Kinetic Studies of Thermal Decomposition Reactions of Amminechromium(III) Complexes in Solid State.

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Kinetics of the thermal decomposition reactions of $[Cr(NH_3)_6]X_3$ (X=Br, I and NCS) and $[Cr(NCS)(NH_3)_5](NCS)_2$ in solid state were studied by the manometric method. The rate constants, activation energies and activation entropies of the substitution reactions of outer-sphere anions for coordinated ammonia molecules were presented, and possible reaction mechanisms were discussed.

It is well-known that the decomposition of chromium(III) complexes having volatile ligands such as ammonia, water and ethylenediamine is initiated by substitution of an outer-sphere anion for ligand; for example, $[Cr(NH_3)_6]Cl_3$ liberates ammonia to form $[CrCl(NH_3)_5]Cl_2$.[1,2] This behavior differs entirely from that of many cobalt(III) complexes of which the decomposition is initiated by electron transfer from a ligand or an outer-sphere anion to a central metal ion.[3,4]

Investigations on these substitution reactions of chromium(III) complexes have been reported, but the mechanisms are not clear. This might be attributed to the lack of kinetic measurements. There are a few works on kinetic measurements: Wendlandt and Bear[5] obtained isothermal kinetic data for the deaquation of $[Cr(H_2O)(NH_3)_5]X_3$ (X=Cl, Br, I and NO_3), and Tanaka and Nagase[2] those for deammonation of $[Cr(NH_3)_6]Cl_3$, $[CrCl(NH_3)_5]Cl_2$ and *cis*-$[CrCl_2(NH_3)_4]Cl$. Tsuchiya and his coworkers also obtained kinetic data for the deaquation of $[Cr(H_2O)(NH_3)_5]X_3$ (X=Cl, Br, I, NO_3, SO_3 and SO_4) from the DTG and DTA curves.

We have studied kinetics of the thermal decomposition of $[Cr(NH_3)_6]X_3$ (X=Br, I and NCS) and $[Cr(NCS)(NH_3)_5](NCS)_2$ by the manometric method, and discussed the mechanisms on the basis of kinetic data.

Experimental

Apparatus and Procedure. Pressure-time curves were obtained by the apparatus described previously.[3] Details of the procedure were reported.[2]

A Hitachi EPI-2G infrared spectrophotometer and a Hitachi EPS-3T spectrophotometer equipped with a standard integrating sphere attachment were used for the measurements of the infrared absorption spectra and diffuse reflectance spectra, respectively.

Materials. The complexes $[Cr(NH_3)_6]Cl_3$[7] and $[Cr(H_2O)(NH_3)_5]Cl_3$[8] were prepared according to literature. $[Cr(NH_3)_6]Br_3$ and $[Cr(NH_3)_6]I_3$ were obtained by adding HBr and HI, respectively, to the aqueous solution of $[Cr(NH_3)_6]Cl_3$. $[Cr(NCS)(NH_3)_5](NCS)_2$ was prepared by a modified Werner's method.[9] A mixture of 15 g of $[Cr(H_2O)(NH_3)_5]Cl_3$ and 20 g of KNCS was dissolved in a solution of 10 ml of glacial acetic acid in 50 ml of water. The filtrate was cooled and orange crystals were separated by filtration. For the preparation of $[CrI(NH_3)_5]I_2$, the solution containing $[Cr(H_2O)(NH_3)_5]Cl_3$ and HI was heated on a water bath until purple crystals were separated. $[Cr(NH_3)_6](NCS)_3$ was prepared as follows: the mixture of $[Cr(NH_3)_6]Cl_3$ and methanol saturated with KNCS was left standing overnight at room temperature, and filtered off. The yellow filtrate was evaporated until crystals of $[Cr(NH_3)_6](NCS)_3$ were separated.

