

# Thermal Decomposition of Copper (II) Calcium (II) Formate

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The presence of different stages in the thermal decomposition process of  $\text{CuCa}(\text{HCOO})_4$  has been established by means of TGA at different heating rates, X-ray powder diffraction of quenched samples, and DSC methods. During the first stage, decomposition of one of the two copper formate structural units contained in the unit cell takes place. The presence of  $\text{CuCa}_2(\text{HCOO})_6$  has been detected. Calcium formate structural units break down at higher temperatures; the last decomposition peak corresponds to the appearance of different calcium-copper oxides. © 1996 Academic Press, Inc.

## INTRODUCTION

Mixed carboxylates have been used to obtain basic metal cuprate precursors to prepare high  $T_c$  superconductors (1–4).

A systematic thermal decomposition study of copper containing alkaline-earth coordination compounds with the formate ligand is being carried out at our laboratory.

We have already studied the thermal decomposition of the copper strontium compound,  $\text{CuSr}(\text{HCOO})_4$ , and we have analyzed the crystal structure modifications of the materials involved during the different stages of decomposition (5). In the present work we study the different stages through which thermal decomposition of  $\text{CuCa}(\text{HCOO})_4$  takes place and propose a decomposition mechanism which takes into account the intermediate reaction products and their crystal structures; finally we compare the behavior of both copper alkaline-earth formates.

## EXPERIMENTAL

Anhydrous copper calcium formate ( $\text{CuCa}(\text{HCOO})_4$ ), hereafter  $\text{ACuCaF}$ , has been synthesized following the method proposed in (6), by slowly adding the required stoichiometric amount of  $\text{CaCO}_3$  to a solution of  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  in the minimum amount needed of a 20% aqueous formic acid solution; good single crystals were obtained by slow evaporation at 40°C. The powder

diffraction pattern of the blue crystalline solid was in good agreement with that calculated from single crystal data given in (6).

Crystals obtained were characterized by optical microscopy, by TGA in a Mettler TG 50 apparatus, between 30 and 1000°C in air, at heating rates of 1, 5, and 10°C/min, and by DSC on a Perkin-Elmer DSC-2 calorimeter between –30 and 250°C scanned at a heating rate of 10°C/min. X-ray powder diffraction patterns of samples quenched at different temperatures were taken on a Philips PW-3710 diffractometer ( $\text{CuK}\alpha$  radiation); X-ray powder diffraction patterns of samples kept at different temperatures were taken in a heating stage on a Philips PW-1030 digitalized diffractometer (HTD).

## RESULTS

From TGA and DTG analysis up to 1000°C, we found that the decomposition of  $\text{ACuCaF}$  takes place, up to 300°C, through well differentiated although somewhat overlapping stages. A step at 770°C is related to the reaction of  $\text{CaCO}_3$  and  $\text{CuO}$  to give different cuprates. At each stage and for all heating rates the resulting quenched products were analyzed by X-ray powder diffraction methods.

### Thermogravimetric Analysis

TGA tracings for different heating rates are shown in Fig. 1; relevant temperatures, weight losses, and composition of the quenched samples obtained at different temperatures for a heating rate of 10°C/min are shown in Table 1.

#### 1. Heating Rate 10°C/min (Fig. 1a)

(a) *First stage.* The first stage of the thermal decomposition of  $\text{ACuCaF}$  up to 200°C with a weight loss of about 12%, and a change in color from blue to reddish, can be related to the decomposition of one of the two copper formate structural units contained in the unit cell.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  evolve; copper is, in part, separated as metallic copper (which is later oxidized to  $\text{Cu}_2\text{O}$ ). These changes are re-

