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COMPARATIVE STUDY OF THERMAL ANALYSIS OF ALKALI METAL SUCCINATES

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ABSTRACT

The thermal decomposition of alkali metal succinates i.e. $M_2(CH_2COO)_2 \cdot xH_2O$ (M = Li, Na, K, NH_4) has been studied up to 823 K by employing simultaneous non-isothermal techniques (DTG, DTA and TG). The final thermolysis products are the corresponding metal carbonates as characterized by chemical analysis and IR spectroscopy. A comparison of the decomposition temperatures leads to the stability order Li > Na > K > NH_4. The results are also compared with analogous oxalates.

INTRODUCTION

The effect of systematically varying the cation, whilst keeping the carboxylate anion the same, on thermal stability has been extensively investigated using isothermal and non-isothermal techniques, Mössbauer and IR spectroscopic methods [1–4]. Bassi et al. studied the thermal decomposition of transition metal(II) propionates [5], iso- and terephthalates [6], maleates and fumarates [7] and compared their thermal stabilities. Dollimore and Griffiths [8] reported the thermolysis of alkali metal oxalates (Li, Na, K) with decomposition temperatures 811, 737 and 754 K, respectively. Ammonium oxalate decomposed at 473 K as reported by Erdey et al. [9]. In order to observe the effect of alkali metal cation (Li^+, Na^+, K^+, NH_4^+) as well as of increasing ring size (oxalate → succinate) on the thermal stability, a study of the thermal decomposition of alkali metal succinates has been undertaken.

EXPERIMENTAL

Alkali metal succinates were prepared by mixing under constant stirring equimolar quantities of aqueous solutions of alkali metal carbonates and succinic acid. The reaction mixture was concentrated on a water bath until a

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TABLE 1

Analytical data for alkali metal succinates

Compound		C(%)	H(%)	N(%)
$Li_2(CH_2COO)_2 \cdot 0.5H_2O$	Calc.	34.6	3.6	–
	Found	36.1	3.4	
$K_2(CH_2COO)_2 \cdot 2H_2O$	Calc.	20.8	3.4	–
	Found	21.5	3.2	
$(NH_4)_2(CH_2COO)_2$	Calc.	31.7	7.9	18.9
	Found	33.6	7.6	19.7

white solid product was obtained on cooling. After filtration the product was dried under vacuum. The identity of these compounds was established by IR spectral and chemical analysis (Table 1). The percentages of sodium and potassium were confirmed by flame photometry. The IR spectra were recorded on a spectrophotometer (Pye Unicam Ltd., England) using KBr pellets in the range 4000–200 cm^{-1}. Simultaneous DTG, DTA and TG curves were recorded on a Stanton Redcroft (STA-780) model at a heating rate of 10 °C min^{-1} in static air atmosphere.

$Na_2(CH_2COO)_2 \cdot 6H_2O$ was purchased from Loba-Chemie Indo-Austranal Co., Bombay, India.

RESULTS AND DISCUSSION

The IR spectrum of lithium succinate hemi-hydrate (Fig. 1A) shows a small distinct doublet with peaks at 2950 and 2990 cm^{-1} due to CH_2 stretching of the succinate group. The band between 3400 and 3500 cm^{-1} is not sharp but is in the form of an impression due to the fact that the salt contains only half a water molecule. A broad and distinct band at 1585 cm^{-1} is due to $\nu_{asym}(C{=}O)$ while a sharp band at 1450 cm^{-1} along with a shoulder at 1460 cm^{-1} is due to $\nu_{sym}(C{=}O)$ of the coordinated carboxylate ligand [10]. The IR spectra of the sodium and potassium analogues are very

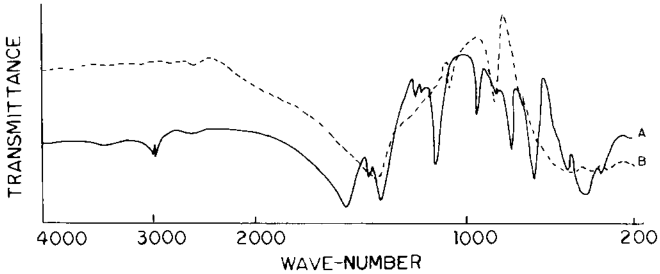

Fig. 1. Infrared spectrum of lithium succinate hemi-hydrate. (A), 298 K; (B), 773 K.

