The Thermal Deaquation-Anation Reactions of Aquopentamminechromium(III) Complexes in the Solid State

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The thermal deaquation-anation reactions of aquopentamminechromium(III) nitrate, chloride, bromide, and iodide in the solid state were investigated by the techniques of TG, DSC, X-ray powder diffraction analysis, and manometry. The first-order rate constants were obtained by isothermal kinetics. The activation enthalpies calculated from the first-order rate constants increased in the order: the nitrate(24.3) < the chloride(26.4) < the bromide(29.7) < the iodide(30.7 kcal/mol). The enthalpy changes by DSC were 12.3, 6.5, 6.3, and 7.0 kcal/mol for the nitrate, chloride, bromide, and iodide respectively. The slight deviation from the first-order kinetics was observed in cases of the nitrate and the chloride.

Although the deaquation-anation reactions of aquopentamminechromium(III) complexes in the solid state have been widely investigated by several workers, some problems still remain. The deaquation-anation reactions of aquopentamminechromium(III) complexes are, in general, represented by this equation:

$$[Cr(H_2O)(NH_3)_5]X_3 \longrightarrow [CrX(NH_3)_5]X_2 + H_2O$$

where X contains of nitrate, chloride, bromide, and iodide anions. The temperature of the initial weight-loss, which is taken as a measure of the thermal stability of the complex, was given by Wendlandt and Bear[1)] as increasing in this order: the chloride < the nitrate < the bromide < the iodide. According to Tsuchiya and his co-workers,[2)] though, the order is as follows:

the nitrate < the chloride < the bromide < the iodide
(40°) (60°) (68°) (70°C)

The thermal stabilities of the complexes depend on the variety of outer-sphere anions, and the order given by Tsuchiya *et al.* differs, of course, from that by Wendlandt and Bear.

Wendlandt and Bear[1)] were the first to obtain the kinetic data of the deaquation-anation reactions of the aquopentamminechromium(III) complexes. They obtained the first-order rate constants by following the increase in the water vapor-pressure as a function of time at given temperature; the activation energies were thereby calculated to be 16, 18, 31, and 18 kcal/mol for the nitrate, chloride, bromide, and iodide respectively. Tsuchiya and his co-workers[2)] also obtained the activation energies of the sulfate and sulfate in addition to those of the four complexes by non-isothermal methods, DTA or DTG curve analyses. The activation energies obtained by two groups of workers are in good agreement with one another except for those of the chloride.

Tsuchiya and his co-workers[2)] discussed the mechanisms of the deaquation-anation reactions on the basis of the activation energies obtained and suggested that the bromide, sulfate, and sulfite, which have the larger activation energies, include, to some extent, the tendency of S_N1; this is attributed to the larger ionic radii of the bromide, sulfate, and sulfite anions. Their discussion seems reasonable, but the question remains of why the iodide, which contains the larger iodide anion has the smaller activation energy.

In the present paper, the deaquation-anation reactions of some aquopentamminechromium(III) complexes will be re-examined in order to explain the problems mentioned above.

Experimental

Materials. Aquopentamminechromium(III) nitrate[3)] was prepared by the method in the literature and was recrystallized by adding a small amount of concentrated nitric acid to an aqueous solution of $[Cr(H_2O)(NH_3)_5](NO_3)_3$ below 20 °C. The chloride, bromide, and iodide were obtained by adding concentrated hydrochloric, hydrobromic, and hydriodic acid respectively to an aqueous solution of pure $[Cr(H_2O)(NH_3)_5](NO_3)_3$ below 20 °C. In each case, this process was repeated two times. The elemental analyses for N and H agreed with the calculated values within ±0.3%.

Measurements. The TG and DSC curves were simultaneously recorded with a Rigaku 8002 CS apparatus at a heating rate of 3 °C/min in a flowing-nitrogen atmosphere of 50 ml/min. Twenty milligrams of the powdered sample were placed in a crucible made from an aluminum sheet 0.1 mm thick. A lid of the same material rested inside the crucible. α-Alumina was used as the reference material. The heats of the deaquation-anation reactions were measured from the areas of the DSC curves. The instrument was calibrated in the sensitivity range of 2 millical/full-scale deflections, from the heat of transition of potassium nitrate, which appears at 128 °C with ΔH(transition) = 12.28 kcal/mol.

