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Thermal Decomposion Reactions of Chromium(III) Complexes. Hexammine, Chloropentammine and *cis*-Dichlorotetrammine Complexes

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The thermal decomposition reactions of $[Cr(NH_3)_6]Cl_3$, $[CrCl(NH_3)_5]Cl_2$ and *cis*-$[CrCl_2(NH_3)_4]Cl$ in solid state were studied by the manometric, infrared spectroscopic and reflectance spectroscopic methods. The decomposition of these complexes in vacuum was initiated by substitution of an outer-sphere chloride ion for a coordinated ammonia. The rate constants, activation energies and activation entropies of these substitution reactions were obtained and the possible reaction processes were discussed. The products *cis,cis*-$[CrCl_3(NH_3)_3]$ and *cis,trans*-$[CrCl_3(NH_3)_3]$ were obtained on the heating of *cis*-$[CrCl_2(NH_3)_4]Cl$.

The thermal decomposition of ammine complexes of chromium(III) has been extensively investigated. Generally, these complexes were found to lose ammonia upon heating and to form non-electrolytes. Schlesinger *et al.*[1,2] obtained a green insoluble product $[CrCl_3(NH_3)_3]$ on the heating of $[CrCl(NH_3)_5]Cl_2$ in an atmosphere of dry hydrogen chloride but its structure has not been proposed. The complex of the same composition, $[CrCl_3(NH_3)_3]$, had been prepared by Werner and Halben[3] from an aqueous solution, but it was described as a blue-green solid.

Wendlandt and Chou[4] studied the thermal properties of several hexamminechromium(III) complexes by means of thermogravimetric analysis, differential thermal analysis and reflectance spectroscopy. They reported that the decomposition took place according to the equations

$$[Cr(NH_3)_6]X_3 \rightarrow [CrX(NX_3)_5]X_2 + NH_3 \quad (1)$$

$$[CrX(NH_3)_5]X_2 \rightarrow [CrX_3(NH_3)_3] + 2NH_3 \quad (2)$$

$$4[CrX_3(NH_3)_3] \rightarrow 3CrX_3 + CrN + 3NH_4X + 8NH_3 \quad (3)$$

where X represents Cl or Br.

Stembridge[5] prepared the triammine intermediate in an atmosphere of hydrogen chloride, ammonia and nitrogen, and reported that each preparation gave an identical compound as determined by X-ray diffraction and differential thermal analysis.

In the present paper, the kinetic studies of the substitution reaction between a coordinated ammonia and an outer-sphere chloride ion are presented. The formation of the blue and the green type of $[CrCl_3(NH_3)_3]$ on the heating of *cis*-$[CrCl_2(NH_3)_4]Cl$ is described, and their infrared and reflectance spectra are demonstrated.

Experimental

Apparatus and Procedure. Pressure-time curves of amminechromium(III) complexes were obtained with the apparatus reported in a previous paper.[6] The temperature of the furnace was kept within ±0.5°C. The pressure was measured with an accuracy of 1/100 mmHg by means of a mercury manometer and a microscope. The samples which were smaller than 200 mesh in size weighed 2 to 10 mg in each measurement.

The sample in a small crucible of about 1 *ml* in volume was placed in the reaction tube. The system of about 300 *ml* in volume was evacuated by a rotary pump for 1 hr. Then, the system was closed by operating a cock and the temperature of the furnace was rapidly elevated to that at which the reaction was to be investigated. After the temperature of the sample reached that of the furnace (about 20 min), the change of pressure with time was measured.

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[2] H. I. Schlesinger and D. N. Rickles, *ibid.*, **51**, 3523 (1929).

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

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

[5] W. W. Wendlandt and J. P. Smith, "The Thermal Properties of Transition-Metal Ammine Complexes," Elsevier, Amsterdam (1967), p. 109.