Results

Hexamminechromium(III) bromide loses one mole of ammonia to form $[CrBr(NH_3)_5]Br_2$ as shown by

$$[Cr(NH_3)_6]Br_3 \longrightarrow [CrBr(NH_3)_5]Br_2 + NH_3 \qquad (1)$$

Pressure-time curves of $[Cr(NH_3)_6]Br_3$ in the temperature range of 213 to 232 °C are given in Fig. 1. Reaction (1) proceeded essentially according to a

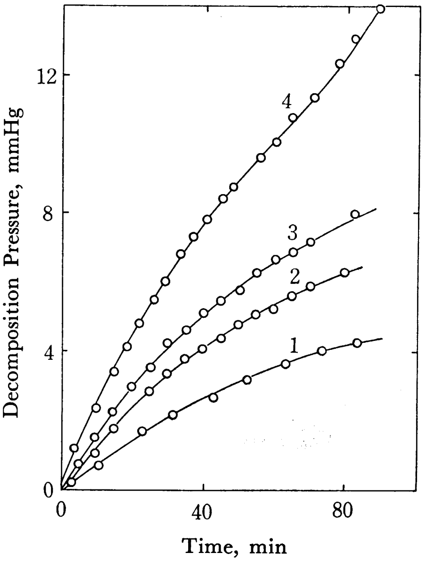

Fig. 1. Pressure-time curves of $[Cr(NH_3)_6]Br_3$ at (1) 213, (2) 221, (3) 225 and (4) 232°C.

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[1] W. W. Wendlandt and J. P. Smith, "The Thermal Properties of Transition-Metal Ammine Complexes", Elsevier, Amsterdam, 1967.

[2] N. Tanaka and K. Nagase, This Bulletin, **42**, 2854 (1969).

[3] N. Tanaka and K. Nagase, *ibid.*, **40**, 546 (1967).

[4] N. Tanaka, K. Nagase, and S. Nagakura, *ibid.*, **41**, 1143 (1968).

[5] W. W. Wendlandt and J. L. Bear, *J. Inorg. Nucl. Chem.*, **26**, 531 (1964).

[6] R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, This *Bulletin*, *42*, *1881 (1969)*.

[7] M. Mori, *Nippon Kagaku Zasshi*, **74**, 253 (1953).

[8] M. Mori, *ibid.*, *74*, *255 (1953)*.

[9] A. Werner and J. von Halben, *Ber.*, **39**, 2668 (1906).

first-order rate equation, but deammonation was suppressed by the increase of decomposition pressure. In the case of $[Cr(NH_3)_6]Cl_3$ the deammonation proceeded almost independently of the decomposition pressure.[2] On the pressure-time curve, there is an inflection point at 232 °C, indicating that the reaction

$$[CrBr(NH_3)_5]Br_2 \longrightarrow [CrBr_3(NH_3)_3] + 2NH_3$$

follows Reaction (1). In fact, the sample heated at 232 °C for 90 min was confirmed to be a mixture of $[CrBr(NH_3)_5]Br_2$ and $[CrBr_3(NH_3)_3]$ from its infrared and reflectance spectra. The infrared spectrum also showed the formation of a small amount of ammonium bromide.

When $[Cr(NH_3)_6]Br_3$ was heated at 230 °C in a vacuum (the system was continuously evacuated with a rotary pump), the main product was not $[CrBr_3(NH_3)_3]$ but chromium nitride. This shows that $[CrBr_3(NH_3)_3]$ is stable above 230 °C in the presence of free ammonia. This was also observed for $[CrCl_3(NH_3)_3]$. In the case of iodide complex, $[CrI_3(NH_3)_3]$ could not be obtained even when the sample was heated in the presence of free ammonia, $[CrI(NH_3)_5]I_2$ only being obtained by heating the sample in a sealed capillary tube.

Plots of $\log(1-x)$ *versus* time are given in Fig. 2, where x denotes fractional decomposition. The kinetic parameters for Reaction (1) are given in Table 2.

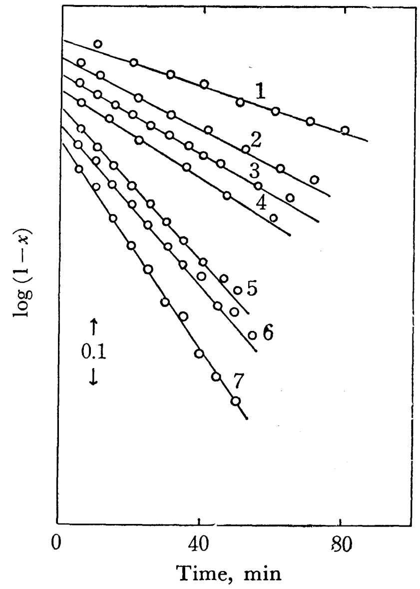

Fig. 2. Plots of a first-order rate equation for $[Cr(NH_3)_6]Br_3$ at (1) 210, (2) 213, (3) 215, (4) 217, (5) 219, (6) 221 and (7) 225 °C.

