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Kinetic Studies of Thermal Decomposition Reactions of Metal Complexes. Hexammine- and Halogenopentamminecobalt(III) Complexes

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The thermal decomposition reactions of amminecobalt(III) complexes in solid state were studied mainly by the polarographic, the manometric and the infrared spectroscopic methods. The decomposition processes of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]Br_3$, $[Co(NH_3)_6]I_3$, $[CoCl(NH_3)_5]Cl_2$, $[CoBr(NH_3)_5]Cl_2$, $[CoCl(NH_3)_5]Br_2$ and $[CoBr(NH_3)_5]Br_2$ *in vacuo*, in air atmosphere and in sealed tube were investigated. In all cases, the decomposition of these complexes was initiated by electron transfer from an outer-sphere anion or a ligand to the central cobalt(III) cation. The reaction processes and products were found to be much different with the different environments, but little different with the different halide ions. The rate constants, frequency factors and activation energies for the electron transfer reactions were obtained.

Many reports on the thermal decomposition reactions of amminecobalt(III) complexes have been presented, but only a few reports are concerned with the kinetics of the reactions.[1-3] In previous papers,[4,5] Tanaka *et al.* suggested that the decomposition of amminecobalt(III) complexes was initiated by the electron transfer from either a ligand or an outer-sphere anion to the central cobalt(III) ion, forming thermally less stable cobalt(II) complexes. Since those studies are rather qualitative and incomplete as to a series of different anions and different environments, a quantitative investigation of the reaction processes of various amminecobalt(III) complexes seems to be worth while.

In this paper, the kinetic parameters of those reactions which were obtained by the polarographic and the manometric methods are presented and the possible reaction processes are discussed.

Experimental

Materials. $[Co(NH_3)_6]X_3$[6] (X : Cl, Br, I), $[CoX(NH_3)_5]Y_2$[7,8] (X, Y: Cl, Br), $[Co(NH_3)_6]Cl_2$[9] and $[CoCl_2(NH_3)_4]Cl\cdot H_2O$[10] were prepared according to the methods given in the literatures.

Apparatus and Procedure. A Yanagimoto PR-2 pen-recording polarograph was used for the determinations of cobalt(III) and cobalt(II) contents in the samples subjected to the thermal treatment. The dropping mercury electrode used had an m value of 1.58 mg/sec, and a drop time, t_d, of 4.0 sec, when measured at -0.7 V *vs.* SCE at 25°C in a deaerated solution containing 0.5 M ammonium chloride, 0.5 M ammonium hydroxide and 0.005% gelatin.

Decomposition pressure - time curves of the amminecobalt(III) complexes were obtained by means of the apparatus which was reported by Mori and Tsuchiya.[1] The temperature of the sample was controlled in a range of ± 0.5°C by means of a mercury regulator and an electric furnace. Samples which were smaller than 200 mesh in size weighed 50 mg in each measurement. The decomposition pressure was measured with a mercury manometer and a cathetometer. A Hitachi EPI-2G recording infrared spectrophotometer equipped with a potassium bromide foreprism and gratings was used for the measurements of infrared absorption spectra. The potassium bromide disk and the Nujol mull method were used.

The rate constants of the electron transfer reactions were determined by the polarographic measurement of the contents of cobalt(III) and cobalt(II) in the sample. The amount of the sample was 10 mg in each case. The samples which had been taken out of the furnace without exposing to air were dissolved in supporting electrolyte solutions containing 0.5 M ammonium chloride, 0.5 M ammonium hydroxide and 0.005% gelatin. The height of the first wave due to the reduction of cobalt(III) to cobalt(II) represents the relative amount of cobalt(III), and that of the second wave due to the reduction of cobalt(II) to cobalt(0), the sum of cobalt(III) and cobalt(II) in the pyrolyzed sample. Mole fractions of cobalt(II) in the pyrolyzed samples were calculated by the measurement of the corrected heights of the waves, since the diffusion current constants of the cobalt(III) species are smaller than those of the cobalt(II) species.

