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Substitution Reactions of Metallic Complexes of β,β',β''-Triaminotriethylamine. VII. Kinetics of Bromide Anation of Diaquo(β,β',β''-Triaminotriethylamine)Cobalt(III) Ion

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The bromide anation reaction of diaquo(triaminotriethylamine)cobalt(III) ion has been studied spectrophotometrically. The kinetics fit a rate law

$$\frac{-d[complex]}{dt}=k_{AN}[Br^-][complex]$$

with k_{AN} *typically* 10^{-4} sec^{-1} M^{-1}. *The activation parameters:* $\Delta H^* = 25.2\pm0.4$ $kcal/mol^{-1}$, $\Delta G^* = 24.3\pm0.3$ $kcal/mol^{-1}$, *and* $\Delta S^* = 0.19\pm1.1$ *cal* deg^{-1} mol^{-1} *at ionic strength* 2.0 M.

Introduction

Most of the substitution reactions of complex ions in aqueous solutions involve the participation of water as a reactant, *i.e.*, hydrolysis, or a displaced ligand, i.e., anation. An extensive amount of kinetic data has been reported for the acid or base hydrolysis reactions of octahedral haloaminecobalt(III) complexes, whereas relatively few studies are reported on the anation reaction of the corresponding aquoamine-cobalt(III) complexes.[2]

In previous work, the kinetics of acid hydrolysis reactions of dihalo(triaminotriethylamine)cobalt(III) ions have been investigated extensively.[3] As a part of a program of studying the kinetics of the substitution reactions of tren-cobalt(III) ions, it was decided to investigate the anation reaction of the diaquo(triaminoriethylamine)cobalt(III) ion, $Co(tren)(H_2O)_2^{3+}$. As a preliminary study of this system, the kinetics of bromide anation reaction of $Co(tren)(H_2O)_2^{3+}$ were examined. The results are presented and a possible mechanism is suggested for the reaction.

Experimental Section

Reagents. Deionized water and reagent grade chemicals were used in all procedures. In the kinetics studies bromide concentrations were adjusted with sodium bromide, sodium perchlorate used to adjust the ionic strength was anhydrous reagent grade quality.

Preparation of Compound. Diaquo(triaminotriethylamine)cobalt(III) ion was generated *in situ* by acid hydrolysis of dibromo(tren)cobalt(III) bromide, $[Co(tren)Br_2]Br$,[3c] in 0.1 *M* perchloric acid.

Electronic Absorption Spectra. The visible spectra of all species were obtained with a Cary Model 14M recording spectrophotometer, and matched cells of 1-cm path length were used.

Kinetic Method for Determining Rate of Anation Reaction. Spectrophotometric Method. The diaquo species used in this study was prepared by dissolving $[Co(tren)Br_2]Br$ in 0.1 *M* $HClO_4$ and allowing it to undergo an acid hydrolysis reaction at 60°C. The scan of the visible spectrum of the solution at the end of the secondary hydrolysis step was found to be identical to that reported for $Co(tren)(H_2O)_2^{3+}$.[3c,e] A series of scans of the spectrum during the bromide anation of $Co(tren)(H_2O)_2^{3+}$ in 0.1 *M* $HClO_4$, 1.0 *M* NaBr, and at 50.0°C is shown in Figure 1. The scans showed two well-defined isosbestic points at 516 and 442 nm which did not change during the course of the reaction, and the wavelengths were in good agreement with those reported for the acid hydrolysis of $Co(tren)BrH_2O^{2+}$.[3c] These observation indicate that the total concentration of the bromoaquo and the diaquo complexes is constant during the course of the reaction, and no other product is formed to any great extent. However, the spectrum of the final solution was intermediate to those of the diaquo and the bromoaquo complexes. Thus instead of having all the diaquo complex converted into the bromoaquo complex, there is an equilibrium between these two species under the given experimental conditions.

In a typical experiment the solution of Co(tren)-

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[1] Based in part on a dssertation submitted by K. Kuo to the Graduate School of the State Unversity of New York at Binghamton in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1971.

(2) For review see: (a) D.R. Stranks in « Modern Coordination Chemistry », J. Lewis and R.G. Wilkins (Eds.), Interscience Publishers, Inc., New York, N.Y., 1960; (b) F. Basolo and R.G. Pearson, « Mechanism of Inorganic Reactions », Wiley, New York, N.Y., 1967.