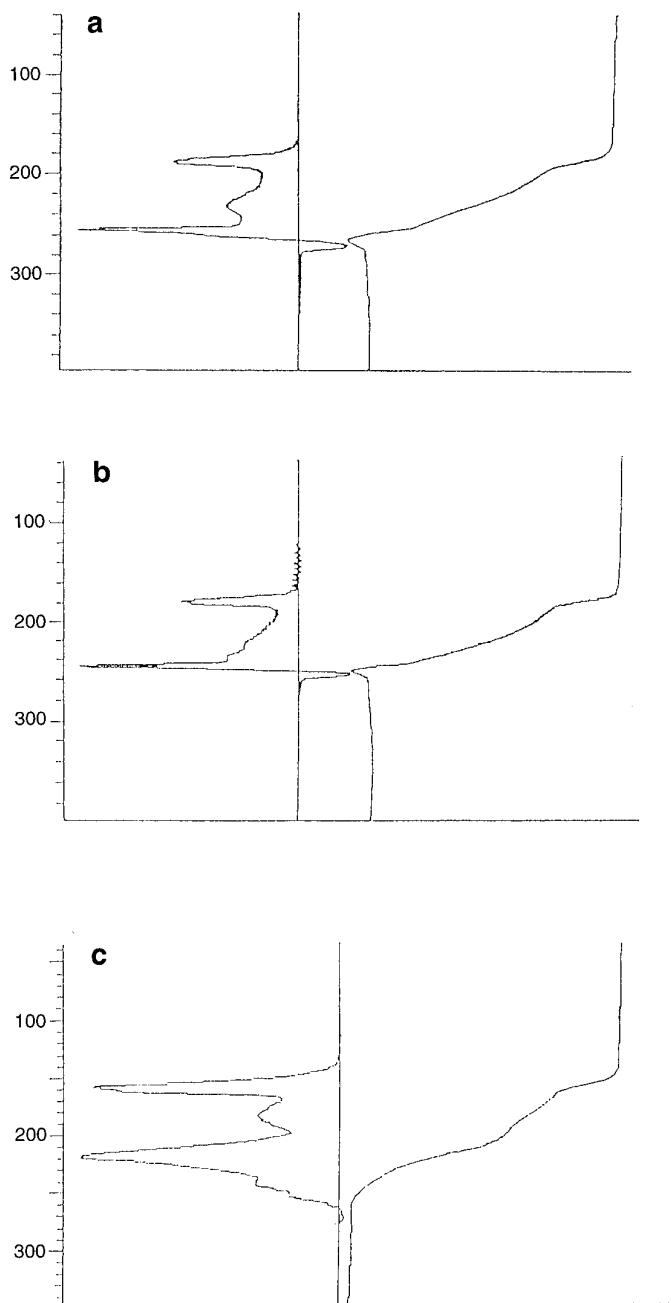


FIG. 1. DTG and TG tracing of ACuCaF. (a) Heating rate of 10°C/min; (b) Heating rate of 5°C/min; (c) Heating rate of 1°C/min.

flected in the widening of the ACuCaF diffraction peaks. The calculated weight loss considering that Cu is present as  $\text{Cu}_2\text{O}$  is 14.45%. In samples quenched at 200°C, where the first stage of decomposition has not been completed (weight loss about 8%), X-ray diffraction patterns show ACuCaF as the main component together with Cu and  $\text{Cu}_2\text{O}$ ; some  $\text{CuCa}_2(\text{HCOO})_6$  (hereafter ACuCa<sub>2</sub>F) and a broad, very weak peak belonging to beta  $\text{Ca}(\text{HCOO})_2$  have

TABLE 1  
Decomposition Temperature and Weight Loss of ACuCaF

Heating rate	$T$ (°C)	Weight loss %		Calculated value
		<i>a</i>	<i>b</i>	
10°C/min	150–200	11.99	11.55	14.45 <sup>c</sup>
	200–243	15.40	15.56	14.45 <sup>c</sup>
	243–265			10.60 <sup>d</sup>
	Partial sum	13.89	13.94	39.50
	265–270	41.28	41.05	
	580–800	+3.53	+2.96	15.59

<sup>a</sup> On single crystal between 35 to 500°C.

<sup>b</sup> On powder samples between 35 to 1000°C.

<sup>c</sup> Calculated with Cu remaining as  $\text{Cu}_2\text{O}$ .

<sup>d</sup> Calculated with Cu as  $\text{Cu}_2\text{O}$  and Ca remaining as  $\text{CaCO}_3$ .

also been detected. Cu atoms are either separated or rearrange to give the ACuCa<sub>2</sub>F structure (Fig. 2).

No copper formate was ever found.

