THE THERMAL STABILITIES OF ALKALI METAL ALKANOATES.
PART IV.

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The thermal stabilities of long-chain lithium and potassium n-alkanoates from tridecanoate to eicosanoate have been investigated up to 873 K with a MOM derivatograph. The results obtained, together with available data of different kinds, allowed the findings that: (i) in an oxygen atmosphere, stability is limited to crystalline polymorphs; (ii) in nitrogen, the isotropic liquid stability range goes up to $\simeq 1.3\ T_F/\mathrm{K}$ when the melt forms on fusion of a lithium soap, but has only a narrow extent when the melt forms on clearing of a potassium soap.

Information on the thermal stabilities of the lithium and potassium n-alkanoates from pentanoate to dodecanoate was given in Parts II and III [1, 2] of this series, respectively. The higher homologues up to eicosanoate of both salt families are dealt with in the present paper where, for the sake of simplicity, MC_x (M = Li or K) is used as the general formula instead of $n\text{-}C_xH_{2x-1}O_2M$.

The recent DSC investigations carried out by two of us [3, 4], together with the X-ray diffraction patterns taken by Gallot and Skoulios [5] on LiC_{14}, LiC_{16}, LiC_{18}, KC_{14}, KC_{16} and KC_{18}, and with other data from different sources [6], point to the following conclusions.

(i) The $LiC_{13} - LiC_{20}$ homologues can exist in the range from room temperature to decomposition either as a crystalline solid, or in a "plastic" mesomorphic (e.g. waxy) or in the isotropic liquid state.

(ii) In the case of the $KC_{13} - KC_{20}$ n-alkanoates, before the isotropic liquid state is reached, a turbid liquid-crystalline mesomorph always forms, which at the clearing temperature, T_{Cl}, turns into an isotropic clear melt.

(iii) In either soap series the fusion temperatures, T_F, which may be understood as the melting temperatures of the polar end groups, are approximately constant, whereas the transition temperatures, T_A, which may be understood as the melting temperatures of the paraffinic chains, tend to decrease as n_C increases (n_C: number of carbon atoms).+

+ The (always occurring) intercrystalline and the (often occurring) interplastic transitions are unimportant as regards the present considerations.

Experimental

A MOM derivatograph was employed to record simultaneously DTA, TG and DTG traces on samples (coming from the same lots used in the previous [3, 4] DSC study) of the salts in question up to 873 K, in both oxygen and nitrogen atmospheres. The procedure adopted, as well as a few points relevant to the different sensitivities and temperature scale accuracies offered by a Perkin–Elmer DSC-2 device and by the derivatograph, have already been described [1, 2, 7].

Results

A comprehensive picture of the thermal behaviour of the $LiC_{13} - LiC_{20}$ soaps in the region above 400 K is given in Fig. 1; the following points may be stressed. In oxygen atmosphere the passage (at T_A) from a crystalline to a non-crystalline ("plastic") state is approximately concomitant with the beginning of decomposition, whereas in nitrogen there exists a remarkably large stability range of the isotropic liquid, extending from T_F up to about $1.3\ T_F$. The decomposition processes involve a succession of several steps in the former atmosphere, but apparently occur through a much simpler mechanism in the latter one: as an example, the curves obtained with the derivatograph on LiC_{15} are shown in Fig. 2, while, for the sake of completeness, the DSC trace recorded over A and F on the same salt (using nitrogen as the purge gas) is reproduced in Fig. 3.

