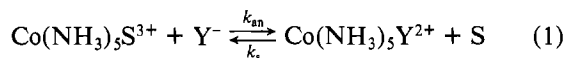
believed to occur via dissociative interchange, I_d, processes involving ion-pair formation in aqueous[2–5] and nonaqueous[6] media. In one study Reynolds and Barber[7] quantitatively disproved the existence of a D (dissociation) mechanism in ion-pairing media, provided the rate of breaking of the cobalt(III)–solvent bond during the formation of activated complexes was essentially the same for activated complexes leading to solvent–anion interchange within the ion pair as for activated complexes leading to solvent exchange in the absence of anions. This provision is a very important one and its validity is far from being settled at the present time. In one experiment[8] the rate of water exchange between bulk water and $Co(NH_3)_5OH_2^{3+}$ sites was determined in the presence of HSO_4^- and SO_4^{2-} ions and compared with the rate in the absence of the sulfate ions; the half-time for exchange was somewhat increased at 27 °C from 24.4 h in the absence of sulfate ions to 27.8 h in the presence of the ions. The effect of the presence of anions on the solvent-exchange rates of $Rh(NH_3)_5OH_2^{3+}$,[9] of $Ir(NH_3)_5OH_2^{3+}$,[10] and of $Cr(DMF)_6^{3+}$,[11] where DMF = *N,N*-dimethylformamide, is not large, although significant, as might be expected for reactions proceeding by I_a mechanisms[4,11] and having partial bonds between the central metal and leaving and entering ligands. For these latter complexes rate constants k_i for interchange of leaving solvent and entering anion within the ion pair may markedly exceed rate constants k_{ex} for solvent exchange in the absence of ion pairs. It has been pointed out[6] that the rate of cobalt(III)–solvent bond breaking in $Co(NH_3)_5S^{3+}$ complexes is probably greater than the rate of solvent exchange because of internal return of the solvent molecule to its original coordination site

with attendant failure to consummate solvent exchange. It was likewise pointed out[6] that k_i values could therefore become somewhat larger than k_{ex} values in an I_d process if the entering anion effectively prevented internal return. To this it may be added that finding a common k_i/k_{ex} ratio slightly greater than unity for a number of different ligands can be taken as good evidence that internal return has been prevented and that the rate of cobalt(III)–solvent bond breaking is unaffected by formation of an ion pair. Here we report on solvent exchange and anation rates in the $Co(NH_3)_5(Me_2SO)^{3+}$–Br⁻ system in Me_2SO solvent.

Experimental Section

Materials. The compounds $[Co(NH_3)_5(Me_2SO)](ClO_4)_3 \cdot 2H_2O$[12] and $[Co(NH_3)_5Br]Br_2$[13] were prepared by literature methods. The bromide salt was converted to the perchlorate salt by dissolving in warm water, adding $HClO_4$, and cooling until a purification cycle produced a product free of uncoordinated bromide ion. Dimethyl sulfoxide from Aldrich Chemical Co. Inc. was distilled under reduced pressure and the middle two-thirds fraction collected. Dimethyl-d_6 sulfoxide, 99.5 atom %, from Stohler Isotope Chemicals was used without further purification. *p*-Toluenesulfonic acid (PTSA) was obtained from Eastman Kodak Co. and recrystallized from ethanol. Tetraethylammonium bromide and perchlorate were obtained from Fisher Scientific Co. and recrystallized from ethanol and dried in a vacuum oven.

Rate Measurements. Ion-pair formation constants K_0 for $Co(NH_3)_5(Me_2SO)^{3+},Br^-$ were determined in Me_2SO spectrophotometrically at 301 nm. The absorbance of each freshly prepared solution in a series of solutions containing 5.00×10^{-4} M Me_2SO complex, variable Et_4NBr and Et_4NClO_4 concentrations, and constant PTSA concentration at constant ionic strength μ was measured against a blank containing the same concentrations of all reagents with the omission of the complex. The wavelength setting of the spectrophotometer was not changed throughout the series. The weights of the $[Co(NH_3)_5(Me_2SO)](ClO_4)_3$ stock solution and of the total mixture used were recorded for each solution in the series so that the complex content of each solution containing Br⁻ could be carefully corrected to the complex content of the first solution in the series which contained no Br⁻. These precautions were necessary because at 301 nm the absorbance coefficients are large and changing rapidly with wavelength.

