

THERMOSTABILITY OF ALKALI BENZENECARBOXYLATES

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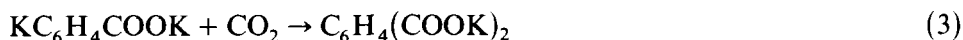
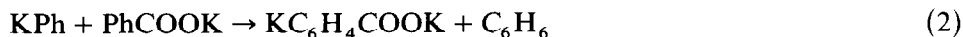
ABSTRACT

The thermostability of alkali benzenecarboxylates in a stream of nitrogen was studied by thermogravimetry (TG). The decomposition temperature at which each salt decomposes into one half of its weight loss, as determined by TG, was used as a measure of the thermostability of the salt. The results are: 528°C (Li), 510°C (Na), 488°C (K), 482°C (Rb), 462°C (Cs) for benzoate; 516°C (Na), 499°C (K), 492°C (Rb), 485°C (Cs) for phthalate. The results of dipotassium isophthalate and terephthalate are: 502°C (isophthalate), 625°C (terephthalate). The decomposition temperatures of benzoate and phthalate decrease with the size of the cation.

INTRODUCTION

The catalytic conversion of potassium benzoate, dipotassium phthalate and isophthalate into dipotassium terephthalate is often called the Henkel reaction [1]. The mechanism has been investigated by many authors and several different mechanisms have been proposed [2–13].

One of these is the decarboxylation–carboxylation mechanism proposed by Sorm and Ratusky [5–8]. They assume a phenyl anion intermediate for alkali benzoate.

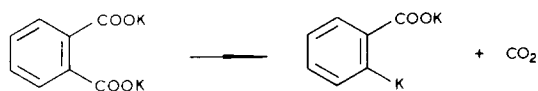


Thermostabilities of alkali benzoates [14] and potassium benzenecarboxylates [15] were studied by Szammer and Ötvös. The thermostability data showed that the benzoates, phthalate and isophthalate are thermostable at the Henkel reaction temperature.

Regularities in the formation of products during the thermal disproportionation of alkali metal salts of benzenecarboxylic acids was reported by Khlestkin et al. [16]. Thermal disproportionation of PhCOOK to *p*-C₆H₄(COOK)₂ and C₆H₆ was accompanied by additional weight loss owing to

thermal decomposition of the intermediates. The reactivity of aromatic carboxylic salts of alkali metals increased with the size of the cation.

Thermal disproportionation of benzoate is started by the decarboxylation of the salt [reaction (1)]. Thermal displacement of dialkali phthalate is also started by decarboxylation. The decarboxylation is irreversible [14].



The influence of the alkali metal ion on the thermostabilities of the benzoate and phthalate was studied by thermogravimetry. The results are discussed.

EXPERIMENTAL

Preparation of compounds

The alkali benzoate and phthalate were prepared by mixing the alkali metal hydroxide with the stoichiometric proportion of benzoic acid or phthalic anhydride. The procedure was controlled by adjusting the pH of the solution.

$$\text{pH} = 7 + [\text{p}K_a + \log c]$$

where $\text{p}K_a$ = dissociation constant of benzenecarboxylic acid and c = concentration of the salt.

The mixture was concentrated using a vacuum rotary evaporator and the residue was dried at 65–70°C. The salts were milled and dried in a desiccator, with or without vacuum. Dipotassium isophthalate and terephthalate were prepared by the same procedure as was used for the benzoate.

Instrumentation

The Shimadzu differential thermal analysis apparatus MTG-11 was used to study the thermostabilities of the salts. The samples in the 200 mg range were carefully weighed in a platinum crucible. The sample weights of dipotassium isophthalate and dipotassium terephthalate were 115 mg. The reference sample used in the differential thermal analysis was 500 mg α -alumina. Starting at room temperature, the sample was heated to 700°C at a uniform heating rate of 2.0°C min⁻¹ in a stream of nitrogen (50 ml min⁻¹).

TABLE 1

Decomposition temperatures of alkali benzoates and ionic radii of the alkali metals

Compound	Decomposition temperature (°C)	Ionic radius (pm)
Li benzoate	528	60
Na benzoate	510	95
K benzoate	488	133
Rb benzoate	481	148
Cs benzoate	462	169

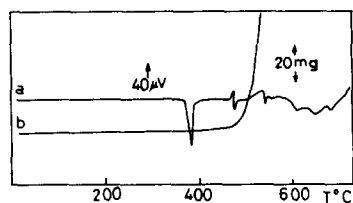


Fig. 1. Lithium benzoate. (a) DTA in nitrogen; (b) TG in nitrogen.

