*Thermodynamic Studies on Cobalt Complexes. III. Thermal Dissociation of Hexamminecobalt(III) Chloride and Chloropentamminecobalt(III) Chloride**

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Compared with a great number of studies on the reaction of complex salts in the aqueous solution, the investigations on the thermal decomposition of complexes in the solid state are few. These include studies on ammines of cobalt(1,2), nickel(3), platinum(4) and indium(5) and on nitroammines of platinum(6) and cobalt(7,8). Among these studies the data on dissociation pressure were reported only for cobalt- and nickelammine complexes(1,3) and thermodynamic discussion of them has never been made. For this reason we started the present study and determined the dissociation pressure of hexamminecobalt(III) chloride and chloropentamminecobalt(III) chloride. The free energy change of dissociation of the former complex was calculated and the standard free energy of formation of the latter complex was obtained.

Experimental

Hexamminecobalt(III) chloride was prepared by Bjerrum's method(9) and chloropentamminecobalt(III) chloride, by the method of Jörgensen(10). The apparatus used for the determination of the dissociation pressure is shown in Fig. 1.

After the sample was put into the reaction vessel, made of heat resistant borosilicate glass, A, the whole apparatus was evacuated. The cocks B and C were closed and the temperature of the electric furnace F was held at the desired constant temperature by an automatic regulator. The dissociation pressure was determined by the manometer M.

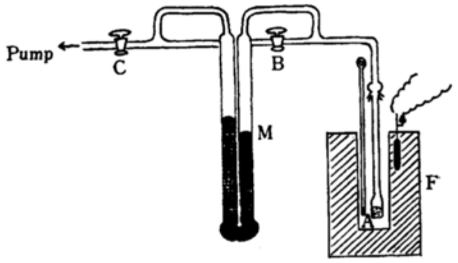

Fig. 1. Apparatus.

Results and Discussion

Dissociation Pressure of Hexamminecobalt(III) Chloride. — The dissociation pressure of hexamminecobalt(III) chloride was measured at several temperatures in the range of 83～173°C. As we found that the decomposition products consist of chloropentamminecobalt(III) chloride and ammonia, but not of cobaltous chloride, the decomposition reaction can be expressed by the following equation,

$$[Co(NH_3)_6]Cl_3(s) = [Co(NH_3)_5Cl]Cl_2(s) + NH_3(g)$$

The values of dissociation pressure determined for hexamminecobalt(III) chloride are listed in Table I.

Biltz(1) reported that the decomposition of hexamminecobalt(III) chloride began at 175～180°C and chloropentamminecobalt(III) chloride was formed at 216～220°C. Clark et al(2). reported that the decomposition began at 173°C and ammonium chloride appeared at 181°C. However, we detected the evolution of ammonia at 160°C by passing the decomposition gas into water containing phenolphthalein, and could determine the dissociation pressure at a temperature lower than that pointed out by Biltz(1) and Clark(2).

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1) W. Biltz, *Z. anorg. Chem.*, **83**, 177 (1913).

2) G. L. Clark, A. J. Quick and W. D. Harkins, *J. Am. Chem. Soc.*, **42**, 2483 (1920).

3) W. Biltz and B. Fetkenheuer, *Z. anorg. Chem.*, **83**, 163 (1913).

4) A. A. Grinberg and B. V. Ptitzuin, *Izv. Inst. Platin*, **9**, 73 (1932); *Chem. Abstr.*, **27**, 1290 (1933),

5) V. G. Tronev and A. P. Kochetkova, *Khim. Redkikh Elementov, Akad. Nauk S. S. S. R., Inst. Obshchei i Neorg. Khim.*, (1957), No. 3, p. 87; *Chem. Abstr.*, **52**, 2634b (1958).

6) L. A. Chugaev and S. S. Kil'tuinovich, *Izv. Inst. Platin*, **2**, 70 (1921); *Chem. Abstr.*, **20**, 2961 (1926).

7) A. V. Ablov and N. I. Lobanov, *Zhur. Obshchei Khim.*, **25**, 648 (1955); *Chem. Abstr.*, **49**, 12170h (1955).

8) A. V. Ablov, E. A. Popa and T. A. Malkova, *Zhur. Neorg. Khim.*, **1**,2716 (1956); *Chem. Abstr.*, **50**, 13634i (1956).

9) W. C. Fernelius, "Inorganic Syntheses", Vol II. McGraw Hill Book Co., Inc., New York, N. Y. (1946), p. 216.

10) S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 281 (1892).

