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The Thermal Decomposition of Metal Oxalato Complexes

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The thermal decomposition of trioxalato complexes of cobalt(III), iron(III) and chromium(III) has been investigated by the thermogravimetric, the polarographic and the infrared spectroscopic method. The results indicate that, in the case of the iron(III) and the cobalt(III) complexes, the decomposition reaction is initiated by the electron transfer from the coordinated oxalate ion to the central metal ion. In the case of oxalatoamminecobalt(III) complexes, the oxalate ion is considered to be an electron donor; the more oxalate ions are coordinated, the complexes are thermally less stable.

There have been many reports on the photolytic and the pyrolytic decomposition of oxalato complexes in solutions,[1)] but only a few reports on the decomposition in the solid state.[2-6)] It has been reported in the previous papers[7,8)] that the thermal decomposition of hexamminecobalt(III) chloride is often initiated by the electron transfer from either a ligand or an outer-sphere ion to a central cobalt(III) ion, forming a less stable cobalt(II) complex.

In the case of potassium trioxalatocobaltate(III) and potassium trioxalatoferrate(III), the same type of electron transfer was expected, because these complexes are easily reduced by photoradiation in aqueous solutions and in the solid state.

In this study, it became clear that the lower stability of potassium trioxalatocobaltate(III) against the thermal treatment than potassium trioxalatochromate(III) is due to the electron transfer from a coordinated oxalate ion to a central cobalt(III) ion, as was found in the case of the thermal decomposition of hexamminecobalt(III) chloride.[7,8)] This result has been confirmed by polarographic and infrared spectroscopic measurements of the pyrolytic products of trioxalatocomplexes. The result will be briefly presented in this paper. A similar conclusion has been obtained recently by Wendlandt and Simmons[5)] from the thermomagnetic measurement.

Experimental

Potassium trioxalatocobaltate(III),[9)] potassium trioxalatoferrate(III),[10)] potassium trioxalatochromate(III),[11)] oxalatotetramminecobalt(III) chloride,[12)] ammonium dioxalatodiamminecobaltate(III),[13)] oxalatotetramminechromium(III) chloride[11)] and potassium dioxalatocobaltate(II)[14)] were prepared by the methods given in the literatures cited. They were identified by the measurement of their infrared absorption spectra.

The automatic recording thermobalance has previously been described.[7)] The samples of 400 mg in weight and 100 to 200 mesh in particle size were pyrolysed in a dynamic nitrogen atmosphere. The furnace heating rate was approximately linear with time and about 3°C per min.

Polarograms were recorded with a pen-recording polarograph, Yanagimoto Polarorecorder PR-2, equipped with an automatic potential scanner. The samples which had been taken out of the furnace were dissolved in a supporting electrolyte solution containing 1 M ammonium chloride and 1 M aqueous ammonia in the case of the oxalatoamminecobalt(III) complexes, in a 1 M potassium chloride solution in the case of potassium trioxalatocobaltate(III), and in a 0.5 M potassium oxalate solution in the case of potassium trioxalatoferrate(III). Gelatin was added as a maximum suppressor by 0.005% in concentration. The dropping mercury electrode used had an m value of 2.06 mg/sec, and a drop time, t_d, of 3.72 sec, being measured at -0.80 V *vs.* SCE in a deaerated solution containing 1 M ammonium chloride and 1 M aqueous ammonia at 25°C.

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A Hitachi EPI-2G double-beam infrared spectrometer with a potassium bromide foreprism and gratings was used for the measurement of the infrared absorption spectra. The potassium bromide disk method was employed.

Results and Discussion

The thermogravimetric curves of the trioxalato complexes are reproduced in Fig. 1. As is seen from the curves, the decomposition of the cobaltate(III) began at 45°C with a loss of hydrated water.

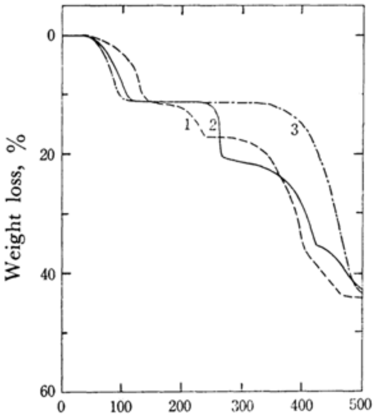

Fig. 1. Thermogravimetric curves of (1) $K_3[Co(C_2O_4)_3]\cdot 3H_2O$, (2) $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and (3) $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ obtained in nitrogen atmosphere.