The bromide anation of the Me_2SO complex in Me_2SO solvent at a given temperature was followed spectrophotometrically at 580 nm in a thermostated cell compartment for a series of solutions containing variable Et_4NBr and Et_4NClO_4, but fixed PTSA, concentrations at constant μ. A surplus of reaction mixture was suspended in a sealed flask in a water bath at the same temperature with exclusion of light. After 10 half-lives the infinite-time absorbance, A_∞, was read, and then after 24 h it was read again to ensure that the reading had not

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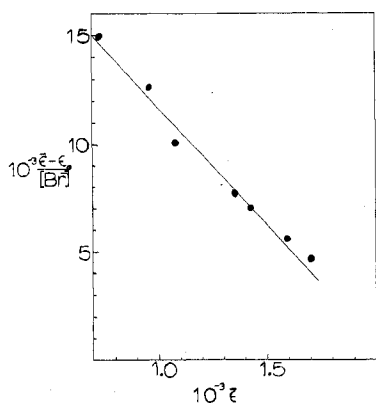
Figure 1. Plot of $10^{-3}(\bar{\epsilon} - \epsilon_0)/[Br^-]$ vs. $10^{-3}\bar{\epsilon}$ for determination of the $Co(NH_3)_5(Me_2SO)^{3+},Br^-$ ion-pair formation constant at 301 nm and 25 °C.

changed.[14] An aliquot of infinite-time reaction mixture was diluted with cold water and passed through ion-exchange resin, AG 50W-X4, 200–400 mesh, maintained at approximately 7 °C to minimize any further substitution reactions. The bromo complex was eluted with 2 M HClO₄ and determined spectrophotometrically at 550 nm by using $\epsilon = 57.7$ M^{-1} cm^{-1}; the Me₂SO complex was eluted with 4 M HCl and determined at 516 nm by using $\epsilon = 61.6$ M^{-1} cm^{-1}. The quotients $[Co(NH_3)_5Br^{2+}]/[Co(NH_3)_5(Me_2SO)^{3+}]$ thus determined for solutions at equilibrium were used to obtain the individual first-order solvolysis and anation rate constants.

The rate of the Me₂SO-exchange reaction in the absence of Br⁻ was determined at 45.0 ± 0.1 °C by using $Co(NH_3)_5(Me_2SO-h_6)^{3+}$ initially dissolved in 99.5 atom % Me₂SO-d_6 solutions of known μ and PTSA content. Samples of reaction mixture were withdrawn at times t and immediately frozen in acetone–dry ice mixtures. After all samples were collected, they were thawed singly, the ¹H NMR spectrum was taken with an HFT-80 spectrometer, and the coordinated Me₂SO-h_6 and ammonia peak areas were integrated. When the Me₂SO-h_6 complex was converted to the bromo complex, the NH₃ peak split, but both peaks could be integrated without interference from other peaks to get the total ammonia proton area. The relative peak areas gave the relative amounts of coordinated Me₂SO-h_6 and ammonia at time t. Sometimes peak heights were measured as well; both methods gave essentially the same results. In the presence of Br⁻ the rate of loss of bound Me₂SO-h_6 was corrected for loss due to Br⁻ anation but otherwise the general procedure remained the same.

Results and Discussion

Determination of K_0. Formation constants K_0 of the ion pair $Co(NH_3)_5(Me_2SO)^{3+},Br^-$ in Me₂SO were determined at 0.4 and 1.0 M ionic strength from plots of $(\bar{\epsilon} - \epsilon_0)/[Br^-]$ against $\bar{\epsilon}$ such as shown in Figure 1; ϵ_0 is the molar extinction coefficient of the free complex cation and $\bar{\epsilon}$ is the measured, corrected absorbance divided by the total cobalt(III) concentration. The slope of a plot was equal to $-K_0$ and the ratio of intercept to |slope| was equal to ϵ_i, the molar extinction coefficient of the ion pair. A least-squares treatment of the data gave $K_0 = 10.7 \pm 0.6$ M^{-1} and $\epsilon_i = 2.1 \times 10^3$ M^{-1} cm^{-1} for [PTSA] = [Co(III)] and $K_0 = 11.4 \pm 1.3$ M^{-1} and $\epsilon_i = 2.0 \times 10^3$ M^{-1} cm^{-1} for [PTSA] = 10[Co(III)] at 0.4 M ionic strength (μ) and $K_0 = 5.5 \pm 0.2$ M^{-1} and $\epsilon_i = 2.3 \times 10^3$ M^{-1} cm^{-1} for [PTSA] = [Co(III)] at 1.0 M μ. There was no significant change in the results when a series of measurements was carried out at 45 °C and 0.4 M ionic strength; hence the enthalpy of formation of the ion pair was small.