TABLE I. DISSOCIATION PRESSURE OF HEXAMMINECOBALT(III) CHLORIDE

Temp. (°C)	$1/T\times10^3$	Dissociation pressure (mmHg)	$\log p_{mm}$
83	2.808	0.70	−0.1549
92	2.739	1.15	0.0607
102	2.666	1.45	0.1614
114	2.583	2.19	0.3404
124	2.518	2.89	0.4609
129	2.487	3.49	0.5428
133	2.462	3.94	0.5955
138	2.432	4.59	0.6618
143	2.403	5.33	0.7267
149	2.369	6.04	0.7810
153	2.347	6.98	0.8439
158	2.320	7.73	0.8882
162	2.298	8.87	0.9479
168	2.267	10.33	1.0141
173	2.242	12.21	1.0867
176	2.227	14.26	1.1541

Biltz[1] observed 14 mmHg as the dissociation pressure of hexamminecobalt(III) chloride at 174°C, which is relatively close to our value, but he did not measure it at a temperature lower than 174°C. On the other hand, it was found by us that ammonium chloride began to form at about 170°C and the decomposition pressure rapidly increased at higher temperatures.

The logarithm of the dissociation pressure was plotted against the reciprocal of the absolute temperature (Curve a in Fig. 2). The obtained curve is approximately linear except the two points at 173 and 176°C. The equation of the straight line is calculated by the least square method as follows:

$$\log p_{mm}=5.7705-2101.40/T \qquad (1)$$

From this equation the heat of dissociation is obtained as $\Delta H=9612$ cal.

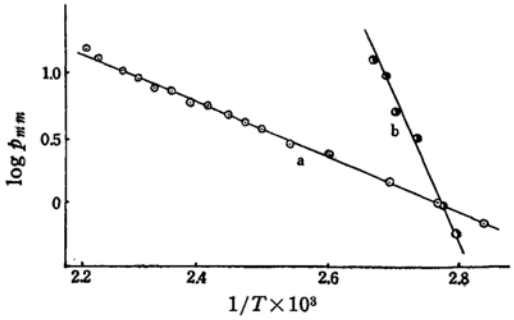

Fig. 2. The relationship between the dissociation pressure and the temperature for
a: hexamminecobalt(III) chloride
b: chloropentamminecobalt(III) chloride.

Biltz[1] obtained the value of about 18 kcal. as the heat of dissociation from his data determined at 174∼216°C by means of the Nernst formula, but we recalculated the value of 28 kcal. from his data.

If the value of $\Delta H=9612$ cal. determined above at the temperature in the range of 83∼173°C is assumed to be approximately equal to that at 25°C, it agrees fairly well with the value of 8.56 kcal. calculated from the heats of formation of $[Co(NH_3)_6]Cl_3(s)$, (−274.1 kcal.[11]), $[Co(NH_3)_6Cl]Cl_2(s)$, (−254.5 kcal.[12]) and $NH_3(g)$ (−11.04 kcal.[13]).

The standard free energy change of decomposition calculated by the formula 1 is:

$$\Delta G^\circ=-\boldsymbol{R}T\ln p=9612-13.218T \qquad (2)$$

The values of $\Delta G^\circ_{298}=5672$ cal. and $\Delta S^\circ_{298}=13.22$ e. u. are obtained.

The standard free energy of formation of complex salts in the solid state has never been known except that of $[Co(NH_3)_6]Cl_3(s)$, which was calculated by the present authors from the solubility data in the preceding paper[14]. By using this value and the equation 2 the standard free energy of formation of $[Co(NH_3)_5Cl]Cl_2(s)$ in the solid state is calculated to be:

$$\Delta G^\circ=-254008+365.99T$$

and the value of $\Delta G^\circ_{298}=-144.90$ kcal. is obtained.

Dissociation Pressure of Chloropentamminecobalt(III) Chloride. — The dissociation pressure of chloropentamminecobalt(III) chloride was measured by the same apparatus as that shown in Fig. 1. The results are given in Table II.

TABLE II. DISSOCIATION PRESSURE OF CHLOROPENTAMMINECOBALT(III) CHLORIDE

Temp. (°C)	$1/T\times10^3$	Dissociation pressure (mmHg)	$\log p_{mm}$
88	2.769	0.50	−0.3010
93	2.732	1.49	0.1732
96	2.709	3.08	0.4886
99	2.687	5.93	0.7731
101	2.673	9.51	0.9782
103	2.659	12.15	1.0846

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[11] K. B. Yatsimirskiĭ and L. L. Pankowa, *Zhur. Obshchei Khim.*, **19**, 617 (1949); K. B. Yatsimirskiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 162.

