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THERMAL DECOMPOSITION OF BARIUM CITRATE *

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ABSTRACT

The thermal decomposition of barium citrate occurs in three stages. During the first stage anhydrous salt is formed while the second stage results in intermediates, possibly aconitic acid and modified itaconic acid moieties formed by dehydration and decarboxylation, and barium carbonate. In the third stage complete decomposition to barium carbonate takes place.

INTRODUCTION

In recent years the "liquid mix technique" [1,2] has gained prominence for the preparation of materials for solid-state devices. This is because these have better physical and electrical properties, compared to those prepared by conventional ceramic techniques, and require no milling. In this technique mixtures of citrates, oxalates, formates or tartarates are used to achieve homogeneous mixing on an atomic scale. However, to apply this technique the mechanism of decomposition of these organic salts has to be understood both individually, and when in the presence of one another.

The thermal decomposition of several organic acid salts of alkaline earth metals (e.g. oxalates and formates) have been studied extensively. However, similar information about citrates is scarce [3,4]. In this paper, therefore, the thermal analysis of barium citrate is reported, and a tentative scheme is proposed for its multistage decomposition. The thermogravimetric data supported by infrared (IR), and X-ray diffraction (XRD) analyses of the various stages are used in the study.

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EXPERIMENTAL

Preparation

Solutions of barium chloride ($BaCl_2 \cdot 2\ H_2O$, AR grade, BDH) and sodium citrate ($Na_3C_6H_5O_7 \cdot 2\ H_2O$, AR grade, Merck) in stoichiometric proportions were mixed by adding the sodium citrate solution dropwise to the barium chloride solution with continuous stirring (5 min). The thick white precipitate of barium citrate obtained was filtered, washed several times with distilled water until free from all soluble impurities, then air-dried.

Instrumental

The thermal measurements were carried out in a Netzsch STA 409 differential thermal analyzer which plots simultaneously the results of differential thermal analysis (DTA), thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG) along with the sample temperature (T). A Pye Unicam IR spectrometer (SP3-300) was used to record the spectra of TG residues in Nujol, hexachlorobutadiene (HCB) and in KBr pellets. The X-ray diffraction patterns were recorded on a Philips 1730 diffractometer.

For differential thermal analysis, 56 mg of sample was placed in a cylindrical-type platinum crucible mounted on one of the 2-mm alumina rods of the sample carrier covering the Pt/Pt–10% Rh differential thermocouple which measures simultaneously the sample temperature. The sample was heated in dynamic air atmosphere at a rate of 10°C min^{-1}. A chart speed of 120 mm h^{-1} was used for the thermogravimetric scan. Activation energies were calculated from the thermogravimetric data using the method of Freeman and Carrol [5].

RESULTS AND DISCUSSION

The decomposition of barium citrate ($Ba_3(C_6H_5O_7)_2 \cdot 2\ H_2O$) takes place in three stages as shown in the thermogravimetric curve (Fig. 1). The weight losses obtained at various stages of the decomposition process are summarised in Table 1.

In the first step of the TG curve an endothermic change having an activation energy of 18.5 kcal mol^{-1} leading to dehydration was observed in the temperature range 27–300°C (step A). This dehydration begins at 64°C and is completed by 300°C. The IR spectrum of this stage shows a considerable reduction in the broad hydroxyl band intensity observed at 3380 cm^{-1} and sharpening of the bands in the region 1200–800 cm^{-1} as compared to the starting material (Fig. 2). The observed weight loss of 5.0% may be

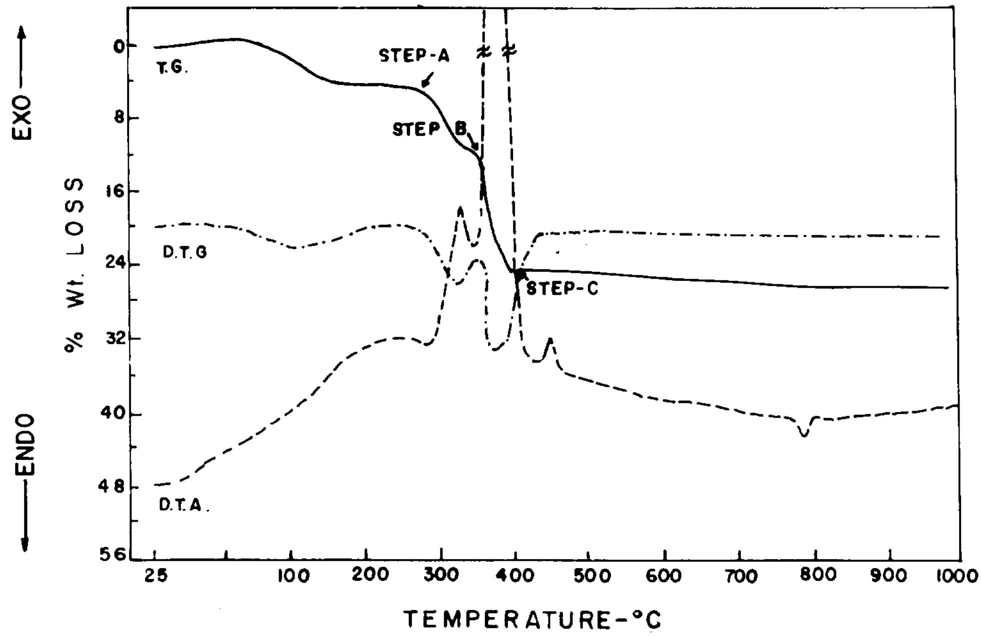


Fig. 1. TG, DTG and DTA curves of barium citrate in air.