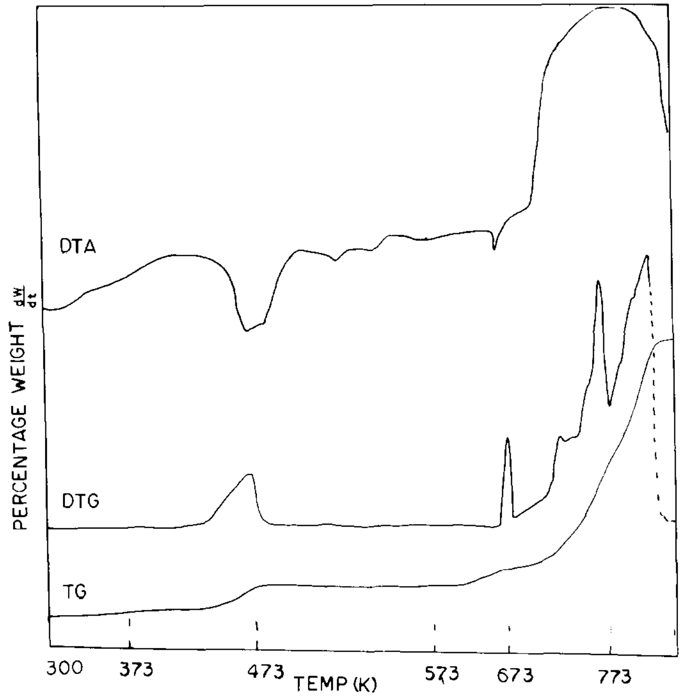

Fig. 2. Simultaneous DTG, DTA and TG curves of lithium succinate hemi-hydrate.

similar to that of lithium succinate; the only difference lies in the presence of a large broad band centred at about 3350 cm^{-1} due to ν(O–H) of water molecules. Other parameters being almost similar, ammonium succinate shows a broad band in the range 3350–3050 cm^{-1} due to NH_4^+ stretching [11].

Figure 2 shows the simulataneous DTG, DTA and TG curves of lithium succinate hemihydrate at a heating rate of 10 °C min^{-1} in static air atmosphere. DTG shows five distinct peaks at 465, 668, 720, 758 and 799 K. There are corresponding peaks in DTA i.e. one broad endotherm at 461 K and another small endotherm at 647 K followed by an exothermic region between 661 and 813 K, indicating that thermal changes are accompanied by weight losses. The TG curve shows the commencement of dehydration at 433 K. A weight loss of 6.0% has been observed in TG at 473 K indicating the removal of half a water molecule (calc. loss = 6.47%). After remaining stable up to 633 K, the anhydrous salt undergoes a multistep decomposition reaction. The TG curve shows a weight loss of 46.0% at 817 K suggesting the formation of Li_2CO_3 (calc. loss = 46.5%). The formation of the final thermolysis product, i.e. lithium carbonate, has been confirmed by the presence of a distinct characteristic band at 1420 cm^{-1} (Fig. 1B) in the IR spectrum [12] and by chemical analysis.

TABLE 2

Decomposition temperatures of alkali metal carboxylates (K)

Alkali metal	Succinate	Oxalate
Li	661	811
Na	640	737
K	633	754
NH_4	360	473

The mode of decomposition for sodium and potassium succinates is similar to that of the lithium analogue, i.e. the first step is the dehydration and the second is the decomposition of the anhydrous salt into its carbonate. However in the case of ammonium succinate the whole of the compound evaporated at 573 K. Table 2 lists the decomposition temperatures of alkali metal succinates as well as alkali metal oxalates [8,9] to enable a comparison of thermal stability to be made.

A comparison of decomposition temperatures of the individual alkali metal succinates suggests the thermal stability order $Li > Na > K > NH_4$. This sequence is expected from the different electrostatic properties (electronegativity, cationic size, polarizing power, etc.) of the alkali metal cations.

A comparative study of alkali metal succinates with their oxalate analogues shows that the former are thermally less stable than the latter. Thus it can be concluded that the seven-membered ring (succinate) is less stable than the five-membered ring (oxalate). A decrease in stability upon ring enlargement causes a reduction in stability due to chelate effect. Irving et al. [13] on the basis of the entropy factor have reported that with an increase in n (chain length) in the series $MOOC(CH_2)_nCOOM$ for a large number of metal dicarboxylates, the stability decreased.

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