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The Thermal Decomposition Reactions of Bivalent Metal Succinates in the Solid State

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The thermal decomposition reactions of $MC_4H_4O_4$ (M : Mg(II), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II)) in nitrogen or helium were investigated by means of TG-DTA, X-ray diffraction measurements, gas chromatography, and combustion analysis for carbon. The decomposition residues of the Mg and Zn salts were composed of the corresponding metal oxides and some carbon, while those of the Co, Ni, Cu, and Pb salts were composed of the corresponding metals and some carbon. H_2, O_2, CO, CO_2, H_2O, CH_4, C_2H_2, C_2H_4, $HCOOCH_3$, $HCOOC_2H_5$, $CH_3COOC_2H_5$, $C_2H_5COOC_2H_5$, and $(CH_2CO)_2O$ were identified as the gaseous decomposition products; the compositions of the gaseous mixtures varied a great deal with the metals. Possible reaction mechanisms were discussed mainly on the basis of the decomposition products.

The thermal decomposition reactions of metal formates and oxalates have been widely investigated. In the case of metal oxalates, the primary decomposition stages was divided in three types, forming (i) metal oxide and an equimolar mixture of CO and CO_2, (ii) metal and CO_2, and (iii) metal carbonate and CO.[1] The tendency to form either metal or metal oxide is consistent with the prediction on thermodynamic grounds of the Ellingham diagram.[2]

The thermal decomposition reactions of metal salts of carboxylic acids with high proportions of both hydrogen and carbon have also been investigated by many workers, but the reactions are not well established in terms either of decomposition product or mechanism. Limited to metal succinates, only fragmentary information is available in the literature.[3–5]

In the present study, the solid and gaseous decomposition products of the anhydrous succinates of Mg(II), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) will be determined in detail, and the reaction mechanisms of these salts will be discussed on the basis of the results obtained systematically.

Experimental

Materials. The metal succinates were prepared by dissolving the corresponding metal carbonates in an aqueous solution of succinic acid. The values of the elemental analyses of C and H agreed with the calculated values within ±0.3% for all the salts.

Measurements. The thermogravimetric(TG) and differential thermal analytic(DTA) curves were obtained with a Shinku Riko TGD-3000 apparatus at a heating rate of 10 °C/min. In each measurement, *ca.* 20 mg of powdered sample was placed in a platinum crucible. X-Ray diffraction measurements were carried out with a Toshiba ADG-101 diffractometer in a nitrogen atmosphere. Except for the cobalt samples, Cu*Kα* radiation and a nickel filter were used. Fe*Kα* radiation and a manganese filter were used for the cobalt samples.

The evolved gas curves were obtained by the conductometric technique at a heating rate of 10 °C/min in a helium atmosphere. The procedure was described in a previous paper.[6] Analyses of evolved gas were performed with a Shimadzu GC-1C gas chromatograph and a Shimadzu PYR-1A pyrolyzer. A column (2 meters long) packed with 60—80 mesh active carbon was used for the analysis of nonpolar gases, and a column (2 meters long) with 60—80 mesh Gaskuro Kogyo Chromosorb-101 was used for that of polar gases. The procedure was as follows: the temperature of the pyrolysis chamber was adjusted to the peak temperature on the evolved gas curves. *Circa* 3 mg of a powdered sample in a platinum boat was introduced into the pyrolysis chamber, and it was then maintained at that temperature for 3 min. By changing the two-way valve, helium carrier gas (60 ml/min) was routed through the pyrolysis chamber so that the evolved gases were carried out into the column which was maintained at a constant temperature. The column temperatures were 100 °C for active carbon and 60, 90, and 120 °C for Chromosorb-101. The retention times were as follows: active carbon column (at 100 °C): 0.5 (H_2), 0.9(O_2), 1.1(CO), 2.0(CH_4), 3.7(CO_2), 13.5(C_2H_2), and 19.8(C_2H_4) min. Chromosorb-101 column (at 120 °C):1.2(H_2O), 2.2($HCOOCH_3$), 5.2 ($HCOOC_2H_5$), 11.7 ($CH_3COOC_2H_5$), and 27.5($C_2H_5COOC_2H_5$). The assignments were checked by using columns coated with liquid paraffin or triacetin.