attributed to the removal of about 2 moles of crystal water. Barium citrate is reported to crystallize with either 7, 5 or 3.5 moles of H_2O [6]. The freshly precipitated amorphous material had 7 moles of H_2O, whereas the needle-like crystals had 5 moles and those with 3.5 moles were microcrystalline. The microcrystalline sample obtained in the present case has apparently lost 1.5 moles of crystalline water during vacuum-drying of the sample at 27°C.

The IR spectrum (Fig. 2) of the sample in the second stage of the TG

TABLE 1

Thermal analysis data for the decomposition of barium citrate

Thermal change	% wt. loss observed at the end of each stage	% wt. loss calcd.	Temp. range (°C)	Activation energy (kcal $mole^{-1}$)	Type of reaction
Formation of anhydrous salt	5.0	4.3	27–300	18.5	endothermic
Decomposition to intermediates and barium carbonate	9.1	9.2	300–373	3.5	exothermic
Complete decomposition to barium carbonate	14.4	14.6	373–412	17.6	exothermic

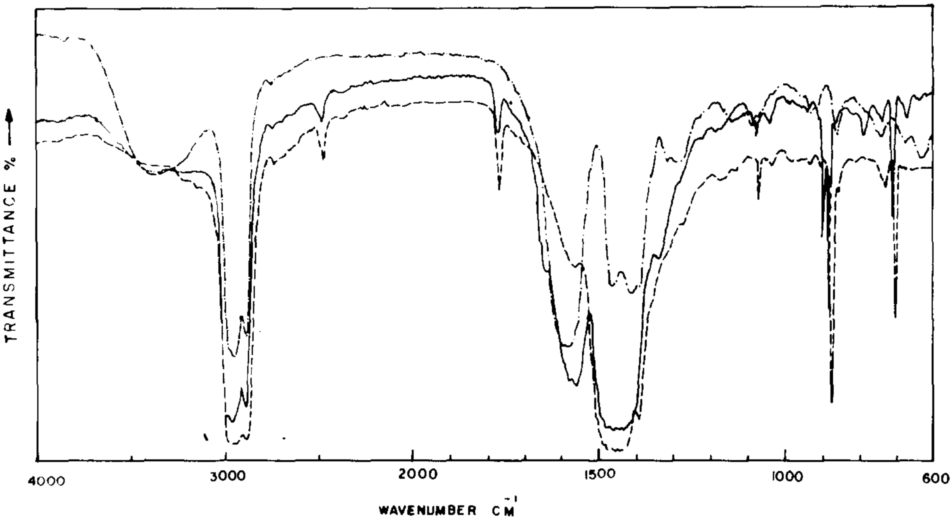
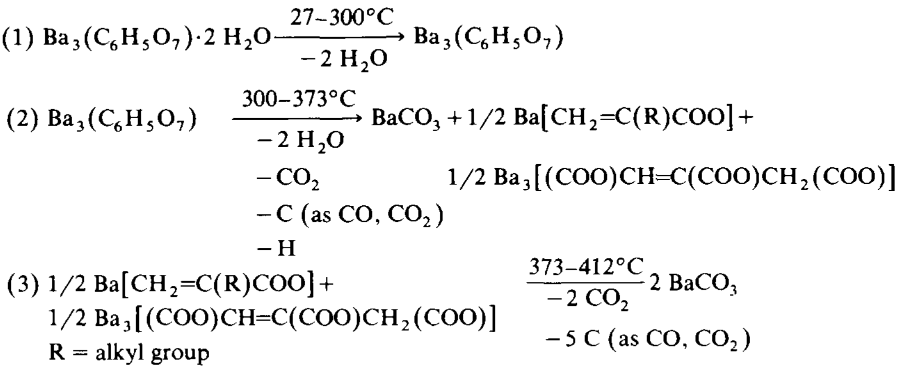


Fig. 2. IR spectra of barium citrate (·—·—·), decomposition stage II (———), and stage III (— — —).

