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Thermal Decomposition Reactions of Metal Oxalato Complexes in the Solid State. I. Thermographic Studies of Metal Oxalato Complexes

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The thermal decomposition reactions of metal oxalato complexes in the solid state were studied by the TG and DSC methods. The results from TG indicated that the thermal stability of the anhydrous complex decreases approximately with the increase in the electron affinity of the central metal ion. From DSC, the complexes can be divided into two groups, giving endothermic and exothermic peaks on the decomposition of their anhydrous complexes respectively. The two enthalpy changes, ΔH, corresponding to the dehydration and to the decomposition of the anhydrous complexes, are also presented.

Although the thermal properties of metal oxalates have been extensively studied, few studies have been made of metal oxalato-type complexes. Wendlandt and George[1] carried out the thermogravimetry (TG) of $K_3[Cr(ox)_3]3H_2O$, $K_3[Fe(ox)_3]3H_2O$, $K_3[Co(ox)_3]3H_2O$, and $K_3[Rh(ox)_3]2.5H_2O$.

Tanaka and Nanjo[2] have followed the change in the valence state of the central metal ions on the thermal decomposition reactions of $K_3[Fe(ox)_3]$ and $K_3[Co(ox)_3]$; they have suggested that the decomposition of these complexes is initiated by the electron transfer from the coordianted oxalate ion to the central metal ion.

Information on the intermediates and kinetic data on the thermal decomposition reactions of $K_3[Mn(ox)_3]3H_2O$,[3] $K_3[Fe(ox)_3]3H_2O$,[4–7] and $K_3[Co(ox)_3]3H_2O$,[8,9] have been presented by several workers.

In this study, the TG and DSC curves of a number of metal oxalato complexes will be presented, and the relations between the thermal property of the complex and the nature of the central metal ion will be examined.

Experimental

TG and DSC. Thermogavimetric (TG) and Differential scanning calorimetric (DSC) curves were obtained with a Rigaku 2008 CS thermobalance equipped with a standard differential scanning calorimeter in a dynamic nitrogen atmosphere. About ten milligrams of a powdered sample in an aluminum crucible were used in each measurement. The heating rate was exactly linear with the time at about 4°C per min.

Materials. The complexes of Al(III),[10] V(III),[11] Cr(III),[12] Mn(III),[13] Fe(III),[14] Co(III),[15] Rh(III),[16] Cu(II),[17], Pd(II),[18] and Pt(II),[19] were prepared according to the litterature. The $K_2[Zn(ox)_2]2H_2O$ was prepared by boiling $Zn(OH)_2$ with a stoichiometric amount of aqueous $H_2C_2O_4 \cdot 2H_2O$ and $K_2C_2O_4 \cdot H_2O$ until the solution was neutral. The analytical results on the complexes were as follows: $K_3[Al(ox)_3]3H_2O$; C, found, 15.45, calcd, 15.85; H, found, 0.90, calcd, 1.30; $K_3[V(ox)_3]3H_2O$; C, found, 14.76, calcd, 14.79; H, found, 1.19, calcd, 1.23; $K_3[Cr(ox)_3]3H_2O$; C, found, 14.77, calcd, 14.78; H, found, 0.86, calcd, 1.23; $K_3[Fe(ox)_3]3H_2O$; C, found, 14.49, calcd, 14.65; H, found, 0.81, calcd, 1.22; $K_3[Co(ox)_3]3H_2O$; C, found, 14.41; calcd, 14.57; H, found, 1.21, calcd, 1.21; $K_3[Rh(ox)_3]4.5H_2O$; C, found, 12.43, calcd, 12.74; H, found, 1.25, calcd, 1.25; $K_2[Cu(ox)_2]2H_2O$; C, found, 13.48, calcd, 13.56; H, found, 0.93, calcd, 1.13; $K_2[Zn(ox)_2]2H_2O$; C, found, 13.39, calcd, 13.48; H, found, 0.83, calcd, 1.12; $K_2[Pd(ox)_2]3H_2O$; C, found, 11.54, calcd, 11.56; H, found, 1.43, calcd, 1.45; $K_2[Pt(ox)_2]2H_2O$; C, found, 9.55, calcd, 9.89; H, found, 0.66, calcd, 0.83.

