BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2093—2095 (1970)

Intramolecular Electron-transfer Reactions of Ethylenediaminetetraacetatocobaltate(III) and Its Related Complexes in Solid State

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(Received January 23, 1970)

Electron transfer from a ligand to a central cobalt(III) in solid state was investigated by following the change of the valence state of coblat(III) to cobalt(II). The reaction was carried out in a vacuum as a function of sample amount, temperature and nature of a ligand and an outer-sphere cation. The electron-transfer reaction followed the first-order rate law. An outer-sphere cation had a slight effect on the reaction of the complex ion. The kinetic parameters obtained for potassium ethylenediaminetetraacetatocobaltate(III) ($E_a=38$ kcal/mol, $A=10^{14}$) differed greatly from those for potassium propylenediaminetetraacetatocobaltate(III), potassium cyclohexanediaminetetraacetatocobaltate(III) and potassium trimethylenediaminetetraacetatocobaltate(III) ($E_a\simeq 22$ kcal/mol, $A\simeq 10^6$). The kinetic behavior of the pentadentate complex, potassium hydrogen halogenoethylenediaminetetraacetatocobaltate(III), was compared with that of the hexadentate complex, potassium ethylenediaminetetraacetatocobaltate(III).

The electron-transfer reactions of cobalt(III) complexes in solid state were discussed in detail by Tanaka *et al.*[1] They proposed that the values of the activation energies increased in parallel with the increase of the ligand field.

However, it is considered that the electron-transfer reaction depends on the structure of the ligand in addition to the electronic state of the complex ion.

In the present study, a series of diaminotetraacetatocobaltate(III) complexes whose electronic spectra are almost the same but structure different were adopted, and their structural effects on the electron-transfer reaction were discussed.

Experimental

Materials. Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate, K[Coedta]$2H_2O$,[2] potassium propylenediaminetetraacetatocobaltate(III) dihydrate, K[Copdta]$2H_2O$,[3] potassium cyclohexanediaminetetraacetatocobaltate(III) trihydrate, K[Cocydta]$3H_2O$,[4] potassium trimethylenediaminetetraacetatocobaltate(III) dihydrate, K[Cotrdta]$2H_2O$,[5] potassium hydrogen chloroethylenediaminetetraacetatocobaltate(III) monohydrate, K[CoCledtaH]H_2O[6], and potassium hydrogen bromoethylenediaminetetraacetatocobaltate(III) dihydrate, K[CoBredtaH]$2H_2O$,[7] were prepared according to the methods given in literature.

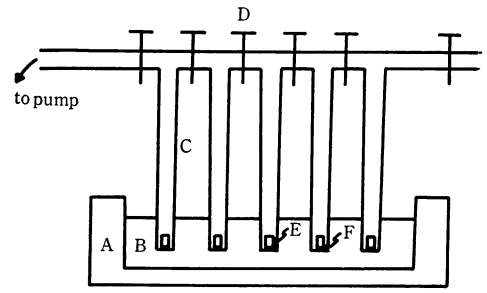

Fig. 1. Schematic diagram of apparatus: (A) bath, (B) silicone oil, (C) reaction tube, (D) cock, (E) crucible and (F) sample.

Apparatus and Procedure. Figure 1 shows the apparatus used for the thermal treatment. Samples which were smaller than 100 mesh in size weighed 2 to 4 mg in each kinetic measurement and the temperature of the sample was controlled in a range of ± 0.3°C by means of a silicone oil bath. The system was continu-

1) N. Tanaka, K. Nagase and S. Nagakura, This Bulletin, **41**, 1143 (1968).

2) H. Brintzinger, H. Thiele and U. Mueller, *Z. Anorg. Chem.*, **251**, 285 (1943).

3) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **81**, 2955 (1959).

4) F. P. Dwyer and F. L. Garvan, *ibid.*, **83**, 2610 (1961).

5) N. Tanaka and H. Ogino, This Bulletin, **37**, 877 (1964).

6) M. Mori, M. Shibata, E. Kyuno and H. Nakajima, *ibid.*, **29**, 887 (1956).

7) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

ously evacuated by a rotary pump during the reaction. Every one hour, the heated sample was taken out of the reaction tube and dissolved in a 25 ml deaerated solution containing 0.5 M potassium chloride. A Yanagimoto PR-2 pen-recording polarograph was used for the determination of cobalt(III) content in the solution.