[12] A. B. Lamb and J. P. Simmons, *J. Am. Chem. Soc.*, **43**, 2188 (1921).

[13] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances", Reinhold Publishing Corp., New York, N. Y. (1936).

[14] M. Mori, R. Tsuchiya and Y. Okano, This Bulletin, **32**, 462 (1959).

Biltz[1] found that chloropentamminecobalt(III) chloride decomposed at 180~220°C, but our results show that the decomposition takes place at a lower temperature. In contrast to hexamminecobalt(III) chloride, the increase of the dissociation pressure of chloropentamminecobalt(III) chloride with the rise of temperature is quite large. In other words, although the dissociation pressure of chloropentamminecobalt(III) chloride is less than that of hexamminecobalt(III) chloride at a temperature lower than 90°C, the thermal dissociation of the former exceeds that of the latter at a temperature higher than 92°C, and the dissociation pressure of the former at 103°C is nearly the same as that of the latter at 173°C. It is concluded from these facts that chloropentamminecobalt(III) chloride is stable at a temperature below 90°C and becomes suddenly unstable at a temperature above 192°C.

The plots of the logarithm of the dissociation pressure against the reciprocal of the absolute temperature give a straight line as shown by the line b in Fig. 2. The equation of the straight line is calculated as follows:

$$\log p_{mm} = 36.4869 - 13288.3/T$$

From this equation as the heat of dissociation the value of $\Delta H = 60.78$ kcal. is obtained. It is in good agreement with the value, 60.84 kcal., which is calculated from the heats of formation of components of the following dissociation reaction,

$$[Co(NH_3)_5Cl]Cl_2(s) = CoCl_2(s) + 1/6\,N_2(g)$$
$$+ NH_4Cl(s) + 11/3\,NH_3(g)$$

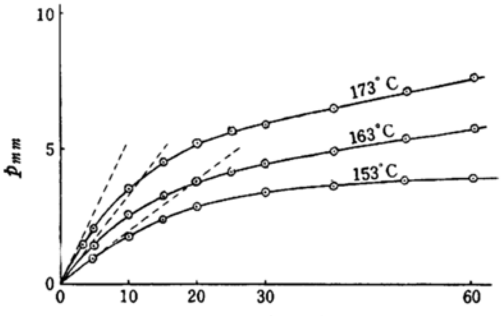
$$\Delta H_{f[Co(NH_3)_5Cl]Cl_2} = -254.5 \text{ kcal.}^{12)}$$
$$\Delta H_{fCoCl_2} = -77.8 \text{ kcal.}^{15)}$$
$$\Delta H_{fNH_4Cl} = -75.38 \text{ kcal.}^{13)} \text{ and}$$
$$\Delta H_{fNH_3} = -11.04 \text{ kcal.}^{13)}$$

The Rate of Thermal Dissociation of Hexamminecobalt(III) Chloride.—The rate of the thermal dissociation of this complex was determined by tracing the pressure change of ammonia produced in the decomposition by the apparatus shown in Fig. 1. The results are shown in Table III and Fig. 3.

The velocity constant k at the time when the dissociation begins to take place is given by the tangent of the velocity curve at zero point in Fig. 3. The plots of logarithm of the velocity constant against the reciprocal of the absolute temperature give a straight line as shown in Fig. 4, from which the value of 17.98

TABLE III. RATE OF DISSOCIATION OF HEXAMMINECOBALT(III) CHLORIDE

Temp. (°C)	153	163	173
Time (min.)	Dissociation pressure p mmHg		
3	—	1.05	1.50
5	0.95	1.55	2.35
10	1.65	2.59	3.64
15	2.29	3.14	4.54
20	2.84	3.58	5.18
25	—	3.98	5.53
30	3.14	4.33	5.83
40	3.54	4.98	6.67
50	3.74	5.33	7.32
1 (hr.)	3.99	5.58	7.67
1.5	4.44	6.17	9.01
2	4.84	6.47	10.26
2.5	5.13	7.02	10.86
3	5.28	7.42	11.31
4	5.83	—	11.55
k	0.2005	0.3390	0.5220
$\log k$	$\bar{1}.3021$	$\bar{1}.5302$	$\bar{1}.7177$
$1/T \times 10^3$	2.347	2.293	2.242



Time (min.)

Fig. 3. Rate of dissociation of hexamminecobalt(III) chloride.

