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STUDY OF THE THERMAL STABILITIES OF ALKALI-METAL NAPHTHENATES

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ABSTRACT

The thermal analyses of sodium and potassium cyclohexane butyrates were performed between room temperature and 823 K under both oxygen and nitrogen atmospheres. Information was obtained on the thermal stability of these salts and the thermal decomposition processes they underwent.

INTRODUCTION

Naphthenic acids are mono-carboxylic acids mainly containing a saturated ring structure with a side chain of varying length. The rings are predominantly of C_5 and C_6 number.

Naphthenic acids occur in virtually all crude oils and in amounts ranging from trace to commercially and technically significant quantities [1]. These acids are of importance to industry and are obtained largely from oil fractions boiling between 175 and 370°C. They are used industrially mainly in the form of soaps. The sodium soaps of these acids have found wide application as emulsifiers and as a soap base possessing bactericidal action. They also have application in agriculture and horticulture functioning as fertilizers [2].

The literature offers a remarkable amount of data on the thermal behaviour of alkali-metal alkanoates and investigation by several authors through a variety of experimental techniques have provided a picture of the phase transitions and thermal stabilities of these products [3]. Alkali-metal naphthenates in contrast have so far received little attention and information on their thermal stabilities is limited in spite of their importance in industrial applications.

The present paper deals with studying the thermal properties in both nitrogen and oxygen atmospheres of sodium and potassium cyclohexane butyrates salts. Phase transitions, thermal and thermogravimetric data were measured and collected.

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EXPERIMENTAL

Apparatus

Differential scanning calorimetery (DSC), thermogravimetric (TG) and differential thermogravimetric (DTG) measurements were carried out on a Heraeus TA 500 thermal analyser. In the DSC measurements, samples weighing 10–20 mg were heated at a rate of 10°C min^{-1} in an aluminium crucible under the chosen atmosphere. The reference cell was filled with pure and dried powdered aluminium oxide.

TG and DTG curves were recorded simultaneously by placing a sample weighing 15–30 mg in a platinum crucible and heating at a rate of 20°C min^{-1} under a flowing atmosphere of nitrogen or oxygen gas. In all the thermal measurements gas flow rates were 10–15 l h^{-1}.

Materials

Sodium and potassium cyclohexanebutyrates of more than 97% purity were purchased from Alfa Products (VENTRON). Samples were kept at 373 K until constant weight was attained in order to remove any absorbed moisture.

RESULTS AND DISCUSSION

It is well established that the thermal decomposition of alkali-metal alkanoates under an inert atmosphere is often represented as in the following scheme

$$2\ \text{R–COOM} \rightarrow \text{R–CO–R} + \text{M}_2\text{CO}_3 \qquad (1)$$

where M = univalent metal, $\Delta H > 0$.

In fact, however, carbon, water, carbon monoxide, hydrogen and organic molecules other than R–CO–R may also be formed, the yield in R–CO–R actually being affected by the nature of both the anion and the cation and also of the inert gas [4].

On the other hand, decomposition in an oxygen atmosphere seems to be a rather complicated process, in spite of the obvious and usually adopted scheme

$$2\ \text{R–COOM} \overset{\text{O}_2}{\rightarrow} \text{M}_2\text{CO}_3 + \text{water} + \text{carbon dioxide} \qquad (2)$$

where M = univalent metal, $\Delta H < 0$.

A comparison of the DSC traces of sodium and potassium cyclohexane butyrate with that of a sodium alkanoate under oxygen and nitrogen

TABLE 1

Clearing, fusion and decomposition temperature (K) detected by DSC measurements [a]

Type of compound	Nitrogen atmosphere							Oxygen atmosphere						
	T_t	T_{cl}	T_F	T_i	T_m [b]	T_f	R	T_t	T_{cl}	T_F	T_i	T_m [b]	T_f	R
Sodium cyclohexane butyrate	498	628	539	703	775	798	1.3	498	d	537	586	600 680 760	785	1.1
Potassium cyclohexane butyrate	498	698	540	723	785	798	1.34	498	d	540	563	580 680 750	786	1.04
Sodium isocaproate [c]	453	625	534	625	735	785	1.17	453	d	534	525	555 665 685 725	745	0.98

[a] d = decomposition; T_t = temperature of solid state transition; $R = T_i/T_F$.

[b] From DTG trace.

[c] From ref. 5.

