BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1886—1891 (1969)

Derivatographic Studies on Transition Metal Complexes. II.[*1] Thermal Reaction in the Solid State of Chromium(III) and Cobalt(III) Aquo-EDTA-like Complexes[*2]

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(Received August 13, 1968)

The thermal reaction processes in the solid state of the following chromium(III) and cobalt(III) aquo complexes with EDTA or the related aminopolycarboxylic acids were investigated by means of derivatography: $[CrHedta(H_2O)]$ (I), $[CrHpdta(H_2O)]\cdot H_2O$ (II), $[CrHtmta(H_2O)]\cdot H_2O$ (III), $[Cr(OH)Hapda(H_2O)_2]$ (IV) and $[Co(OH)Hapda(H_2O)_2]$ (V) (edta, pdta, tmta and apda are the abbreviated forms of ethylenediaminetetraacetate, propylenediaminetetraacetate, trimethylenediaminetetraacetate and ammoniapropionicdiacetate anions, respectively.). With complex I, the carboxylate anion free from coordination to metal coordinated when the dehydration took place at *ca.* 280°C. It resulted in the change of the coordination number of EDTA from quinquedentate to sexadentate. In the case of complexes II and III, the transition appeared below *ca.* 100°C where the coordinated water molecule in the coordination sphere is thermally expelled to the outer sphere as the protonated form due to the coordination of a carboxylate anion. PDTA and TMTA (conjugated acids of pdta and tmta respectively) also changed from quinquedentate to sexadentate ligands in this step. Of complexes IV and V, the coordinated hydroxo group was excluded as a water molecule together with the hydrogen in a free carboxylate anion at *ca.* 140°C to make the coordination number of APDA(conjugated acid of apda) change from terdentate to quadridentate. The activation energies and the enthalpy changes in each thermal reaction process were determined by the analysis of their derivatograms.

The thermal behaviors in the deaquation-anation reaction of a series of the aquopentaamminechromium(III) complexes in the solid phase have been discussed on the basis of the data obtained from "Derivatograms" in the preceeding paper.[*1] One merit in the simultaneous measurements of TGA and DTA curves by "Derivatograph" is being able to deduce whether the enthalpy change appearing in the DTA curve is due to the weight loss of the sample or due to only the phase change. The combination of the IR data concerning the samples before and after the thermal reactions with the results obtained by Derivatograph may give detailed information about the structural transformations in the reactions.

Several aquo complexes of chromium(III) and cobalt(III) with EDTA or the related ligands, PDTA, APDA or TMTA were prepared. Investigations were carried out (1) to obtain information on the structural change in the successive, thermal reaction processes for these complexes and (2) to determine, if possible, the enthalpy changes and the energies of activation concerning the respective reactions. The ligands used in this study are given in Fig. 1.

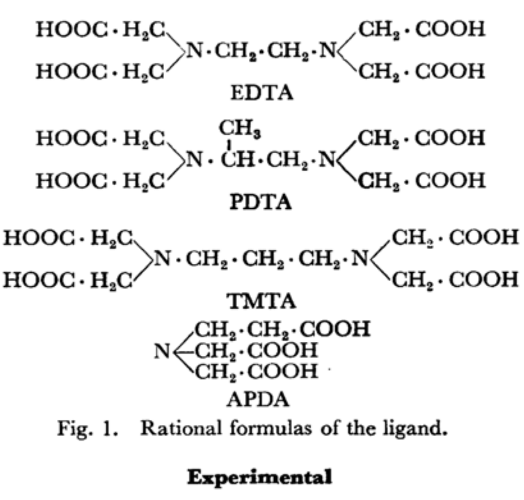

Fig. 1. Rational formulas of the ligand.