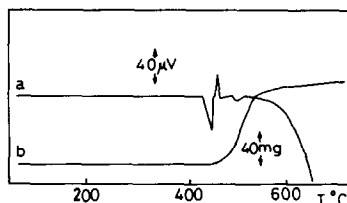


Fig. 2. Sodium benzoate. (a) DTA in nitrogen; (b) TG in nitrogen.

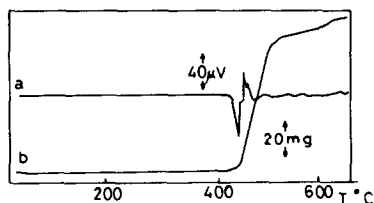


Fig. 3. Potassium benzoate. (a) DTA in nitrogen; (b) TG in nitrogen.

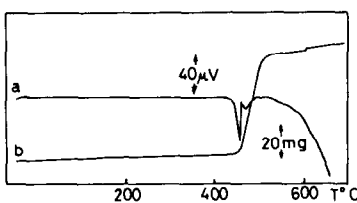


Fig. 4. Rubidium benzoate. (a) DTA in nitrogen; (b) TG in nitrogen.

TABLE 2

Decomposition temperatures of dialkali phthalates and ionic radii of the alkali metals

Compound	Decomposition temperature (°C)	Ionic radius (pm)
Na ₂ phthalate	516	95
K ₂ phthalate	499	133
Ru ₂ phthalate	492	148
Cs ₂ phthalate	485	169

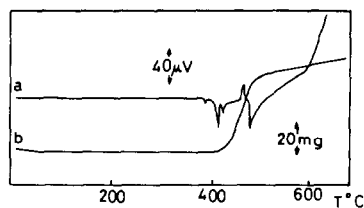


Fig. 5. Cesium benzoate. (a) DTA in nitrogen; (b) TG in nitrogen.

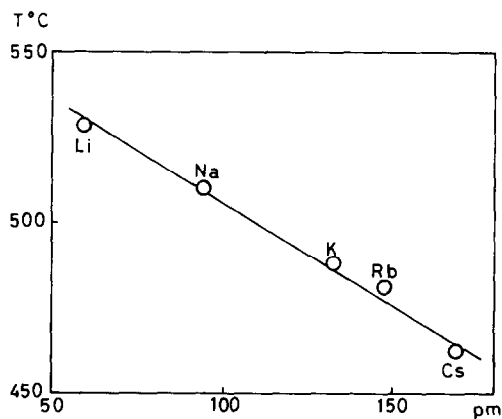


Fig. 6. Relationship between the decomposition temperature and the ionic radius of the alkali metal for alkali benzoates.

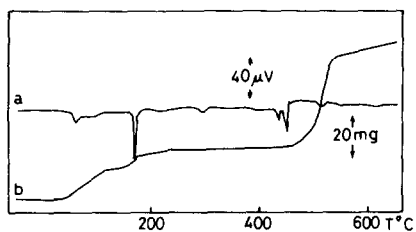


Fig. 7. Disodium phthalate. (a) DTA in nitrogen; (b) TG in nitrogen.

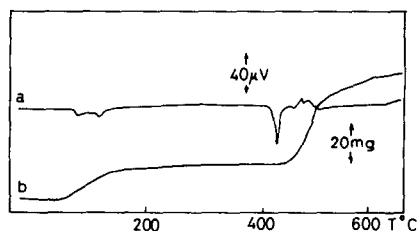


Fig. 8. Dipotassium phthalate. (a) DTA in nitrogen; (b) TG in nitrogen.