Results and Discussion

TG Study. The thermogravimetric curves of the metal oxalato complexes obtained in this work are given in Figs. 1 and 2. The TG curves of Al(III), V(III), Cu(II), Zn(II), Pd(II), and Pt(II) complexes seem to be the first to appear. Although the TG curves of the remaining metals have been presented by several workers, these curves were reproduced under the experimental conditions employed in the present work. The temperature range and the percentage of mass loss are summarized in Table 1. Except for $K_3[Mn(ox)_3]3H_2O$, all the complexes evolved hydrated water at about 100°C to form the corresponding anhydrous complexes. The dehydration of $K_3[Mn(ox)_3]3H_2O$ took place, along with the decomposition of the anhydrous complex. Except for

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Table 1. Temperature range and mass loss of metal oxalato complexes

Complex	Dehydration			Decomposition of anhydrous complex		
	Tamperature range, °C	Mass loss, %		Temperature range, °C	Mass loss, %	
		Obsd.	Calcd.		Obsd.	Calcd.
$K_3[Al(ox)_3]3H_2O$	55—100	9.2	11.7 for $3H_2O$	335—426	28.8	31.2 for $2CO+2CO_2$
$K_3[V(ox)_3]3H_2O$	35—124	10.2	11.1 for $3H_2O$	331—414	23.9	23.9 for $CO+2CO_2$
$K_3[Cr(ox)_3]3H_2O$	32—162	10.5	11.1 for $3H_2O$	325—450	18.8	—
$K_3[Mn(ox)_3]3H_2O$	45—225	16.7	20.0 for $3H_2O+CO_2$			
$K_3[Fe(ox)_3]3H_2O$	30—122	9.1	11.1 for $3H_2O$	230—265	8.7	8.8 for CO_2
$K_3[Co(ox)_3]3H_2O$	48—115	9.5	10.9 for $3H_2O$	115—231	8.7	8.8 for CO_2
$K_3[Rh(ox)_2]4.5H_2O$	25—150	14.6	14.3 for $4.5H_2O$	225—260	23.4	23.4 for $3CO_2$
$K_2[Cu(ox)_2]2H_2O$	85—117	9.8	10.2 for $2H_2O$	247—285	24.4	24.9 for $2CO_2$
$K_2[Zn(ox)_2]2H_2O$	80—130	5.8	10.1 for $2H_2O$	360—430	11.0	11.0 for $1/2CO+1/2CO_2$
$K_2[Pd(ox)_2]3H_2O$	28—110	13.7	13.0 for $3H_2O$	116—190	21.2	21.2 for $2CO_2$
$K_2[Pt(ox)_2]2H_2O$	75—110	6.7	7.4 for $2H_2O$	207—223	18.7	18.1 for $2CO_2$

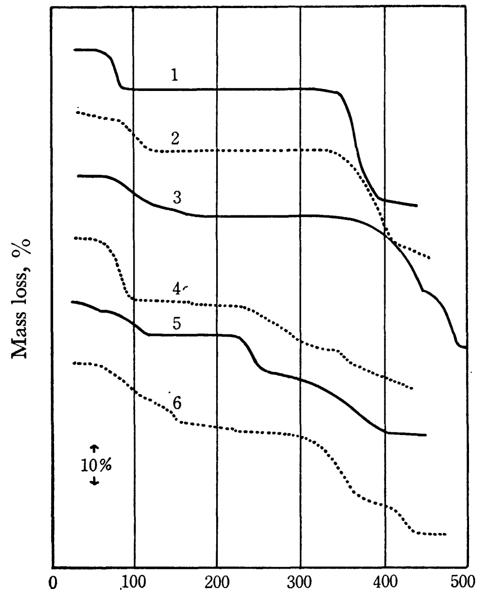

Fig 1. TG curves of (1) $K_3[Al(ox)_3]3H_2O$, (2) $K_3[V(ox)_3]3H_2O$, (3) $K_3[Cr(ox)_3]3H_2O$, (4) $K_3[Mn(ox)_3]3H_2O$, (5) $K_3[Fe(ox)_3]3H_2O$ and $K_3[Co(ox)_3]3H_2O$ in a nitrogen atmosphere.