1) M. Mori and R. Tsuchiya, This Bulletin, **32**, 467 (1959).
2) W. W. Wendlandt and J. L. Bear, *J. Phys. Chem.*, **65**, 1516 (1961).
3) W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 843 (1963).
4) N. Tanaka and M. Nanjo, This Bulletin **37**, 1330 (1964).
5) N. Tanaka, M. Sato and M. Nanjo, *Sci. Repts. Tohoku Univ., Ser. I*, **48**, No. 1, 1 (1964).
6) J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," **2**, ed. by W. C. Fernelius, McGraw-Hill, New York (1946), p. 216.
7) W. A. Hynes, L. K. Yanowski and M. Shiller, *J. Am. Chem. Soc.*, **60**, 3053 (1938).
8) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 463 (1898).
9) W. Biltz and B. Fetkeuheuer, *ibid.*, **89**, 130 (1914).
10) S. M. Jörgensen, *ibid.*, **14**, 33 (1897).

The preliminary measurements with different initial amounts of the samples had confirmed the relation given by the equation,

$$-dN/dt = kN \quad (1)$$

where N represents the number of cobalt(III) ions in the sample and k the rate constant. They indicated that the kinetics of the electron transfer reaction followed a first-order rate law. For the convenience of experiments Eq. (1) was modified to

$$\ln(1-x) = -kt \quad (2)$$

where x is the mole fraction of cobalt(II) in the sample subjected to the thermal treatment.

Results and Discussion

Decomposition Processes. The decomposition products of amminecobalt(III) halides subjected to the thermal treatment *in vacuo* were found to consist of mainly cobalt(II) halides, and minute amounts of ammonium halides, molecular halogens and ammonia. Upon the decomposition of $[Co(NH_3)_6]Br_3$, $[CoBr(NH_3)_5]Cl_2$ and $[CoCl(NH_3)_5]Br_2$, purple-colored liquid bromine was observed on the inside wall of the end of the reaction tube where the reaction tube was cooled with dry ice. Hexamminecobalt(III) iodide gave purple-red iodine crystals by the same treatment.

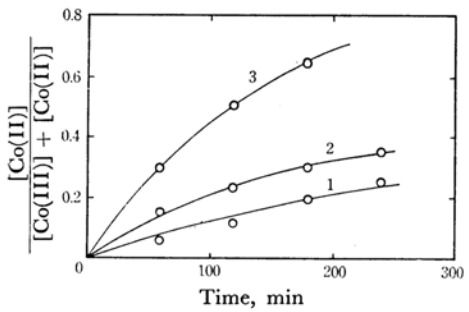

Fig. 1. Mole fractions of cobalt(II) in the pyrolyzed samples of (1) $[Co(NH_3)_6]Cl_3$ at 165°C, (2) $[Co(NH_3)_6]Br_3$ at 165°C and (3) $[Co(NH_3)_6]I_3$ at 119°C as a function of time.

Figure 1 shows the time dependence of the ratio of cobalt(II) content to the sum of cobalt(III) and cobalt(II) contents in the pyrolyzed samples of $[Co(NH_3)_6]X_3$ (X: Cl, Br and I). The order of the increasing rates of the electron transfer reaction was as follows:

$$[Co(NH_3)_6]Cl_3 < [Co(NH_3)_6]Br_3 < [Co(NH_3)_6]I_3$$

This order suggests that the rate depends considerably on the nature of outer-sphere halide ions. The rate of the electron transfer reaction was increased by substituting a chloride ion for a coordinated ammonia, as is clearly shown in Fig. 2. These results indicate that the substance which donates an electron to the central cobalt(III) ion would not be a coordinated ammonia, but a

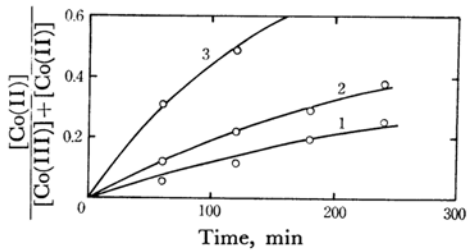

Fig. 2. Mole fractions of cobalt(II) in the pyrolyzed samples of (1) $[Co(NH_3)_6]Cl_3$, (2) $[CoCl(NH_3)_5]Cl_2$ and (3) $[CoCl_2(NH_3)_4]Cl$ as a function of time at 165°C.

halide ion. A possible process of the decomposition reaction of $[Co(NH_3)_6]Cl_3$ *in vacuo* is therefore considered as,

$$[Co^{III}(NH_3)_6]Cl_3 \rightarrow [Co^{II}(NH_3)_6]Cl_2 + Cl$$
$$\rightarrow CoCl_2 + 6NH_3 + \frac{1}{2}Cl_2 \quad (3)$$

where Cl represents a chlorine atom. The first step which is rate-determining is the electron transfer process from the outer-sphere chloride ion to the central cobalt(III) ion. The reaction of the second step is very fast, because hexamminecobalt(II) chloride is thermally much unstable. The formation of ammonium chloride may be due to the reaction between ammonia gas and chlorine.