Experimental

Preparation of Starting Materials. *Hydrogenethylenediaminetetraacetatoaquochromium(III)*: $[CrHedta(H_2O)]$ (I). This was prepared by a method given in literature[1] and was identified by elemental analysis

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[*1] Part I of this series: R. Tsuchiya, Y. Kaji, A. Uehara and E. Kyuno, This Bulletin, **42**, 1881 (1969).

[*2] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, March, 1968.

1) D. T. Sawyer and J. M. Mckinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).

and IR spectral measurement.

Hydrogen propylenediamine tetraacetato aquo chromium (III) Monohydrate: [CrHpdta(H_2O)]·H_2O (II). The preparation was carried out by the same method[1] and the chemical formula was checked by elemental analysis and IR spectra.

Hydrogen trimethylenediaminetetraacetatoaquochromium(III) Monohydrate: [CrHtmta(H_2O)]·H_2O (III). Thirteen grams of chromium(III) chloride hexahydrate were dissolved in 100 m*l* of water and then 15 g of TMTA were added. After the solution was heated on a water bath at about 80°C for a while, 25 g of potassium hydrogencarbonate was added little by little. After being evaporated to half the volume by aeration, the solution was when necessary, quickly filtered and the filtrate was kept to stand for a while. When red crystals were deposited, they were filtered and washed with a small amount of ethanol-water (1:1) mixture and then with ethanol-ether (1:1) mixture and air-dried. Yield about 18 g. The product was recrystallized in water.

Found: C, 33.77; N, 6.95; H, 4.69%. Calcd for [CrHtmta(H_2O)]·H_2O: C, 33.75; N, 7.16; H, 4.61%.

Hydroxohydrogenammoniapropionicdiacetatodiaquochromium(III): [Cr(OH)Hapda(H_2O)$_2$] (IV). This was prepared by the method reported previously[2] and the identification was carried out in a way similar to that described above.

Hydroxohydrogenammoniapropionicdiacetatodiaquocobalt (III): [Co(OH)Hapda(H_2O)$_2$] (V). Twelve grams of cobalt(II) chloride hexahydrate were dissolved into 100 m*l* of water and another 100 m*l* of water containing 10 g of APDA neutralized with 10 g of potassium hydrogencarbonate was added, and then the mixture was heated on a water bath for about one hour. The clear pink solution obtained was oxidized by 10 m*l* of 10% hydrogen peroxide solution to produce the cobalt(III) complex. After the pH of the solution was adjusted to 2—3, the solution was stood for a few hours. Purple crystals were obtained. The products were recrystallized from its concentrated aqueous solution. Yield about 5 g.

Found: C, 26.49; N, 4.72; H, 4.65%. Calcd for [Co(OH)Hapda(H_2O)$_2$]: C, 26.65; N, 4.44; H, 4.47%.

Derivatographic Measurement. The derivatograms of these complexes expressing simultaneously the results of thermogravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermogravimetric analysis (DTG) were obtained with a Metrimpex Derivatograph Typ-OD-102 made in Hungary. All the experiments were carried out in a nitrogen stream under the heating rate of 1°C/min, and 500 mg of the sample was used in each run. The analyses of derivatograms for each reaction process were carried out in a manner similar to that explained in a previous paper.*1

IR Measurement. The IR spectra were measured with a JASCO Model IR-E Spectrophotometer in Nujol mull state for the samples in the successive, appropriate heating steps appointed from the derivatograms.

Conductivity Measurement. The conductivities of the samples were determined with a Yokogawa Universal Bridge BV-Z-13A.