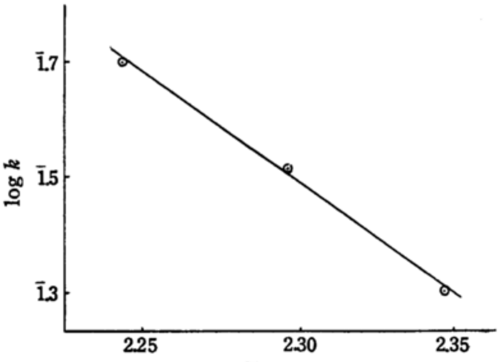


Fig. 4. The relationship between the velocity constant and the temperature for hexamminecobalt(III) chloride.

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15) K. Sano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **58**, 370 (1937).

kcal. is obtained as the activation energy of the thermal dissociation of hexamminecobalt(III) chloride.

The Rate of Thermal Dissociation of Chloropentamminecobalt(III) Chloride.—The determination was made by the same method as that used in the above experiment for hexamminecobalt(III) chloride. The results are shown in Table IV and Fig. 5.

The plots of the logarithm of the velocity constant k at the time when the dissociation begins to take place against the reciprocal of the absolute temperature give a straight line as shown in Fig. 6, from which the value of 54.06 kcal. is obtained as the activation energy of the thermal dissociation of chloropentamminecobalt(III) chloride.

TABLE IV. RATE OF DISSOCIATION OF CHLOROPENTAMMINECOBALT(III) CHLORIDE

Temp. (°C)	96	100	103
Time (min.)	Dissociation pressure p mmHg		
2	—	—	0.25
5	—	0.35	0.60
8	—	—	0.90
10	0.40	0.65	1.10
15	—	0.90	1.55
20	0.65	1.10	2.05
25	—	1.30	2.29
30	0.95	1.50	2.49
40	1.10	1.75	3.34
50	1.35	2.00	3.83
1 (hr.)	1.44	2.19	4.23
1.5	1.78	2.69	5.78
2	1.93	3.14	6.57
2.5	2.19	3.64	7.42
3	2.45	3.99	8.27
4	2.58	4.29	9.31
k	0.0354	0.0782	0.135
$\log k$	$\bar{2}.5490$	$\bar{2}.8932$	$\bar{1}.1303$
$1/T \times 10^3$	2.709	2.680	2.659

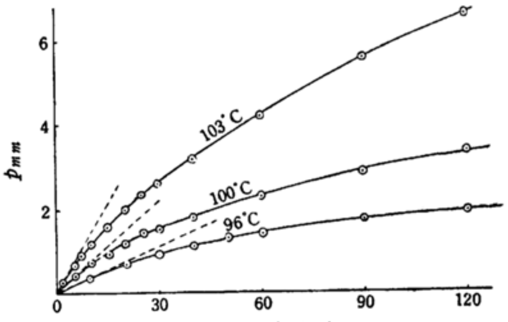

Fig. 5. Rate of dissociation of chloropentamminecobalt(III) chloride.

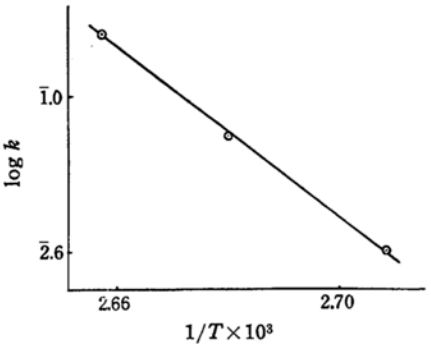

Fig. 6. The relationship between the velocity constant and the temperature for chloropentamminecobalt(III) chloride.

As shown above, the heat of dissociation and the activation energy of chloropentamminecobalt(III) chloride are very high compared with those of hexamminecobalt(III) chloride. These data give an explanation for the fact that chloropentamminecobalt(III) chloride produced in the thermal dissociation of hexamminecobalt(III) chloride does not suffer from further decomposition so far as the latter is present, even if the dissociation pressure of the former is very high.

Summary

1. The thermal dissociation of hexamminecobalt(III) and chloropentamminecobalt(III) chlorides was studied. The heats of dissociation calculated from the the data of dissociation pressure determined are in good agreement with the values calculated from other sources.

2. The free energy change of dissociation of hexamminecobalt(III) chloride was calculated and by combining this value with the standard free energy of formation of that complex previously obtained, the standard free energy of formation of chloropentamminecobalt(III) chloride in the solid state was determined.

3. The rate of the thermal dissociation of hexamminecobalt(III) and chloropentamminecobalt(III) chlorides was determined and the activation energies of the dissociation were calculated.

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