The X-ray diffraction patterns were measured with a Toshiba diffractometer ADG 101 equipped with a standard high-temperature sample holder in a vacuum. Copper-$K\alpha$ radiation with a nickel filter was used.

Pressure-time curves were obtained at a constant temperature with the apparatus reported in a previous paper.[4)] The temperature of the furnace was kept within ±0.2 °C. The pressure was measured with a mercury manometer and cathetometer reading to 0.01 mm. About twenty milligrams of the sample in a Pyrex crucible were used in each measurement. The final water vapor-pressure became about 4 mmHg for $[Cr(H_2O)(NH_3)_5](NO_3)_3$. The procedure was as follows. A system about 300 ml in volume was previously evacuated for 1 hr by means of a rotary pump in order to remove any adsorbed gases. After the system was purged with N_2 gas, the reaction tube was taken out of a furnace held at the required temperature. The sample was placed in the reaction tube, and then the reaction tube was again inserted in the furnace, which was immediately evacuated for 3 min. The system was closed by operating two stopcocks, and the change in the pressure with the time was measured.

Results

TG and DSC Studies. The DSC curves of the aquopentamminechromium(III) complexes gave a single endothermic peak in the 60—100 °C temperature region. It was found that a crystalline sample and a less crystalline sample of the nitrate gave different thermal stabilities, while the stability of the bromide and iodide were almost independent of their crystalline states, and that the chloride depended, to some extent, on its crystalline state. The corresponding weight-losses from the TG curves were 5.42(5.27), 5.48(5.27), 6.78(6.88), 4.55 (4.56), and 3.52(3.36%) for the nitrate[I], nitrate[II], chloride, bromide, and iodide respectively. Each calculated value of weight-losses is described in parentheses. The nitrate[I] is a crystalline sample which was prepared by the method described in the Experimental section, while [II] is a less crystalline sample which was prepared by adding a large amount of ethanol, all at once, to a saturated aqueous solution of $[Cr(H_2O)(NH_3)_5](NO_3)_3$. The X-ray diffraction patterns of both nitrates are given in Fig. 1, along with those of the nitrate[I] subjected to heat treatment. The temperatures of the initial weight-loss(t_i) and the enthalpy changes (ΔH) corresponding to the deaquation-anation reactions are summarized in Table 1, along with the data described previously.

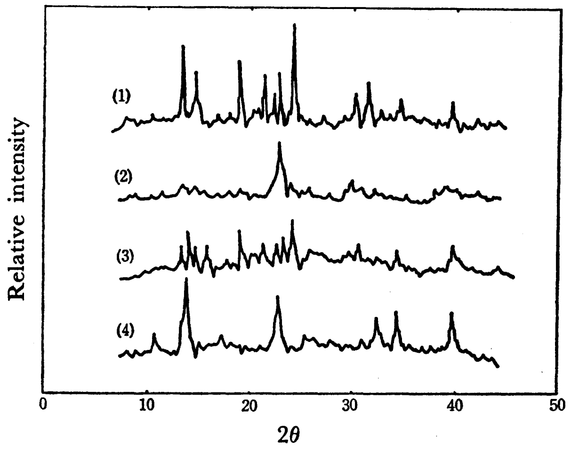

Fig. 1. X-ray diffraction patterns of $[Cr(H_2O)(NH_3)_5](NO_3)_3$ [I](line 1) and [II](2), and of the products after heating the nitrate[I] in a vacuum at 77 °C for 1 hr(3) and 3 hr(4).

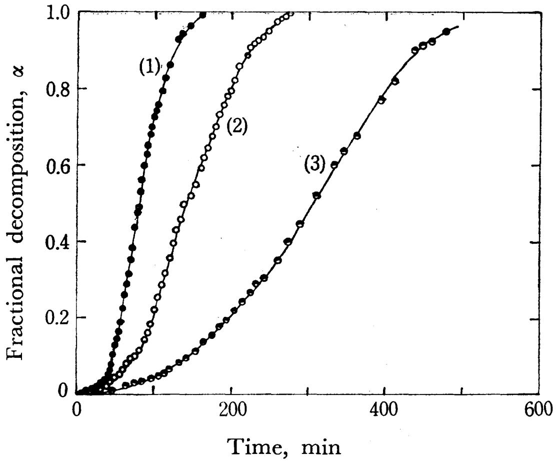

Fig. 2. Kinetic runs of $[Cr(H_2O)(NH_3)_5](NO_3)_3$[I] at (1) 86.5, (2) 81, and (3) 76 °C.