curve (step B) in the temperature range 300–373°C shows little resemblance to that of the first stage except for the carboxylate bands at 1550 and 1330 cm^{-1}. Thus, the hydroxyl stretching band at 3380 cm^{-1} is absent. New bands at 2495(w), 1770(w), 1450(vvs), 1060(w), 875(s), 725(w) and 700(ms) cm^{-1} corresponding to those of barium carbonate [7] are found. Unsaturation has begun in the acid moiety as shown by the additional medium strong bands at 890 and 790 cm^{-1} ascribable to the $-$CH out of plane deformation modes of $R_2R_1C{=}CH_2$ and $R_1CH{=}CR_2R_3$ groups, respectively [8]. Thus, during this stage, barium citrate has decomposed partly into barium carbonate and partly into intermediates resulting from dehydration and decarboxylation of the citrate moieties. Dehydration and decarboxylation of citric acid [9] and its alkaline earth metal salts (e.g., calcium [4]) have been reported. The formation of aconitic acid [(COOH)CH=C(COOH)CH_2-(COOH)] by dehydration during the pyrolysis of calcium citrate [4] and barium isocitrate [3] has been established. Thermal decomposition of citric acid at 100–120°C was also found to yield aconitic acid and further to itaconic acid by decarboxylation [CH_2=C(COOH)CH_2(COOH)]. In the present communication, there is clear evidence for the formation of an aconitic acid moiety as one of the intermediates in the second stage of the decomposition of barium citrate. The second intermediate could be a modified itaconic acid moiety formed by its decarboxylation as shown in Scheme 1.

In order to ascertain the quantity of $BaCO_3$ formed at the end of this stage, a semiquantitative estimation was carried out using the IR intensity in KBr pellet of the strong barium carbonate bands at 1450 and 875 cm^{-1}. The



$$(1)\ \mathrm{Ba_3(C_6H_5O_7)\cdot 2\,H_2O} \xrightarrow[-2\,\mathrm{H_2O}]{27\text{–}300^\circ\mathrm{C}} \mathrm{Ba_3(C_6H_5O_7)}$$

$$(2)\ \mathrm{Ba_3(C_6H_5O_7)} \xrightarrow[\substack{-2\,\mathrm{H_2O}\\ -\mathrm{CO_2}\\ -\mathrm{C}\ (\text{as CO, CO}_2)\\ -\mathrm{H}}]{300\text{–}373^\circ\mathrm{C}} \mathrm{BaCO_3} + 1/2\,\mathrm{Ba[CH_2{=}C(R)COO]} + 1/2\,\mathrm{Ba_3[(COO)CH{=}C(COO)CH_2(COO)]}$$

$$(3)\ 1/2\,\mathrm{Ba[CH_2{=}C(R)COO]} + 1/2\,\mathrm{Ba_3[(COO)CH{=}C(COO)CH_2(COO)]} \xrightarrow[\substack{-2\,\mathrm{CO_2}\\ -5\,\mathrm{C}\ (\text{as CO, CO}_2)}]{373\text{–}412^\circ\mathrm{C}} 2\,\mathrm{BaCO_3}$$

R = alkyl group

Scheme 1. Decomposition scheme of barium citrate.

results showed that barium carbonate was present as approximately one third of the total weight of the sample at this stage.

The experimental weight loss of 9.1% obtained from the thermogravimetric analysis during this stage is in agreement with the formation of the two intermediate products suggested earlier during the dehydration and decarboxylation of the citrate moieties (Scheme 1). The activation energy calculated for the exothermic decomposition at this stage is 3.5 kcal mol^{-1}.

In the third stage (step C) in the temperature range 373–412°C further decomposition of the intermediates takes place and the IR spectrum (Fig. 2) shows bands due to barium carbonate only. The formation of barium carbonate [10] is confirmed by the XRD data (Fig. 3). The decomposition of this stage is exothermic with an activation energy of 17.6 kcal mol^{-1}. The observed weight loss of 14.4% during this stage is in good agreement with the calculated loss of 14.6% required for the formation of barium carbonate.

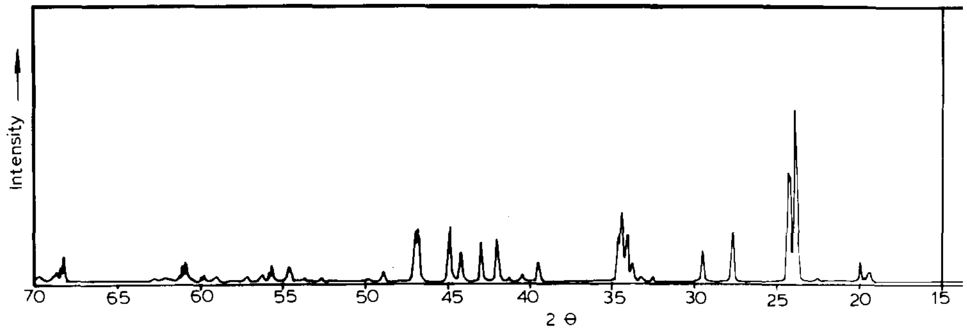


Fig. 3. XRD pattern of barium carbonate.

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