Rate of Br⁻ Anation. The results for the Br⁻ anation rate measurements at $\mu = 0.4$ M are given in Table I for PTSA concentrations equal to the cobalt(III) concentration and to

Table I. Anation of $Co(NH_3)_5(Me_2SO)^{3+}$ by Br⁻ in Dimethyl Sulfoxide Solutions[a]

[Br⁻]/M	K_a/M^{-1}	$10^5 k_{app}$/s^{-1}	$10^5 k_{an}$[b]/ s^{-1}	$10^5 k_{sol}$[b]/ s^{-1}
		0.003 00 M PTSA		
0.0300	93.2	2.08	1.51	0.6
0.0500	68.5	2.82	2.15	0.7
0.0700	72.1	3.73	2.76	0.6
0.100	48.5	4.26	3.51	0.8
0.150	23.2	4.87	3.77	1.1
0.250	14.0	6.58	5.10	1.5
0.300	16.1	6.68	5.53	1.2
		0.0300 M PTSA		
0.0300	87.3	2.44	1.74	0.7
0.0400	75.6	3.23	2.38	0.9
0.0500	59.5	3.61	2.66	1.0
0.0700	48.5	4.21	3.22	1.0
0.100	41.9	5.26	4.22	1.0
0.150	21.6	6.73	5.12	1.5
0.250	13.8	8.29	6.41	1.9
0.300	15.6	6.63	5.20	1.4

[a] 3.00×10^{-3} M Co(III); 45.3 ± 0.1 °C; $\mu = 0.40$ M (Et₄NClO₄). [b] The standard deviation in k was approximately 10% and was calculated from the experimental standard deviations of k_{app} and K_a by using the equation for propagation of error.

Table II. Anation of $Co(NH_3)_5(Me_2SO)^{3+}$ by Br⁻ in Dimethyl Sulfoxide Solutions[a]

[Br⁻]/M	K_a/M^{-1}	$10^5 k_{app}$/s^{-1}	$10^5 k_{an}$[b]/ s^{-1}	$10^5 k_{sol}$/ s^{-1}
0.100	38.3	2.58	1.94	0.6
0.150	22.0	3.47	2.57	0.9
0.204	23.2	3.80	3.08	0.7
0.250	16.6	4.37	3.46	0.9
0.300	15.9	4.67	3.81	0.9
0.350	13.4	5.74	4.68	1.0
0.400	10.7	6.00	4.82	1.2

[a] [PTSA] = [Co(III)] = 0.0200 M; 45.3 ± 0.1 °C; $\mu = 1.0$ M (Et₄NClO₄). [b] See footnote b of Table I.

10 times the cobalt(III) concentration. The absorbance–time data obeyed the integrated rate law

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

where k_{app} is an apparent first-order rate constant given by eq 2a in terms of k_{sol}, the first-order rate constant for the

$$k_{app} = k_{sol} + k_{an} = k_{sol}(1 + K_a) \qquad (2a)$$

solvolysis of $Co(NH_3)_5Br^{2+}$, k_{an}, the pseudo-first-order rate constant for anation of $Co(NH_3)_5(Me_2SO)^{3+}$, and K_a, the conditional equilibrium constant given in eq 2b. With the

$$K_a = k_{an}/k_{app} =$$
$$[Co(NH_3)_5Br^{2+}]/\{[Co(NH_3)_5(Me_2SO)^{3+}] + [Co(NH_3)_5(Me_2SO)^{3+},Br^-]\}[Br^-] \quad (2b)$$

