The Mechanism of the Thermal Decomposition of Hexamminecobalt(III) Chloride

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The thermal decomposition of hexamminecobalt(III) complexes has been extensively studied by several researchers,[1-6] and the stoichiometric relation,

$$6[Co(MH_3)_6]Cl_3(s) \rightarrow$$
$$6CoCl_2(s) + N_2(g) + 6NH_4Cl(s) + 28NH_3(g)$$

has been proposed for the complete decomposition.[6] Its mechanism, however, is not fully understood. In the course of a reinvestigation of the thermal decomposition of metal complexes in this laboratory, some preliminary results suggested that the decomposition of cobalt(III) complexes was often initiated by the electron transfer from either a ligand atom or an outer-sphere ion to the central cobalt(III) atom, forming a less stable cobalt(II) complex. These results have been confirmed by polarographic and infrared spectroscopic measurements of the thermal decomposition product of hexamminecobalt(III) chloride, as well as by the measurement of the infrared spectra of the complex at elevated temperatures. The results will be briefly presented in this paper. A similar conclusion has been obtained by Wendlandt and Smith[7] from the thermomagnetic measurement of cobalt(III) ammine complexes.

Experimental

Hexamminecobalt(III),[8] hexamminecobalt(II)[9] and hexamminechromium(III)[10] chlorides were prepared by the methods given in the literature cited; they were identified by the measurement of their infrared absorption spectra.

The thermogravimetric curves were recorded with an automatic-recording thermobalance, Shimadzu Thermano Balance Type RT-2, in a nitrogen atmosphere. A 400-mg. sample was used in each measurement unless otherwise stated. The furnace heating rate was approximately linear with the time at about 3°C per min. The particle sizes of the samples ranged between 100 and 200 mesh.

Polarograms were recorded with a Yanagimoto PR-2 Polarorecorder equipped with an automatic potential scanner. The samples which had been taken out of the furnace were dissolved in supporting electrolyte solutions containing 1 M ammonium chloride, 1 M ammonium hydroxide and 0.005% gelatin. The dropping mercury electrode used had an m value of 2.06 mg./sec. and a drop time, t_d, of 3.72 sec., when measured at -0.80 V. vs. SCE in the same supporting electrolyte solution.

A Hitachi EPI-2G double-beam instrument with a KBr foreprism and gratings was used for the measurement of the infrared absorption spectra. The KBr disk method was employed unless otherwise stated.

Results and Discussion

The thermogravimetric curves of hexamminecobalt(III), hexamminecobalt(II) and hexamminechromium(III) chlorides are reproduced

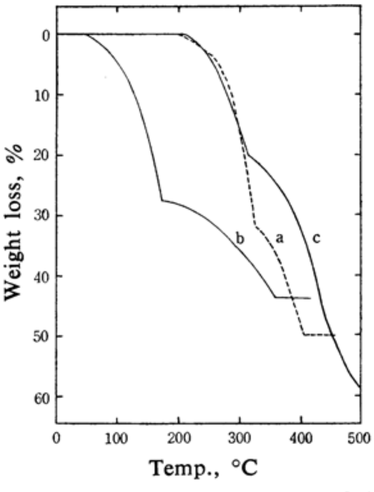

Fig. 1. Thermogravimetric curves of (a) $[Co(NH_3)_6]Cl_3$, (b) $[Co(NH_3)_6]Cl_2$ and (c) $[Cr(NH_3)_6]Cl_3$ obtained in nitrogen atmosphere.

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[7] W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 1267 (1963).

[8] J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," Vol. II, Ed. by W. C. Fernelius, McGraw-Hill, New York (1946), p. 216.

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in Fig. 1. The decomposition of hexamminecobalt(III) chloride begins at 205°C, whereas that of hexamminecobalt(II) chloride begins at 50°C.