Kinetic Studies. The pressure-time curves of the complexes were obtained at various temperatures. The curves of the nitrate[I] and bromide are given, respectively, in Figs. 2 and 3, as examples, where α means the mol-ratio of liberated water to the complex.

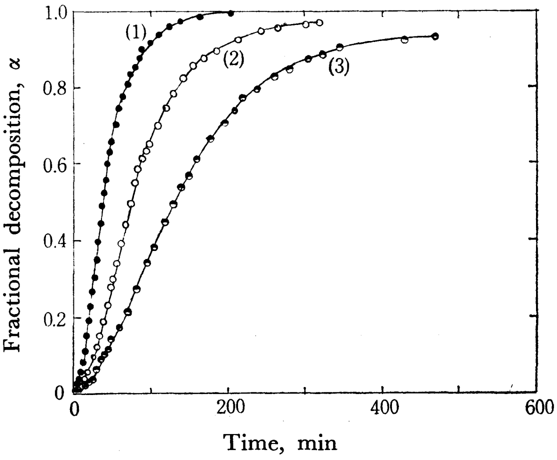

Fig. 3. Kinetic runs of $[Cr(H_2O)(NH_3)_5]Br_3$ at (1) 81, (2) 76, and (3) 70.8 °C.

Table 1. Temperatures of initial weight-loss(t_i) and enthalpy changes(ΔH) for deaquation-anation reactions of $[Cr(H_2O)(NH_3)_5]X_3$ in the solid state

X	t_i, °C		ΔH, kcal/mol		
	This work	Tsuchiya[2]	This work	Wendlandt[1]	Tsuchiya[2]
NO_3[I][a]	75	40	12.3	5.6	11.9
NO_3[II][b]	51		—		
Cl	56	60	6.5	6.1	6.1
Br	76	68	6.3	7.8	9.0
I	83	70	7.0	6.3	10.8

a) The crystalline sample, X-ray diffraction pattern(1) in Fig. 1. b) The less crystalline sample, X-ray diffraction pattern(2) in Fig. 1.

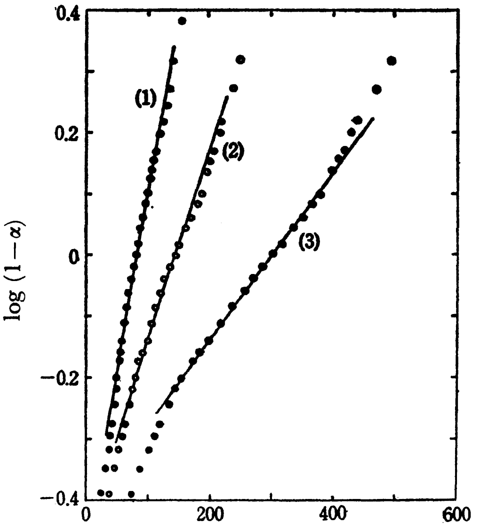

Fig. 4. Plots of log $(1-\alpha)$ *versus* time of $[Cr(H_2O)(NH_3)_5]Br_3$ at (1) 81, (2) 76, and (3) 70.8 °C. The rate constants obtained are a first-order.

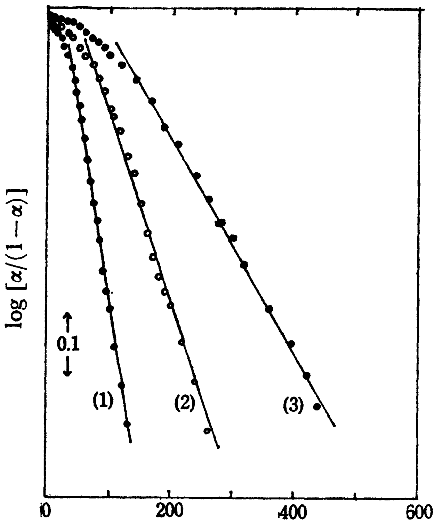

Fig. 5. Plots of log $[\alpha/(1-\alpha)]$ *versus* time of $[Cr(H_2O)(NH_3)_5](NO_3)_3$[I] at 86.5, (2) 81, and (3) 76 °C. The rate constants obtained are a second-order.