We must take into account that decomposition temperatures are close, therefore decomposition peaks in all the experiments are overlapping so it is possible that reactions occurring mainly in the second heating stage start even before the first peak is over.

(b) *Second stage.* The second stage of the thermal decomposition of ACuCaF takes place between 200 and 243°C and is accompanied by a weight loss of about 15%. This stage is closely related to the behavior of the remaining copper formate structural units contained in both ACuCaF and ACuCa<sub>2</sub>F; again  $\text{CO}_2$  and  $\text{H}_2\text{O}$  evolve. The calculated weight loss considering that Cu is present as  $\text{Cu}_2\text{O}$  is again 14.45%. In samples quenched at 240°C, where the second stage of decomposition has not been completed, X-ray diffraction patterns show the presence of  $\text{Cu}_2\text{O}$  and Cu as the main crystalline components and broad peaks belonging to the remaining ACuCaF, ACuCa<sub>2</sub>F, and beta  $\text{Ca}(\text{HCOO})_2$  structures (Fig. 2). No calcium carbonate was detected.

(c) *Third stage.* The third stage of the thermal decomposition of ACuCaF takes place between 244 and 268°C with a weight loss of about 14% followed by a small weight gain. The calculated weight loss is 10.6%. This stage is related to the decomposition of beta  $\text{Ca}(\text{HCOO})_2$ . X-ray powder diffraction patterns show the presence of  $\text{CaCO}_3$  and CuO as the only components of the quenched samples. Only at this stage the calcium formate structural units are broken down, although decomposition of pure  $\text{Ca}(\text{HCOO})_2$  should occur at about 470°C.

To explain this anomaly the thermal behavior of pure  $\text{Ca}(\text{HCOO})_2$  and of its molecular 1:1 mixture with CuO was studied. Pure  $\text{Ca}(\text{HCOO})_2$  shows a weight loss peak

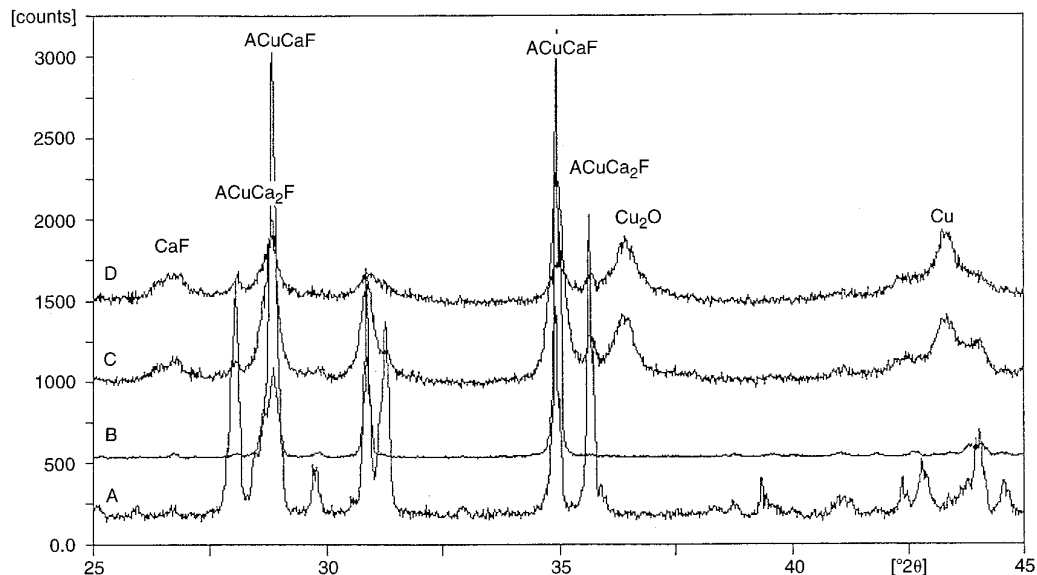


FIG. 2. Powder X-ray diffraction diagrams of (A)  $\text{ACuCaF} + \text{ACuCa}_2\text{F}$  (1 + 1) used as a standard, (B)  $\text{ACuCaF}$ , (C) quenched samples of  $\text{ACuCaF}$  at  $200^\circ\text{C}$ , (D) quenched samples of  $\text{ACuCaF}$  at  $240^\circ\text{C}$ .

at about  $460^\circ\text{C}$  and the 1:1 mixture show a weight loss peak at  $340^\circ\text{C}$ . This difference in the decomposition temperatures can be explained by the catalytic influence of copper in the thermal behavior of alkaline-earth formates, as shown for  $\text{CuSr}(\text{HCOO})_2$  (5).