Result and Discussion

Dehydration Mechanisms in Aquo-EDTA-Like Complexes. Some chemical properties of the samples, I—V, including their IR data are shown in Table 1. Their IR spectra show two characteristic bands near at 1730 and 1640 cm^{-1} which correspond to those assigned by Busch and Bailar[3] in cobalt(III) EDTA complex to the stretching vibration concerning the non-coordinated and coordinated carboxylate anions, respectively. In complexes III, IV and V, above all, the band at 1730 cm^{-1} is shifted to about 1690 cm^{-1} probably due to the stronger interaction between the non-coordinated carboxylate and the neighboring, coordinated H_2O or OH group.[2]

TABLE I. SOME CHEMICAL PROPERTIES OF COMPLEXES

Complex	IR ($\nu_{C=O}$)(cm^{-1}) -COOH	-COO-M	Molar conductivity* (mho cm^{-1})	pH**
I	1738 (s)	1640 (vs)	211.6	2.5
II	1728 (s)	1635 (vs)	278.1	2.6
III	1685 (s)	1630 (vs)	153.8	4.2
IV	1690 (s)	1640 (vs)	2.8	6.4
V	1689 (s)	1640 (vs)	3.2	6.2

* 1.0×10^{-3} mol/*l* aqueous solution was used.

** 1.0×10^{-2} mol/*l* aqueous solution was used.

The lower values of pH and the higher values of the conductivities in complexes, I, II and III, show that they dissociate, to a great extent, into the hydrogen ion and complex anion. But complexes IV and V are all non-electrolytic species in aqueous solution.

The derivatograms for each complex, I—V, are shown in Figs. 2 and 3. The IR spectra of the samples taken at the appropriate step of the thermal reaction processes appearing in the derivatograms were measured. They are shown in Fig. 4.

Complex I loses one mole of the coordinated water about 280°C as seen in Fig. 2, and Fig. 4-a shows that the absorption peak at 1738 cm^{-1} assigned to the non-coordinated carboxylate disappears after the heating at 280°C. It may suggest that, in complex I, the non-coordinated carboxylate comes into the coordination to metal as soon as one water molecule is liberated at the temperature.

In the case of complex II, a small but distinct endothermic change is observed in the DTA curve just before the TGA curve begins to show any weight decrease of the sample as seen in Fig. 2. Fig. 4-b shows that the band assigned to the non-coordinated carboxylate also disappears but the band assigned to the coordinated one remains

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[2] A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **41**, 2385 (1968).

[3] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

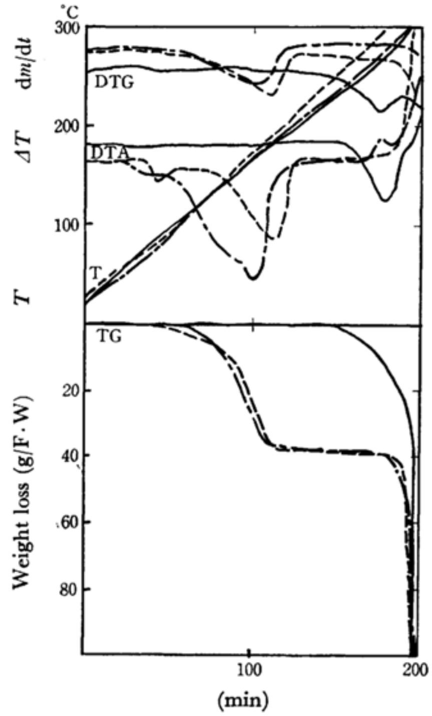


Fig. 2. Derivatograms for I (——), II (------) and III (–·–·–).