Results

The TG-DTA curves of the salts of Mg, Co, Ni, Cu, Zn, and Pb in a nitrogen atmosphere are given in Figs. 1 and 2. A weight-loss beginning at 25—62 °C for the salts of Mg, Co, Ni, and Cu corresponded to the removal of the water molecules contained in these salts. The anhydrous salts of Mg, Co, and Ni just after the dehydration were amorphous, and the anhydrous salts of Mg and Co recrystallized at 306 and 272 °C respectively, with a sharp exotherm on each DTA curve. The lead salt showed an endotherm at 160 °C on its DTA curve. The endothermic passage corresponded to the phase transition from tetragonal to cubic. The details of the thermal behavior before the decomposition of the anhydrous salts will be reported elsewhere.

The decomposition of the anhydrous salts began at 237—426 °C. The decomposition temperatures (t_i) which were determined by means of the initial weight-loss temperatures, varied a great deal with the metal as may be seen in Table 1. Except for the magnesium salt, the DTA peaks splits into two or more, suggesting that these salts decomposed through multiple steps. The infrared absorption measurements at several magnitudes of the decomposition showed no presence of solid intermediates in the course of the decomposi-

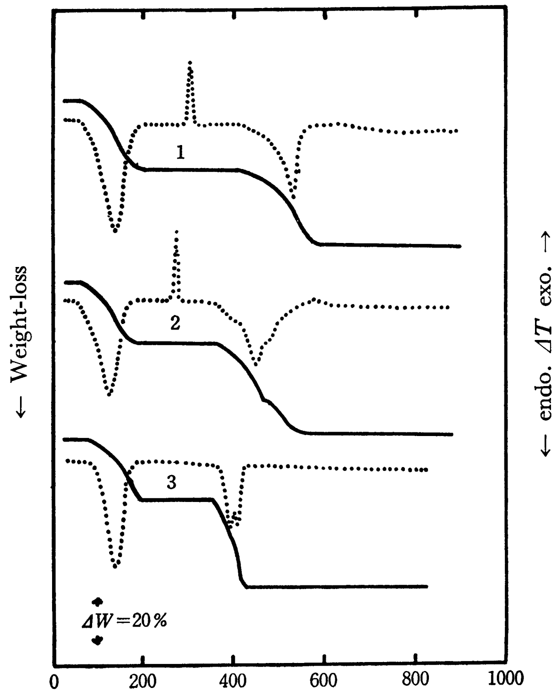

Fig. 1. TG-DTA curves of (1) $MgC_4H_4O_4 \cdot 4H_2O$, (2) $CoC_4H_4O_4 \cdot 4H_2O$, and (3) $NiC_4H_4O_4 \cdot 4H_2O$ in a nitrogen atmosphere: — indicates TG and ···, DTA.

tion processes. Except for the salts of Mg, Zn, and Pb, however, the values of CO/CO_2 in the gaseous mixtures were greatly different between the primary and following steps. In the case of the copper salt, which decomposed in two steps, the CO/CO_2 ratio at the primary step was 2.3, while that at the secondary step was near zero. The salts of CO and Ni showed a similar tendency. On the other hand, the salts of Mg, Zn, and Pb predominantly evolved CO_2 over the decomposition processes.

The X-ray diffraction measurements confirmed that the final decomposition products for the salts of Co, Ni, Cu, and Pb were the metals, while those for the magnesium and zinc salts were the metal oxides. In the case of the zinc salt, however, the vaporization of zinc metal was observed above 600 °C, so no well-difined plateau for zinc oxides was seen on its TG curve, the reduction of zinc oxide probably taking place above that temperature. Although the product of the lead salt was identified as lead metal by the X-ray diffraction, it did not melt even well above the melting point of pure lead (327.3 °C). The lead metal obtained might be finely divided pyropholic lead metal, as indicated in the thermal decomposition of lead citrate[7] and tartarate.[8]