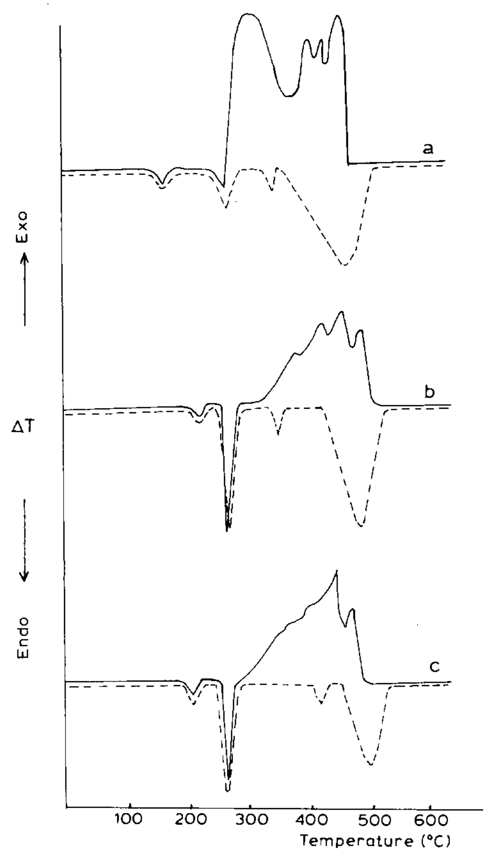

Fig. 1. DSC curves for: (a) sodium alkanoate; (b) sodium cyclohexane butyrate; and (c) potassium cyclohexanebutyrate. (———) under O_2 atmosphere; (- - - - - -) under N_2 atmosphere.

atmospheres are shown in Fig. 1. In Table 1, the clearing, T_{cl}, and fusion, T_F, temperatures are presented. The data for the sodium alkanoate were obtained from ref. 5. The initial, T_i, and final, T_f, decomposition temperatures are also recorded in the same table, together with the T_m values at which maxima peak temperatures are exhibited by the DTG traces under oxygen and nitrogen atmospheres.

It is clear from Table 1 that the sodium and potassium cyclohexane butyrates possessed a wider stability range of their melts than the sodium alkanoate. Their ratios, R, between T_i and the temperature of isotropic liquid formation (T_F in this case) varies from about 1.34 under nitrogen and 1.1 under oxygen atmosphere, while the R value for the sodium alkanoate is 1.17 under nitrogen and 0.98 under oxygen atmosphere. R increases on substitution of the alkanoate anion with that of the naphthenate.

It is also noted that under oxygen atmosphere, the R value decreases on replacing the sodium with the potassium cation. This is furthur confirmed

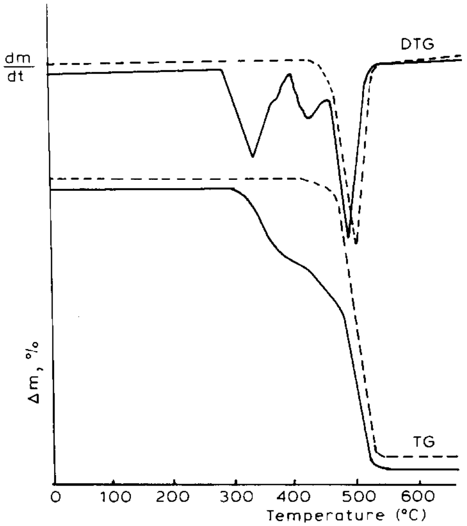

Fig. 2. Typical thermogravimetric curves for the alkalimetal naphthenates. (———) under O_2 atmosphere; (- - - - -) under N_2 atmosphere.

from Table 1 and Fig. 1 whereby the decomposition under oxygen starts at 586 K for the sodium salt and 563 K in the case of potassium. It is also clear from Fig. 1 that the fusion peak for the sodium and potassium naphthenates can be fully recorded under both nitrogen and oxygen atmospheres while the fusion peak for the sodium alkanoate can be fully recorded only under nitrogen atmosphere, since decomposition under oxygen apparently starts as soon as the crystal lattice begins to collapse.

Solid-state transitions were also detected for the three salts as shown in

TABLE 2

Thermogravimetric data [a]

Type of compound	$(\Delta m,\%)_c$	N_2 atmosphere		O_2 atmosphere	
		$(\Delta m,\%)_e$	Δ	$(\Delta m,\%)_e$	Δ
Sodium cyclohexane butyrate	72.5	73	+1	68	−6
Potassium cyclohexane butyrate	66.5	65	−2	64	−4
Sodium isocaproate [b]	62	62.5	+1	60	−3

[a] $(\Delta m,\%)_c$ = Calculated weight loss (%); $(\Delta m,\%)_e$ = Experimental weight loss (%); $\Delta = 100 \times \frac{(\Delta m\%)_e - (\Delta m\%)_c}{(\Delta m\%)_c}$.

[b] From ref. 5.

Fig. 1. Sodium and potassium naphthenate possessed transition temperatures 50 K higher than the sodium alkanoate.

The DTG traces shown in Fig. 2 indicated that the weight loss process proved to be of a more complex nature under oxygen than under nitrogen gas, while the single peak recorded under nitrogen gas lied close to the highest temperature peak recorded in the DSC measurements. In Table 2 the calculated and experimental wt.% losses are presented and accuracy seems to be within the accepted limit of ±3–5%, although some of the disturbing factors mentioned in the reaction schemes seem to play a role in the decomposition of sodium cyclohexane butyrate under oxygen atmosphere.

It can be concluded that, while alkalimetal naphthenates underwent similar chemical decomposition schemes to that of alkali-metal alkanoates under both nitrogen and oxygen atmospheres, the former salts possessed a higher degree of thermal stability than the latter type.

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