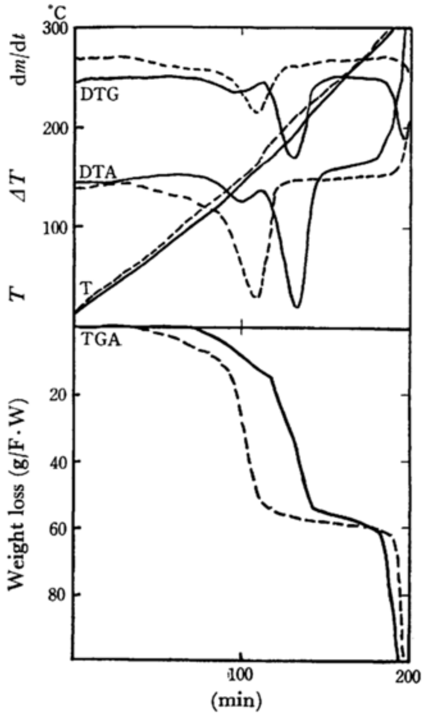
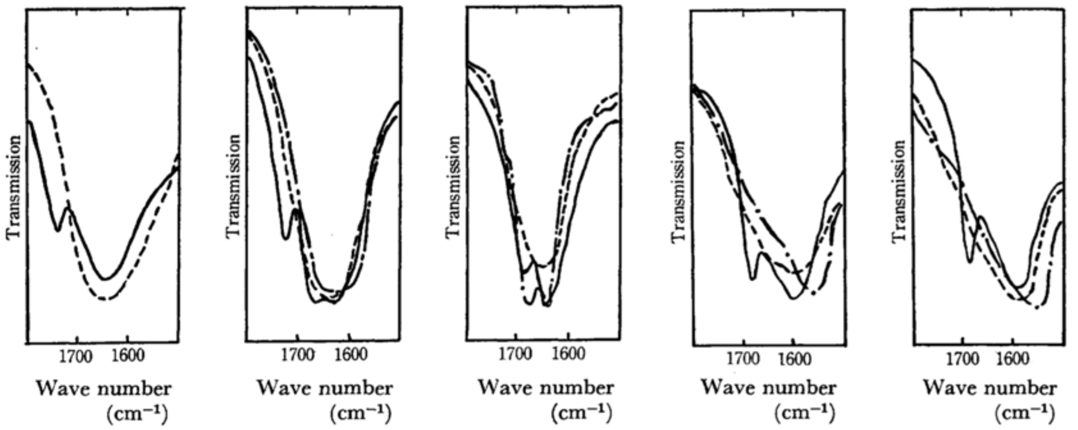


Fig. 3. Derivatograms for IV (——) and V (------).



(a) I (b) II (c) III (d) IV (e) V

Fig. 4. Infrared spectra.

upon heating at *ca.* 95°C. In this step, PDTA anion behaving as a quinquedentate ligand may turn to a sexadentate ligand in the same way as EDTA in complex I. However, differing from I, the change occurring in the coordination number in complex II is due not to the complete liberation of water molecule from the complex, but probably to the separation of water molecule from coordination sphere in the complex itself, without any weight loss.

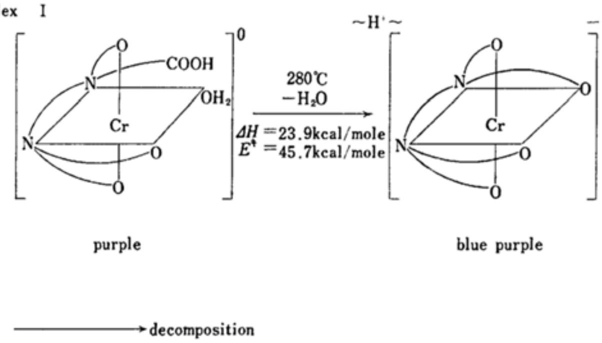
Above 95°C, the weight loss of the sample begins, and two moles of water are successively liberated up to 220°C, which are shown by TGA and DTA curves in Fig. 2. The IR spectrum concerning the carboxylate stretching vibration at 200°C is shown to be similar to that at 95°C as seen in Fig. 4-b, which may indicate no structural change in the coordinated PDTA molecule.

