Thermal Decomposition Reactions of Metal Oxalato Complexes in the Solid State. II.[1] Evolved Gas Analyses of Metal Oxalato Complexes

Kenzo Nagase

Department of Chemistry, Tohoku University, Kawauchi, Sendai

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The thermal decomposition reactions of a number of metal oxalato complexes in the solid state were studied by an EGA method in a helium atmosphere. As regards the decomposition stage of an anhydrous complex, the complexes investigated could be divided into three groups: the complexes of Mn(III), Fe(III), Co(III), Rh(III), Cu(II), Pd(II), and Pt(II), this first group giving only CO_2 as a gaseous product, decomposed by electron transfer from an oxalato ligand to a central metal ion; the complexes of Al(III) and Zn(II), this second group giving CO and CO_2 in the molar ratio of 1 : 1, decomposed by C–O bond breaking to form a metal oxide with no change in the oxidation number of a central metal; and the complexes of V(III) and Cr(III), this third group giving CO_2 and a smaller amount of CO, decomposed through both the processes, electron transfer and C–O bond breaking. The subsequent decomposition reactions of the bivalent metal oxalato complexes formed upon heating the corresponding trivalent metal oxalato complexes were divided into two types: one is associated with further reduction of a central metal ion, while the other is associated with C–O bond breaking.

The thermal decomposition reactions of metal oxalato complexes have been studied by several techniques, and the stoichiometries for several complexes have been examined on the basis of their gaseous and solid products.

Broadbent *et al.*[2] have studied the thermal decomposition of $K_3[Fe(ox)_3]$ in a nitrogen atmosphere and found $K_2C_2O_4$ and a chalky yellow solid at 260°C, and, beyond 460°C, a mixture of K_2CO_3 and free iron, by a method of X-ray diffraction identification.

Wendlandt and Simmons[3,4] have suggested that the bivalent metal complexes formed upon heating $K_3[Mn(ox)_3]$ and $K_3[Co(ox)_3]$ below 200°C in a nitrogen atmosphere can be represented by the $K_2[Mn(ox)_2]$ and $K_2[Co(ox)_2]$ formulae on the basis of their reflectance spectra. Tanaka and Sato[5] have assigned the chalky yellow compound, which had been found by Broadbent,[1] to $K_2[Fe(ox)_2]$ on the basis of the infrared and reflectance spectra.

Bancroft *et al.*[6] have also examined the thermal decomposition of $K_3[Fe(ox)_3]$ and suggested the presence of $K_6[(C_2O_4)_2Fe(OX)Fe(C_2O_4)_2]$ (OX=quadridentate oxalato group) on the basis of the infrared spectrum; this differs from the conclusions reported by Broadbent[2] and Tanaka.[5]

Broadbent *et al.*[7] have reported that $K_3[Al(ox)_3]$ decomposes in two stages upon heating above 375°C and that the residue contains Al_2O_3, K_2CO_3, and K_2O, as determined by X-ray diffraction identification.

The studies mentioned above, however, are incomplete, particularly in gaseous products. In the present study, the thermal decomposition reactions of the metal oxalato complexes were studied by a method of EGA (evolved gas analysis) in the temperature range of 25—600°C, and on the basis of the gaseous products, the stoichiometries of the thermal reactions were reexamined; moreover, the stoichiometries for the other metal oxalato complexes will be newly presented.

Experimental

Materials. The complexes used in this study were prepared according to the literature. Analyses of the complexes have been reported in the preceding paper.[1]

Measurements of EG Curves. Evolved gas (EG) curves were obtained with an apparatus consisting of a Shimadzu GC-1C gas chromatograph and a Shimadzu PYR-1A pyrolyzer in a helium atomosphere, at a flowing rate of 50 ml/min. With the rearrangement, the exit line from a pyrolysis chamber is directly connected to a thermal conductivity detector, without passing through a column. The procedure is as follows: about a 3-milligram sample in a platinum boat is introduced into a pyrolysis chamber. After the air is swept out, the temperature of the sample is raised to 600°C at a heating rate of 5°C/min. Changes in the thermal conductivity by the evolved gas are recorded as a function of the temperature of the sample.

Analyses of Gaseous Products. Analyses of gaseous products were performed by the use of the above apparatus equipped with a column, composed of 2-meter-long and 3-millimeter-indiameter stainless steel tubing, packed with 60—80 mesh activated charcoal. The temperature of the detector and the column were maintained at 200°C and 150°C respectively. The procedure was as follows: the temperature at which a peak maximum is observed on a EG curve, and then a sample was introduced into the furnace and it was maintained at that temperature for about 5 min while helium carrier gas was routed through the bypass by means of a two-way valve. By changing the valve, carrier gas is routed through the pyrolysis chamber and gaseous products are carried into the chromatographic column. The retention times are 1.5 min for CO and 3.0 min for CO_2 under the conditions employed in this study.

