Short communications

THE THERMAL STABILITIES OF ALKALI METAL ALKANOATES PART III

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Simultaneous DTA, TG and DTG analysis has been performed on potassium n-alkanoates from pentanoate to dodecanoate in the range between room temperature and 873 K. Information has been obtained on the thermal decomposition processes they undergo in both oxygen and nitrogen atmospheres.

Among the alkali metal n-alkanoate families, that characterized by lithium as the cation is the only one in which the stepwise melting process leading to isotropic liquid never involves passage through any anisotropic (mesomorphic) liquid-crystalline phase.

The investigation with the derivatograph reported in Part II [1] allowed establishment of the temperature ranges where, in both oxygen and an inert atmosphere, the lithium salts from n-pentanoate to n-dodecanote are thermally stable in the molten state.

It now seems worth while taking the corresponding potassium homologues into account for comparison hereafter these will be denoted for the sake of brevity as KC_5, ..., KC_{12}. This group of salts, for which the temperatures and enthalpies of phase transitions have recently been determined through an extensive DSC study [2, 3], includes the homologues exhibiting both the highest clearing temperature and the largest field of existence of the liquid-crystalline phase among all the alkali metal n-alkanoates, i.e. KC_6 (for which $T_{Cl} = 725.8 \pm 0.8$ K) and KC_9 (for which the difference between the clearing and fusion temperatures amounts to $\simeq 158$ K) (*).

A few operational details were already given in Part I [4], while the samples submitted to measurement were portions of the same lots as employed in the previous DSC investigation.

The simultaneous recording of the DTA, TG and DTG traces was carried out with a MOM derivatograph up to 873 K.

(*) The fusion temperature, T_F/K, is here taken as that at which liquid crystals form (on heating), independently of the nature of the phase in equilibrium with them at T_F, although other authors may prefer a different terminology.

Owing to the different sensitivities of the DSC and derivatograph, the DTA picture of the phase relationships obtained with the latter technique was in some cases less detailed (e.g. the intercrystalline transition occuring in KC_5 at 400 K with an enthalpy change of 0.1 kcal mol^{-1} was clearly perceivable only by DSC).

Another point worthy of some comment concerns the clearing phenomenon. Let us consider as an example the case of KC_{10}, for which previous DSC [3] and
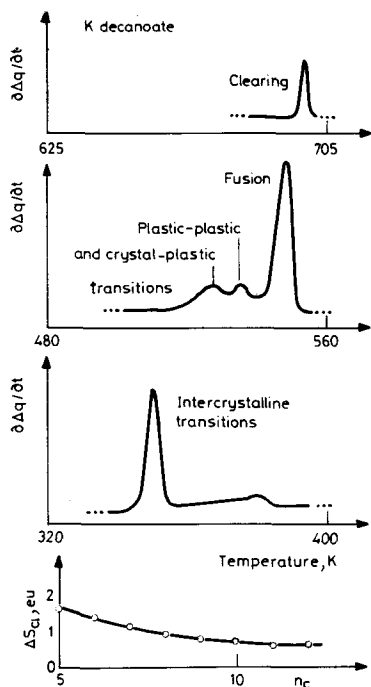

Fig. 1. Upper part: phase relationships in KC_{10} as obtained by DSC (sample wt. 4.296 mg; scan speed 10° min^{-1}). The self-consistency of the clearing temperatures and enthalpy changes through the whole homologous series is supported by the regular trend of the $\triangle S_{Cl}$'s when plotted vs. n_C (see the lower part of the Figure). Plastic phases do not occur when $n_C < 9$

present DTA traces are shown in the upper part of Figs 1 and 2, respectively. It can be observed that the clearing peak is sharper and occurs at a somewhat higher temperature in the DSC than in the DTA record. This is a common feature of the whole homologous series $KC_5, \ldots, KC_{12}$ (the above difference in temperature amounting on average to $\simeq 7$ K), and is reasonably justifiable as follows: (i) all of the salts concerned are characterized by a more or less marked hygroscopicity; (ii) the operational procedure adopted in the case of DSC allowed measurements on samples which had not been exposed to atmospheric moisture; (iii) for instrumental reasons, contact with the atmosphere could not be avoided

in the case of the derivatograph: during transfer of the salt into the open sample holder, weight increases of several percent usually occurred; (iv) a preliminary heating to constant weight within the instrument at about 100° was therefore necessary. Under such circumstances, one cannot exclude the occurrence (related to the thermal history) of minor alterations, surely contained within very narrow limits (since DSC and DTA always gave substantially agreeing results, as proved
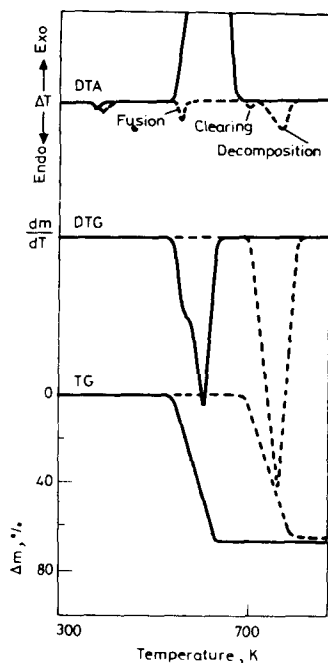

