BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1143—1146 (1968)

Kinetics and Mechanisms of Thermal Decomposition Reactions of Cobalt(III) Complexes. Hexammine-, Halogenoammine- and Oxalatoamminecobalt(III) Complexes

Nobuyuki TANAKA and Kenzo NAGASE[*1]
Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

and Saburo NAGAKURA
Institute of Solid State Physics, The University of Tokyo, Minato-ku, Tokyo

(Received November 29, 1967)

Kinetics of the thermal decomposition reactions of hexammine-,halogenoammine- and oxalatoamminecobalt(III) complexes in solid state has been studied by following the change in the cobalt(III) contents with time. It was found that the decomposition of these complexes was initiated by the change of the valence state of cobalt(III) to cobalt(II), and that these electron-transfer reactions were kinetically of a first order. The first-order rate constants, the activation energies and the frequency factors of these electron-transfer reactions were obtained. The values of the activation energies were found to increase in parallel with the increase in the difference between t_{2g} and e_g orbitals of the cobalt(III) complexes investigated. (The notations, t_{2g} and e_g, are used in the expression of an O_h-symmetry approximation for halogenoammine- and oxalatoamminecobalt(III) complexes.)

It has been reported that the thermal decomposition of cobalt(III) complexes in solid state is caused by the change of the valence state of cobalt(III) to cobalt(II); Tanaka and his co-workers[1–5] proposed that the decomposition of cobalt(III) and iron(III) complexes was initiated by an electron transfer from a ligand or an outer-sphere anion to the central metal(III) cation. Wendlandt *et al.*[6–8] also found the change of the valence state on the thermal decomposition of cobalt(III) and manganese(III) complexes.

In order to proceed a general consideration of the electron-transfer reactions on the thermal decomposition of cobalt(III) complexes, the present authors have undertaken the determination of the rates of these reactions. The activation energies and frequency factors were calculated from the first-order rate constants using the Arrhenius equation, and the mechanisms of the electron-transfer reactions were discussed.

Experimental

The apparatus and the procedure are described in a previous paper.[8] $[Co(NH_3)_6]X_3$(X=Cl, Br, I), $[Co(en)_3]Cl_3\cdot 3H_2O$, $[CoX(NH_3)_5]Y_2$(X, Y=Cl, Br), *trans*-$[CoCl_2(NH_3)_4]Cl\cdot H_2O$, $[Co(ox)(NH_3)_4]Cl$, $K[Co(ox)_2(NH_3)_2]\cdot H_2O$ and $M_3[Co(ox)_3]\cdot 3H_2O$(M=Na, K) were prepared according to the methods given in the literature (see Refs. 3 and 4).

Results

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

$$-\mathrm{d}N/\mathrm{d}t = kN \tag{1}$$

where N represents the number of cobalt(III) ions in the sample and k the first-order rate constant. Figure 1 shows the dependence of the reaction rate on the initial amount of the sample, indicating that the reaction follows the first-order rate law.

For the convenience of the treatment, Eq. (1) was modified to

$$\ln(1-x) = -kt \tag{2}$$

where x is the mole fraction of cobalt(II) in the sample. A plot of $\log(1-x)$ *versus* time was made for each complex at various temperatures, and nearly

---

[*1] Present address: Department of Chemistry, College of General Education, Tohoku University, Kawauchi, Sendai.

1) N. Tanaka and M. Nanjo, This Bulletin, **37**, 1330 (1964).
2) N. Tanaka, M. Sato and M. Nanjo, *Sci. Repts. Tohoku Univ., Ser. I*, **48**, No. 1, 1 (1964).
3) N. Tanaka and K. Nagase, This Bulletin, **40**, 546 (1967).
4) N. Tanaka and M. Nanjo, *ibid.*, **40**, 330 (1967).
5) N. Tanaka, K. Nagase and S. Nagakura, *Inorg. Nucl. Chem. Letters*, **3**, 169 (1967); in press (1967).
6) W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 1267 (1963).
7) W. W. Wendlandt and E. L. Simmons, *ibid.*, **27**, 2317 (1965).
8) E. L. Simmons and W. W. Wendlandt, *ibid.*, **27**, 2325 (1965).