All the curves, except for those of the nitrate[I], were analyzed by means of the first-order rate equation: $\ln(1-\alpha)=-kt$. The first-order plots of $[Cr(H_2O)(NH_3)_5]Br_3$ are given in Fig. 4 as examples. The linear relations of $\ln(1-\alpha)$ *versus* the time were maintained in the rang of $0.1<\alpha<0.7$, $0.1<\alpha<0.7$, $0.2<\alpha<0.9$, and $0.2<\alpha<0.9$ for the nitrate[II], chloride, bromide and iodide, respectively. The curves of the nitrate[I] were analyzed by means of the Prout-Tompkins equation.[5] The plots of $\ln[\alpha/(1-\alpha)]$ *versus* the time for the nitrate[I] gave linear relations in the range of $0.1<\alpha<0.8$, as is shown in Fig. 5.

From the rate constants at various temperatures, the activation parameters were calculated. The rate constants(k), activation enthalpies ($\Delta H^{\neq}$), and activation entropies ($\Delta S^{\neq}$) obtained are presented in Table 2, along with those of the previous works.[1,2]

Discussion

The investigated deaquation-anation reactions of the aquopentamminechromium(III) complexes are essentially initiated by the substitution of an outer-sphere anion for a coordinated water molecule. The nitrate gives different thermal stabilities and shapes of kinetic runs between the crystalline sample and the less crystalline one. The former was dehydrated at temperatures higher than 24 °C, and the shape of the kinetic runs was sigmoidal. Since the reaction of the former gave an induction period and could be described by the $d\alpha/dt=k\alpha(1-\alpha)$ equation in the acceleration and decay periods, the reaction may be supposed to proceed through a nucleation and growth mechanism.[5,6] Therefore, the disagreement with the nitrate results reported in the previous works[1,2] may be due to the difference in the crystalline states of the samples used.

The activation enthalpies obtained from the first-order rate constants at various temperatures increased parallel to the increase in the temperatures of the initial weight-loss. The results differ from those of the previous works, as may be seen in Tables 1 and 2. Since the complexes containing larger anions have larger activation enthalpies, the reactions of the complexes investigated may proceed through the displacement mechanism(S_N2).[7] Although the reactions of the nitrate[II] and chloride have negative activation

Table 2. Rate constants(k), activation enthalpies($\Delta H^{\neq}$) and activation entropies($\Delta S^{\neq}$) for the deaquation-anation reactions of $[Cr(H_2O)(NH_3)_5]X_3$ in the solid state

X	$k\times10^4$, s^{-1} (°C)		$\Delta H^{\neq}$, kcal mol^{-1}				$\Delta S^{\neq}$, e.u.
	This work	Wendlandt[1]	This work	Wendlandt[1]	Tsuchiya[2] DTG	Tsuchiya[2] DTA	This work
NO_3[I]	1.21(81)[a]	1.86(85.4)	34.5	16	18	14	20.2
NO_3[II]	1.38(55)		24.3(25.1)[b]				−2.49
Cl	2.41(65)	10.0 (85)	26.4	18	28	25	−2.53
Br	2.43(76)	1.86(83.6)	29.7	31	38	36	9.2
I	1.61(82)	3.55(86.2)	32.7	18	—	19	15.4

a) The second-order rate constant, obtained from $kt=\ln[\alpha/(1-\alpha)]$. b) This value was obtained from the change of weight at constant temperature in a nitrogen atmosphere.

entropies, those of the bromide and iodide have positive values. The latter complexes may not form rigid activated complexes because of the larger ionic sizes of the entering outer-sphere anions.

The activation enthalpies obtained for the deaquation-anation reactions of the aquopentamminechromium(III) complexes are smaller than those for the deammonation-anation reactions of hexamminechromium(III) complexes:[7] $[Cr(NH_3)_6]Cl_3$, 30; $[Cr(NH_3)_6]Br_3$, 43; $[Cr(NH_3)_6]I_3$, 49 kcal/mol. This may be due to the smaller bond strength in $Cr–OH_2$ in the former complexes than those in $Cr–NH_3$ in the latter complexes.

It may be noted that, when the enthalpy changes obtained in this work are compared with the previous data, as in Table 1, there is an approximate agreement among them, only with a few exceptions. The data in the previous works were obtained by DTA. The values chloride, bromide, and iodide are similar to each other, while that of the nitrate is larger. This tendency has also been observed for the deaquation-anation reactions of aquopentamminecobalt(III) complexes.[8]

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