Results and Discussion

The evolved gas (EG) curves of the metal oxalato

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[1] Paper I of this series: K. Nagase, This Bulletin, **45**, 2166 (1972).

[2] D. Broadbent, D. Dollimore, and J. Dollimore, *J. Chem. Soc.*, **1967**, 451.

[3] W. W. Wendlandt and E. L. Simmons, *J. Inorg. Nucl. Chem.*, **27**, 2317 (1965).

[4] E. L. Simmons and W. W. Wendlandt, *ibid.*, **27**, 2325 (1965).

[5] N. Tanaka and K. Sato, This Bulletin, **43**, 789 (1970).

[6] G. M. Bancroft, K. G. Dhamawardhena, and A. G. Maddock, *Inorg. Nucl. Chem. Lett.*, **6**, 403 (1970).

[7] D. Broadbent, D. Dollimore, and J. Dollimore, *Analyst*, **94**, 543 (1969).

Table 1. Analyses of gaseous products on each decomposition stage (%)

Complex	Stage I	Stage II	Stage III	Stage IV
$K_3[Al(ox)_3]\cdot 3H_2O$	H_2O	$CO(50)$, $CO_2(50)$	—	$CO(81)$, $CO_2(19)$
$K_3[V(ox)_3]\cdot 3H_2O$	H_2O	$CO(27)$, $CO_2(73)$	—	$CO(88)$, $CO_2(12)$
$K_3[Cr(ox)_3]\cdot 3H_2O$	H_2O	$CO(32)$, $CO_2(68)$	$CO(48)$, $CO_2(52)$	$CO(77)$, $CO_2(23)$
$K_3[Mn(ox)_3]\cdot 3H_2O$	H_2O, CO_2		$CO(45)$, $CO_2(55)$	$CO(87)$, $CO_3(13)$
$K_3[Fe(ox)_3]\cdot 3H_2O$	H_2O	CO_2	$CO(19)$, $CO_2(81)$	$CO(23)$, $CO_2(77)$
$K_3[Co(ox)_3]\cdot 3H_2O$	H_2O	CO_2	CO_2	$CO(45)$, $CO_2(55)$
$K_3[Rh(ox)_3]\cdot 4.5H_2O$	H_2O	CO_2	—	$CO(82)$, $CO_2(18)$
$K_2[Cu(ox)_2]\cdot 2H_2O$	H_2O	CO_2	—	$CO(89)$, $CO_2(11)$
$K_2[Zn(ox)_2]\cdot 2H_2O$	H_2O	$CO(44)$, $CO_2(56)$	—	$CO(87)$, $CO_2(13)$
$K_2[Pd(ox)_2]\cdot 3H_2O$	H_2O	CO_2	—	$CO(91)$, $CO_2(9)$
$K_2[Pt(ox)_2]\cdot 2H_2O$	H_2O	CO_2	—	$CO(70)$, $CO_2(30)$
$K_2C_2O_4\cdot H_2O$	H_2O	—	—	$CO(87)$, $CO_2(24)$

complexes and potassium oxalate in the temperature range of 25—600°C are given in Figs. 1—3. These curves show that the complexes investigated decomposed in 3 or 4 stages. Gas analyses of each decomposition stage are sammarized in Table 1.

Dehydration (Stage I). All of the complexes immediately lost hydrated waters upon heating at about 100°C. Except for $K_3[Mn(ox)_3]\cdot 3H_2O$, the complexes showed the corresponding anhydrous plateaus on the EG curves. The dehydration of $K_3[Mn(ox)_3]\cdot 3H_2O$ took place with the decomposition of the anhydrous complex. For the complexes of Al(III), V(III), Cr(III), Fe(III), and Co(III), the peak corresponding to the dehydration splits into two or three, suggesting that water molecules are not held in the crystal lattice in an identical manner. On the other hand, the peaks of Rh(III), Pd(II), and Pt(II) are smooth, with no shoulder, water molecules being held equally in the crystal lattice.

Decomposition of Anhydrous Complexes (Stage II). In contrast to the dehydration, there are big variations in the temperatures at which the anhydrous complexes begin to decompose. Most of the complexes investigated decomposed in one step, but the complexes of Mn(III), Co(III), and Pd(II), which showed no anhydrous plateau, or only a short one, decomposed in two steps. The reason for this difference is not yet clear.