As shown in Fig. 2, in the case of complex III, a small change on the DTA curve also appears at relatively low temperature region, 60—80°C, without giving any weight loss in TGA curve, where the complex shows only a slight color change from red to reddish-violet. The sharp band at 1685 cm^{-1} in IR spectra at room temperature could not be detected in the sample at 80°C as seen in Fig. 4-c, giving the verification that a coordinated carboxylate may come out from the coordination sphere as H_3O^+ in this step, resulting in the coordination of the carboxylate ion, where TMTA molecule turns from a quinquedentate ligand to a sexadentate one. At 90—220°C the DTA curve shows a split peak, probably due to the stepwise liberation of two moles of water from the intermediate, H_3O-[Crtmta]$\cdot H_2O$. Further decomposition begins to proceed at about 280°C and a small exothermic peak appears immediately before decomposition, its significance not being so clear. The reappearance of the peak assigned to the non-coordinated carboxylate in IR spectra in Fig. 4-c may suggest the formation of the ionic intermediate, but its structure is unknown.

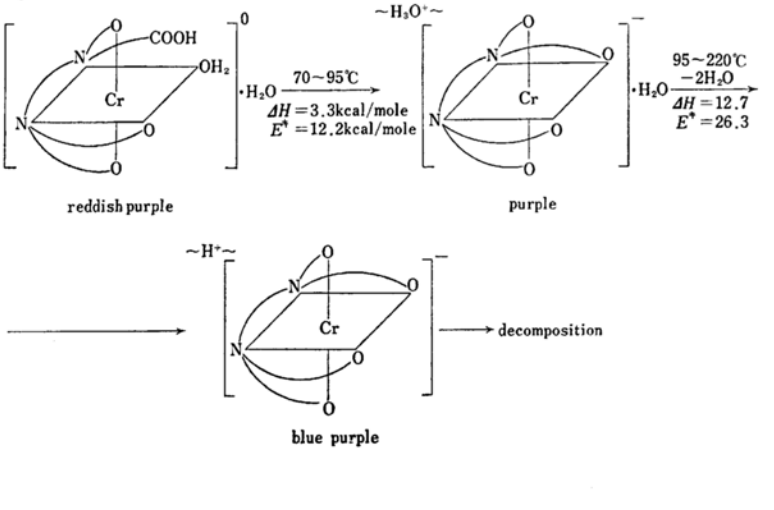
The derivatogram for complex IV in Fig. 3 shows the relatively small, distinct changes in both DTA and DTG curves at 130—160°C corresponding to the weight loss for just one mole of water, and they are accompanied by the great sharp peaks in DTA and DTG at 160—210°C corresponding to the liberation of two moles of water. The IR spectra of IV at 160°C and 210°C, as shown in Fig. 4-d, do not give the band assigned to the non-coordinated carboxylate which was presented at 1690 cm^{-1} at room temperature. These results may suggest that APDA which acted as a terdentate ligand keeping one of the carboxylate group non-coordinated behaves as a quadridentate at 160—210°C owing to the liberation of the first one mole of water which comes from the coordinated OH^- and H^+ of the free carboxylate group.

With complex V, it is found in Fig. 3 that one mole and another two moles of water are gradually liberated, successively. The IR spectra of V at 150°C and 180°C in Fig. 4-c also give no band assigned to non-coordinated carboxylate group