A color change of the complex from green to redish violet was observed at about 120°C. On the other hand, the corresponding chromium(III) complex lost hydrated water at higher than 35°C, and the dehydrated complex was obtained at 105°C, which was very stable up to 345°C. Potassium trioxalatoferrate(III) began to lose hydrated water at about 45°C, and at 115°C the dehydrated complex was formed which was also stable up to 250°C. The comparison of the thermal stability for these oxalato complexes gave the following order:

$$K_3[Cr(C_2O_4)_3] > K_3[Fe(C_2O_4)_3] > K_3[Co(C_2O_4)_3]$$

Cobalt(III) contents in potassium trioxalatocobaltate(III) subjected to the thermal treatment are given in Table 1, which were determined by the polarographic method described previously.[7] Table 1 shows that the amount of cobalt(III) in the sample was smaller when treated at a higher temperature, and that the color change of the complex from green to redish violet observed at about 120°C was due to the reduction of cobalt(III) to cobalt(II). The decrease in the iron(III) content was also observed with the trioxalatoferrate(III) at higher than 250°C.

TABLE 1. LOSS IN THE Co(III) CONTENT OF THE $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ SUBJECTED TO THE THERMAL TREATMENT

Temp.* °C	Loss of the Co(III) content, %
80**	0
115	29
120	66
125	96
195	100
215	100

* Temperature at which the sample was taken out of the furnace.

** At this temperature, the sample was kept for 1 hr.

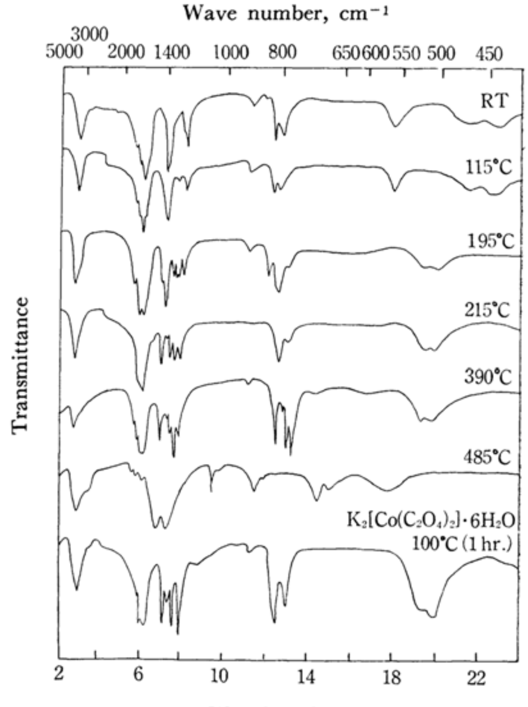

Fig. 2. Infrared absorption spectra of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ and $K_2[Co(C_2O_4)_2]\cdot 6H_2O$ (the last curve) subjected to the thermal treatment. Temperature at which the sample was taken out of the furnace is indicated on the curve. RT means room temperature.

Infrared spectra of the trioxalato complexes subjected to the thermal treatment at various temperatures are given in Figs. 2, 3 and 4. In the case of the cobalt(III) complex, new absorption bands appeared at 1621, 1425, 1337, 1304, 1282, 783.1, 772.2, 765.1, 519.5 and 504.3 cm⁻¹ upon the thermal decomposition. On the other hand, the original absorption bands of the complex at 1397, 1252, 902.5, 824.4, 807.8, 565.9, 475.1 and 440.0 cm⁻¹ decreased in intensity as temperature increased. According to the band assignment of

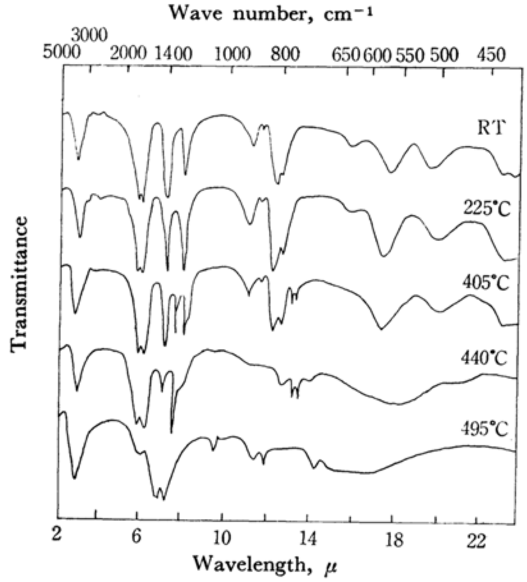

Fig. 3. Infrared absorption spectra of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ subjected to the thermal treatment. Temperature at which the sample was taken out of the furnace is indicated on the curve. RT means room temperature.