aid of eq 2a and 2b k_{app} was separated into k_{sol} and k_{an} values as listed in Table I. Triplicate rate experiments were carried out at each Br⁻ concentration; the accompanying error in k_{app} was approximately 3–4% and in K_a approximately 8%. From the known K_0 and K_a values the free Br⁻ concentration at the beginning and end of each anation experiment was calculated. Thus for 0.300 M total Br⁻, $[Br^-]_0 = 0.298$ M and $[Br^-]_\infty = 0.297$ M; for 0.0300 M total Br⁻, $[Br^-]_0 = 0.0293$ M and $[Br^-]_\infty = 0.0276$ M. The average values of 0.297_5 M and 0.0284_5 M were taken for the "constant" free Br⁻ concentration throughout the anation. Plots of eq 2 were linear to 3 half-lives. The results at $\mu = 1.0$ M are given in Table II.

If the anation proceeds by a dissociative interchange (I_d) within the ion pair, the first-order anation rate constants in

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(14) At the end of this time tests for the presence of cobalt(II) formed by reduction of the Me₂SO-Co^{III} complex were negative. Reference 6 reports the presence of small amounts of cobalt(II) too small to affect the rate of the anation reaction.

Tables I and II are given by eq 3 and plots of k_{an}^{-1} against

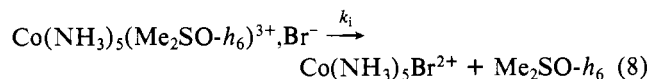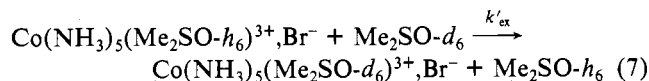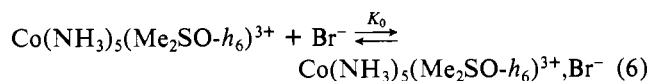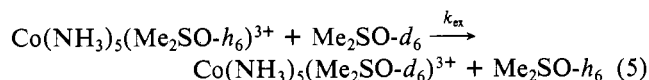$$k_{an} = \frac{k_i K_0 [\text{Br}^-]}{1 + K_0 [\text{Br}^-]} \tag{3}$$

$[\text{Br}^-]^{-1}$ are linear with intercept equal to k_i^{-1} and an intercept-to-slope ratio equal to K_0. Such plots yielded straight lines within the experimental error. At $\mu = 0.4$ M values of k_1 were $(6.7 \pm 0.4) \times 10^{-5}$ and $(8.1 \pm 0.7) \times 10^{-5}$ s^{-1} for PTSA concentration equal to and 10 times greater than the total cobalt(III) concentration, respectively, and the corresponding K_0 values were 10.4 ± 0.8 and 10.5 ± 1.1 M^{-1}, respectively. The values of k_i obtained in this way are not significantly different. At $\mu = 1.0$ M the k_i and K_0 values were $(7.0 \pm 0.6) \times 10^{-5}$ s^{-1} and 4.6 ± 0.5 M^{-1}, respectively. The values of K_0 are in excellent agreement with the values obtained independently by absorbance measurements at 301 nm.

In both of the reaction series listed in Table I k_{sol} shows a tendency to increase with increasing Br$^-$ concentration. This increase is apparently real and outside of experimental error. This can be seen as follows. The apparent first-order rate constant for approach to anation equilibrium, k_{app}, is related to k_{sol} and K_a by eq 2a. If k_{sol} should be constant throughout a series at, e.g., the average value of 0.9×10^{-5} s^{-1} for 0.003 M PTSA, then K_a for 0.0300 M Br$^-$ must be approximately 48 M^{-1} instead of 93 M^{-1} as observed. This value of 48 M^{-1} is far outside the experimental error in determining K_a by chromatographic separation of the 2+ and 3+ cations followed by spectrophotometric determination of the separate cations. The increase in k_{sol} possibly arises from an increased solvolysis rate in an ion pair such as Co(NH$_3$)$_5$Br^{2+},Br$^-$ as compared to Co(NH$_3$)$_5$Br^{2+}. Table II shows a lesser tendency for k_{sol} to increase at the higher ionic strength as might be expected for decreased ion-pair formation.