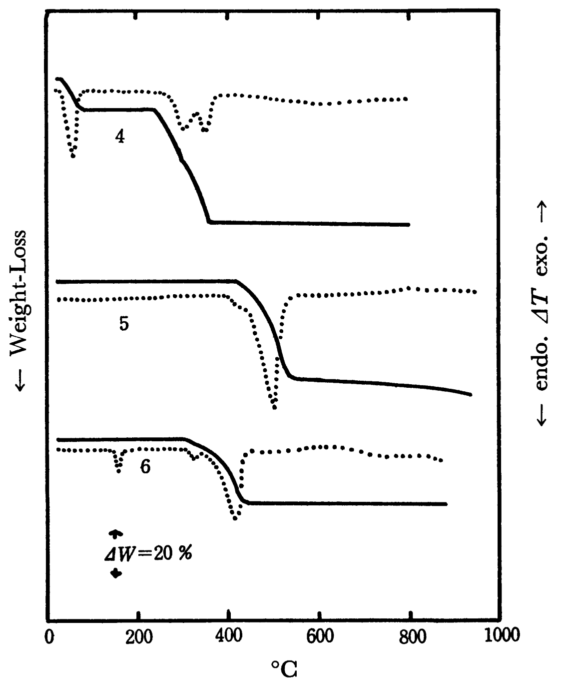

Fig. 2. TG-DTA curves of (4) $CuC_4H_4O_4 \cdot 2H_2O$, (5) $ZnC_4H_4O_4$, and (6) $PbC_4H_4O_4$ in a nitrogen atmosphere: — indicates TG and ···, DTA.

The decomposition residues for all the salts contained some carbon in addition to the metals or the metal oxides. The amount of carbon included was determined by combustion analysis (Table 1). There is possibility of the formation of the metal carbides, as has been reported in connection with the thermal decomposition of nickel malonate in a vacuum.[9] In the present work, however, no X-ray diffraction lines corresponding to the metal carbides were observed. The weight-losses (ΔW_{obsd}) agreed approximately with the values calculated (ΔW_{cald}) for the compositions which were evaluated from X-ray diffraction measurements and combustion analysis for carbon, as may be seen in Table 1.

The gas chromatograms of the salts of Mg, Co, and Cu are given in Figs. 3 and 4 as examples. They correspond to the evolved gases when the anhydrous salts were pyrolyzed at the final peak temperature of

TABLE 1. INITIAL DECOMPOSITION TEMPERATURES (t_i), WEIGHT-LOSSES (ΔW) AND DECOMPOSITION RESIDUES OF THE SUCCINATES, AND HEATS OF FORMATION (ΔH_f°) OF THE METAL OXIDES $M + 1/2O_2 \rightarrow MO$

Salt	t_i/°C	ΔW_{obsd}/%	ΔW_{calcd}[a]/%	Residue	ΔH_f°/kcal
$MgC_4H_4O_4 \cdot 4H_2O$	409	34.9	35.8	MgO+2.0C	−143.8
$CoC_4H_4O_4 \cdot 4H_2O$	356	39.3	40.2	Co+1.4C	−57.2
$NiC_4H_4O_4 \cdot 4H_2O$	351	39.6	39.7	Ni+1.5C	−58.4
$CuC_4H_4O_4 \cdot 2H_2O$	237	50.2	51.6	Cu+0.4C	−37.1
$ZnC_4H_4O_4$	426	42.9	41.9	ZnO+1.2C	−83.2
$PbC_4H_4O_4$	309	27.7	29.7	Pb+1.6C	−52.1[b]

a) The values calculated from the compositions in the the column of "Residue." b) Yellow form.

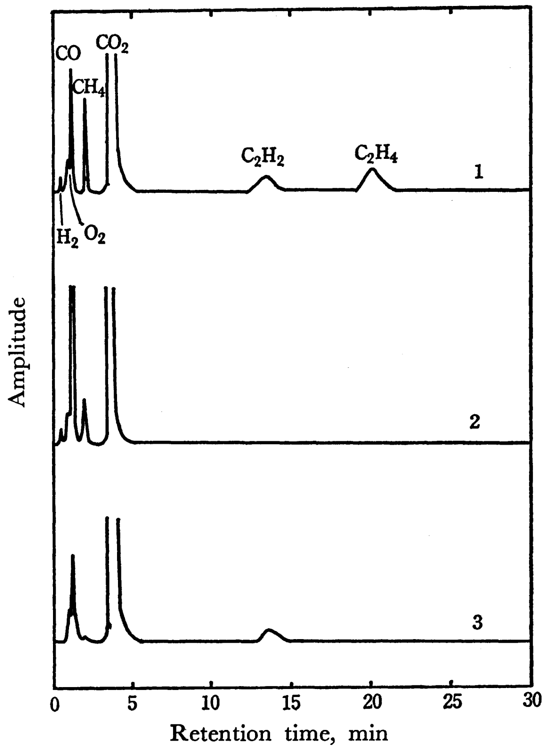

Fig. 3. Gas chromatograms of (1) $MgC_4H_4O_4$, (2) $CoC_4H_4O_4$, and (3) $CuC_4H_4O_4$, using an active carbon column.

