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Note

The solid-state kinetics of the deaquation and anation of some $[Co(NH_3)_5H_2O]X_3$ complexes

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The kinetics of the deaquation and anation reaction of complexes of the type $[Co(NH_3)_5H_2O]X_3$, where X is chloride, bromide or nitrate, were first studied by Mori *et al.*[1,2]. By measurement of the rate of evolution of the water as a function of temperature, they found the activation energy for the chloride complex to be 21.47 kcal/mole. Wendlandt and Bear[3], using a similar method but at three different temperatures, found activation energies of 19 ± 2, 25 ± 2, and 31 ± 3 kcal/mole for the chloride, bromide and nitrate complexes, respectively.

We wish to report here new data concerning the kinetics of these reactions. These data were obtained using the non-isothermal mass-loss method recently reported by Broido[4]. The basis of this method, the mathematical approximations of which were first suggested by Horowitz and Metzger[5], is to determine the fraction of material undecomposed, y, as a function of temperature, T, and to plot $\ln\ln(1/y)$ as a function of $1/T$. As in a conventional Arrhenius plot, the slope of the straight line obtained is proportional to the activation energy. Draper[6] has developed a virtually identical method derived from purely thermodynamic considerations which did not involve an approximation in the exponential portion of the rate equation.

EXPERIMENTAL

Apparatus

Thermogravimetric data were taken using a DuPont Model 950 Thermogravimetric Analyzer. Sample sizes of 10–12 mg were employed. A heating rate of 10°C/min and a dynamic nitrogen atmosphere were used for all of the studies.

Preparation of compounds

The $[Co(NH_3)_5H_2O]X_3$ complexes were prepared as previously described[3]. Water contents of the complexes were determined by mass-loss on the thermobalance. Analytical data found for water were: $[Co(NH_3)_5H_2O]Cl_3$, 6.76% found, 6.70% theor.; $[Co(NH_3)_5H_2O]Br_3$, 4.60% found, 4.48% theor.; and $[Co(NH_3)_5H_2O](NO_3)_3$, 5.13% found, 5.17% theor.

RESULTS AND DISCUSSION

The kinetics curves for the deaquation and anation reactions are shown in Fig. 1, while the activation energies, *E*, are given in Table I.

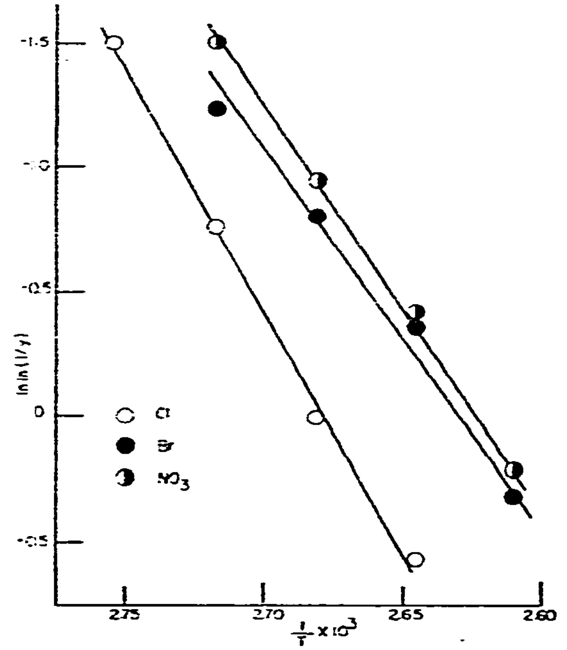

Fig. 1. Kinetics curves for the $[Co(NH_3)_5H_2O]X_3$ complexes.

TABLE I

ACTIVATION ENERGIES FOR THE DEAQUATION AND ANATION REACTIONS OF $[Co(NH_3)_5H_2O]X_3$ COMPLEXES

Compound	*E, kcal/mole*		
	Mori et al.[1,2]	*Wendlandt and Bear*[3]	*This work*
$[Co(NH_3)_5H_2O]Cl_3$	21.47	19 ± 2	37 ± 4
$[Co(NH_3)_5H_2O]Br_3$		25 ± 2	31 ± 3
$[Co(NH_3)_5H_2O](NO_3)_3$		31 ± 3	33 ± 3

There does not appear to be any correlation between the energies of activation determined by the TG method with those obtained by the vapor pressure method; the former are of greater magnitude and appear to have a different order of anion effect.