Rate of Solvent Exchange. In both the absence and presence of Br$^-$ the data for the loss of coordinated Me$_2$SO-h_6 obeyed the integrated rate law given in eq 4, where (A_D/A_{NH_3}) is the

$$\ln (A_D/A_{NH_3})_t = \ln (A_D/A_{NH_3})_0 - k_{loss}t \tag{4}$$

relative area of the coordinated Me$_2$SO-h_6 and ammonia peaks at the indicated time from an NMR spectrum. The k_{loss} values are given in Table III. In the absence of Br$^-$ the value was $(6.33 \pm 0.39) \times 10^{-5}$ s^{-1} at 45.0 °C, in excellent agreement with the previously reported[6] value of $6.3_5 \times 10^{-5}$ s^{-1} in the presence of PTSA. In the presence of Br$^-$ the loss of coordinated Me$_2$SO-h_6 occurs by the reactions shown in eq 5–8.

$$\text{Co(NH}_3)_5(\text{Me}_2\text{SO-}h_6)^{3+} + \text{Me}_2\text{SO-}d_6 \xrightarrow{k_{ex}}$$
$$\text{Co(NH}_3)_5(\text{Me}_2\text{SO-}d_6)^{3+} + \text{Me}_2\text{SO-}h_6 \quad (5)$$

$$\text{Co(NH}_3)_5(\text{Me}_2\text{SO-}h_6)^{3+} + \text{Br}^- \underset{}{\overset{K_0}{\rightleftharpoons}}$$
$$\text{Co(NH}_3)_5(\text{Me}_2\text{SO-}h_6)^{3+},\text{Br}^- \quad (6)$$

$$\text{Co(NH}_3)_5(\text{Me}_2\text{SO-}h_6)^{3+},\text{Br}^- + \text{Me}_2\text{SO-}d_6 \xrightarrow{k'_{ex}}$$
$$\text{Co(NH}_3)_5(\text{Me}_2\text{SO-}d_6)^{3+},\text{Br}^- + \text{Me}_2\text{SO-}h_6 \quad (7)$$

$$\text{Co(NH}_3)_5(\text{Me}_2\text{SO-}h_6)^{3+},\text{Br}^- \xrightarrow{k_i}$$
$$\text{Co(NH}_3)_5\text{Br}^{2+} + \text{Me}_2\text{SO-}h_6 \quad (8)$$

In this case the apparent pseudo-first-order rate constant for loss of coordinated Me$_2$SO-h_6 is given by eq 9, where $k_{ex} =$

$$k_{loss} = \frac{k_{ex} + (k'_{ex} + k_i)K_0[\text{Br}^-]}{1 + K_0[\text{Br}^-]} \tag{9}$$

$(6.33 \pm 0.39) \times 10^{-5}$ s^{-1}, $k_i = (7.0 \pm 0.6) \times 10^{-5}$ s^{-1}, and $K_0 = (5.5 \pm 0.2)$ M^{-1}. Values of k'_{ex}, listed in Table III, were calculated from eq 9, by using the values of the average free

Table III. Loss of Me$_2$SO-h_6 from Co(NH$_3$)$_5$(Me$_2$SO-h_6)$^{3+}$ in Me$_2$SO-d_6 in Absence and Presence of Et$_4$NBr[a]

[Br$^-$][b]/M	[Br$^-$][c]/M	$10^5 k_{loss}/\text{s}^{-1}$	$10^5 k'_{ex}/\text{s}^{-1}$
...	...	6.33 ± 0.39	...
0.200	0.136	7.23 ± 0.55	1.4
0.300	0.227	8.72 ± 0.96	3.6
0.402	0.362	8.12 ± 0.36	2.0
0.500	0.458	7.79 ± 0.67	1.3
0.647	0.604	9.72 ± 0.90	3.7

[a] 45.0 ± 0.1 °C; $\mu = 1.0$ M (Et$_4$NClO$_4$); [PTSA] = [Co(III)] = 0.0500 M. [b] Total Et$_4$NBr concentration. [c] Average free Br$^-$ concentration throughout the solvent-exchange process.

Br$^-$ concentration listed in column 2 of the table. The average free Br$^-$ concentration was calculated as explained in the section on the anation rate. The values of k'_{ex} cannot be determined with precision because they are obtained as a difference between two much larger, and comparable, numbers. However, it seems that some solvent exchange occurs within the ion pair although anation within the ion pair is much more important.

