Anation of Penta-ammineaquocobalt(III) by Bromide Ion in Aqueous Media

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The aquation rate constant of the ion $[Co(NH_3)_5Br]^{2+}$ is $(3{\cdot}9 \pm 0{\cdot}08) \times 10^{-6}$ s^{-1} at 25·0 °C, 1·00M ionic strength, and 0·0100M-$HClO_4$. The anation rate constant for the same conditions is $(1{\cdot}32 \pm 0{\cdot}06) \times 10^{-6}$ l mol^{-1} s^{-1} over the range $0{\cdot}1000\text{M} \leqslant [Br^-] \leqslant 0{\cdot}750\text{M}$ and shows no saturation effect with increasing bromide-ion concentration. The mechanistic implication of this result is discussed. By independent measurements the concentration quotient for formation of the inner-sphere bromo-complex has been found to be $0{\cdot}283 \pm 0{\cdot}030$ l mol^{-1} for the same conditions. Attempts to determine ion-pairing constants of Br^- with $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(NH_3)_5Br]^{2+}$ failed.

THE competition ratio R_x defined by Haim and Taube is given by equation (1),[1] where rate and equilibrium

$$R_x = \frac{[Co(NH_3)_5X^{2+}]}{[Co(NH_3)_5H_2O^{3+}][X^-]} = \frac{k_x + k_x'K_{\text{int}}}{k_w + k_w'K_{\text{int}}[X^-]} \qquad (1)$$

constants are as defined by these authors. Buckingham *et al.*[2] have found that competition ratios for the ions $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5Br]^{2+}$ as products are essentially equal and independent of halide-ion concentration,[1,2] indicating that $k_w'K_{\text{int}}[X^-]$ is negligible compared to k_w. For example, R_x for both complexes is equal to 0·24 when the ion $[Co(NH_3)_5N_3]^{2+}$ and HNO_2 react in 1M-HCl and 1M-HBr. Therefore, the numerators of R_x for Cl^- and Br^- are equal and the intermediate $[Co(NH_3)_5]^{3+}$ reacts equally rapidly with both ions. If this intermediate occurs in anation of $[Co(NH_3)_5H_2O]^{3+}$ by Cl^- and Br^- then the rate laws for the two anation

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[1] A. Haim and H. Taube, *Inorg. Chem.*, 1963, **2**, 1199.

[2] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, 1967, **6**, 1027.

reactions *must* be the same. The rate law for the Cl^- anation at 1·0M ionic strength[3,4] has the form (2),

$$\text{Rate} = \frac{A[Cl^-]}{B + C[Cl^-]}[Co(NH_3)_5H_2O^{3+}]_{tot} \qquad (2)$$

which can be interpreted on the basis of either a D or an I_d mechanism.[5] Consequently we have studied the anation reaction for Br^- at 1·0M ionic strength. This could be studied directly at 0·3, 0·5, and 0·75M-Br^-. At 0·1- and 0·2M-Br^- it was necessary to study the aquation reaction of the ion $[Co(NH_3)_5Br]^{2+}$ and obtain the anation rate constant using the equilibrium constant determined for this medium. Here we report the results of these anation, aquation, and equilibrium studies.

EXPERIMENTAL

The salts $[Co(NH_3)_5Br]Br_2$ [6] and $[Co(NH_3)_5H_2O](ClO_4)_3$ [7] were prepared as described in the literature. Water was distilled from potassium permanganate, sodium hydroxide, and sulphuric acid. Other chemicals were reagent grade and used without purification.

Equilibrium Measurements.—For determination of the concentration equilibrium quotient for the inner-sphere complex, solid complex was dissolved in stock solvent containing the desired concentrations of $HClO_4$, $NaClO_4$, and NaBr and the equilibrium approached from both sides. The solutions were equilibrated in sealed containers for 1 month in a water-bath at 25·0 ± 0·1 °C. Absorbances were then determined with a Beckman DU spectrophotometer having a cell compartment thermostatted at the same temperature, the solution equilibrated for an additional month in the water-bath, and the absorbances redetermined. Equilibrium was attained before the first absorbances were recorded.

For determination of the ion-pairing constant of $[Co(NH_3)_5H_2O]^{3+}$, Br^- stock solutions of the ion $[Co(NH_3)_5H_2O]^{3+}$ and Br^- at 25·0 °C were mixed giving 0·2475—0·9900M-Br^- and the absorbance determined as rapidly as possible; negligible substitution occurred in the short period required. For determination of the ion-pairing constant of $[Co(NH_3)_5Br]^{2+},Br^-$, the salt $[Co(NH_3)_5Br]Br_2$ was first dissolved in thermostatted perchlorate solution for rapid dissolution and then Br^- stock solution was added. The time at which the absorbance was read was noted and a correction applied for aquation occurring from the known aquation rate. Each absorbance determination was made in triplicate and always with the same solvent in the reference cell as was being used in the sample cell.