The relevant DSC phase transition temperatures (rounded to the nearest unit) are listed in Table 1, along with the T_m values in the DTG curves at which main (M) or secondary (m) maxima and shoulders (s) occur, and with the T_f values around which decomposition appears to be completed (all rounded to the nearest 5 or 10). The initial decomposition temperatures, T_i, unavoidably established with
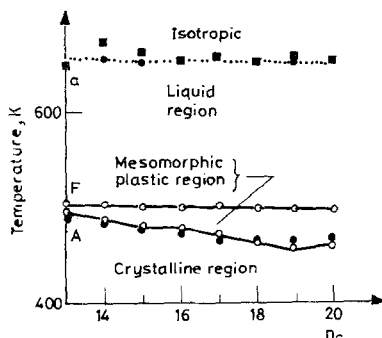

Fig. 1. Empty circles "A" and "F": crystal-plastic transitions and fusion temperatures of $LiC_{13} - LiC_{20}$, as obtained from DSC records; dotted line "a": temperatures corresponding to $1.3\ T_F/K$; filled circles and squares: temperatures of decomposition start T_i, as found with the derivatograph in oxygen and nitrogen atmospheres respectively
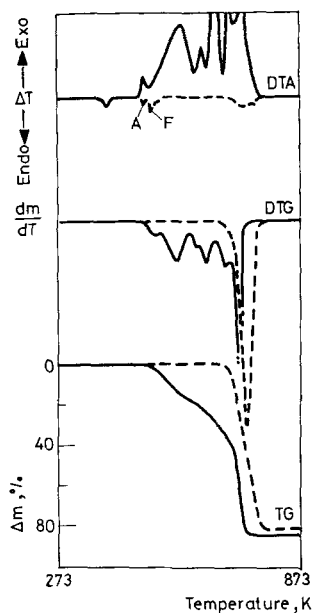
Fig. 2. DTA, TG and DTG curves taken on LiC_{15} with the derivatograph, as replotted from the original photographic records (solid and dashed lines refer to oxygen and nitrogen atmospheres, respectively)
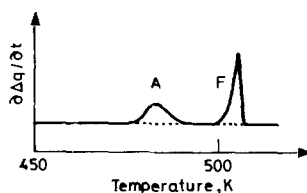

Fig. 3. A DSC trace recorded over A and F for LiC_{15}, using nitrogen as the purge gas

only moderate accuracy, are shown in Fig. 1, where they are indicated by rather large black symbols.

In the potassium $C_{13}-C_{20}$ series the T_A's range between 483 and 450 K, with a noticeable odd-even alternating effect; the T_F's are approximately constant around 540 K, and the T_{Cl}'s decrease monotonously from 671 K for the tridecanoate to 613 K for the eicosanoate. As regards the initial decomposition temperatures, it must be said that they exhibit a larger spread and a less definite trend than in the case of the corresponding lithium series. It could, anyhow, be stated that the T_i's (i) in oxygen always lie between the relevant T_A's and T_F's, and (ii) in nitrogen atmosphere fall not far from the T_{Cl}'s, in such a way that the stability range of the isotropic liquid, practically negligible for the shorter homologues, may extend for

Table 1

Temperatures, T/K, of fusion, transition A and decomposition in $LiC_{13}-LiC_{20}$ n-alkanoates

Salt	DSC [3] (a)		Derivatograph (present work)			
			N_2 atm.		O_2 atm.	
	T_F	T_A	T_m	T_f	T_m	T_f
LiC_{13}	505	497	745	785	545 m 610 m 670 m 730 M	795
LiC_{14}	505	489	750	805	505 s 530 m 575 m 635 m 675 M	730
LiC_{15}	502	479	740	785	510 m 565 m 615 m 635 m 685 m 720 M	760
LiC_{16}	502	480	745	790	560 m 625 m 660 m 705 s 730 M	790
LiC_{17}	503	473	740	785	565 m 625 m 690 m 720 M	790
LiC_{18}	501	465	735	790	515 s 560 m 620 m 665 m 710 M	740
LiC_{19}	500	456	725	780	540 s 580 m 650 m 680 M	715
LiC_{20}	499	462	735	795	515 s 575 m 660 m 720 M	800

(a) *Samples sealed in Al pans and scanned using N_2 as the purge gas*

few tens of degrees in the case of the longer ones. Analogously to lithium soaps, the decomposition process involves several steps in oxygen, but possibly only one in nitrogen atmosphere: the pertinent data are listed in Table 2.