In Table 1, it should be noticed that the complexes can be divided into three groups: the complexes of Mn(III), Fe(III), Co(III), Rh(III), Cu(II), Pd(II), and Pt(II), giving only CO_2, belong to the first group; the complexes of Al(III) and Zn(II), giving CO and CO_2 in the molar ratio of 1: 1, belong to the second group; and the complexes of V(III) and Cr(III), giving CO_2 and a smaller amount of CO, belong to the third group.

The giving of only CO_2 suggests that electron transfer takes place from an oxalate to a central metal ion. The stoichiometries for the complexes in the first group may be represented by the following equations:

$$K_3[M^{III}(ox)_3] \longrightarrow K_2[M^{II}(ox)_2] + 1/2K_2C_2O_4 + CO_2 \quad (M=Mn,\ Fe,\ and\ Co)$$

$$K_3[M^{III}(ox)_3] \longrightarrow M + 3/2K_2C_2O_4 + 3CO_2 \quad (M=Rh)$$

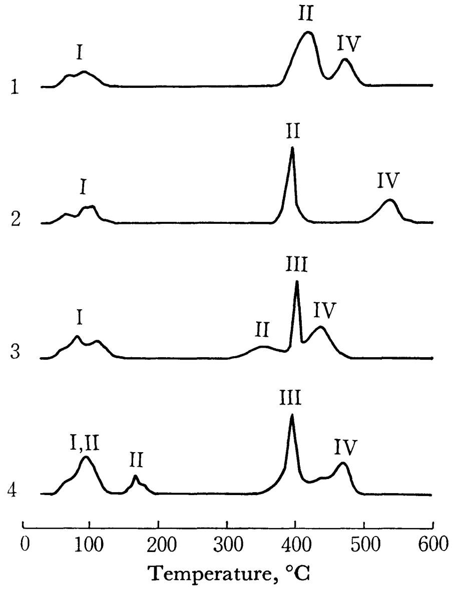

Fig. 1. EG curves of (1) $K_3[Al(ox)_3]\cdot 3H_2O$, (2) $K_3[V(ox)_3]\cdot 3H_2O$, (3) $K_3[Cr(ox)_3]\cdot 3H_2O$, and (4) $K_3[Mn(ox)_3]\cdot 3H_2O$ in a helium atmosphere.

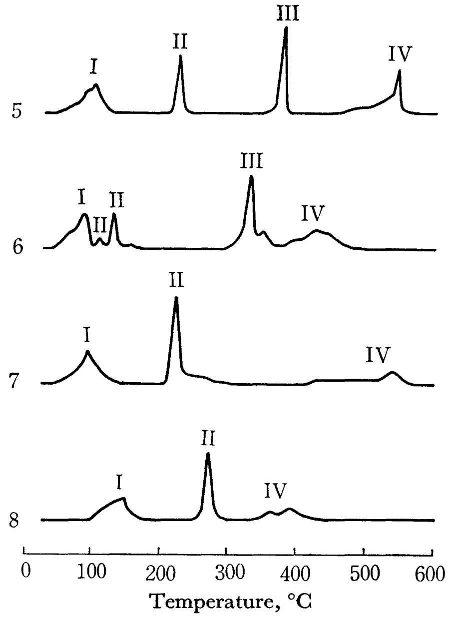

Fig. 2. EG curves of (5) $K_3[Fe(ox)_3]\cdot 3H_2O$, (6) $K_3[Co(ox)_3]\cdot 3H_2O$, (7) $K_3[Rh(ox)_3]\cdot 4.5H_2O$, and (8) $K_2[Cu(ox)_2]\cdot 2H_2O$ in a helium atmosphere.

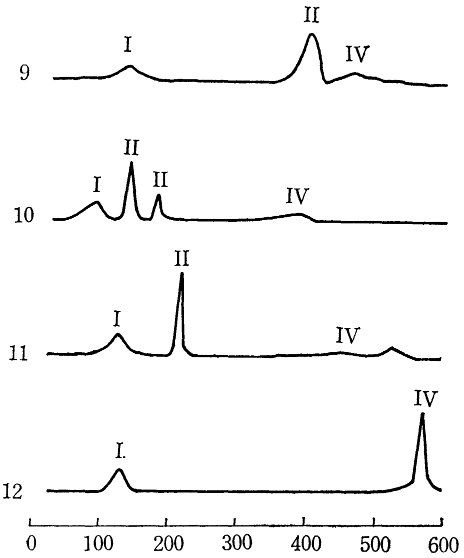

Fig. 3. EG curves of (9) $K_2[Zn(ox)_2]\cdot 2H_2O$, (10) $K_2[Pd(ox)_2]\cdot 3H_2O$, (11) $K_2[Pt(ox)_2]\cdot 2H_2O$, and (12) $K_2C_2O_4\cdot H_2O$ in a helium atmosphere.

$$K_2[M^{II}(ox)_2] \longrightarrow M + K_2C_2O_4 + 2CO_2 \qquad (M=Cu,\ Pd,\ and\ Pt)$$

The results from the TG and the DSC, which have been reported in the preceding paper, are consistent with these equations.