When hexamminechromium(III) iodide was heated in an inert gas atmosphere or in a vacuum, the complex decomposed to chromium nitride. The reaction is represented by

$$[Cr(NH_3)_6]I_3 \longrightarrow CrN + 3NH_4I + 2NH_3 \qquad (2)$$

It proceeded essentially according to a first-order rate equation, but decomposition was suppressed by the increase of decomposition pressure, as seen for the bromide complex. The first-order rate constants of Reaction (2) were determined by the measurement of initial rates. The activation parameters obtained are given in Table 2.

The order of the thermal stabilities of the hexamminechromium(III) halides heated under the conditions of manometric measurement is as follows:

$$[Cr[NH_3)_6]Cl_3 < [Cr(NH_3)_6]Br < [Cr(NH_3)_6]I_3$$

This differs from that of the thermal stabilities reported by Wendlandt and Chou.[10] The order they obtained from the temperature of initial mass-loss in the air is as follows:

$$\begin{array}{ccccc} [Cr(NH_3)_6]I_3 & < & [Cr(NH_3)_6]Cl_3 & < & [Cr(NH_3)_6]Br_3 \\ (190°C) & & (200°C) & & (250°C) \end{array}$$

By heating $[Cr(NH_3)_6]I_3$ in the air, free iodine was observed which is considered to be formed by the reaction of the iodide ion and the oxygen in air.

$[CrI(NH_3)_5]I_2$ was obtained almost quantitatively when $[Cr(NH_3)_6]I_3$ was heated in a sealed capillary tube, in which the decomposition pressure became very high and the whole system was maintained at a furnace temperature. The infrared absorption peaks of the product are given in Table 1, together with those of $[Cr(NH_3)_6]I_3$ and $[CrI(NH_3)_5]I_2$.

TABLE 1. WAVE NUMBERS OF THE PRODUCT,[a] $[Cr(NH_3)_6]I_3$ AND $[CrI(NH_3)_5]I_2$

	$\delta_d(NH_3)$	$\delta_s(NH_3)$	$\rho_r(NH_3)$
Product	1586	1292	746
$[Cr(NH_3)_6]I_3$	1595	1307	738
$[CrI(NH_3)_5]I_2$	1587	1292	747

a) The product was obtained by heating $[Cr(NH_3)_6]I_3$ at 225 °C for 24 hr in a sealed capillary tube.

Kinetic runs of hexamminechromium(III) thiocyanate in a temperature range of 99 to 116 °C are given in Fig. 3, where α denotes the mole ratio of free ammonia to chromium(III) complex. The reaction is represented by

$$[Cr(NH_3)_6](NCS)_3 \longrightarrow [Cr(NCS)_3(NH_3)_3] + 3NH_3 \qquad (3)$$

It proceeded almost independent of the pressure of free ammonia, obeying the Prout-Tompkins equation, $dx/dt=kx(1-x)$, where x denotes fractional decompo-

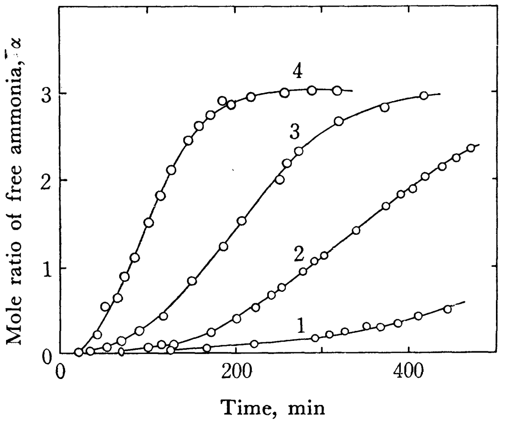

Fig. 3. Kinetic runs of $[Cr(NH_3)_6](NCS)_3$ at (1) 99, (2) 106, (3) 110 and (4) 116°C.