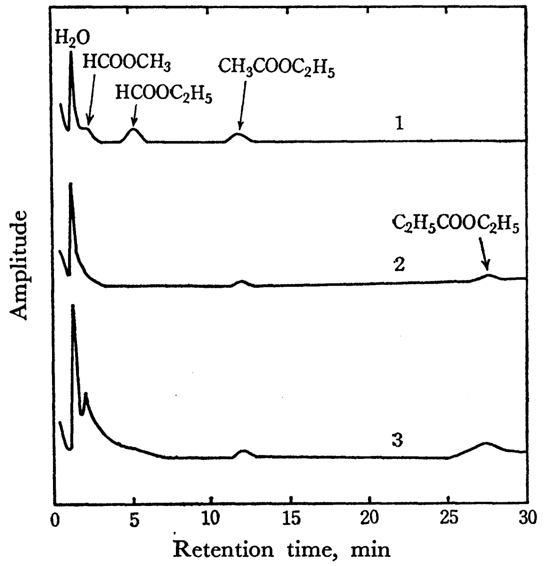

Fig. 4. Gas chromatograms of (1) $MgC_4H_4O_4$, (2) $CoC_4H_4O_4$, and $CuC_4H_4O_4$, using a Chromosorb-101 column.

each evolved gas curve. Although CO_2 predominated in the gaseous products for all the salts, the compositions of the gaseous mixtures varied considerably with the metals. The salts investigated could be divided in three groups. The magnesium and zinc salts, which gave similar chromatographic patterns, evolved hydrogen-rich compounds, such as H_2, CH_4, and C_2H_4, while the copper and lead salts in another group tended to evolve O_2, H_2O, $HCOOCH_3$, and C_2H_2. The latter gases are relatively oxygen-rich or hydrogen-poor compounds. Although H_2O and $HCOOCH_3$ were observed for all the salts, the latter salts were richer in them. The cobalt and nickel salts were intermediate between the two groups in the quantities of CH_4 and H_2O and were characterized as evolving a large amount of CO. All the salts gave succinic anhydride in addition to the gases shown in the gas chromatograms. Its formation was confirmed by infrared measurements.

Discussion

The values of t_i increased with the decrease in the heats of formation of metal oxide (ΔH_f°), as may be seen in Table 1, with the exception of the magnesium salt. The values of t_i for the salts of Co, Ni, Cu, and Pb, which gave the metals as decomposition residues, were correlated by a straight line with ΔH_f° (Fig. 5), suggesting that the decomposition of these salts may be initiated by electron transfer from a succinate anion to a metal cation, as has been indicated for metal oxalates and metal oxalato complexes.[10)]

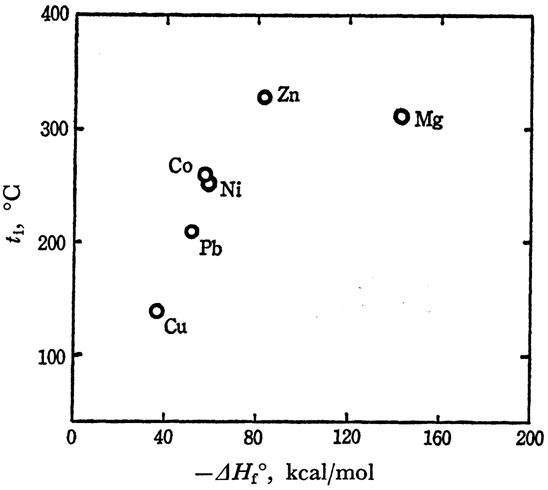

Fig. 5. Correlation of initial decomposition temperatures(t_i) of the anhydrous succinates with heats of formation(ΔH_f°) of the metal oxides.

The amounts of carbon in the decomposition residues are considered to correlate, to some extent, with ΔH_f°, since such secondary reaction as

$$MO + C \longrightarrow M + CO$$

or

$$MO + 1/2C \longrightarrow M + 1/2CO_2$$

are possible at the decomposition temperatures. In fact, the amount of carbon decreased with the increase in ΔH_f°, with a few exceptions (Table 1).

The amounts of H_2 and O_2 are also considered to correlate with ΔH_f° as a result of possible secondary reactions, such as

$$M + 1/2O_2 \longrightarrow MO$$
$$MO + H_2 \longrightarrow M + H_2O$$

In the case of the salt of Cu, which is thermodynamically most stable in the metallic state, the evolution of

H_2 was not observed. It is difficult to discuss the reaction schemes in detail, since the overall reactions might be composed of a number of elementary reactions whose contributions might vary with the reaction temperature, the decomposition pressure, and the extent of decomposition.

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