$K_3[Rh(ox)_3]4.5H_2O$ and $K_2[Pd(ox)_2]3H_2O$, the observed values of mass loss corresponding to the dehydration were somewhat lower than the calculated values for the formula described. This difference may be due to the partial evolution of the hydrated water before measurement. In a previous paper,[1] it has been reported that the rhodium(III) complex evolved 2.5 mol of water in two steps; however, it evolved 4.5 mol of water in one step in the present work.

The order of the decomposition temperatures of the anhydrous complexes is as follows:

$$K_3[Mn(ox)_3]<K_3[Co(ox)_3]<K_2[Pd(ox)_2]<K_2[Pt(ox)_2]<K_3[Rh(ox)_3]<K_3[Fe(ox)_3]<K_2[Cu(ox)_2]<K_3[Cr(ox)_3]<K_3[V(ox)_3]<K_3[Al(ox)_3]<K_2[Zn(ox)_2]$$

This order has no relation to the strength of the metal-oxygen bond as obtained by the infrared spectroscopic

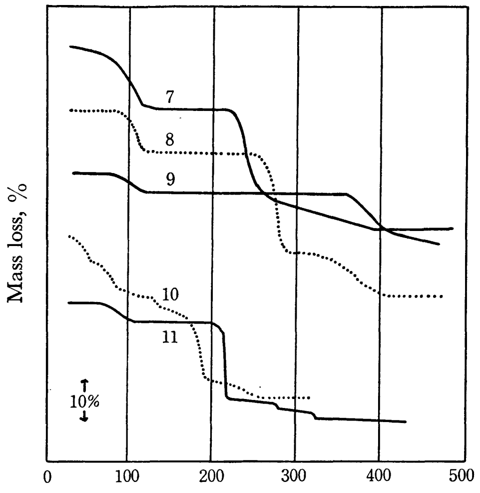

Fig. 2. TG curves of (7) $K_3[Rh(ox)_3]4.5H_2O$, (8) $K_2[Cu(ox)_2]2H_2O$, (9) $K_2[Zn(ox)_2]2H_2O$, (10) $K_2[Pd(ox)_2]3H_2O$ and (11) $K_2[Pt(ox)_2]2H_2O$ in a nitrogen atmosphere.

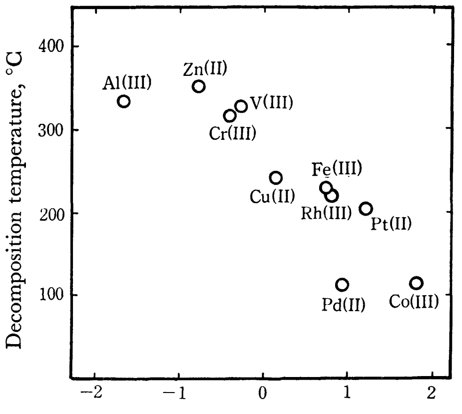

Fig. 3. Correlation of decomposition temperatures of metal oxalato complexes with oxidation-reduction potentials of central metal ions in aqueous solution. The redox potentials adopted correspond to the couples M(II)/M(III) for V, Cr, Fe, and Co, M(0)/M(III) for Al and Rh, and M(0)/M(II) for Cu, Zn, Pd, and Pt, respectively.