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Results

[Cr(NH$_3$)$_6$]Cl$_3$. Figure 1 shows pressure-time curves which were obtained with various amounts of [Cr(NH$_3$)$_6$]Cl$_3$. The initial rate was found to increase linearly with the increase of the sample amount. A series of kinetic runs for [Cr(NH$_3$)$_6$]Cl$_3$ in a temperature range from 174°C to 210°C are given in Fig. 2, where the term α means the mole fraction of liberated ammonia to chromium(III) complex. The results in Fig. 2 suggest that [Cr(NH$_3$)$_6$]Cl$_3$ liberates one mole of ammonia below 190°C, but three moles of ammonia at higher temperatures. The infrared spectra of the product obtained at 190°C were identical with those of [CrCl(NH$_3$)$_5$]Cl$_2$. The product obtained at 210°C was green in color as reported by Schlesinger,[1,2] but was found to be accompanied by a small amount of ammonium chloride. The analytical data of the green compound after being washed with cold water agreed with the calculated values for [CrCl$_3$(NH$_3$)$_3$]. These results support the processes of Eqs. (1) and (2) which were reported by Wendlandt.[4] The first-order rate constants for the reaction of Eq. (1) were calculated from the plots given in Fig. 3.

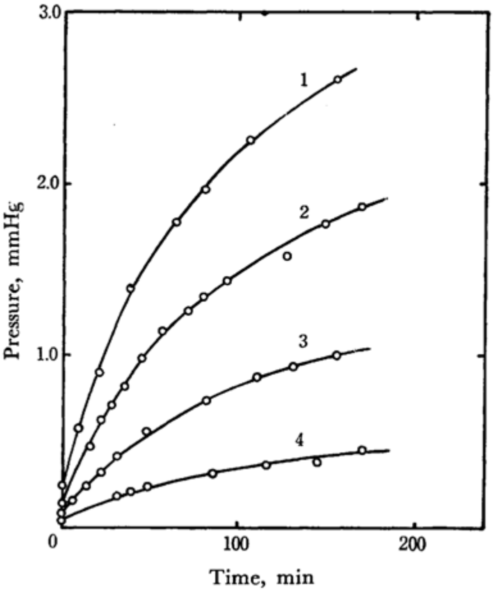


Fig. 1. Reaction rates with various sample amounts for [Cr(NH$_3$)$_6$]Cl$_3$ at 178°C.
(1) 15.2, (2) 10.1, (3) 5.0 and (4) 2.2 mg

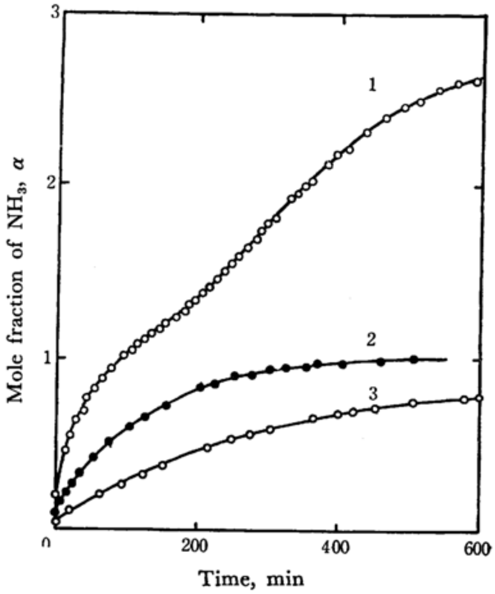


Fig. 2. Fractional decomposition curves of [Cr(NH$_3$)$_6$]Cl$_3$ at (1) 210, (2) 190 and (3) 174°C.