Polarograms of heated samples of hexamminecobalt(III) chloride are given in Fig. 2, where, for convenience of comparison, the current is represented with a value for one millimolar of the total concentration of cobalt(III) and cobalt(II). The temperatures at which the samples were taken out of the furnace are given in Table I. On curves 1 to 4, the first wave starts around −0.1 V. vs. SCE, which corresponds to the reduction of cobalt(III) to cobalt(II). The change in the limiting current with various heights of the mercury reservoir shows that the limiting current is diffusion-controlled. The second wave can be attributed to the reduction of cobalt(II) to cobalt(0). The height of the first wave decreased with an increase in the temperature at which the samples were treated. This indicates that the amount of cobalt(III) in the sample is less when treated at a higher temperature. Curve 5, which was obtained with the sample taken out of the furnace at 305°C, shows that the cobalt(III) was completely reduced to cobalt(II). Percentages of the decrease in weight and cobalt(III) content are given in Table I.

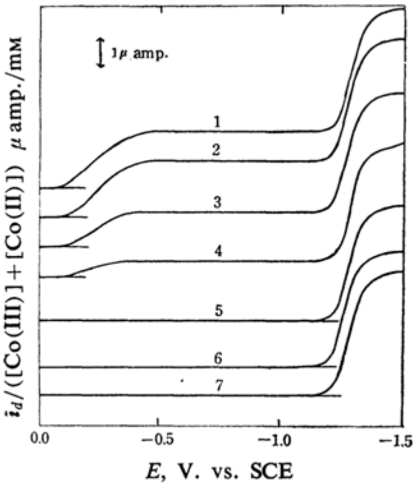

Fig. 2. Polarograms of the $[Co(NH_3)_6]Cl_3$ subjected to the thermal treatment, being recorded in 1 M NH_4Cl - 1 M NH_4OH containing 0.005% gelatin: The numbers represent the sample numbers given in Table I. Polarograms are corrected for the residual currents and the current is represented with the value for one millimolar of the total concentration of Co(III) and Co(II).

TABLE I. LOSS IN WEIGHT AND Co(III) CONTENT IN THE $[Co(NH_3)_6]Cl_3$ SUBJECTED TO THE THERMAL TREATMENT

Sample no.	Temp.* °C	Loss in weight, %	Loss in Co(III) content, %
1	Not treated	—	—
2	170	0	0
3	285	11.9	35
4	295	22.8	76
5	305	30.7	100
6	340	37.6	100
7	475	48.6	100

* Temperatures at which the samples were taken out of the furnace.

Infrared spectra of hexamminecobalt(III) chloride treated at various temperatures are given in Fig. 3. The absorption band due to the NH_3 symmetric deformation vibrations at 1320 cm^{-1} and that due to the NH_3 rocking vibrations at 830 cm^{-1} decrease in intensity as temperature increases until they disappear at 340°C. A new absorption band appears at 1400 cm^{-1}; this is assigned to the ν_4 vibration of NH_4^+ ions. In samples 6 and 7, the NH_3 degenerate deformation band at 1608 cm^{-1} overlaps with a sharp ν_4 band of free ammonia molecules. These changes in the infrared absorption spectra may indicate a decrease in cobalt(III) content as well as

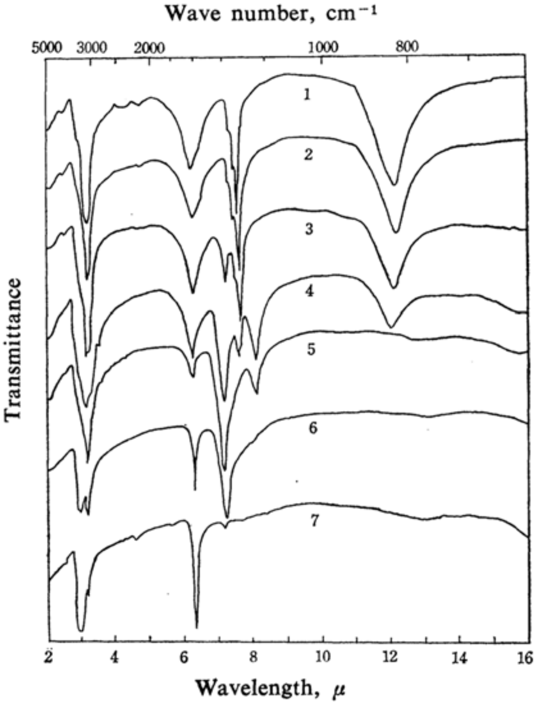

Fig. 3. Infrared absorption spectra of the $[Co(NH_3)_6]Cl_3$ subjected to the thermal treatment: The numbers represent the sample numbers given in Table I. Transmittance scale displaced arbitrarily.