Results and Discussion

The decomposition processes of diaminotetraacetatocobaltate(III) complexes were investigated by thermogravimetric analysis, gas evolution analysis and polarographic analysis. For example, the process for potassium ethylenediaminetetraacetatocobaltate(III) in a vacuum is given by the equations

$$K[Co^{III}\,edta]2\,H_2O \xrightarrow[\sim 50°C]{\text{dehydration}} K[Co^{III}\,edta] + 2\,H_2O \quad (1)$$

$$K[Co^{III}\,edta] \xrightarrow[\sim 170°C]{\text{electron transfer}} K[Co^{II}(edta')] \quad (2)$$

$$K[Co^{II}(edta')] \xrightarrow{\text{decarbonation}} \text{Products containing cobalt(II)} + CO_2 \quad (3)$$

where edta' represents the edta radical which was formed by the electron transfer from an edta to a central cobalt(III). The rate of reaction (2) was followed by the measurement of the change of the valence state of cobalt(III) to cobalt(II).

The Order of the Electron-transfer Reaction. The measurements which were carried out with various initial amounts of the sample confirmed, as shown in Fig. 2, the relation given by the equation

$$-dN/dt = kN \quad (4)$$

where N represents the number of cobalt(III) ions in the heated sample and k the rate constant. Equation (4) is modified to

$$2.303 \log x = -kt \quad (5)$$

where x is the mole fraction of cobalt(III) in the sample. A plot of $\log x$ *versus* time was made for each complex and nearly straight lines were obtained. The plots for K[Cocydta] are shown in Fig. 3 as an example.

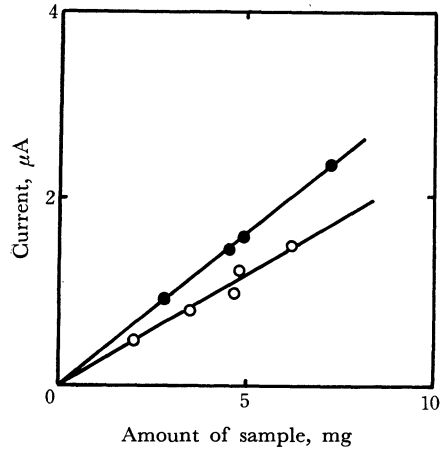

Fig. 2. Determination of cobalt(III) content for Na[Coedta] (●) before and (○) after heating at 172°C for 5 hr.

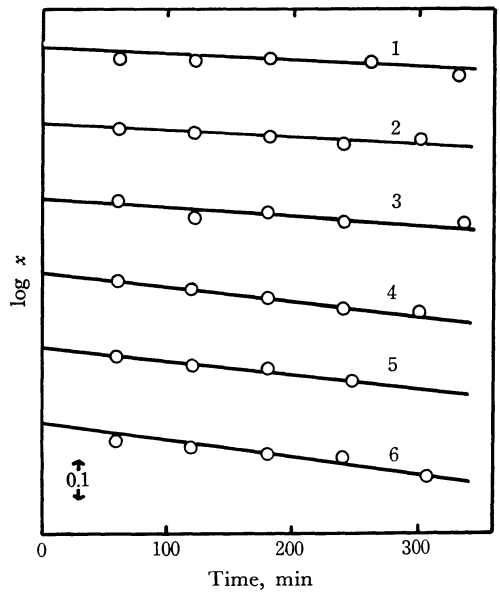

Fig. 3. Plots of $\log x$ *versus* time for K[Cocydta] at various temperatures: (1) 190, (2) 192, (3) 196, (4) 200, (5) 203 and (6) 204°C.

From these results, it is confirmed that the electron-transfer reaction follows the first-order rate law.

Effects of Outer-sphere Cations on the Electron-transfer Reaction. The kinetic parameters of ammonium, sodium and potassium salts of ethylenediaminetetraacetatocobaltate(III) are given in Table 1. The temperatures at which the rate constants are equal to 1×10^{-5} sec^{-1} are almost the same among these complexes, but the activation energies (E_a) and frequency factors (A) are slightly different. Therefore, a precise comparison of the kinetic behavior of the complex ion should be made among the complexes containing the same outer-sphere ion.

