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Comparative Study of the Polymorphic Species of Strontium and Calcium Formates. I. Differential Thermal Analysis (DTA)

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The existence of new polymorphic varieties of strontium formate (β, δ) and calcium formate (γ, δ) has been established by differential thermal analysis. In our experimental conditions the following species are detected: β-$Sr(HCOO)_2$ below 235°C; δ-$Sr(HCOO)_2$ above 235°C; γ-$Ca(HCOO)_2$ between 150 and 300°C; and δ-$Ca(HCOO)_2$ beyond 300°C. It is shown that some of the corresponding polymorphic transitions for these formates are possible only in the presence of water traces.

Introduction

To date, two polymorphic species of calcium formate have been reported, and only one for each of the three formates of strontium, barium and lead II. According to the literature, they are called α- and β-$Ca(HCOO)_2$, α-$Sr(HCOO)_2$, α-$Ba(HCOO)_2$ and α-$Pb(HCOO)_2$, respectively. All these species exist at room temperature and atmospheric pressure. The α species of strontium (*1*), barium (*2*) and lead II (*3*) formates are isomorphous, but α-$Ca(HCOO)_2$ (*4*) and α-$Sr(HCOO)_2$ (*1*) are not.

If other species of these formates appear at higher temperatures or in peculiar experimental conditions, some of them could be isomorphous. The investigation of new polymorphic species of strontium and calcium formates has been attempted first by differential thermal analysis, and the experimental results obtained with this technique are mentioned in this work. A second article will deal with the results obtained by infrared spectroscopy and X-ray diffraction.

Experimental

1. Sample Preparation

The preparation of α-$Ca(HCOO)_2$ and β-$Ca(HCOO)_2$ has already been described elsewhere (*5*). Strontium formate has been obtained in solution by reaction of formic acid (40% by volume) on the carbonate. After evaporation, this solution yields $Sr(HCOO)_2 \cdot 2H_2O$ crystals which have been recrystallized twice from aqueous solution. At 130°C this dihydrate gave the "anhydrous" salt α-$Sr(HCOO)_2$; this compound is not rehydrated in the air at room temperature.

2. Apparatus

A differential thermal microanalyser, "B.D.L." type, M_3 model, with hollow thermocouples, 25 μl in capacity has been used. This apparatus functions to provide a controlled atmosphere and it may be run without any perturbation with a gaseous flow not exceeding 0.6 liter hr^{-1}. The heating rate is nearly linear, but in our temperature range (25–400°C) the cooling rate cannot be controlled.

3. Experimental Conditions

Except in some particular cases, where single crystals were used, the formate samples were ground in a mortar. The granulometry had no noticeable influence on the recordings. No more than 10 mg were used in each run. Alumina has been chosen as a reference material, and the usual heating rate was 5°C min^{-1}. The running (T) and differential (ΔT) temperatures were recorded simultaneously.

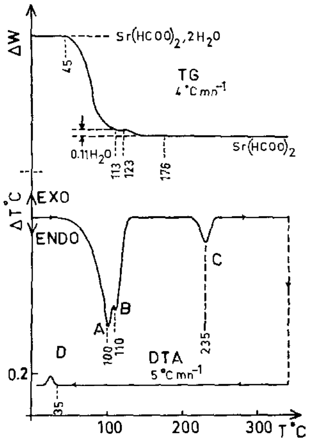

FIG. 1. TG and DTA on $Sr(HCOO)_2 \cdot 2H_2O$, first thermal cycle at $p_{H_2O} = 17.4$ Torr.

4. *Other Experimental Techniques*

When necessary, thermogravimetry (TG) has also been performed. The apparatus was a D.A.M.-Ugine-Eyraud, B 28 model thermobalance.

X-ray diffraction and infrared absorption (ir) were used in order to detect and characterize the encountered phases at the beginning, in the course or at the end of the DTA experiments. Specially adapted heating devices have been used for carrying out the latter investigations at higher temperatures (*6–8*).