TABLE 3

Decomposition temperature of dipotassium isophthalate and terephthalate

Compound	Decomposition temperature (°C)
K_2 isophthalate	502
K_2 terephthalate	625

RESULTS AND DISCUSSION

Alkali benzoates

Thermogravimetry (TG) and differential thermal analysis (DTA) curves for alkali benzoates are shown in Figs. 1–5. There is hardly any difference in the decomposition starting temperature for Li, Na, K and Rb salts of benzoic acid. It is difficult to determine exactly the decomposition starting temperature by TG curves. The temperature at which each salt decomposes into one half of its weight loss is taken as the decomposition temperature. The results are given in Table 1 together with ionic radii of the alkali metals. The relationship between the decomposition temperature of the salt and the ionic radii of the alkali metal is given in Fig. 6. The decomposition temperatures give a fairly good straight line plot. The temperatures decrease with increasing size of the cation. Szammer reported the decomposition starting temperatures of benzoates to be 450°C (Na), 430°C (K), 410°C (Rb), 390°C

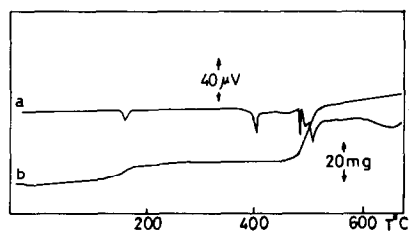


Fig. 9. Dirubidium phthalate. (a) DTA in nitrogen; (b) TG in nitrogen.

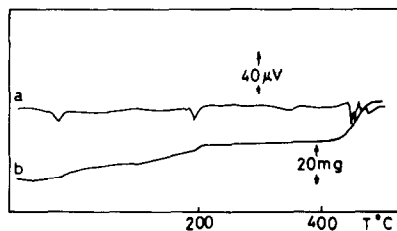


Fig. 10. Dicesium phthalate. (a) DTA in nitrogen; (b) TG in nitrogen.

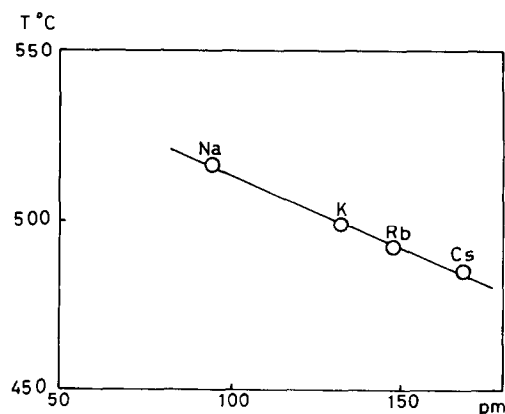


Fig. 11. Relationship between the decomposition temperature and the ionic radius of the alkali metal for dialkali phthalates.

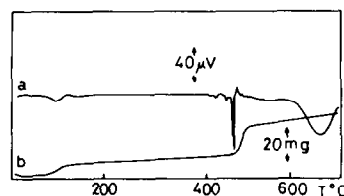


Fig. 12. Dipotassium isophthalate. (a) DTA in nitrogen; (b) TG in nitrogen.

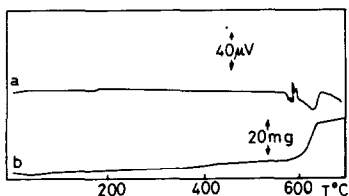


Fig. 13. Dipotassium terephthalate. (a) DTA in nitrogen; (b) TG in nitrogen.

(Cs). The temperature decreases with increasing size of the cation. It was reported by Khlestkin et al. that the reactivity of alkali aromatic carboxylates increased with the size of the cation [16].

Dialkali phthalates

Thermogravimetry (TG) and differential thermal analysis (DTA) curves for dialkali phthalates are shown in Figs. 7–10. The temperature at which each salt decomposes into one half of its weight loss is taken as the decomposition temperature. The results are given in Table 2. The relationship between the decomposition temperature of the salt and the ionic radius of the alkali metal is given in Fig. 11. The temperature decreases with increasing size of the cation. This was also found for the benzoates. The decomposition temperature is higher than the corresponding temperature for benzoates in every alkali metal salt. Therefore, dialkali phthalates are more thermostable than alkali benzoates in the same alkali salt. Szammer reported initial decomposition temperatures for potassium benzoate and dipotassium phthalate of 430°C and 460°C, respectively [15].

Dialkali isophthalate and terephthalate

Thermogravimetry (TG) and differential thermal analysis curves (DTA) for dialkali isophthalate and terephthalate are shown in Figs. 12 and 13. The decomposition temperatures are given Table 3. The thermostability of potassium salts increase in the order benzoate < phthalate < isophthalate < terephthalate.

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