On the other hand, the reactions taking place when the samples were treated in a sealed tube or in air were more involved. The decomposition pressure - time curves of the hexammine complexes are shown in Fig. 3. The order of the initial rates of the decomposition reactions was found to be $[Co(NH_3)_6]Cl_3 < [Co(NH_3)_6]Br_3 < [Co(NH_3)_6]I_3$. This order agrees with that of the electron transfer reaction *in vacuo*, but the reaction rate decreased to a larger extent with the proceeding of the decomposition reaction. The dependence of the reaction rate on the decomposition pressure is shown in Fig. 4, which shows that, when the

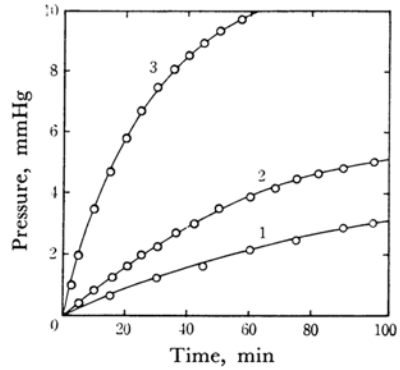

Fig. 3. Decomposition pressure of (1) $[Co(NH_3)_6]Cl_3$ at 171°C, (2) $[Co(NH_3)_6]Br_3$ at 173°C and (3) $[Co(NH_3)_6]I_3$ at 149°C as a function of time.

TABLE 1. INFRARED ABSORPTION SPECTRA OF $[Co(NH_3)_6]Cl_3$, $[CoCl(NH_3)_5]Cl_2$ AND THE DECOMPOSITION PRODUCT OF $[Co(NH_3)_6]Cl_3$ PYROLYZED AT 220°C IN A SEALED TUBE

	$\delta_d(NH_3)$	$\delta_s(NH_3)$	$\rho_r(NH_3)$	ν(M–N)		
$[Co(NH_3)_6]Cl_3$	1603	1325	829.9	500	476	448
$[CoCl(NH_3)_5]Cl_2$	1600	1305	842.5	496	488	464
Product	1595	1305	841.8	497	488	463

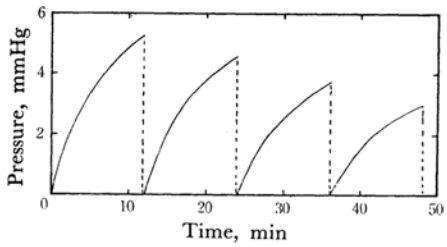

Fig. 4. Decomposition pressure of $[CoCl(NH_3)_5]Cl_2$ as a function of time at 217°C. The system was evacuated every 12 min.

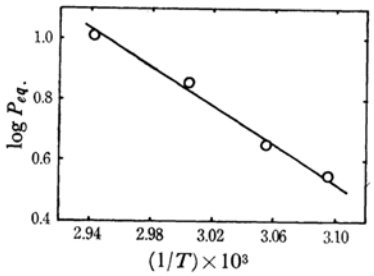

Fig. 5. Equilibrium pressure *versus* the reciprocal of absolute temperature for $[Co(NH_3)_6]Cl_2$.

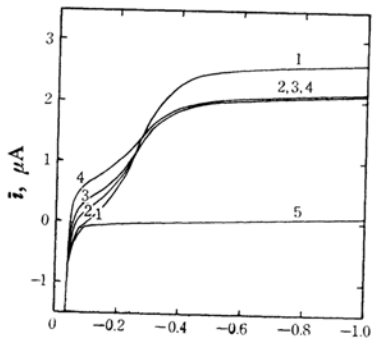

Fig. 6. Polarograms of 0.75 mM $[Co(NH_3)_6]Cl_3$ before (curve 1) and after pyrolysis in a sealed tube at 220°C for 30 min (2), 60 min (3), and 120 min (4). Curve 5 shows a residual current curve of supporting electrolyte solution containing 0.5 M ammonia, 0.5 M ammonium chloride and 0.005% gelatin.