(3) (a) Part I: S.K. Madan, W.M. Reiff, and J.C. Bailar, Jr., *Inorg. Chem.*, *4*, 1366 (1965); (b) Part II: S.K. Madan and Peone, Jr., *ibid.*, *6*, 463 (1967); (c) Part IV: W.V. Miller and S.K. Madan, *ibid.*, 9, 3362 (1970); (d) Part V: K. Kuo and S.K. Madan, *ibid.*, *10*, 229 (1971); (e) Part VI: W.V. Miller and S.K. Madan, *ibid.*, *10*, 1250 (1971).

Table I. Rate Data for Bromide Anation Reaction of Diaquo-(triaminotriethylamine)cobalt(III). Ion in 0.1 *M* $HClO_4$ [a]

Temp.(°C)	$k_{-2}\times10^4$ sec^{-1} [Br$^-$] *M* 0.35	0.55	0.75	0.95	1.25	1.55	$k_{AN}\times10^4$ sec^{-1}
50.0 [b]	—	1.27	—	2.24	3.04	3.70	2.40
55.0 [b]	—	2.60	—	4.65	5.86	7.15	4.70
60.0 [b]	—	4.30	—	7.48	10.0	12.4	8.00
60.0 [c]	2.90	4.60	6.23	7.88	—	—	8.35
65.0 [b]	—	7.82	—	13.8	18.0	23.0	14.6

[a] Concentration of diaquo complex = 1.02×10^{-3} *M* and 9.42×10^{-4} *M*. [b] Ionic strength (μ) = 2.0 *M*. [c] μ = 1.0 *M*.

$(H_2O)_2^{3+}$ ($\sim1\times10^{-3}$ *M*) was thermostated at reaction temperature and then solid NaBr and $NaClO_4$ were added to give desired bromide concentration and ionic strength. The reaction mixture was transferred to a spectrophotometric cell and the rate of appearance of the bromoaquo species was measured spectrophotometrically using a Cary Model 14M recording spectrophotometer. The temperature was controlled to within ±0.1°C by pumping water from a constant temperature bath through the compartment surrounding the cell. All kinetic measurements were made at 560 nm where the molar absorbtivity of the diaquo species was 52 M^{-1} cm^{-1} and that of bromoaquo species was 161 M^{-1} cm^{-1} at 50°C.

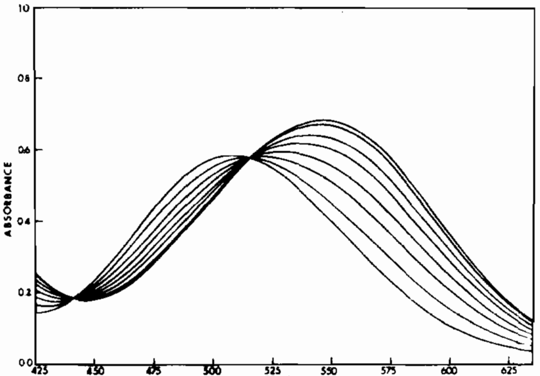

Figure 1. Spectral Change During the Bromide Anation of Diaquo(triaminotriethylamine)cobalt(III) Ion in 0.1 *M* $HClO_4$ and 1.0 *M* NaBr at 50.0°C. Reading upward at 600 nm, reaction time is 200, 900, 1700, 2600, 3900, 5300, 9150, 21500, and 75500 sec.

For the amount of excess bromide ion used, the reaction was found to be an opposed first-order-first-order reaction in the aqueous solution. Plots of log $(x_e/x_e\text{-}x)$ *vs.* time were linear with slopes equal to $k_{-2}\,a/2.303\,x_e$, where x and x_e are formed concentrations of the bromoaquo complex at time t and equilibrium, respectively, and a is the initial complex concentration. The value of k_{-2}, pseudo-first-order rate constant of the anation reaction, could be calculated. Consecutive runs always agreed to within 4%.

Bromide Concentration Dependence of Anation Reaction Rate. In order to calculate the second-order rate constant, k_{AN}, of the bromide anation reaction of $Co(tren)(H_2O)_2^{3+}$, the reaction rates have been measured in bromide concentration range 0.35-1.55 *M* at constant ionic strengths. A second-order rate law

$$\text{Rate}=k_{AN}[\text{Br}^-][\text{complex}] \tag{1}$$

or

$$\text{Rate}=k_{-2}[\text{complex}] \tag{2}$$

was used to calculate k_{AN}. From eq. (1) and (2), the plot of k_{-2} *vs.* [Br$^-$] should give a straight line having a slope k_{AN}, and typical data in this study at 50.0°C and ionic strength 2.0 *M* are plotted in Figure 2.