The data of Table III allow one to gain some insight into the details of solvent exchange and anation within the ion-pair Co(NH$_3$)$_5$(Me$_2$SO)$^{3+}$,Br$^-$. The 1,4,2 geometry is accepted for the transition state of the I_d solvent-exchange reaction in the absence of Br$^-$; five NH$_3$ ligands occupy the coordination sites on the $-z$, $\pm x$, and $\pm y$ axes whereas the two equivalent exchanging solvent molecules occupy sites above the xy plane and somewhat off the $+z$ axis of the complex. The two exchanging solvent molecules must be equivalent to satisfy the principle of microscopic reversibility. Thus, in the absence of Br$^-$ the rate constant for bond fission must be twice k_{ex} or 12.6×10^{-5} s^{-1} because each of the two solvent molecules has a 50% chance of occupying the vacant sixth coordination site and a 50% chance of being lost to the bulk solvent phase upon deactivation of the transition state. In the presence of Br$^-$ ion pairs are formed. When some of these become activated to form transition states, Br$^-$ ion will be present as well as solvent. Unless proven otherwise, it will be assumed that both solvent exchange and anation can occur in these transition states. We may enquire: Is the rate of Co(III)–Me$_2$SO bond fission in these transition states affected by the presence of Br$^-$? We may answer this question as follows. When the Co(III)–Me$_2$SO bond breaks, one of three events can occur: (1) The original Me$_2$SO molecule can return to the vacant coordination site (internal return). (2) A different Me$_2$SO molecule can proceed to occupy this site (solvent exchange). (3) The Br$^-$ ion can proceed to occupy the site (anation). When solvent exchange occurs, the two Me$_2$SO molecules must again occupy equivalent positions in the transition state because no overall chemical reaction occurs—only isotope redistribution. Consequently, the specific rate for Co(III)–Me$_2$SO bond fission is $(2k'_{ex} + k_i)$. If a median value of $k'_{ex} = 2 \times 10^{-5}$ s^{-1} from Table III is used and if an average value of $k_i = 7.0 \times 10^{-5}$ s^{-1} is used, the value of 11×10^{-5} s^{-1} is calculated for the specific rate of bond fission. The agreement with the specific rate of bond fission in the absence of Br$^-$ is good, and possibly fortuitously so. However, increasing the number of equivalent solvent molecules in the transition states formed from the free cation and from the ion pair decreases both specific rates of bond fission but does not bring them into serious disagreement. We conclude that, within our margin of experimental error, the rate of Co(III)–Me$_2$SO bond breaking is not affected by the presence of Br$^-$ in the ion pair.

Summary

We assume that the solvent-exchange and anation reactions of Co(NH$_3$)$_5$(Me$_2$SO)$^{3+}$ occur by the I_d mechanism. For this model we have measured the rate of solvent exchange within

the ion pair, obtained estimates of the rate of Co(III)–Me$_2$SO bond fission in the transition states formed from the free and from the ion-paired complex ion, concluded that the presence of Br$^-$ had only a small effect, at most, on the rate of bond fission, and observed that anation occurs more frequently than

solvent exchange as a result of this bond fission. Since the rate of solvent exchange is relatively small for the ion pair, so is the rate of internal return.

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 17. Carbon Dioxide Uptake by and Decarboxylation of the cis-Bis(ethylenediamine)rhodium(III) System in Aqueous Solution[1]