Experimental Results

1. *Strontium Formate*

a. $Sr(HCOO)_2 \cdot 2H_2O$. Our first study has been devoted to following, by DTA and TG, the formation under controlled atmosphere ($p_{H_2O} =$ 17.4 Torr) of α-$Sr(HCOO)_2$ from the dihydrate $Sr(HCOO)_2 \cdot 2H_2O$. These experiments gave the recordings drawn on Fig. 1, on which the following may be noticed:

(1) the first endothermic effect on the DTA curve, which occurs between 45 and 135°C, corresponds to the complete weight-loss of the two water molecules of the dihydrate, as indicated by the TG curve; in fact, this thermal effect is constituted of two peaks *A* (at 100°C) and *B* (at 110°C) related respectively to two successive weight-losses;
(2) the endotherm *C* at 235°C has no connection with any weight-loss;
(3) during the first cooling, followed by DTA only, an exotherm *D* is observed close to 30°C, and, according to the anhydrous formate preparation process, is attributed to α-$Sr(HCOO)_2$ formation.

In the course of a second thermal cycle, which has been performed immediately after the first one, the DTA curve of Fig. 2 has been obtained, on which can be seen:

(1) an endotherm at 235°C on heating, which is the peak *C* on Fig. 1;
(2) an exotherm on cooling, located exactly at the same place as the peak *D* on Fig. 1.

b. α-$Sr(HCOO)_2$. Using α-$Sr(HCOO)_2$, we carried out a thermal cycle similar to the previous ones, but in a dry air-flow and got the DTA curve of Fig. 3a. Again the endotherm at 235°C is observed on heating, but there is no thermal effect on cooling. When a dry atmosphere is always kept

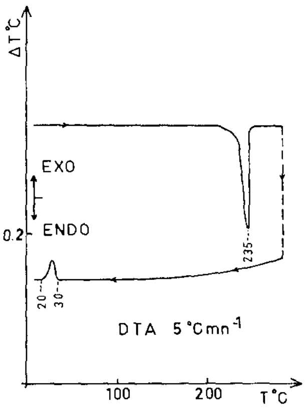

FIG. 2. DTA on $Sr(HCOO)_2 \cdot 2H_2O$, second thermal cycle at $p_{H_2O} = 17.4$ Torr.

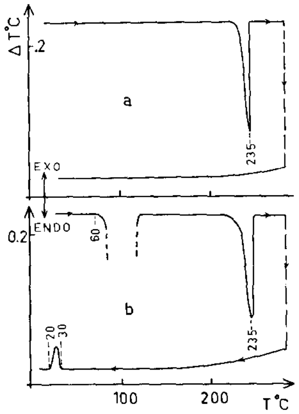

FIG. 3. DTA on α-$Sr(HCOO)_2$. (a) Thermal cycle in a dry air-flow; (b) same sample treated 16 hr at $p_{H_2O} = 17.4$ Torr and then heated and cooled in the humid air-flow.

on the same sample, no thermal effect at all is observed, neither on heating nor on cooling.

If the same sample is subjected to a humid air-flow, it will be found that each time the sample has been in the presence of water on cooling, the exotherm *D* appears (cf. Fig. 1 and 3b).

All these observations can be indefinitely reproduced. They show that α-Sr(HCOO)$_2$ exhibits on heating, without any appreciable weight-loss, an endothermic transformation *C* which can therefore be ascribed to the formation of a new polymorphic high temperature variety, namely δ-Sr(HCOO)$_2$. This has been confirmed by X-ray investigations, which furthermore reveal the existence of a third polymorphic species, β-Sr(HCOO)$_2$, obtained after δ-Sr(HCOO)$_2$ has been cooled. This β-Sr(HCOO)$_2$ phase is exothermally transformed into α-Sr(HCOO)$_2$ in the presence of water vapor. In the absence of water traces, the reversible $\beta \rightleftarrows \delta$ transformations can indefinitely be observed only by X rays (*9*), without any thermal effect as detected by DTA.