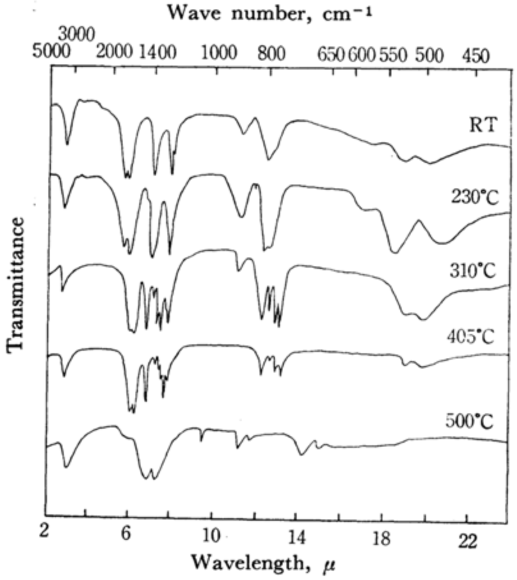

Fig. 4. Infrared absorption spectra of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ subjected to the thermal treatment. Temperature at which the sample was taken out of the furnace is indicated on the curve. RT means room temperature.

oxalato complexes,[15] the disappearance of the original absorption bands indicates that the stretching vibrations of C–O, Co–O and C–C and the deformation vibration of C–C=O were weakened by the thermal treatment. The absorption bands of potassium trioxalatocobaltate(III) subjected to the thermal treatment did not coincide with those of either cobalt(II) oxalate or potassium dioxalatocobaltate(II), but potassium dioxalatocobaltate(II) subjected to the thermal treatment at 100°C for an hour gave almost the identical absorption spectra to those of the trioxalatocobaltate(III) pyrolysed at 195°C. The results obtained by the polarographic and the infrared spectroscopic study lead to a conclusion that cobalt(III) is reduced to cobalt(II) by an electron transfer from a coordinated oxalate ion to a central cobalt ion.

Oxalate radicals have been confirmed to be formed in the photolysis of potassium trioxalatocobaltate(III) in solutions,[16] and proposed also as an intermediate species in the thermal decomposition of the same compound in solid state.[5] From the chemical analysis and the reflectance spectra of the decomposition products, Wendlandt and Simmons[5] reported that the thermal decomposition of potassium trioxalatocobaltate(III) proceeds according to the reaction,

$$2K_3[Co(C_2O_4)_3]\cdot 3H_2O \xrightarrow{150°C} 2K_2[Co(C_2O_4)_2] + KHC_2O_4 + KHCO_3 + CO_2 + 5H_2O$$

In the present study, however, potassium dioxalatocobaltate(II) was not detected as an intermediate species.

In the case of the trioxalatoferrate(III), the change of infrared absorption spectra was found to be similar to that of the corresponding cobalt(III) complex. This means that the thermal decomposition of the both complexes may proceed through similar paths, which involve the intramolecular electron transfer. The chromium(III) complex, on the other hand, did not give such absorption bands as due to the electron transfer reaction, and was very stable up to 345°C.

It has been found out by the infrared spectroscopic investigation[15] that the strength of metal-oxygen bond in trioxalato complexes is in the decreasing order of

$$Co^{III}\text{-}O > Cr^{III}\text{-}O > Fe^{III}\text{-}O$$

On the other hand, the thermal stability of the trioxalato complexes is in the decreasing order of

$$K_3[Cr(C_2O_4)_3] > K_3[Fe(C_2O_4)_3] > K_3[Co(C_2O_4)_3]$$

The reduction potentials[18] of aquo ions suggest that the degree of reducibility is in the decreasing order of

$$Co^{III} > Fe^{III} > Cr^{III}$$

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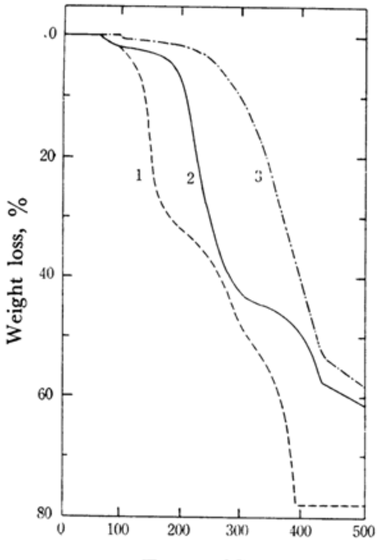

Fig. 5. Thermogravimetric curves of (1) $NH_4[Co(C_2O_4)_2(NH_3)_2]\cdot H_2O$, (2) $[Co(C_2O_4)(NH_3)_4]Cl\cdot H_2O$ and (3) $[Cr(C_2O_4)(NH_3)_4]Cl$ obtained in nitrogen atmosphere.