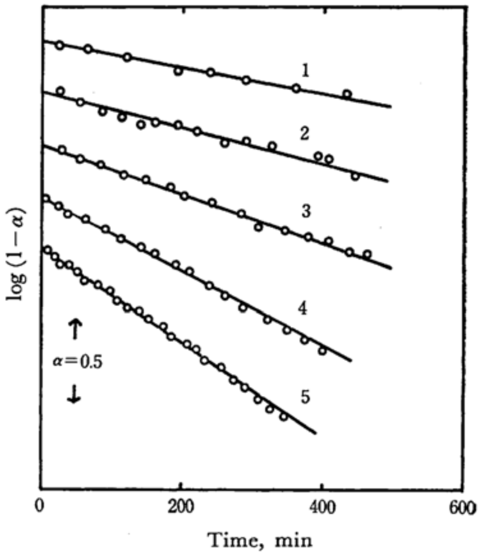


Fig. 3. Plots of the first-order rate function for [Cr(NH$_3$)$_6$]Cl$_3$ at (1) 170, (2) 174, (3) 177, (4) 183 and (5) 188°C.

[CrCl(NH$_3$)$_5$]Cl$_2$. In Fig. 4 are shown fractional decomposition curves of [CrCl(NH$_3$)$_5$]Cl$_2$ measured at various temperatures. The curve at 222°C indicates that [CrCl(NH$_3$)$_5$]Cl$_2$ liberates about two moles of ammonia. The product was green and its infrared spectra agreed with those of the product obtained from [Cr(NH$_3$)$_6$]Cl$_3$. On the curve at 210°C, however, the inflection point was observed, which suggests that an intermediate such as [CrCl$_2$(NH$_3$)$_4$]Cl exists. In order to detect the intermediate, [CrCl(NH$_3$)$_5$]Cl$_2$ was heated at 220°C for 5 hr in a sealed tube. A green product was formed, and when it was treated with cold water, part of it was dissolved to give a green solution, suggesting the formation of *trans*-[CrCl$_2$(NH$_3$)$_4$]Cl.

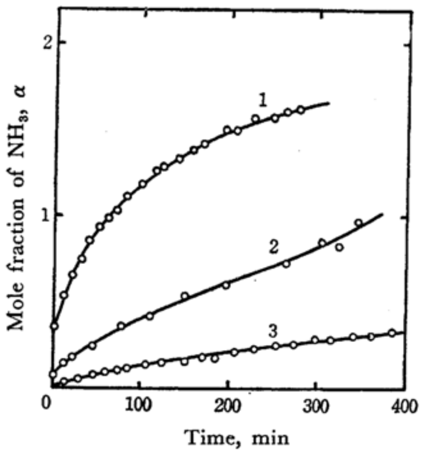


Fig. 4. Fractional decomposition curves of [CrCl-$(NH_3)_5$]Cl_2 at (1) 222, (2) 210 and (3) 191°C.

***cis*-[CrCl$_2$(NH$_3$)$_4$]Cl.** In Fig. 5 are shown fractional decomposition curves of *cis*-[CrCl$_2$-$(NH_3)_4$]Cl measured at various temperatures. One mole of ammonia was liberated from *cis*-[CrCl$_2$-$(NH_3)_4$]Cl. The product which was obtained by treating at 153°C for 3 hr was blue and its analytical data agreed with the calculated values for [CrCl$_3$-$(NH_3)_3$]. When this blue compound was heated at 153°C for 3 days, the blue color gradually changed into green without any decomposition. The infrared spectra of both compounds are shown in Fig. 6. The blue compound gives symmetric deformation bands at 1280 and 1255 cm^{-1} and the NH$_3$ rocking bands at 780, 735 and 700 cm^{-1}, whereas the green compound gives the corresponding bands at 1280 and 735 cm^{-1}, respectively.

The reflectance spectra of both compounds are shown in Fig. 7. The blue compound in solid state has two absorptions at 17200 (the first band) and 23300 cm^{-1} (the second band), whereas the

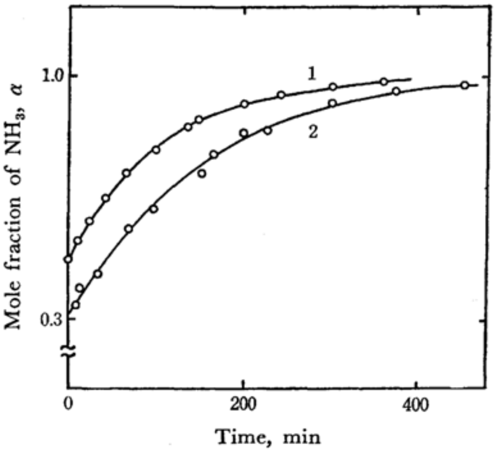


Fig. 5. Fractional decomposition curves of *cis*-[CrCl$_2$(NH$_3$)$_4$]Cl at (1) 142 and (2) 136°C.