### 2. Heating Rate $5^\circ\text{C}/\text{min}$ (Fig. 1b)

The differences observed when heating at  $5^\circ\text{C}/\text{min}$  are essentially the strong overlapping of the second and third peaks observed when working at  $10^\circ\text{C}/\text{min}$ , and only one broad nonsymmetric peak is observed above  $190^\circ\text{C}$  with a weight loss of 27%, followed by a small weight gain. Comparison of the results of both heating rates show that the first stages for both heating rates are similar.

### 3. Heating Rate $1^\circ\text{C}/\text{min}$ (Fig. 1c)

The decomposition process evolves in three different stages similar to the  $10^\circ\text{C}/\text{min}$  rate results. The oxidation of copper and cuprous oxide to cupric oxide takes place within the third stage of the decomposition process.

Similar results were obtained when using single crystals, when using powdered samples, and when HTD experiments were performed.

Heating up to  $1000^\circ\text{C}$  a weight loss of 15.6% at  $770^\circ\text{C}$  takes place for all heating rates; X-ray diffraction patterns of quenched samples show only the presence of a mixture of calcium cuprates. The presence of  $\text{Ca}_2\text{CuO}_3$  is in good agreement with the observations of Sanchis *et al.* (7); but besides, in our samples quenched from above  $800^\circ\text{C}$  we

always observed the presence of  $\text{CaCu}_2\text{O}_3$ . We have never observed the presence of  $\text{CaCuO}_2$ .

## Differential Thermal Calorimetry

Using a heating rate of  $10^\circ\text{C}/\text{min}$  a slight change in the  $dC_p/dT$  vs  $T$  curves at about  $110^\circ\text{C}$  was observed in differential scanning calorimetry experiments; this slight change is compatible with an enhancement of the thermal vibration of some of the structural groups. The sample was still blue and transparent after cooling. At  $150^\circ\text{C}$  the base line turns noisy, probably due to the breaking of some of the bonds in the copper formate structural units, before decomposition starts at  $180^\circ\text{C}$ . These DSC anomalies are quite similar to those observed in orientation-switching transitions where the degree of disorder is a continuous function of temperature. Often the onset of disorder is marked by a sharp change of the slope of the specific heat curve. This, however, is not itself a transition; it is the beginning of the premonitory region (8).

## Optical Microscopy

In samples kept under silicon oil while heated in the heating stage of a Kofler optical microscope, bubbles appear before any darkening of the blue transparent single crystals is detected. Only after some time elapses the crystals darken, suggesting that decomposition begins by the separation of the formate ions coordinated to the copper atoms.

TABLE 2  
Comparative Weight Loss

% wl	rel wl	SrCu(HCOO) <sub>4</sub>	% wl	rel wl	CaCu(HCOO) <sub>4</sub>
			12	29.2	A (Cu, V) Ca (F, Vf) + ACuCa <sub>2</sub> F + Cu + Cu <sub>2</sub> O + bACaF
18	64.3	aASF + bASF + CuO + Cu <sub>2</sub> O	15	36.6	bACaF + CuO
10	35.7	SrCO <sub>3</sub> + CuO	14	34.1	CaCO <sub>3</sub> + CuO

Note. wl = weight loss; rel wl = relative weight loss; a = alpha phase; b = beta phase.

## DISCUSSION AND CONCLUSIONS

The most interesting result obtained from TGA and X-ray diffraction study of samples of ACuCaF quenched at different temperatures is that the two crystallographically equivalent copper atoms contained in the unit cell (6) behave quite differently under heating. This is true for all the different heating rates used in this work: only one copper formate structural unit decomposes at about 200°C.