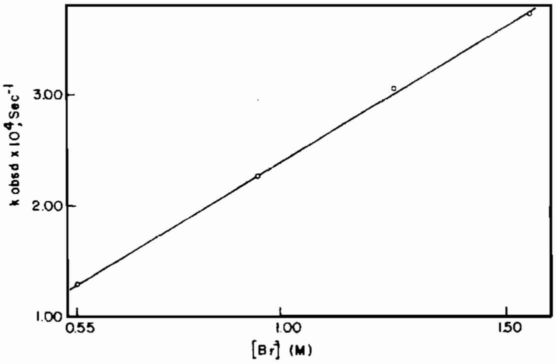

Figure 2. Plot of k_{-2} *vs.* [Br$^-$] for the Bromide Anation Reaction of Diaquo(triaminotriethylamine)cobalt(III) Ion at 50.0°C and Ionic Strength 2.0 *M*.

Results and Discussion

The pseudo-first-order rate constants, k_{-2}, of the bromide anation reaction of diaquo(tren)cobalt(III) ion were determined in 0.1 *M* $HClO_4$ and constant ionic strength under various conditions of bromide concentration and temperature. The data obtained are given in Table I. As in the case of most anation reactions of aquo complexes with anionic ligands, the bromide anation reaction of $Co(tren)(H_2O)_2^{3+}$ was found to be second-order with a rate dependent on bromide concentration. Also, the reaction rate increases with decreasing ionic strength of the reaction medium, which is expected for the reaction involving oppositely charged ions.

The activation enthalpy corresponding to the second-order rate constant of the reaction, k_{AN}, obtained from the linear Arrhenius plot over the range 50.0-65.0°C and at an ionic strength 2.0 *M* is $\Delta H^* = 25.2\pm0.4$ kcal mol^{-1}. The values of ΔG^* and ΔS^* were calculated to be 24.3±0.3 kcal mol^{-1} and 0.19±1.1 cal deg^{-1} mol^{-1}, respectively.

Based on the anation results and the previous reported acid hydrolysis rate constants,[3c] the equilibrium constants for the reaction

$$Co(tren)(H_2O)_2^{3+} + Br^- \rightleftarrows Co(tren)BrH_2O^{2+} + H_2O$$

were calculated to be 3.0 and 2.7 at ionic strength 2.0 *M*, and at 65.0 and 55.0°C, respectively.

The fact that the anation reaction conforms to a second-order rate law does not permit a distinction to be made beween a dissociative mechanism and an associative mechanism because of the possible outer-sphere association. However, in an S_N1 process, water exchange and complex formation will compete for the same intermediate, whereas in S_N2 processes the reactions are independent.[4]

Recently, Broomhead and Kane-Maguire[5] have investigated the halide anation reactions of ruthenium(III)-amine complexes. Their results indicated no S_N1 type mechanism, but either a direct S_N2 mechanism or an outer-sphere into inner-sphere interchange process was suggested.

From the present data obtained in this study, it is not possible to determine a definite mechanism for the anation reacion of $Co(tren)(H_2O)_2^{3+}$. However, because of the microscopic reversibility, the anation reaction should have a transition state similar to that of the reverse acid hydrolysis reaction. In the previous studies,[3] a dissociation type mechanism has been found for the acid hydrolysis reaction of cobalt (III) tren complexes. Therefore, the direct S_N2 mechanism can be ruled out at this point, even though it has been suggested for the halide anation reactions[5] and the reverse acid hydrolysis reactions[6] of the ruthenium(III)-amine complexes. For a limiting S_N1 mechanism the pentacoordinated intermediate has to be formed. Haim, *et al.*[7] have shown that without a stabilizing π-bonding ligand, the five-coordinated ion, $Co(tren)H_2O^{3+}$, would be too high in energy to exist. Furthermore, the calculated values of $k_{-2}/[Br^-]$ at a given temperature and ionic strength were found to be fairly constant within the experimental error, as is shown by the straigth lines from the plots of k_{-2} *vs.* $[Br^-]$ (Figure 2). This is not expected for a limiting S_N1 mechanism, in which the dependence of the observed rate constant becomes less than first-order, and a nonlinearity is observed in the plot of the observed rate constant *vs.* the entering-group concentration at high concentration of the entering group.[2b,7]

Under our experimenal conditions, i.e., a cationic complex and high bromide concentration, the equilibrium formation of an outer-sphere complex has to be considered. Therefore, an outer-sphere to inner-sphere interchange process (which has been discussed by Basolo and Pearson,[2b] and is kinetically second-order) is believed to be the reaction pathway for the anation reaction of diaquo(tren)cobalt(III) ion. For the transition state, the most appropriate choice would be an octahedral wedge-type geometry, which has been suggested for most of the acid hydrolysis reactions of cobalt(III)-amine complexes.

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