Complex I



Complex II



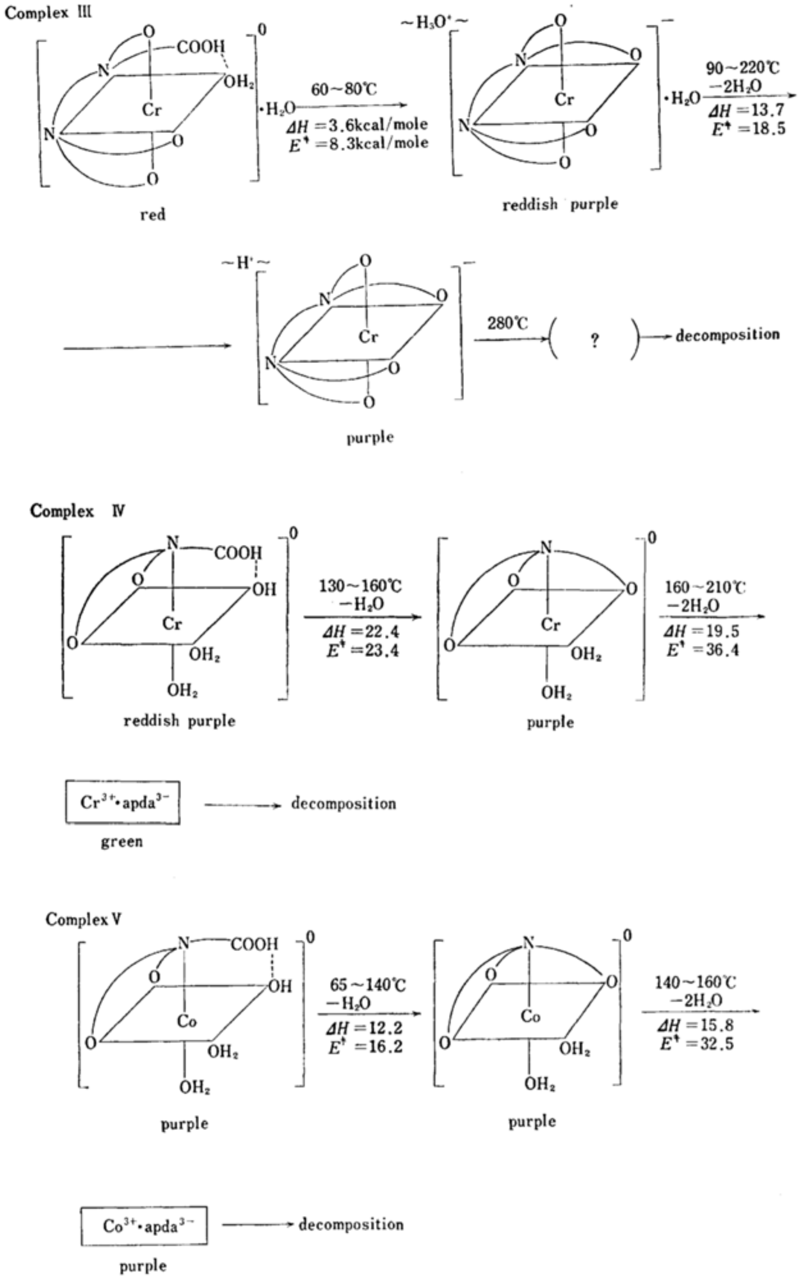


Fig. 5. Possible thermal reaction schemes.

which appeared at room temperature in the same way as those of complex IV. It may suggest that, in complex V also, APDA turns to a quadridentate ligand from a terdentate one at 150°C. The possible thermal reaction schemes for complexes, I—V, are proposed in Fig. 5.

Enthalpy Change and Activation Energy. The enthalpy changes, ΔH, for each step of the thermal decomposition of these complexes were estimated from DTA in the same way as described previously.*1 The activation energies, $E^{\neq}$, for the corresponding steps were calculated by using DTA[4] or DTG[5] curves and by applying the Arrhenius plots to this calculation. The representative Arrhenius plots, $\log k$ *vs.* $1/T$, where k is the rate constant for complexes III and IV are shown in Fig. 6-a, b and Fig. 7-a, b, respectively. The values

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4) H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).

5) N. G. Dave and S. K. Chopra, *Z. Phys. Chem.*, **48**, 257 (1966).

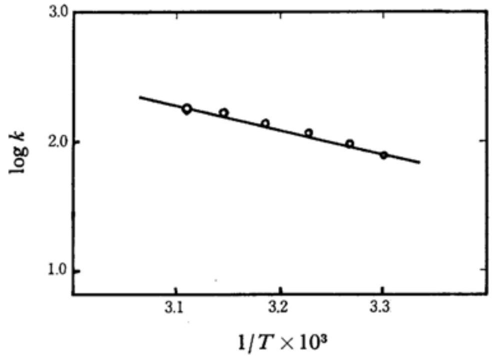

Fig. 6-a. Arrhenius plots for the endothermic reaction at 60—80°C of [CrHtmta (H_2O)]$\cdot H_2O$ from DTA.