decomposition gas is removed, the reaction rate increases again. These facts suggest the existence of the reversible reaction between the solid and the gas phase. Reactions of the cobalt(II) complexes with ammonia could be reversible, because cobalt(II) complexes are more labile for substitution reactions than cobalt(III) complexes. The equilibrium pressures of the cobalt(II) complex were measured without any difficulty. The results are shown in Fig. 5. In addition, there seems to exist another reversible reaction, which is an electron transfer from a cobalt(II) complex to a halogen molecule. Polarograms of $[Co(NH_3)_6]Cl_3$ subjected to the thermal treatment in a sealed tube of about 3 m*l* in volume at 220°C are given in Fig. 6. The curves 1 to 4 indicate that the wave which corresponds to the reduction of cobalt(III) to cobalt(II) splits to two steps after a certain period of the thermal treatment. This change suggests the formation of $[CoCl(NH_3)_5]Cl_2$[11,12]; the first wave is considered to be of $[CoCl(NH_3)_5]Cl_2$. After twenty hours, the yellow color of $[Co(NH_3)_6]Cl_3$ turned into a red-colored product. Infrared absorption spectra of the latter given in Table 1 showed that $[Co(NH_3)_6]Cl_3$ was converted to $[CoCl(NH_3)_5]Cl_2$. Nevertheless, the ratios of cobalt(III) to cobalt(II) of the pyrolyzed samples did not change after the initial lapse of 30 min, suggesting the existence of the reversible reaction of electron transfer. Chloropentamminecobalt(III) chloride may be formed by the side reaction which involves the substitution reaction of an outer-sphere ion for a ligand. Since the rate of this side reaction is considered to be much smaller than that of the electron transfer reaction, $[CoCl(NH_3)_5]Cl_2$ may be produced when the electron transfer reaction is strongly interfered. From these results, the possible mechanisms of the decomposition reaction of $[Co(NH_3)_6]Cl_3$ in a sealed tube may be given as follows:

$$\begin{aligned}[Co(NH_3)_6]Cl_3 &\overset{A}{\rightleftharpoons} [Co(NH_3)_6]Cl_2 + \frac{1}{2}Cl_2 \rightleftharpoons R \\ &\overset{B}{\rightarrow} [CoCl(NH_3)_5]Cl_2 + NH_3 \overset{A'}{\rightleftharpoons} \\ &\quad [Co(NH_3)_5]Cl_2 + \frac{1}{2}Cl_2 + NH_3 \rightleftharpoons R\end{aligned} \qquad (4)$$

where R represents the mixture of the decomposition products, that is, lower complexes of amminecobalt(II), ammonia, hydrogen chloride and nitrogen. The process A of Eq. (4) is a reversible

11) W. Biltz, *Z. anorg. Chem.*, **83**, 177 (1913).
12) G. W. Watt, *Inorg. Chem.*, **3**, 325 (1964).

electron transfer reaction while the process B is a substitution reaction. In air also, $[CoCl(NH_3)_5]Cl_2$ and $[CoBr(NH_3)_5]Br_2$ were obtained by the decomposition reactions of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Br_3$. This suggests that oxygen in air oxidizes the cobalt(II) to cobalt(III) complexes instead of halogen molecules.

Kinetic Studies of the Electron Transfer Reactions. The kinetics of the electron transfer reaction was investigated by the polarographic measurements. A plot of $\log(1-x)$ *versus* t was made for each complex at various temperatures; the plots for $[Co(NH_3)_6]I_3$ are shown in Fig. 7 as an example. Nearly straight lines were obtained for all of the hexamminecobalt(III) halides and chloropentamminecobalt(III) chloride, indicating that the electron transfer reactions obey a first-order rate law. On the other hand, $[CoBr(NH_3)_5]Cl_2$, $[CoCl(NH_3)_5]Br_2$ and $[CoBr(NH_3)_5]Br_2$ gave nearly straight lines, when the values of $(1-x)$ were plotted against time. Nevertheless, the initial rates obtained with various initial amounts of these complexes indicated that the reactions of these complexes obey also a first-order rate law.