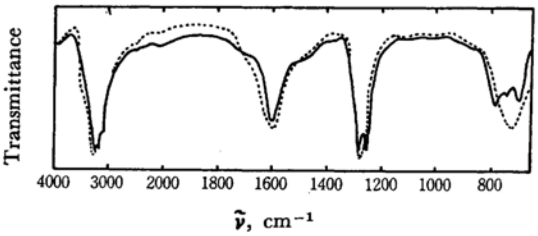


Fig. 6. Infrared absorption spectra of blue (solid line) and green (broken line) compounds in KBr disk.

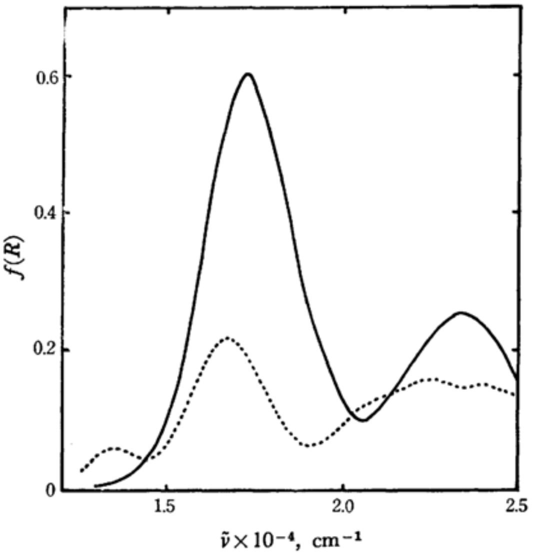


Fig. 7. Reflectance spectra of blue (solid line) and green (broken line) compounds. The spectra were plotted used the Kubelka-Munk function $f(R)=(1-R)^2/2R$, where R is the reflectance.

TABLE 1. X-RAY DIFFRACTION PATTERN OF [CrCl$_3$(NH$_3$)$_3$] (CuK_α, $\lambda=1.5418$ Å)

Blue compound		Green compound	
d	*i*	*d*	*i*
5.609	m	5.644	m
5.539	s	5.574	s
5.215	f	5.277	m
4.901	m	5.126	m
4.796	f	4.928	m
3.739	m	3.969	m
3.708	m	3.900	f
3.132	f	3.770	f
2.979	m	2.849	m
2.867	f	2.831	f
2.747	m	2.763	m
2.557	s	2.747	m
2.398	f	2.730	m

s, strong; m, medium; f, fine

green compound has three absorptions. The weak absorption in a low energy region (13400 cm^{-1}) may be due to the spin-forbidden transition ($^4A_{2g} \rightarrow {}^2E_g$). The absorptions in the region of the second band split into three parts. The X-ray diffraction pattern of the blue compound was different from that of the green compound as shown in Table 1.

When *cis*-$[CrCl_2(NH_3)_4]Cl$ was heated at 165°C for 10 days in a sealed tube, a product which was partly dissolved in cold water to give a green solution was obtained. This fact suggests that the product contained an electrolyte such as *trans*-$[CrCl_2(NH_3)_4]Cl$.