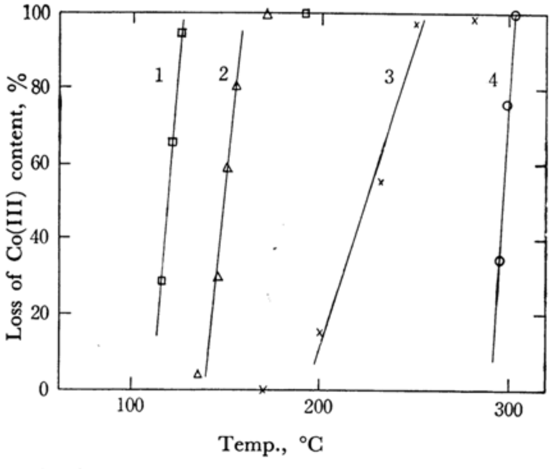

Fig. 6. Loss of Co(III) contents of (1) $K_3[Co(C_2O_4)_3]$, (2) $NH_4[Co(C_2O_4)_2(NH_3)_2]$, (3) $[Co(C_2O_4)(NH_3)_4]Cl$ and (4) $[Co(NH_3)_6]Cl_3$ by the thermal treatment. The samples were taken out of the furnace at the temperature indicated.

From these results, it may be concluded that the mechanism and the ease in the thermal decomposition of trioxalato complexes are determined by the electron affinity of the central metal ion.

The thermogravimetric curves of the oxalatoammine complexes are reproduced in Fig. 5, and the loss of cobalt(III) contents are given in Fig. 6; the latter depends on the number of oxalate ions coordinated. From the thermogravimetric and the polarographic measurements, the thermal stability of the oxalatoamminecobalt(III) complexes is in the decreasing order of

$$[Co(NH_3)_6]Cl_3 > [Co(C_2O_4)(NH_3)_4]Cl > NH_4[Co(C_2O_4)_2(NH_3)_2] > K_3[Co(C_2O_4)_3]$$

The thermal stability of the corresponding chromium(III) complexes which was determined by the measurement of thermogravimetric curves decreased in the following order:

$$K_3[Cr(C_2O_4)_3] > [Cr(NH_3)_6]Cl_3 > [Cr(C_2O_4)(NH_3)_4]Cl$$

This may indicate that the mechanism of the thermal decomposition of the cobalt(III) complexes is entirely different from that of the chromium(III) complexes. The order of the thermal stability of the oxalatoamminecobalt(III) complexes suggests that oxalate ions have electron-donating ability exceeding ammonia molecules or outer-sphere ions. This is considered to be analogous to the following two phenomena. (See Table 2). One is observed in radiolysis[18] of the oxalatoamminecobalt(III) complexes in the solid state; the $G(Co^{2+})$ values of those complexes have the same tendency. This may be explained by assuming that the electron-transfer process from the oxalate ion to the central cobalt(III) ion by the radiation induced the decomposition of the complex. The other[19] is a shift of polarographic half-wave potentials of the oxalatoamminecobalt(III) complexes with the variation of the ligands. (See Table 2). The cobalt(III) complex coordinating with more oxalate ions is more easily reduced at the dropping mercury electrode.

TABLE 2. $G(Co^{2+})$ VALUE AND $E_{1/2}$ OF OXALATOAMMINECOBALT(III) COMPLEXES

Complex	$G(Co^{2+})$ %	$E_{1/2}$ V *vs.* SCE
$K_3[Co(C_2O_4)_3]\cdot 3H_2O$	11.6 ± 0.2	>0
$NH_4[Co(C_2O_4)_2(NH_3)_2]\cdot H_2O$	8.9 ± 0.05	-0.03
$[Co(C_2O_4)(NH_3)_4]Cl\cdot H_2O$	4.3 ± 0.2	-0.21
$[Co(NH_3)_6](NO_3)_3$	0.8 ± 0.02	-0.23

In conclusion, it may be mentioned that the thermal decomposition of oxalato-, oxalatoammine- and ammine-cobalt(III) complexes is initiated by the electron transfer from either a ligand or an outer-sphere ion to the central cobalt(III) ion. The ease with which the electron transfer takes place is determined by the electron affinity of a central metal ion and the ionization potential of a ligand or an outer-sphere ion.

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