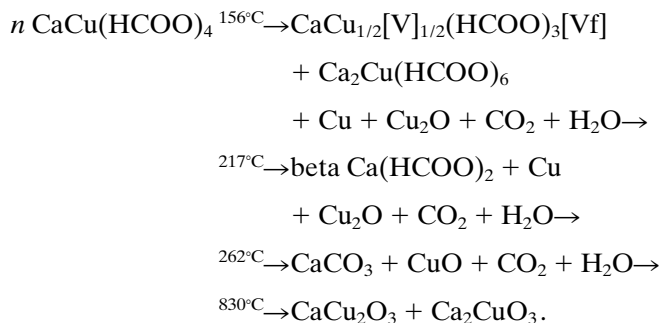
It is not easy to correlate the crystal structures of ACuCa<sub>2</sub>F and ACuCaF with the thermal behavior of the latter. As we have seen, during the first stage of the thermal decomposition of ACuCaF the crystal structure of most of the sample is not much altered, except for an increase in the width of the diffraction peaks of ACuCaF. Notwithstanding there is a weight loss which we have assigned to the decomposition of one of the two copper formate structural units because of the presence of copper and copper oxide and the absence of calcium compounds in the quenched samples. The copper formate groups separate from the ACuCaF structure leaving a disordered (CaCu<sub>1/2</sub>[V]<sub>1/2</sub>(HCOO)<sub>3</sub>[Vf]) structure, where [V] means a copper vacancy and [Vf] a formate ion vacancy, which partially rearranges to give ACuCa<sub>2</sub>F.

The copper vacancies will either be statistically disordered or have an ordered structure depending on the crystallographical equivalence or nonequivalence of the copper atoms in the ACuCaF unit cell. The crystal structure determination of Sanchis *et al.* (6) with both copper atoms occupying equivalent crystallographic sites points to a statistically disordered structure for CaCu<sub>1/2</sub>[V]<sub>1/2</sub>(HCOO)<sub>3</sub>[Vf]; if it were possible to obtain a single crystal of the copper-deficient phase this hypothesis could be confirmed through X-ray structural analysis.

On the other hand, there are two crystallographically nonequivalent groups of formate ions. The formate ions containing O1 atoms (6) joint two copper atoms through a short and a long bond; we believe that this long bond is

the most likely to break during the first stage of the thermal decomposition of ACuCaF.

Taking into account all our experimental results and the behavior of the different formate groups as a function of temperature, the following typical decomposition path for ACuCaF can be given:



Beta Ca(HCOO)<sub>2</sub> can only originate from the defective ACuCaF structure as it has not been detected in the thermal decomposition study of pure ACuCa<sub>2</sub>F (9). From the structural point of view these results are not unexpected. ACuCAF and beta Ca(HCOO)<sub>2</sub> show similar calcium atom coordination: both have two formate ion chelating units while in ACuCa<sub>2</sub>F only one chelating unit is present.

Traces of beta Ca(HCOO)<sub>2</sub> have been detected after the first heating stage, due to the overlapping of the different decomposition peaks.

## Comparison of the Behavior under Heating of Anhydrous Copper Strontium and Copper-Calcium Formates

In spite of their isomorphous crystal structures at room temperature (5, 6), thermal decomposition of these alkaline earth copper formates are not identical, as shown in Table 2.

In both compounds thermal decomposition starts by the breaking down of the copper formate structural units, but while in the strontium compound the formate units coordinating the two copper atoms contained in one unit cell are lost in the first stage, in the calcium compound they are lost in two stages. The thermal decomposition path is easily related to the crystal structure in ACSF: both copper atoms in the ACSF unit cell are crystallographically equivalent (5) and they behave indistinctively on heating.

On the other hand it is difficult to explain the first decomposition peak observed in ACuCaF, which is related to the breaking down of half of the crystallographically equivalent (6) copper formate structural units contained in the unit cell.

The behavior of ACuCaF on heating seems to point to two nonequivalent copper formate structural units. DSC tracings show no evidence of a phase transition before decomposition.

The reason for the different thermal behavior of ACSF and ACuCaF is probably the existence of the ACuCa<sub>2</sub>F phase which controls the decomposition path in the Cu–Ca system and has no parallel structure in the Cu–Sr system.

## ACKNOWLEDGMENTS

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