Kinetic Measurements.—Reaction mixtures were thermostatted in a water-bath at 25·05 ± 0·05 °C, aliquot portions being withdrawn and discarded after determination of absorbance. Both Beckman DU and Unicam SP 500 spectrophotometers were used.

RESULTS

Equilibrium Measurements.—Attempts were made to determine the $[Co(NH_3)_5H_2O]^{3+},Br^-$ ion-pairing constant using the increased intensity of absorption at 310 and 320 nm in the presence of Br^-. Over the concentration range $0·2475\text{M} \leqslant [Br^-] \leqslant 0·9900\text{M}$ at 310 nm and $0·5000\text{M} \leqslant [Br^-] \leqslant 0·9900\text{M}$ at 320 nm (since the effect was smaller at this wavelength) the average molar absorption coefficient was strictly linear in bromide-ion concentration and showed no saturation effect with increasing bromide-ion content in accordance with relation (3), which is readily derived for

$$\bar{\varepsilon} = \varepsilon_a + \varepsilon_1 K_1[Br^-] \qquad (3)$$

the condition $K_1[Br^-] \ll 1$. Here $\bar{\varepsilon}$ is the measured absorbance for a 1·00 cm cell divided by the total aquo-complex concentration, ε_a the molar absorption coefficient of the $[Co(NH_3)_5H_2O]^{3+}$ ion, and ε_1 and K_1 refer to molar absorption coefficient and ion-pairing constant of $[Co(NH_3)_5H_2O]^{3+},Br^-$, respectively. A similar relation can also be written for the $[Co(NH_3)_5Br]^{2+},Br^-$ ion-pair substituting ε_b for ε_a and $\varepsilon_2 K_2$ for $\varepsilon_1 K_1$, since the average molar absorption coefficient was linear in bromide-ion concentration in this system also. Values obtained for ε_a, ε_b, $\varepsilon_1 K_1$, and $\varepsilon_2 K_2$ are listed in Table 1.

TABLE 1

Values of ε_a, ε_b, $\varepsilon_1 K_1$, and $\varepsilon_2 K_2$ at 25·00 ± 0·05 °C, 1·00M ionic strength ($NaClO_4$ + NaBr), and 0·0100M-$HClO_4$

Wavelength/nm	ε_a/l mol⁻¹ cm⁻¹	ε_b/l mol⁻¹ cm⁻¹	$\varepsilon_1 K_1$/l² mol⁻² cm⁻¹	$\varepsilon_2 K_2$/l² mol⁻² cm⁻¹
310	16·58 ± 0·27	776·6 ± 4·6	39·3 ± 1·1	137 ± 11
320	25·54 ± 0·33	726·8 ± 3·0	18·8 ± 0·6	86 ± 6
343	45·57 ± 0·40	405·6 ± 5·0		

The concentration equilibrium quotient defined by equation (4) for the inner-sphere complex was calculated

$$K_c = \frac{[Co(NH_3)_5Br^{2+}] + [Co(NH_3)_5Br^{2+},Br^-]}{\{[Co(NH_3)_5H_2O^{3+}] + [Co(NH_3)_5H_2O^{3+},Br^-]\}[Br^-]} \qquad (4)$$

from (5), since $K_1[Br^-]$, $K_2[Br^-] \ll 1$. Values of K_c are

$$K_c = \frac{\{(\varepsilon - \varepsilon_a)/[Br^-]\} - \varepsilon_1 K_1}{(\varepsilon_b - \varepsilon) + \varepsilon_2 K_2[Br^-]} \qquad (5)$$

given in Table 2 and are independent of bromide-ion concentration as expected from equation (4) if these inequalities apply. The three values of K_c obtained at the three wavelengths are in satisfactory agreement and give $K_c = 0·283 \pm 0·030$ l mol⁻¹ when combined.

Kinetic Measurements.—Values of k_{obs}, the observed pseudo-first-order rate constant for approach to equilibrium, were obtained from gradients of plots of $\log_e (A - A_\infty)$ against time (A and A_∞ are absorbances at time t and after 10 half-lives). At 0·300-, 0·500-, and 0·750M-bromide ion values of the pseudo-first-order anation rate constants, $k_{an,1}$, were obtained from k_{obs} by substituting $k_{aq} = k_{an,1}/K_c$

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[3] C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, 1967, **89**, 3141.

[4] E. Barber and W. L. Reynolds, *Inorg. Chem.*, 1973, **12**, 951.

[5] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' W. A. Benjamin, New York, 1966.

[6] H. Diehl, H. Clark, and H. H. Willard, *Inorg. Synth.*, 1939, **1**, 186—188.