the formation of ammonium ions and free ammonia molecules. These experimental results indicate that, at higher temperatures, cobalt(III) in a hexammine complex is reduced to cobalt(II) to form a less stable cobalt(II) ammine complex, which then immediately dissociates ammonia molecules and undergoes decomposition, as may be seen from the thermogravimetric curve of hexamminecobalt(II) chloride in Fig. 1. Mori and Tsuchiya[6] have proposed that the thermal decomposition of hexamminecobalt(III) chloride proceeds according to the reaction,

$$[Co(NH_3)_6]Cl_3(s) \rightarrow [CoCl(NH_3)_5]Cl_2(s) + NH_3(g)$$

However, they also found the formation of ammonium chloride at temperatures higher than 170°C. This result seems to indicate that the decomposition reaction is not so simple as they proposed.

In this connection, the infrared absorption spectra of hexamminecobalt(III) chloride which were recorded at elevated temperatures by means of the potassium chloride disks should be noted (Fig. 4). The NH_4^+ band at 1400 cm^{-1} appears on the spectra obtained at 200°C and higher. At temperatures higher than 260°C, two new absorption bands are observed, at 1160 cm^{-1} and 655 cm^{-1}; these are considered to be due to the NH_3 symmetric deformation vibration and the NH_3 rocking vibration of cobalt(II) ammine complexes respectively. Cobalt(III) in the hexammine complex is reduced to cobalt(II) by accepting an electron from either a ligand molecule or an outer-sphere ion to form a cobalt(II) ammine complex. Since the complex is kept in the potassium chloride disk, it retains its structure without dissociating all of the ammonia molecules and gives the absorption bands characteristic of the cobalt(II) ammine complex.

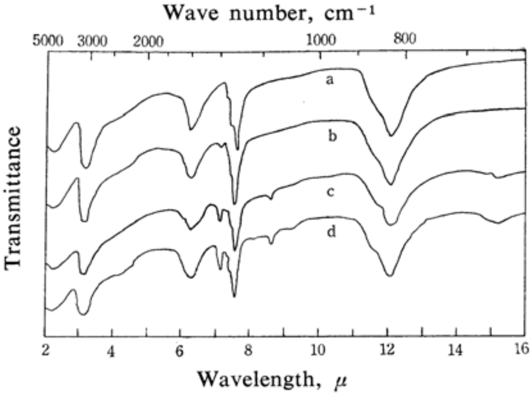

Fig. 4. Infrared absorption spectra of the $[Co(NH_3)_6]Cl_3$ in KCl disks at (a) room temperature, (b) 200°C, (c) 260°C and (d) after cooling of (c). Transmittance scale displaced arbitrarily.

It has been known that the Co–N bond in cobalt(III) ammine complexes is stronger than the Cr–N bond in chromium(III) ammine complexes.[11] This seems to contradict the result obtained from the thermogravimetric measurement, that hexamminecobalt(III) chloride does not decompose more easily than hexamminechromium(III) chloride (see Fig. 1). This contradiction may be explained by considering that the decomposition of hexamminecobalt(III) chloride is initiated by the electron transfer from either a ligand or an outer-sphere ion and that the decompositions of these two complexes, consequently, proceed according to entirely different mechanisms.

Summary

The thermal decomposition of hexamminecobalt(III) chloride has been investigated by thermogravimetric, polarographic and infrared spectroscopic method. The results indicate that the reaction is initiated by the electron transfer from either a ligand molecule or an outer-sphere ion to the central cobalt atom, forming a less stable cobalt(II) complex, which immediately dissociates ammonia molecules and undergoes decomposition.

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