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[10] W. W. Wendlandt and C. Y. Chou, *J. Inorg. Nucl. Chem.*, **26**, 943 (1964).

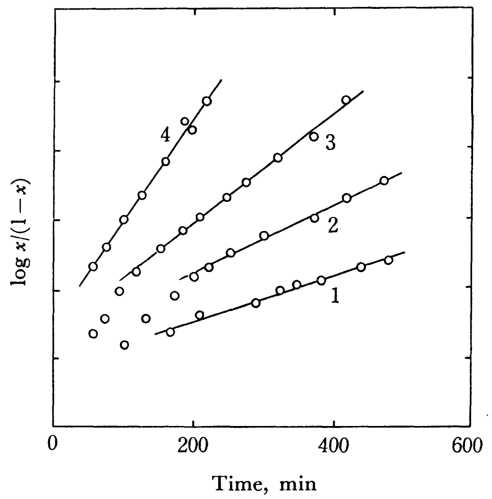

Fig. 4. Plots of $\log x/(1-x)$ versus time of $[Cr(NH_3)_6](NCS)_3$ at (1) 99, (2) 106, (3) 110 and (4) 116 °C.

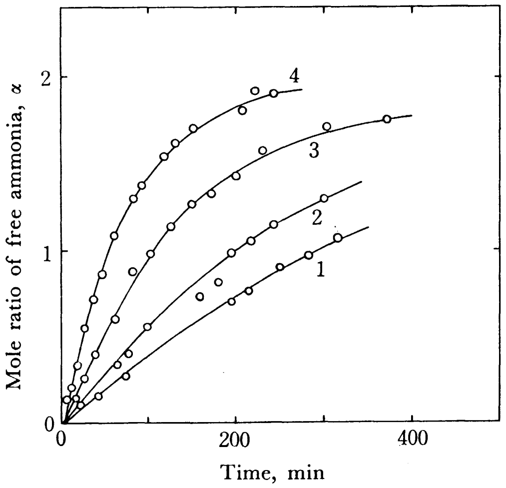

Fig. 5. Kinetic runs of $[Cr(NCS)(NH_3)_5](NCS)_2$ at (1) 91, (2) 94, (3) 101.5 and (4) 105.5 °C.

sition. Plots of $\log [x/(1-x)]$ *versus* time are given in Fig. 4, from which the second-order rate constants were determined. The kinetic parameters of Reaction (3) are given in Table 2.

Kinetic runs of $[Cr(NCS)(NH_3)_5](NCS)_2$ in the temperature range 91—105.5 °C are given in Fig. 5. The reaction is represented by

$$[Cr(NCS)(NH_3)_5](NCS)_2 \longrightarrow [Cr(NCS)_3(NH_3)_3] + 2NH_3 \qquad (4)$$

This obeys a first-order rate equation although this complex contains thiocyanate ions as in the case of $[Cr(NH_3)_6](NCS)_3$. The kinetic parameters are given in Table 2.

Discussion

Kinetic parameters of amminechromium(III) complexes are given in Table 2. The data of $[Cr(NH_3)_6]Cl_3$, $[CrCl(NH_3)_5]Cl_2$ and *cis*-$[CrCl_2(NH_3)_4]Cl$[2] are also given for the sake of comparison. For $[Cr(NH_3)_6]I_3$, the substituted complexes such as $[CrI(NH_3)_5]I_2$ and $[CrI_3(NH_3)_3]$ could not be obtained under the conditions for manometric measurement, but $[CrI(NH_3)_5]I_2$ was obtained by heating $[Cr(NH_3)_6]I_3$ in a sealed capillary tube. This indicates that the reactions including a partial equilibrium such as

$$[Cr(NH_3)_6]I_3 \longrightarrow [CrI(NH_3)_5]I_2 + NH_3$$

$$[CrI(NH_3)_5]I_2 \rightleftharpoons CrN + NH_3 + 3NH_4I$$

may take place in the case of the iodide complex; the formation of the triammine complex, as seen for $[Cr(NH_3)_6]X_3$ (X=Cl, Br and NCS), is considered to be small because of the steric hindrance, *i.e.*, an iodide ion is too large to form $[CrI_3(NH_3)_3]$.