[7] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 1318.

for k_{aq}, the first-order aquation rate constant, in $k_{obs} = k_{an,1} + k_{aq}$. At 0·100- and 0·200M-bromide ion values of $k_{an,1}$ were obtained by substituting $k_{an,1} = k_{aq}K_c[Br^-]$ into the expression for k_{obs} obtained from aquation rate measurements at these concentrations. Values of $k_{an,1}$ are reported in Table 3. The values are satisfactorily independent of wavelength and the average value of $k_{an,2}$, the second-order anation rate constant, at each bromide-ion concentration is (1·29 ± 0·02) × 10^{-6} (0·100), (1·28 ± 0·03) × 10^{-6} (0·200), (1·26 ± 0·03) × 10^{-6} (0·300), (1·41 ± 0·02) × 10^{-6} (0·500), and (1·35 ± 0·02) × 10^{-6} s^{-1} (0·750M). The average value of $k_{an,2}$ obtained from all measurements was (1·32 ± 0·06) × 10^{-6} l mol^{-1} s^{-1}. The value of k_{aq} in the absence of added bromide ion was (4·04 ± 0·10) × 10^{-6} s^{-1} at 343 nm, (3·90 ± 0·05) × 10^{-6} s^{-1} at 320 nm, and (3·96 ± 0·04) × 10^{-6} s^{-1} at 310 nm and showed no dependence on wavelength; the average value was (3·97 ± 0·08) × 10^{-6} s^{-1}.

TABLE 2

Values of the concentration inner-sphere formation quotient, K_c, for the ion $[Co(NH_3)_5Br]^{2+}$ at 25·00 ± 0·05 °C, 1·00M ionic strength ($NaClO_4$ + NaBr), and 0·0100M-$HClO_4$

Wavelength/nm	$[Br^-]$/M	$10^4[Co^{III}]$/M	K_c/l mol^{-1}
310	0·4000	14·4—18·0	0·308 ± 0·031 [a]
	0·5000	3·60—6·00	0·315 ± 0·032
	0·6000	3·84—4·80	0·295 ± 0·020
	0·7000	1·44—3·36	0·310 ± 0·025
	0·8000	1·92—2·40	0·282 ± 0·025
	0·9120	0·960—2·00	0·286 ± 0·030
	0·9900	1·20—1·92	0·270 ± 0·030
	Average value =		0·295 ± 0·030
320	b	b	0·280 ± 0·032
343	b	b	0·274 ± 0·027

[a] The errors are standard deviations for a single measurement. [b] Same solutions as for 310 nm.

TABLE 3

Values of $k_{an,1}$ and $k_{an,2}$ at various bromide-ion concentrations, 25·00 ± 0·05 °C, 0·0100M-$HClO_4$, and 1·00M ionic strength ($NaClO_4$ + NaBr)

	10^7 $k_{an,1}$/s^{-1}				10^6 $k_{an,2}$/l mol^{-1} s^{-1}			
$[Br^-]$/M	310	320	343	590	310	320	343	590nm
0·100	1·30	1·29	1·27		1·30	1·29	1·27	
0·200	2·61	2·50	2·56		1·31	1·25	1·28	
0·300	3·66		3·82	3·86	1·22		1·27	1·29
0·500	7·12	7·10	6·95		1·42	1·42	1·39	
0·750		9·99	10·1	10·2		1·33	1·35	1·36

DISCUSSION

When the values of $K = 0·30$ l mol^{-1} and $k_{aq} = 3·97 \times 10^{-6}$ s^{-1} for the ion $[Co(NH_3)_5Br]^{2+}$ at 25 °C and 1·0M ionic strength are used in the expression for R_{Br^-} the calculated value is 0·20 in reasonable agreement with experimental values.[2] The disagreement [2] between experimental and calculated values of R_{Br^-}, which argued against a common intermediate in spontaneous and induced aquations of the ion $[Co(NH_3)_5Br]^{2+}$, has been removed. However we have shown that the rate law for anation of the ion $[Co(NH_3)_5H_2O]^{3+}$ by Br^- does not have the form given in equation (2) for Cl^- for essentially the same concentration range. If the $[Co(NH_3)_5]^{3+}$ intermediate is formed in the competition experiments of Haim and Taube [1] and of Buckingham *et al.*[2] then we have proved that it is not formed in anation of the ion $[Co(NH_3)_5H_2O]^{3+}$ by Br^- and by Cl^-. The most probable mechanism for these two anations is the I_d mechanism involving ion-pairs; in the case of Cl^- the ion-pairing constant is sufficiently large to cause $C[Cl^-]$ in the denominator of equation (2) to be comparable to B whereas it is not in the case of Br^-. It has previously been shown [8] that aquation of the ion $[Co(NH_3)_5NO_3]^{2+}$ also does not pass through the same intermediate formed in the competition studies.[1,2]

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[8] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, 1964, **3**, 1334.