For the complexes in the second group, the following equations are possible:

$$K_3[Al(ox)_3] \longrightarrow 1/2Al_2O_3 + 3/2K_2C_2O_4 + 3/2CO + 3/2CO_2$$

$$K_2[Zn(ox)_2] \longrightarrow ZnO + K_2C_2O_4 + CO + CO_2$$

In this case, the decomposition of the complexes may be initiated by C–O bond breaking, thus forming a metal oxide with no change in the valency of the central metal. In fact, Dollimore *et al.* have confirmed the formation of Al_2O_3 upon the thermal decomposition of $K_3[Al(ox)_3]$. The results from the TG and the DSC, which have reported in the preceding paper, also support the above equations.

The decreasing order of the redox potentials of metal ions forming aquo ions is as follows:

$$Co(III>Mn(III)>Pt(II)>Pd(II)>Rh(III)>Fe(III)$$
$$Cu(II)>V(III)>Cr(III)>Zn(II)>Al(III)$$

The complexes involving the metal ions listed on the left-hand side of Cu(II) in this series caused an electron transfer from an oxalate to a central metal upon heating, while the complexes of Al(III) and Zn(II), with the most negative potential, did not cause the electron transfer. The metal ions, V(III) and Cr(III) in reducibility, exist in the critical region. In view of the reducibility, in addition to the observation that the CO/CO_2 ratio was considerably smaller than 1, it may be supposed that the complexes of V(III) and Cr(III) in the third group decompose through both the processes, electron transfer and C–O bond breaking.

Subsequent Decomposition (Stage III). The decomposition of the bivalent metal oxalato complexes, probably $K_2[Cr(ox)_2]$, $K_2[Mn(ox)_2]$, $K_2[Fe(ox)_2]$, and $K_2[Co(ox)_2]$, which were formed by heating the corresponding trivalent complexes, can be divided into two types. One may be represented by the equation:

$$K_2[M^{II}(ox)_2] \longrightarrow M + K_2C_2O_4 + 2CO_2 \qquad (M=Fe\ and\ Co)$$

which involves electron transfer from an oxalate to a central metal ion, while the other may be represented by the equation:

$$K_2[M(ox)_2] \longrightarrow MO + K_2C_2O_4 + CO + CO_2 \qquad (M=Cr(II)\ and\ Mn(II))$$

which involves C–O bond breaking.

This division is supported by the reducibility of a bivalent metal ion as well as by the analyses of gaseous products. The decreasing order of the redox potentials of bivalent metal ions forming aquo ions is as follows:

$$Pt(II)>Pd(II)>Cu(II)>Co(II)>Fe(II)>$$
$$Zn(II)>Mn(II)$$

Subsequent Decomposition (Stage IV). The decomposition of the $K_2C_2O_4$ formed on the thermal decomposition of the complexes was the final decomposition stage in the temperature range of 25—600°C. From the EG curves, the peak maximum corresponding to the decomposition of $K_2C_2O_4$ appears at a lower temperature than that of pure $K_2C_2O_4$. This suggests that an included metal or a metal oxide may act as a catalyzer.

The analyses of the gaseous products in Table 1 show that the peak corresponding to the decomposition of $K_2C_2O_4$ involved CO and CO_2, which suggests that the decomposition of $K_2C_2O_4$ can be represented by the following equations:

$$K_2C_2O_4 \left\{ \begin{array}{l} \xrightarrow{\text{I}} K_2CO_3 + CO \\ \xrightarrow{\text{II}} K_2O + CO + CO_2 \\ \xrightarrow{\text{III}} K_2O + 1/2C + CO_2 \end{array} \right.$$

where Process I may be the main one for most of the complexes investigated, since CO is the main product for these complexes. The formations of K_2CO_3 and K_2O have been confirmed, by X-ray diffraction identification,[7] upon the thermal decomposition of $K_3[Al(ox)_3]$. The residue obtained by heating $K_3[Al(ox)_3]$ at 500°C was white, but the residue of pure $K_2C_2O_4$ at 600°C was gray. This difference suggests that Process III is possible for the decomposition of pure $K_2C_2O_4$, but impossible for the $K_2C_2O_4$ formed on the thermal decomposition of $K_3[Al(ox)_3]$. The $2CO \rightarrow CO_2 + C$ reaction which has been suggested by several workers, may not occur under the conditions employed in this work, since carbon was not always formed upon heating the complexes at 600°C. The details of this stage will be reported later on the basis of analyses of solid products.

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