Table 1. Effects of outer-sphere cation on the electron-transfer reaction of EDTA complex

Complex	Temp., °C ($k = 1 \times 10^{-5}$ sec^{-1})	E_a kcal/mol	A
NH_4[Coedta]	171	43	10^{16}
Na[Coedta]	170	41	10^{15}
K[Coedta]	171	38	10^{14}

Kinetic Studies of K[Coedta], K[Copdta], K[Cocydta] and K[Cotrdta]. The first-order rate constants for potassium salts of ethylenediaminetetraacetatocobaltate(III) and its related complexes were determined from the plots of log x *versus* time. The order of the temperatures at which the rate constant is equal to 1×10^{-5} sec^{-1} is as follows:

$$\text{K[Coedta]} < \text{K[Cotrdta]} < \text{K[Cocydta]} < \text{K[Copdta]}$$

This suggests that the rate depends considerably on the nature of the ligand. The activation energies and frequency factors were obtained from the temperature dependence of the rate. The kinetic parameters obtained are given in Table 2. It is noticed that the kinetic parameters of EDTA complex are considerably higher than those of PDTA, CyDTA and TRDTA complexes, which are almost the same.

Table 2. Kinetic parameters of the electron-transfer reaction for various cobalt(III) complexes in solid state

Complex	Temp., °C ($k = 1 \times 10^{-5}$ sec^{-1})	E_a kcal/mol	A
K[Coedta]	171	38	10^{14}
K[Copdta]	199	22	10^{5}
K[Cocydta]	194	24	10^{6}
K[Cotrdta]	187	23	10^{6}

According to a previous paper,[1] the activation energies of the electron-transfer reaction of cobalt(III) complexes are somewhat lower than the energies of the A band of their absorption spectra and the frequency factors are smaller than the normal values for a first-order reaction, 10^{13}. From this conclusion, the values expected for EDTA, PDTA, CyDTA and TRDTA complexes are $E_a =$ 20 to 25 kcal/mol and $A = 10^5$ to 10^8.

Electron transfer from a ligand to a central cobalt(III) will occur after reorganization of the structure of the cobalt complex in the formation of the transition state. Such a rearrangement in the complex containing polydentate ligand will be caused by increasing the bond distance and by varying the direction of the coordinated atom. The latter will be caused by the twist of the chelate ring as observed in racemization. From the steric relationship, the twist is easy for the EDTA complex but difficult for the other three. The difficulty of the twist for the PDTA complex results from the repulsion between methyl hydrogen atoms and methylene hydrogen atoms. The twist of the chelate ring in the CyDTA complex is impossible since the chelate ring involving two nitrogen atoms is fixed by a cyclohexane ring. In the TRDTA complex, the six-membered chelate ring is formed in contrast with the EDTA, PDTA and CyDTA complexes. The difficulty of the twist for the TRDTA complex has been reported by Ogino *et al.*[8] It is supposed that the activation energy and the frequency factor of the electron-transfer reaction are higher for the twist mechanism than for the mechanism by which the chelate ring is fixed. Therefore, the difference between kinetic parameters obtained for the EDTA complex and those for the other three may be due to whether the twist of the chelate ring is possible or not.

Kinetic Studies of Potassium Hydrogen Halogenoethylenediaminetetraacetatocobaltate(III). The kinetic parameters of the pentadentate complex, K[CoCledtaH] and K[CoBredtaH], are given in Table 3. The order of the temperatures at which the rate constant is equal to 1×10^{-5} sec^{-1} was as follows:

Table 3. Kinetic parameters of the pentadentate cobalt(III) complexes

Complex	Temp., °C ($k = 1 \times 10^{-5}$ sec^{-1})	E_a kcal/mol	A
K[CoCledtaH]	158	33	10^{11}
K[CoBredtaH]	144	28	10^{10}

$$\text{K[CoBredtaH]} < \text{K[CoCledtaH]} < \text{K[Coedta]}$$

This order suggests that the rate of the electron-transfer reaction was increased by substituting a halide ion for a carboxyl group. Also, the activation energies were decreased in the order

$$\text{K[Coedta]} > \text{K[CoCledtaH]} > \text{K[CoBredtaH]}.$$

These facts may be explained by the following:

i) The chelate ring of the pentadentate complex will twist more easily than that of the hexadentate complex.

ii) The energies of ligand field splitting and charge transfer from ligand to metal are lower in the order K[Coedta] > K[CoCledtaH] > K[CoBredtaH].

The authors wish to express their hearty thanks to Dr. Hiroshi Ogino for the supply of K[Cotrdta]–$2H_2O$. They also thank the Ministry of Education for the financial support granted for this research.

8) H. Ogino, M. Takahashi and N. Tanaka, presented at the 18th Symposium on Coordination Chemistry, Kyoto, Japan, October, 1968.