Table 2

Temperatures, T/K, of clearing, fusion, transition A and decomposition in $KC_{12}-KC_{20}$ n-alkanoates

| Salt | DSC [14] (a) | | | Derivatograph (this work) | | | |
| | | | | N_2 atm. | | O_2 atm. | |
	T_{Cl}	T_F	T_A	T_m	T_f	T_m	T_f
KC_{13}	671	542	483	765	795	600 m 620 M	680
KC_{14}	662	540	483	765	800	540 m 580 M 625 m	680
KC_{15}	653	541	471	770	805	590 s 610 s 620 M	700
KC_{16}	643	539	469	765	805	540 M 570 m 600 m 635 m 670 m	710
KC_{17}	635	540	462	760	805	510 m 520 m 600 m 635 m 685 M	740
KC_{18}	627	543	464	770	805	520 m 530 m 570 m 615 m 670 M	720
KC_{19}	618	541	450	770	800	510 m 560 m 635 m 675 M	710
KC_{20}	613	545	457	755	805	515 m 585 m 640 M 685 m	720

(a) *Samples sealed in Al pans and scanned using N_2 as the purge gas*

The decomposition of alkali metal alkanoates (if there are no side-reactions) should simply cause evolution of CO_2 and H_2O in oxygen, and of volatile products, e.g. ketones, in nitrogen atmosphere, leaving metal carbonate as the solid residue. The per cent weight losses, $(\Delta m \%)_c$, calculated according to this assumption are reported in Tables 3 (for the lithium soaps) and 4 (for the potassium soaps), along with the experimental ones, $(\Delta m \%)_e$, and with the corresponding $\Delta = 100$ $[(\Delta m \%)_e - (\Delta m \%)_c]/(m \%)_c$ values.

Table 3

Thermogravimetric data for $LiC_{13}-LiC_{20}$ n-alkanoates

Salt	$(\Delta m \%)_c$	N_2 atm.		O_2 atm.	
		$(\Delta m \%)_e$	Δ	$(\Delta m \%)_e$	Δ
LiC_{13}	83.2	79.6	−4.3	85.5	+2.8
LiC_{14}	84.2	81.7	−3.0	82.2	−2.4
LiC_{15}	85.1	81.2	−4.6	84.3	−0.9
LiC_{16}	85.9	84.8	−1.3	85.2	−0.8
LiC_{17}	86.6	83.6	−3.5	87.5	+1.0
LiC_{18}	87.3	85.4	−2.2	87.0	−0.3
LiC_{19}	87.9	82.7	−5.9	88.3	+0.5
LiC_{20}	88.4	87.8	−0.7	88.7	+0.3

Table 4

Thermogravimetric data for $KC_{13}-KC_{20}$ n-alkanoates

Salt	$(\Delta m \%)_c$	N_2 atm.		O_2 atm.	
		$(\Delta m \%)_e$	Δ	$(\Delta m \%)_e$	Δ
KC_{13}	72.6	71.0	−2.2	74.8	+3.0
KC_{14}	74.1	70.7	−4.6	76.6	+3.4
KC_{15}	75.4	75.3	−0.1	77.2	+2.4
KC_{16}	76.5	73.4	−4.1	78.2	+2.2
KC_{17}	77.6	76.6	−1.3	77.3	−0.4
KC_{18}	78.6	77.0	−2.0	77.1	−1.9
KC_{19}	79.5	76.6	−3.6	78.2	−1.6
KC_{20}	80.3	79.9	−0.5	79.3	−1.2

With the exception of LiC_{19}, the agreement between the experimental and calculated values is always within the usual accuracy of the method [3−5%]. As concerns the lithium soaps in particular, this seems to indicate that side-reactions (possibly affecting the nature and amount of the solid residue) are of less importance here than in the case of the shorter homologues [1, 7]. The fact, however, that in nitrogen the Δ's are always negative and, on an average, three times larger than in oxygen atmosphere might in the former case still suggest a limited formation of by-products.

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