Thus, it is supposed that the decomposition of all the complexes listed in Table 2 is essentially initiated by substitution of an outer-sphere anion for a coordinated ammonia.

For the hexamminechromium(III) complexes, the order of temperature at which the rate constant is equal to $1\times10^{-5}\,\text{sec}^{-1}$ is as follows:

$$\underset{(77^\circ C)}{[Cr(NH_3)_6](NCS)_3} < \underset{(156^\circ C)}{[Cr(NH_3)_6]Cl_3} < \underset{(184^\circ C)}{[Cr(NH_3)_6]Br_3} < \underset{(194^\circ C)}{[Cr(NH_3)_6]I_3}$$

It should be noted that the stability of the complexes depends strongly on an outer-sphere ion. The order is quite different from that of the hexamminecobalt(III) complexes whose decomposition is initiated by electron transfer from an outer-sphere anion to a central cobalt(III).[3]

Two types of mechanism are considered for the substitution reaction which includes the replacement of a ligand, dissociation (S_N1) and displacement (S_N2).

S_N1 *mechanism*:

$$[Cr(NH_3)_6]X_3 \rightleftharpoons \underset{\text{five coordination}}{[Cr(NH_3)_5]X_3} + NH_3 \longrightarrow [CrX(NH_3)_5]X_2 + NH_3$$

TABLE 2. KINETIC PARAMETERS OF THE SUBSTITUTION REACTIONS OF AMMINECHROMIUM(III) COMPLEXES IN SOLID STATE

Reaction	$k\times10^5$, sec^{-1} (t, °C)	E_a kcal/mol	$\Delta S^{\ddagger}$ e. u.
$[Cr(NH_3)_6]Cl_3 \rightarrow [CrCl(NH_3)_5]Cl_2+NH_3$	2.97(170)	30	−12
$[Cr(NH_3)_6]Br_3 \rightarrow [CrBr(NH_3)_5]Br_2+NH_3$	2.16(192)	43	12
$[Cr(NH_3)_6]I_3 \rightarrow CrN+3NH_4I+2NH_3$	3.0 (204)	49	18
$[Cr(NH_3)_6](NCS)_3 \rightarrow [Cr(NCS)_3(NH_3)_3]+3NH_3$	10.7 (99)	28	−3
$[CrCl(NH_3)_5]Cl_2 \rightarrow [CrCl_2(NH_3)_4]Cl+NH_3$	1.70(191)	38	1
$[Cr(NCS)(NH_3)_5](NCS)_2 \rightarrow [Cr(NCS)_3(NH_3)_3]+2NH_3$	1.45(85)	36	15
cis-$[CrCl_2(NH_3)_4]Cl \rightarrow$ *cis, cis*-$[CrCl_3(NH_3)_3]+NH_3$	11.0 (136)	31	−2

S_N2 *mechanism*:

$$[Cr(NH_3)_6]X_3 \rightleftharpoons \underset{\text{seven coordination}}{[CrX(NH_3)_6]X_2} \longrightarrow$$

$$[CrX(NH_3)_5]X_2 + NH_3$$

In the case of S_N1, the rate of deammonation is almost independent of the size of an outer-sphere anion and decreases with the increase of the pressure of free ammonia, while in the case of S_N2, the rate depends strongly on the size of an outer-sphere anion. From the equation

$$\Delta H^{\neq} = \Delta H_1^{\neq} - \Delta H_2^{\neq},$$

where $\Delta H_1^{\neq}$ and $\Delta H_2^{\neq}$ are the enthalpies of activation for bond breaking and bond making, respectively, it is supposed that activation energy of S_N1 is larger than that of S_N2. Moreover, the reaction of S_N1 is considered to have larger entropy of activation from the freedom of the activated complex.

Although it is impossible to assign the reaction of all the complexes listed in Table 2, $[Cr(NH_3)_6]Br_3$ and $[Cr(NH_3)_6]I_3$ might belong to S_N1 and $[Cr(NH_3)_6]Cl_3$ to S_N2 from their kinetic behavior. The reason that $[Cr(NH_3)_6](NCS)_3$ decomposed at the lowest temperature may be due to the fact that the nitrogen atom coordinated directly to chromium(III) is the smallest in size.

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