2. Calcium Formate

It has been previously established (*5*) that calcium formate exhibits four polymorphic species α, β, γ, and δ in the temperature range 25–400°C. DTA investigations performed on α-Ca(HCOO)$_2$ with a dry air-flow lead to the following results:

(1) during the heating of the first thermal cycle, the $\alpha \rightarrow \gamma \rightarrow \delta$ transitions occur, and on cooling $\delta \rightarrow \gamma \rightarrow \beta$;

(2) from the very second cycle, the shape of the DTA curves correspond to β-Ca(HCOO)$_2$.

Similar investigations performed under a humid air-flow ($p_{H_2O} = 17.4$ Torr) give evidence of the following transitions:

on heating, $\alpha \rightarrow \gamma \rightarrow \delta$;
on cooling, $\delta \rightarrow \gamma \rightarrow \beta \rightarrow \alpha$.

The $\beta \rightarrow \alpha$ transition is observed only in the presence of water and the shape of the DTA curves obtained on heating depends on the time of exposure of the samples under humid air-flow at room temperature (Fig. 4). If this time is large enough, the observed recording is that of α-Ca(HCOO)$_2$. These DTA curves are similar to those obtained with artificial mixtures of α- and β-Ca(HCOO)$_2$.

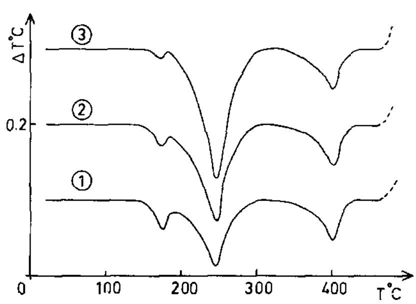

FIG. 4. DTA on α- + β-Ca(HCOO)$_2$ samples obtained after partial transformation at ambient air.

The amount of water involved in the $\beta \rightarrow \alpha$ transition has been evaluated by TG and represents about 0.1% of the sample weight (*5*).

Discussion

We present evidence of the existence, under atmospheric pressure, of two new polymorphic species for strontium formate (β- and δ-Sr(HCOO)$_2$) and for calcium formate (γ- and δ-Ca(HCOO)$_2$). Therefore, in our experimental conditions in the temperature range 20–300°C, strontium formate exhibits three polymorphic species α, β, and δ. The transition between the last two ($\beta \rightleftarrows \delta$) cannot be detected by DTA, and therefore seems to pertain to a transition order higher than one; the $\beta \rightarrow \alpha$ transition requires the presence of water traces.

So far as "anhydrous" calcium formate is concerned, this solid presents, as in the case of thorium tetraformate (*10*) which has been investigated earlier in our laboratory, a relatively complex polymorphism. Present study shows that among the two species α and β, α-Ca(HCOO)$_2$ is thermodynamically the most stable one at room temperature, since β-Ca(HCOO)$_2$ is transformed into α-Ca(HCOO)$_2$ only in the presence of water vapor. Furthermore, the $\gamma \rightarrow \delta$ transition of calcium formate seems to depend strongly on the amount of water in γ-Ca(HCOO)$_2$ (presence of which can be detected by ir absorption).

Summary and Conclusion

The sets of strontium and calcium formates which are detected by DTA under the atmospheric pressure in our experimental conditions are as follows:

Sr(HCOO)$_2$: α and δ;
Ca(HCOO)$_2$: α, β, γ, and δ.

All the above varieties of calcium formate have been found by electrical conductivity measurements (*11*) and by dilatometric analysis (*12*). However, in the case of strontium formate, the β variety escapes detection by DTA.

For both formates, the role played by water vapor on phase transformation kinetic is of paramount importance. This role has long been observed on other solids (*13*), but its mechanism remains unknown. "A priori," it may be assumed that water acts either by insertion into the crystalline structure, or by adsorption on the solid surface. Anyhow, ordinary hydrate formation has to be excluded.

Of course, the characterization of the encountered polymorphic varieties of strontium and calcium formates has to be completed as a result of X-ray investigation, which is to be reported in the following article.

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