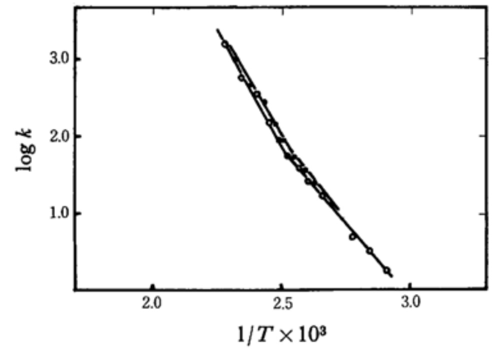

Fig. 6-b. Arrhenius plots for the dehydration reaction at 90—220°C of [CrHtmta (H_2O)]$\cdot H_2O$.

○—○: from DTA ●—●: from DTG

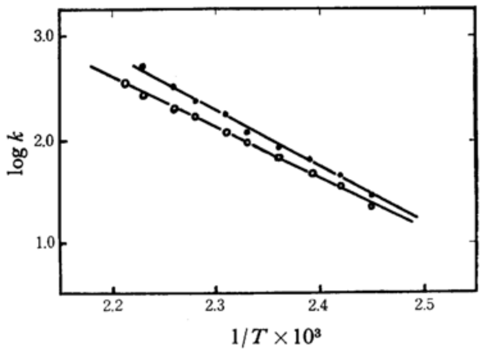

Fig. 7-a. Arrhenius plots for the dehydration reaction at 130—160°C of [Cr(OH)(Hapda)$(H_2O)_2$].

○—○ : from DTA ●—●: fromDTG

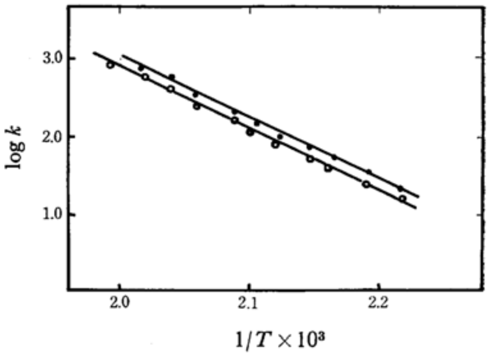

Fig. 7-b. Arrhenius plots for the dehydration reaction of 160—210°C of [Cr(OH)(Hapda)$(H_2O)_2$].

○—○: from DTA ●—●: from DTG

of ΔH and $E^{\ddagger}$ obtained above are given in the corresponding processes in Fig. 5.

The enthalpy changes in the first step of the thermal reaction of complexes II and III, where the coordinated water came out from the coordination sphere to the outer sphere without the liberation of water molecules from the solid phase of the complexes, are obtained in the range of ΔH=3.3—3.6 kcal/mol. On the other hand, those in the second step, where one mole of water was expelled, are estimated within the range of ΔH=12.7—13.7 kcal/mol. Complex III in particular indicates a small exothermic change as ΔH=5.6 kcal/mol at about 280°C. The activation energy for III in the first dehydration process including the transition, 26.8 kcal/mol, is smaller than that in the corresponding process in complex I, 45.7 kcal/mol. It is likely due to the fact that TMTA can coordinate to metal as a sexadentate ligand with less strain than EDTA, owing to a six-membered ring in it.

The activation energies in the first dehydration process for complexes IV and V are approximately close to the respective enthalpy changes. The lower temperature at which the dehydration beings, the smaller enthalpy changes and the lower activation energies in the first and second dehydration processes on cobalt(III) complex V than those on chromium(III) complex IV may indicate that the former is thermally less stable than the latter.

The authors wish to express their appreciation to the Ministry of Education for financial support granted for this research.