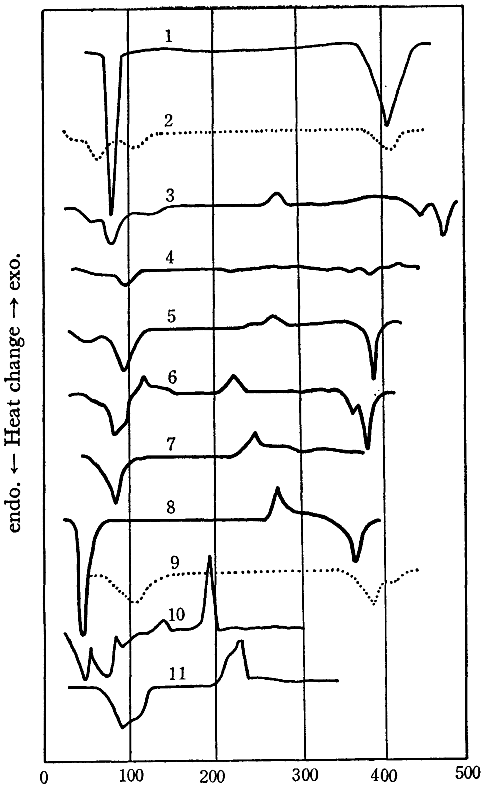

Fig. 4. DSC cruves of (1) $K_3[Al(ox)_3]3H_2O$, (2) $K_3[V(ox)_3]$-$3H_2O$, (3) $K_3[Cr(ox)_3]3H_2O$, (4) $K_3[Mn(ox)_3]3H_2O$, (5) $K_3[Fe(ox)_3]3H_2O$, (6) $K_3[Co(ox)_3]3H_2O$, (7) $K_3[Rh$-$(ox)_3]4.5H_2O$, (8) $K_2[Cu(ox)_2]2H_2O$, (9) $K_2[Zn(ox)_2]$-$2H_2O$, (10) $K_2[Pd(ox)_2]3H_2O$ and $K_2[Pt(ox)_2]2H_2O$ in a nitrogen atmosphere.

study.[20] In Fig. 3, the plots of the decomposition temperatures of the anhydrous complexes *versus* the oxidation-reduction potentials[21] of the central metal ions forming an aquo complex are given. These potentials are considered to measure the relative electron affinities of the central metal ions forming an oxalato complex, since Dq value of H_2O is near to that of $C_2O_4{}^{2-}$. The results in Fig. 3, therefore, indicate that the thermal stability of the anhydrous complex decreases approximately with the increase in the electron affinity of the central metal ion.

DSC Study. The differential calorimetric curves of the complexes obtained in the present work are given in Fig. 4. The values of the enthalpy change, ΔH, corresponding to the dehydration and to the decomposition of the anhydrous complexes are both summarized in Table 2.

Table 2. Enthalpy change of dehydration and decomposition of metal oxalato complexes

Complex	Dehydration (kcal/mol)	Decomposition of anhydrous complex (kcal/mol)
$K_3[Al(ox)_3]3H_2O$	13.9	15.3
$K_3[V(ox)_3]3H_2O$	8.2	4.1
$K_3[Cr(ox)_3]3H_2O$	9.7	−1.9
$K_3[Fe(ox)_3]3H_2O$	12.8	−2.4
$K_3[Co(ox)_3]3H_2O$	13.6	−2.5
$K_3[Rh(ox)_3]4.5H_2O$	12.4	−6.6
$K_2[Cu(ox)_2]2H_2O$	12.1	−3.4
$K_2[Zn(ox)_2]2H_2O$	9.3	2.8
$K_2[Pd(ox)_2]3HO$	9.3	−2.4
$K_2[Pt(ox)_2]2H_2O$	11.3	−6.5

In connection with the enthalpy change corresponding to the dehydration, it should be noticed that there is some difference between the amount of hydrated water from TG and the theoretical value for the formula described. The values calibrated, therefore, are given in Table 2. The values of ΔH corresponding to the dehydration are about 10 kcal/mol for all of the complexes.

From the values of ΔH corresponding to the decomposition of the anhydrous complexes, the anhydrous complexes can be divided into two groups: the complexes of Cr(III), Fe(III), Co(III), Rh(III), Cu(II), Pd(II), and Pt(II), all decomposing with a negative value of ΔH, belong to the first group, while the complexes of Al(III), V(III), and Zn(II), which decompose with a positive value, belong to the second group.

From the analyses of the gaseous products, this division for metal oxalato complexes seems to be suitable; *i.e.*, all the complexes in the first group except for $K_3[Cr(ox)_3]$ evolved only CO_2 upon their decomposition, suggesting an electron transfer from the coordinated oxalate ion to the central metal ion, while the complexes in the second group evolved both CO and CO_2, suggesting the formation of the metal oxide. The details of the gaseous and solid products will be reported later.

The DSC curve of the chromium(III) complex shows a small exothermic peak without any mass loss in the 265—290°C temperature range. This may be due to the transition of the anhydrous complex from the amorphous state (after water removal) to the crystalline state. The ΔH value of this transition was 1.4 kcal/mol. The details of the transition will be reported later.

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