The magnitude of the energy of activation is dependent upon the reaction mechanism. An unequivocal mechanism has not as yet been established for the deaquation–anation reactions; however, Wendlandt *et al.*[7] have postulated an S_N1-type reaction based upon observations of sealed-tube DTA studies. This proposed mechanism involved two steps: (1) the breaking of the Co^{3+}----H_2O bond, and (2) the formation of a Co^{3+}----X^- bond. The possibility that the reaction occurs via a S_N2 reaction cannot, however, be eliminated solely on the basis of calorimetric data. If it is assumed that an S_N1 reaction is involved, then the rate determining step is that of bond breaking and the activation energy must be associated with this step. In the case of the aquopentamminecobalt(III) complexes, the activation energy is associated with the Co^{3+}----H_2O bond breaking. A variation in the energy of activation with the anion would then imply some connection between the anion and ability of the water molecule to be removed and replaced.

The principal difference between the complexes would appear to be that of the differences in the size and charge density of the anions around the octahedral aquopentamminecobalt(III) ion. A limiting term in the size of the lattice of ions is the size of the anions; *i.e.*, how close the anions can approach the central metal ion. For illustrative purposes, a hypothetical model of the complex is shown in Fig. 2. The chloride ion is smaller than either bromide or nitrate ion and would therefore be expected to approach the central ion more closely than the other two. Because of its smaller size, the chloride should have a higher charge density than the other two ions; consequently, the charge density about the central ion in the aquopentammine-cobalt(III)chloride should appear larger than in the other two complexes.

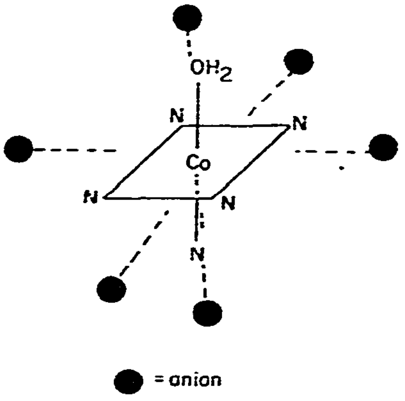

Fig. 2. Proposed model of $[Co(NH_3)_5H_2O]X_3$.

The process of deaquation and anation involves, as a first step, the removal of the water molecule from the central ion. This implies that the water molecule must be evolved from the coordination sphere of the complex. The charge density around the oxygen atom in the water molecule is fairly high; consequently, the amount of energy required to dissociate it from the central ion and remove it from the lattice of surrounding anions should increase as the charge density of the lattice increases. If the lattice contains chloride ions, then the energy required to remove them would be greater than in the case where bromide or nitrate ions are present. Thus the somewhat higher activation energy of the aquopentamminecobalt(III)chloride could be justified. It should be pointed out that the opposing data of Wendlandt and Bear[3] can be justified in terms of an S_N2(lim) mechanism. The rate of reaction in this case is determined by the rate of bond formation. Because of the increased size of the bromide ion, and because of the size and the poor coordination ability of the nitrate ion, an order of activation energies of: $Cl^- < Br^- < NO_3^-$, is not unexpected; these ions are able to enter coordination sphere in the order: $Cl^- > Br^- > NO_3^-$.

Exact knowledge of the type of reaction taking place must await experimental data on the structure of the crystalline complexes both before and after the deaquation reaction. It has not been determined whether or not the lattice changes to accomodate the removal of the anion or if the structure remains the same with holes in the lattice where the anions once were. There is no evidence upon which to postulate the existence of a reaction intermediate of either increased or reduced coordination number (as is the case of kinetics mechanisms postulated in solution). Precise knowledge of the nature of the mechanism will require this formation.

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