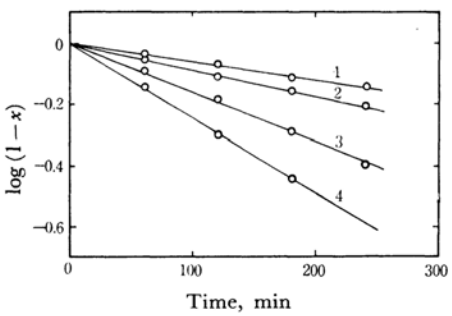

Fig. 7. Relation of $\log(1-x)$ *versus* time for $[Co(NH_3)_6]I_3$ at (1) 103.5, (2) 108.5, (3) 113.5 and (4) 118.5°C.

The first-order rate constants were determined from the initial rates at various temperatures, and the activation energies and frequency factors were calculated using the Arrhenius equation.

The first-order rate constants, the activation energies and the frequency factors for the complexes are given in Table 2. It is seen that little difference in activation energy exists among the hexamminecobalt(III) complexes in spite of a great difference in the rate with different outer-sphere ions. On the other hand, $[CoCl(NH_3)_5]Cl_2$ and $[CoBr(NH_3)_5]Cl_2$ had smaller values of activation energy (20 to 25 kcal/mol), and $[CoCl(NH_3)_5]Br_2$ and $[CoBr(NH_3)_5]Br_2$ had medium values of about 30 kcal/mol. In the case of $[CoBr(NH_3)_5]Cl_2$, the electron donor substance is considered to be a coordinated bromide ion from the observation of the formation of bromine.

It should be noticed that the rate of decomposition of $[CoCl(NH_3)_5]Br_2$ is larger than that of $[CoBr(NH_3)_5]Cl_2$. This seems to mean that an outer-sphere bromide ion donates an electron to the central cobalt(III) ion more easily than a coordinated bromide ion. The π electrons of a bromide ion may transfer to the metal orbitals more easily than the σ electrons. The π orbitals which are not in the direction of bond could overlap the non-bonding d_ε orbitals of the central ion by the thermal vibration. From the experimental results, the most probable process of the electron transfer for $[CoBr(NH_3)_5]Cl_2$ may be considered as follows: A shift of the outer-sphere ion toward the central cobalt(III) ion by the thermal motion would lower the symmetry and consequently would decrease the energy of crystal field splitting. Then, one of the coupled electrons in the d_ε orbitals would go up to a higher d_γ orbital, because the energy for pairing turns out to be greater than the crystal field splitting energy. The electron transfer from a p orbital of bromide ion to the vacant d_ε-type orbital of the activated cobalt(III) ion would then occur. In the case of hexamminecobalt(III) complexes also, analogous processes may take place, that is, the electron transfer could occur from a p orbital of outer-sphere halide ion to a d_ε orbital of the activated cobalt(III) ion.

The activation energies obtained experimentally may correspond to the thermal motions which decrease the crystal field splitting and induce the activated state of the cobalt(III) ion. The frequency factors of the electron transfer would depend on the overlap probability of the corresponding orbitals by the thermal vibration. The overlap

Table 2. Kinetic parameters for various complexes

Complex	$k\times10^5$, sec^{-1} (Temp., °C)	E, kcal/mol	A, sec^{-1}
$[Co(NH_3)_6]Cl_3$	1.87(165), 2.25(167), 3.61(172)	36.0	2×10^{13}
$[Co(NH_3)_6]Br_3$	2.35(155), 4.58(159), 6.12(165)	35.6	3×10^{13}
$[Co(NH_3)_6]I_3$	2.39(104), 3.39(109), 6.08(114)	29.4	3×10^{12}
$[CoCl(NH_3)_5]Cl_2$	2.16(152), 3.36(162), 4.42(167)	21.5	2×10^{6}
$[CoCl(NH_3)_5]Br_2$	2.06(137), 3.83(142), 9.17(153)	30.7	4×10^{11}
$[CoBr(NH_3)_5]Cl_2$	2.29(147), 3.12(152), 4.45(157)	22.7	10^{7}
$[CoBr(NH_3)_5]Br_2$	2.22(132), 3.97(137), 5.37(142)	31.9	5×10^{12}

probability of an inner-sphere halide ion would be smaller than that of an outer-sphere one, because the directions of the *p* orbitals of the former are more fixed than those of the latter. Therefore, the frequency factor obtained experimentally may answer a question of whether the electron donor substance is an outer-sphere anion or a ligand. In the case of $[CoCl(NH_3)_5]Br_2$ and $[CoBr(NH_3)_5]Br_2$ the electron donor substance could be both an inner-sphere and an outer-sphere anion.

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