TABLE 1. KINETIC PARAMETERS FOR COBALT(III) COMPLEXES

Complex	$k\times 10^5$, sec^{-1} (Temp., °C)	E_a 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}
$[CoCl(NH_3)_5]Cl_2$	2.88(155), 3.95(160), 6.40(167)	23.6	3×10^{7}
$[CoCl(NH_3)_5]Br_2$	1.78(132), 2.46(137), 3.80(142)	27.4	8×10^{9}
$[CoBr(NH_3)_5]Cl_2$	1.31(137), 2.19(144), 3.41(152)	22.6	1×10^{7}
$[CoBr(NH_3)_5]Br_2$	1.63(127), 2.31(132), 4.98(142)	24.0	2×10^{8}
trans-$[CoCl_2(NH_3)_4]Cl\cdot H_2O$	1.68(137), 2.66(142), 4.31(155)	19.6	4×10^{5}
$[Co(ox)(NH_3)_4]Cl$	1.12(164), 1.48(170), 3.09(178)	29.9	8×10^{9}
cis-$K[Co(ox)_2(NH_3)_2]\cdot H_2O$	1.60(110), 2.90(117), 4.08(121)	26.6	2×10^{10}
$Na_3[Co(ox)_3]\cdot 3H_2O$	1.69(51), 2.37(56), 3.65(61)	20.0	5×10^{8}
$K_3[Co(ox)_3]\cdot 3H_2O$	2.31(71), 4.03(76), 5.48(81)	20.8	4×10^{8}
$[Co(en)_3]Cl_3\cdot 3H_2O$	1.67(196), 1.99(199), 3.65(207)	34.9	2×10^{11}

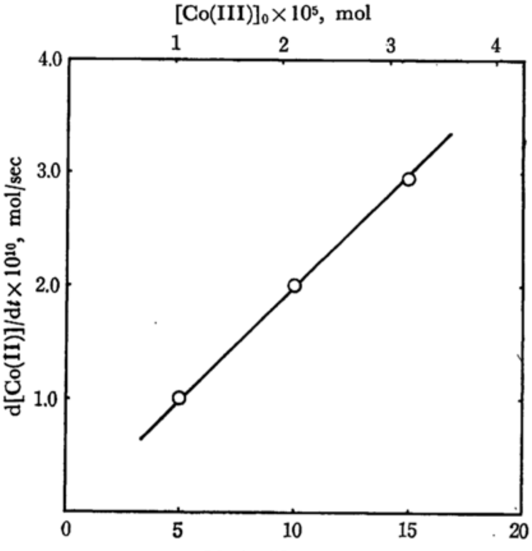

Fig. 1. Reaction rate as a function of the initial amounts of the sample ($[Co(III)]_0$) obtained with $K_3[Co(ox)_3]\cdot 3H_2O$ at 87°C.

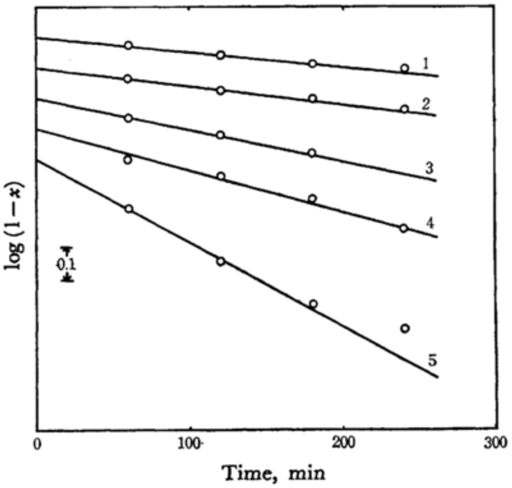

Fig. 2. Relation of $\log(1-x)$ *versus* time for $K_3[Co(ox)_3]\cdot 3H_2O$ at (1) 66, (2) 71, (3) 76, (4) 81 and (5) 87°C.

straight lines were obtained. The plots for $K_3[Co(ox)_3]\cdot 3H_2O$ are shown in Fig. 2 as an example. In the case of $[CoCl(NH_3)_5]Br_2$, $[CoBr(NH_3)_5]Cl_2$, $[CoBr(NH_3)_5]Br_2$ and $[Co(ox)(NH_3)_4]Cl$, the rate was considerably accelerated as the reaction took place and the plots showed a tendency of departing from the straight lines.

The first-order rate constants were determined from the plots of $\log(1-x)$ *versus* t at various temperatures, from which the activation energies and frequency factors were calculated. The kinetic parameters obtained are given in Table 1.