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In acidic solution cis-Rh(en)$_2$(CO$_3$)$^+$ slowly loses carbonate in accordance with the two-term rate law $k_{obsd} = k_0 + k_1[H^+]$, for which the rate parameters are as follows: $k_0 = 9.33 \times 10^{-6}$ s^{-1} at 25 °C, $\Delta H^{*}_0 = 22.8 \pm 1.5$ kcal mol^{-1}, $\Delta S^{*}_0 = -5 \pm 5$ cal deg^{-1} mol^{-1}; $k_1 = 1.00 \times 10^{-5}$ M^{-1} s^{-1} at 25 °C, $\Delta H^{*}_1 = 25.0 \pm 3.6$ kcal mol^{-1}, $\Delta S^{*}_1 = 2 \pm 11$ cal deg^{-1} mol^{-1}. The decarboxylation of the intermediate species cis-Rh(en)$_2$(CO$_3$H)(OH$_2$)$^{2+}$ could be independently studied: $k = 0.72 \pm 0.02$ s^{-1} at 25 °C, $\Delta H^{*} = 19.4 \pm 0.3$ kcal mol^{-1}, $\Delta S^{*} = 5.8 \pm 0.9$ cal deg^{-1} mol^{-1}. Carbon dioxide uptake by cis-Rh(en)$_2$(OH)(OH$_2$)$^{2+}$ yielded cis-Rh(en)$_2$(CO$_3$)(OH$_2$)$^+$ with $k = 69 \pm 18$ M^{-1} s^{-1} at 25 °C, $\Delta H^{*} = 15.9 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{*} = 3.9 \pm 1.6$ cal deg^{-1} mol^{-1}. At higher pH the corresponding dihydroxo complex gave exclusively cis-Rh(en)$_2$(CO$_3$)(OH), with the rate parameters $k = 215 \pm 29$ M^{-1} s^{-1} at 25 °C, $\Delta H^{*} = 14.6 \pm 0.2$ kcal mol^{-1}, and $\Delta S^{*} = 1.1 \pm 0.7$ cal deg^{-1} mol^{-1}. These results are compared with existing rate data on analogous cobalt(III) systems, with emphasis being placed on the relative metal–ligand bond strengths.

Introduction

The kinetics of carbon dioxide uptake and release by a wide variety of cobalt(III) complexes have been studied[4-6] in considerable detail, and the mechanism of reaction now seems to be well understood. All this kinetic evidence indicates that CO$_2$ can only add to a hydroxo ligand and, conversely, carbon–oxygen bond breaking takes place in the decarboxylation of the bicarbonato complex. Furthermore, a linear free energy relationship exists[6] between the rates of CO$_2$ uptake and the dissociation constants of the corresponding conjugate aquo acids, which establishes that the nucleophilicity of the hydroxide bound to the cobalt(III) center determines the rate of CO$_2$ uptake.

The rates of ring opening of the chelated carbonate ligand have also been thoroughly investigated[7-9] and shown to obey a two-term rate expression, $k_{obsd} = k_0 + k_1[H^+]$, where the latter term involves a rapid protonation preequilibrium followed by the rate-determining cleavage of the cobalt–oxygen bond to form a monodentate bicarbonato intermediate.[9]

Limited kinetic data are available for other transition-metal complexes, namely, for the (carbonato)pentaammine complexes of rhodium(III) and iridium(III)[10] and for the ring-closed species cis-(carbonato)bis(oxalato)chromate(III) ion.[11] Nevertheless, these results generally do comply with the accepted behavioral patterns of the cobalt(III) compounds.

We now report a complete kinetic study of the (carbonato)bis(ethylenediamine)rhodium(III) system. One reason for initiating this research was that the known strength of rhodium–oxygen bonds should allow us to observe the monodentate (carbonato)aquo complex as a relatively stable species because ring closure requires the breaking of the Rh–OH$_2$ bond and must therefore be an extremely slow process. Consequently, at high pH, the possibility arises that two CO$_2$ molecules may be independently taken up by the cis-Rh(en)$_2$(OH)$_2^+$ ion. In addition, in the absence of intense light,[12] no detectable isomerization of the cis isomer occurs, eliminating a complicating factor which prevails in the analogous cobalt(III) system.[13] Finally, it is of interest to see whether the increased strength of the metal–oxygen bond plays a role in determining the nucleophilicity of the hydroxo ligand, as was proposed for the Rh(NH$_3$)$_5$OH^{2+} complex.[10]

Experimental Section

Preparation of Compounds. cis-Dichlorobis(ethylenediamine)rhodium(III) perchlorate was prepared by the method of Johnson and Basolo[14] for the corresponding nitrate salt. Using excess base during the refluxing period and reducing the final volume of solution to 25% of its original volume resulted in yields of 30% or more of the cis isomer. It should be noted that it is essential that the solution be maintained at its boiling point during the addition of the aliquots of NaOH

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