

## Short Communications

### ON THE THERMAL STABILITY OF ALKALI METAL ALKANOATES II.

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Lithium *n*-alkanoates from pentanoate ( $\text{LiC}_5$ ) to dodecanoate ( $\text{LiC}_{12}$ ) have been investigated with regard to their thermal stabilities. None of these salts are stable in the molten state when oxygen is present, but in an inert atmosphere the melt appears to be stable over a quite large temperature interval, on the average from the melting point ( $T_F$ ) to about  $1.3 T_F$ .

Up to recent years, molten systems containing organic anions or cations (in spite of the multiple reasons of interest they potentially offer) have received less attention than those involving inorganic salts. This is due, at least in part, to the wide-spread opinion that they generally exhibit poor thermal stability.

Here, however, it is necessary to distinguish between "apparent" and "true" instability; the former can be avoided through the adoption of appropriate experimental conditions.

For salts with organic anions and free from cations of variable valence and from hydroxide ions, e.g. sodium propanoate, Duruz, Michels and Ubbelohde [1] proved (in the absence of oxygen) melts may be obtained with marked stability up to temperatures at which breaking of the carbon-carbon linkages causes true instability.

Within the framework of our current investigations on a variety of thermal properties of the alkali metal alkanates, the present series of communications on simultaneous DTA, TG and DTG analysis is devoted to the collection of systematic information on the temperature ranges in which the melts of such salts can safely be employed.

A previous note [2] reported on a number of isobutanoates, isopentanoates and isohexanoates, while the present one deals with the lithium *n*-alkanoates from pentanoate to dodecanoate, hereafter denoted as  $\text{LiC}_5, \dots, \text{LiC}_{12}$ .

The experimental technique, the operational details and the preparation and handling of materials were described elsewhere [2–5].

DTA, TG and DTG curves were recorded in the range between room temperature and 873 K under nitrogen and oxygen atmospheres. An example of these curves (replotted from the photographic chart record) is shown in Fig. 1 for the case of  $\text{LiC}_{11}$ .

As regards the decomposition process, it is worthwhile to note that: (i) in oxygen atmosphere it always starts at approximately the melting point, and apparently occurs through a succession of steps giving rise to not less than two and up to four DTG peaks or shoulders; (ii) in nitrogen it begins at a markedly higher temperature

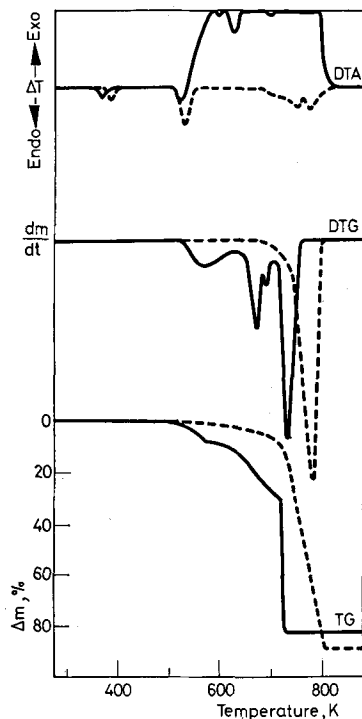


Fig. 1. DTA, TG and DTG curves taken by the derivatograph on lithium hendecanoate in oxygen (solid lines) and nitrogen (dashed lines) atmospheres

and occurs mostly in one step, giving rise to a single DTG peak (only in the cases of  $\text{LiC}_7$  and  $\text{LiC}_8$  was a secondary, much smaller peak observed, respectively preceding and following the main one).

The initial ( $T_i$  in K) and final ( $T_f$  in K) decomposition temperatures are listed in Table 1, together with those  $T_m$  in K relating to maxima (or shoulders) in the DTG curves (all temperatures being rounded to the nearest 5 or 10 K). The last three columns of the Table report the melting temperatures as detected either with the MOM derivatograph ( $T_F(\text{Der})$  in K, (again rounded to the nearest 5 or 10 K) or by DSC ( $T_F(\text{DSC})$  in K, [4, 5]), and the ratios (significant for the thermal stability of the melts)  $R = T_i/T_F(\text{DSC})$ .

The thermogravimetric results are given in Table 2, where  $(\Delta m\%)_c$  and  $(\Delta m\%)_e$  are the calculated and experimental percentage weight losses, respectively, and

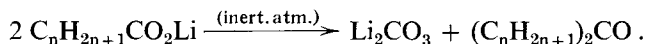
$$\Delta = 100 \frac{(\Delta m\%)_e - (\Delta m\%)_c}{(\Delta m\%)_c}$$

The tabulated data obtained with the derivatograph were supplemented with measurements carried out (in oxygen atmosphere) by means of a micro-TG device of the Cahn type. The two procedures led to satisfactorily agreeing results: the lowest  $\Delta$  was obtained with  $\text{LiC}_{11}$  ( $-0.9$ , Cahn;  $+1.9$ , derivatograph) and the highest one with  $\text{LiC}_{12}$  ( $-14.1$ , Cahn;  $-10.8$ , derivatograph).