Discussion

The observed activation energies increase in parallel with the increase in the difference of e_g and t_{2g} levels, though they are somewhat lower than the transition energies of the A band of the absorption spectra of cobalt(III) complexes. This relation is shown in Fig. 3[*1]; the energies of the A bands are taken from the literatures.[9,10]

The cobalt(III) complexes investigated in this study have a singlet ground state and a triplet lowest excited state. Their symmetry notations are $^1A_{1g}$ and $^3T_{1g}$, respectively, in the expression of an O_h-symmetry approximation. The potential energy curves of the ground state of the cobalt(III) complexes and the lowest triplet state may be represented schematically with curves 1 and 2 in Fig. 4, respectively. The energy state given by curve 2 may

---

[*1] Figure 1 in Ref. 5 should be replaced by this figure, in which the values of $\Delta E(^3T_{1g}-{}^1A_{1g})$ were recalculated.

9) M. Linhard and M. Weigel, *Z. Physik. Chem., N.F.*, **11**, 308 (1957).

10) J. Fujita and Y. Shimura, This Bulletin, **36**, 1281 (1963).

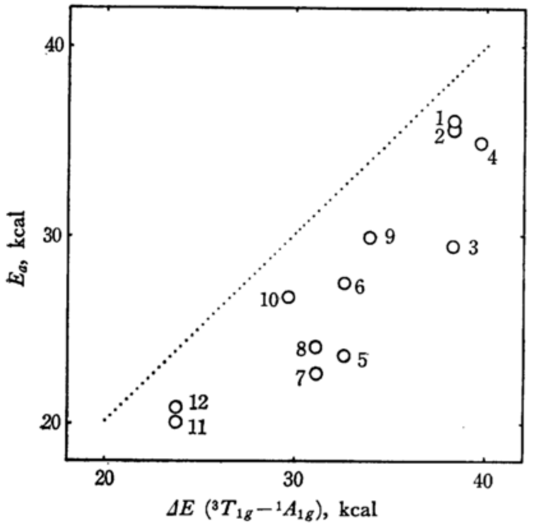

Fig. 3. Relation of the activation energies (E_a) *versus* the energy of the A band (ΔE) for
(1) $[Co(NH_3)_6]Cl_3$, (2) $[Co(NH_3)_6]Br_3$,
(3) $[Co(NH_3)_6]I_3$, (4) $[Co(en)_3]Cl_3\cdot 3H_2O$,
(5) $[CoCl(NH_3)_5]Cl_2$, (6) $[CoCl(NH_3)_5]Br_2$,
(7) $[CoBr(NH_3)_5]Cl_2$, (8) $[CoBr(NH_3)_5]Br_2$,
(9) $[Co(ox)(NH_3)_4]Cl$, (10) $K[Co(ox)_2(NH_3)_2]\cdot H_2O$,
(11) $Na_3[Co(ox)_3]\cdot 3H_2O$ and
(12) $K_3[Co(ox)_3]\cdot 3H_2O$.

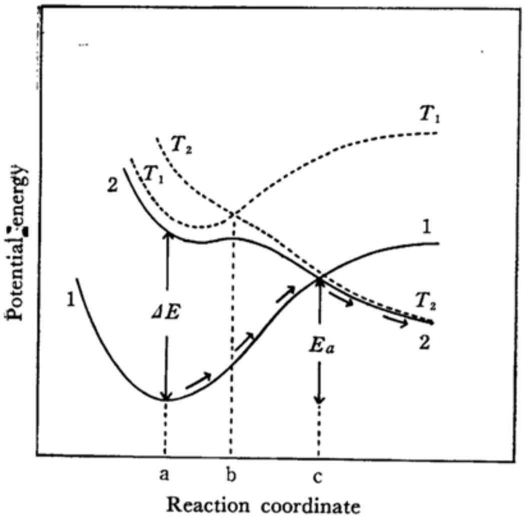

Fig. 4. Schematic potential energy diagram of cobalt complexes.