Discussion

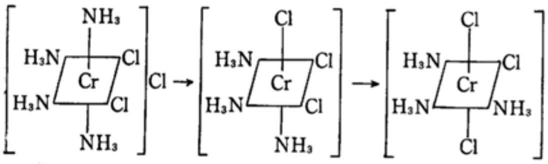
The kinetic parameters of the substitution reactions in solid state are given in Table 2. The order of increasing rates of reaction was as follows:

$$[CrCl(NH_3)_5]Cl_2 < [Cr(NH_3)_6]Cl_3 < cis\text{-}[CrCl_2(NH_3)_4]Cl$$

TABLE 2. KINETIC PARAMETERS FOR THE SUBSTITUTION REACTION OF SOME CHROMIUM(III) COMPLEXES IN SOLID STATE

Complex	$k\times10^5$, sec^{-1} (Temp, °C)	E_a kcal/mol	$\Delta S^{\neq}$ e.u.
$[Cr(NH_3)_6]Cl_3$	4.0(174), 8.5(183)	30	−12
$[CrCl(NH_3)_5]Cl_2$	2.8(198), 7.7(210)	39	1.4
cis-$[CrCl_2(NH_3)_4]Cl$	11 (136), 16 (142)	31	−2.3

From the standpoint of a steric hindrance, *cis*-$[CrCl_2(NH_3)_4]Cl$ may most easily lose ammonia coordinated at the *cis*-position to both chloride ions. This led to the conclusion that trichlorotriammine complex obtained by heating of *cis*-$[CrCl_2(NH_3)_4]Cl$ must have a *cis,cis*-configuration. The *cis,cis*-configuration, however, is less stable than the *cis,trans*-configuration, if a steric hindrance is considered. Therefore, *cis,cis*-$[CrCl_3(NH_3)_3]$ will convert to *cis,trans*-$[CrCl_3(NH_3)_3]$ by heating for a long time.



These considerations suggest that the blue and the green compounds obtained in the present study correspond to *cis,cis*-$[CrCl_3(NH_3)_3]$ and *cis,trans*-$[CrCl_3(NH_3)_3]$, respectively. The reflectance spectra shown in Fig. 7 also support the above consideration, *i. e.*, the absorption bands of the blue compound are symmetrical and their maxima are at higher frequencies than those of the absorption bands of the green compound.

Hexamminechromium(III) chloride had a small activation entropy, which suggests the possibility of a seven-coordinated activated complex. If the substitution reactions of hexammine complexes take place through a seven-coordinated state, kinetic parameters must be strongly influenced by an outer-sphere ion. Actually, the results obtained with $[Cr(NH_3)_6]Cl_3$ greatly differed from those obtained with $[Cr(NH_3)_6]Br_3$. The kinetic parameters for $[Cr(NH_3)_6]Br_3$ are:

$$k = 2.2\times10^{-5}\ \text{sec}^{-1} \text{ at } 192°\text{C},$$

$$E_a = 43\ \text{kcal/mol}$$

$$\text{and } \Delta S^{\neq} = 12\ \text{e.u.}$$

From the above results and consideration, possible reaction processes of ammine chromium(III) complexes could be represented as follows:

$$\begin{tikzcd}
{[Cr(NH_3)_6]Cl_3} \arrow[d, "-NH_3"] & \\
{[CrCl(NH_3)_5]Cl_2} \arrow[d, "-NH_3"] & \\
\boxed{trans\text{-}[CrCl_2(NH_3)_4]Cl} \arrow[d, "-NH_3"] & cis\text{-}[CrCl_2(NH_3)_4]Cl \arrow[l, "\text{isomerization}"', "(A)"] \arrow[d, "-NH_3", "(B)"'] \\
cis,trans\text{-}[CrCl_3(NH_3)_3] & cis,cis\text{-}[CrCl_3(NH_3)_3] \arrow[l, "\text{isomerization}"']
\end{tikzcd}$$

However, the formation of *trans*-$[CrCl_2(NH_3)_4]Cl$ is not yet confirmed. As the process (B) was strongly depressed by the pressure of ammonia, *cis,cis*-$[CrCl_3(NH_3)_3]$ was obtained only by heating in vacuum. Therefore, the process (A) takes place to a considerable extent when *cis*-$[CrCl_2(NH_3)_4]Cl$ is heated under the pressure of ammonia.

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