The fact that the experimental weight losses differ from the calculated ones by amounts considerably in excess of the routine accuracy of  $\pm 3-5\%$  indicates that (although lithium carbonate is expected to be the predominant final solid residue) side-reactions may occur, giving rise to overall decomposition processes more complicated than represented by the schemes:



and



This situation conforms to what was previously [2] observed with a number of short-chain branched alkanooates, for which agreement within 2% was found between calculated and experimental weight losses when the cation was potassium or sodium, whereas discrepancies ranging from 5 to 11% occurred with lithium. In particular, the residue obtained in nitrogen atmosphere may have a non-uniform composition, owing to the presence of crack carbon, carbides, etc., besides the carbonate.

Two conclusive statements can be made.

(i) None of the  $n$ -alkanoates  $\text{LiC}_5, \dots, \text{LiC}_{12}$  are capable of a stable existence in the molten state when oxygen is present, since the approaching of the fusion temperature initiates extensive decomposition.

(ii) In contrast under an inert atmosphere the melt appears to be stable over a quite large temperature interval, which extends from Fig. 1. DTA, TG and DTG curves taken by derivatograph on lithium hendecanoate in oxygen (solid lines) and nitrogen (dashed lines) atmospheres  $\approx 125$  K in the case of  $\text{LiC}_7$  to for  $\text{LiC}_{10}$ , i.e. on the average from  $T_F$  to  $1.3 T_F$ . Such a stability interval is approximately the same as that already found for some branched isomers [2].

Table 1

Fusion and decomposition temperatures of the  $\text{LiC}_5$ – $\text{LiC}_{12}$  *n*-alkanoates

Atmosphere	Salt	$T_1$ (Der), K	$T_m$ (Der), K	$T_f$ (Der), K	$T_F$ (Der), K	$T_F$ (DSC), K	$R = \frac{T_1(\text{Der})}{T_F(\text{DSC})}$
Oxygen	LiC <sub>5</sub>	560	580 655 685 700 m	725	(*)	576	1.0
	LiC <sub>6</sub>	520	545 s 630 720 s 750 m	800		562	0.9
	LiC <sub>7</sub>	530	575 s 655 775 m	805		550	1.0
	LiC <sub>8</sub>	530	560 s 660 m 705	740		539	1.0
	LiC <sub>9</sub>	525	580 s 665 690 m	745		526	1.0
	LiC <sub>10</sub>	525	670 725 m	750		518	1.0
	LiC <sub>11</sub>	510	570 670 685 730 m	770		507	1.0
	LiC <sub>12</sub>	510	570 675 720 m	760		506	1.0
	Nitrogen	LiC <sub>5</sub>	725	770	790	575	576
LiC <sub>6</sub>		725	775	800	555	562	1.3
LiC <sub>7</sub>		675	690 775 m	800	540	550	1.2
LiC <sub>8</sub>		680	750 m 825	865	535	539	1.3
LiC <sub>9</sub>		725	770	790	535	526	1.4
LiC <sub>10</sub>		725	760	775	515	518	1.4
LiC <sub>11</sub>		675	780	805	515	507	1.3
LiC <sub>12</sub>		675	770	795	510	506	1.3

m: main peak  
s: shoulder

(\*) The approximate coincidence of melting and of decomposition starting prevents to take trustworthy  $T_F$ (Der) values in oxygen atmosphere.

Table 2  
Thermogravimetric data

Salt	$(\Delta m, \%)_c$	O <sub>2</sub> atmosphere		N <sub>2</sub> atmosphere	
		$(\Delta m, \%)_c$		$(\Delta m, \%)_c$	
LiC <sub>5</sub>	65.7	61.0	− 7.2	63.0	− 4.1
LiC <sub>6</sub>	69.7	66.7	− 4.3	66.6	− 4.4
LiC <sub>7</sub>	72.8	70.6	− 3.0	67.6	− 7.1
LiC <sub>8</sub>	75.3	69.2	− 8.1	73.4	− 2.5
LiC <sub>9</sub>	77.4	79.4	+ 2.6	78.3	+ 1.2
LiC <sub>10</sub>	79.2	76.0	− 4.0	79.3	+ 0.1
LiC <sub>11</sub>	80.7	82.2	+ 1.9	88.9	+10.2
LiC <sub>12</sub>	82.7	73.8	− 10.8	74.3	− 10.2

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