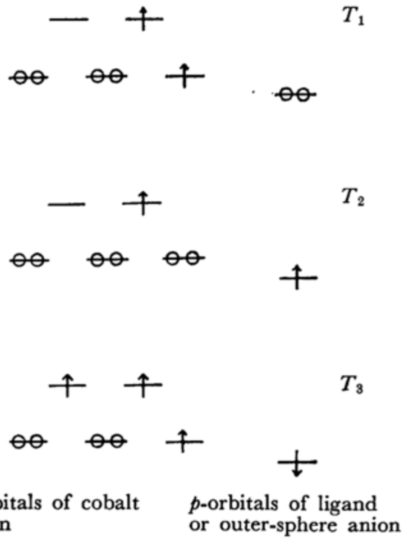

Fig. 5. Electron configurations of the triplet states of cobalt complexes.

mainly consist of electron configurations T_1 and T_2 which are shown in Fig. 5.*[2] The latter is the charge-transfer configuration in the sense that it is brought about by an electron transfer from a ligand or an outer-sphere anion (X^-) to the central metal cation. The potential energy curves of T_1 and T_2 are also schematically shown in Fig. 4.*[3] Curve 2 can be obtained as the result of the configuration interaction between T_1 and T_2.

At or near the point which corresponds to the equilibrium position of the reaction coordinate, T_1 is more stable than T_2, and therefore T_1 is the most important configuration in the lowest triplet state. With the increasing distance in the reaction coordinate, however, T_2 gradually approaches T_1, and they cross each other at point b. At more distant points, T_2 contributes to the lowest triplet state to a

---

*[2] Besides these two configurations, T_3 configuration which is given in Fig. 5 may contribute to the lowest triplet state. Its energy, however, is undoubtedly higher than that of T_2 and the contribution of T_3 to the lowest triplet state may conceivably be small. Therefore, it may safely be disregarded in the qualitative consideration made in the present paper.

*[3] T_1 is stabilized by electrostatic interaction with decreasing distances between X^- and Co^{3+}. On the other hand, we can not expect the large electrostatic attraction in T_2 where X^- approaches Co^{2+}.

*[4] It is difficult to discuss this point quantitatively, because the electron affinity of the central metal cation is very sensitive to its effective charge; namely 35.03 eV for Co^{3+}, 18.29 for Co^{2+} and 5.44 for Co^+. Let us now take as an example the case where X^- is an outer-sphere chloride anion. The energy difference between T_2 and T_1 in the infinite separation may be represented by $E_{T_2}-E_{T_1}=I_{X^-}-A_{Co^{\delta+}}+\Delta$, where I_{X^-} and $A_{Co^{\delta+}}$ are the ionization potential of X^- and the electron affinity of $Co^{\delta+}$, respectively, and Δ is the change in the electrostatic interaction energy between the central metal ion and ligands caused by the electron transfer. The value of Δ is also largely dependent on the δ value, because the positive charge on a ligand molecule, say NH_3, increases with the decreasing δ value.

In the case of $\delta=1$, Δ may be negative, because the electrostatic repulsion between $Co^{\delta+}$ and ligands with positive charge disappears, or at least decreases to a great extent, as the result of the electron transfer. $I_{X^-}-A_{Co^{\delta+}}$ is also negative for $\delta=1$, since $I_{X^-}=3.70$ eV and $A_{Co^+}=5.44$ eV. Therefore, $E_{T_2}-E_{T_1}$ turns out to have a negative sign and T_2 may be expected to be more stable than T_1 in the infinite separation. The above conclusion may conceivably be satisfied for the other δ values than 1.

greater extent than T_1. This may be inferred from the fact that, in the infinite separation between X^- and Co^{3+}, T_2 may conceivably be more stable than T_1.*4 From a similar reason, T_2 or curve 2 crosses curve 1 at point c in the reaction coordinate, as is shown in Fig. 4.

According to the potential energy curves shown in Fig. 4, the electron-transfer process leading to the decomposition of the complexes seems to occur passing through point c as is indicated by arrows given in Fig. 4. In other words, the transfer of the system from curve 1 to curve 2 occurs at point c being accompanied by the change in multiplicity and the electron transfer from a ligand or an outer-sphere anion to Co^{3+}.

In view of the different multiplicity in curves 1 and 2, the probability of the transfer will be small, and consequently the reaction will have a small transmission coefficient, which in turn will give a small value of the frequency factor. The observed frequency factors given in Table 1 support this consideration. The reactions which are kinetically of a first order have in usual the frequency factor of about 10^{13}.

The authors thank the Ministry of Education for the financial support granted for this research.