Fig. 2. DTA, TG and DTG curves for KC_{10} in oxygen (solid lines) and nitrogen (dashed lines) atmospheres, replotted from the original photographic record obtained with the MOM derivatograph

inter alia by the satisfactorily close T_F values obtained for each salt with the two methods, see Table 1), but possibly sufficient to exert a perceivable influence on the clearing temperature and peak shape (both demonstrated [5] to be highly sensitive to manipulation, as well as to the presence of any kind of impurity, even in traces).

Coming now to the decomposition process, the present results allow one to point out the following. In an oxygen atmosphere decomposition starts simultaneously with fusion in the case of the lower homologues, but even at a somewhat lower temperature (falling within the plastic region, see Fig. 1) in the case of the higher ones: the DTG curves prove that the (exothermic) process occurs through a succession of steps and becomes increasingly complicated as n_C increases (n_C

Table 1

Clearing, fusion and decomposition temperatures, K

Salt	DSC [2, 3] (a)		Derivatograph (present work)				
	T_{Cl}	T_F	N₂ atm.			O₂ atm.	
			T_F (b)	T_m	T_f	T_m	T_f
KC₅	716	587	585	775	810	590 m 620 M	645
KC₆	726	582	575	765	800	595 m 615 M	660
KC₇	722	571	565	770	810	570 s 590 s 610 M	640
KC₈	712	561	560	770	805	575 m 615 M	665
KC₉	707	549	545	765	805	575 m 625 M	660
KC₁₀	696	544	545	765	815	555 s 600 M	640
KC₁₁	691	541	540	755	805	535 m 570 m 590 m 625 M	660
KC₁₂	679	541	535	760	800	535 m 555 m 585 m 595 M	625

(a) Samples sealed in Al pans and scanned using N₂ as the purge gas
(b) Peak temperatures

is the number of carbon atoms). In nitrogen, in contrast, the stability range extends up to clearing temperatures or even, a few degrees higher, while decomposition proceeds endothermically, giving rise with all homologues to a single, almost symmetrical DTG peak.

Table 1 lists the clearing temperatures taken by DSC (close to which decomposition starts under nitrogen); the fusion temperatures taken by DSC and DTA agreeing well (and close to which decomposition starts under oxygen); the T_m and T_f values at which maxima or shoulders occur in the DTG curves, and decomposition is completed, respectively. As regards the T'_m s, notations in italics are employed to distinguish main (M) and secondary (m) maxima and shoulders (s). The DSC temperatures are rounded to the nearest unit, and those taken by DTA to the nearest five or ten.

Table 2

Thermogravimetric data

Salt	$(\Delta m \%)_c$	N$_2$ atm.		O$_2$ atm.	
		$(\Delta m, \%)_e$	Δ	$(\Delta m, \%)_e$	Δ
KC$_5$	51	52	+2	51	—
KC$_6$	55	55	—	55	—
KC$_7$	59	59	—	58	−2
KC$_8$	62	62	—	62	—
KC$_9$	65	60	−8	64	−2
KC$_{10}$	67	65	−3	67	—
KC$_{11}$	69	65	−6	66	−4
KC$_{12}$	71	64	−10	69	−3

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

In Table 2 the experimental percentage weight losses, $(\Delta m \%)_e$, are compared with those, $(\Delta m \%)_c$, calculated on the basis of the obvious reaction schemes leading to formation of only alkali metal carbonate as the solid residue, and at the same time to evolution of ketone (and possibly other volatile products) under nitrogen, and of CO_2 and H_2O under oxygen. The Δ values of column 6 are well within the routine accuracy $(3-5\%)$ of the method, whereas those of column 4 may somewhat exceed such limits in the case of the higher homologues. These results apparently indicate that: (i) under oxygen, in spite of the complicated features of the DTG curves, the solid residue should actually be K_2CO_3 only, as expected; (ii) under nitrogen, in spite of the simpler shape of the curves, side-reactions, e.g., crack-carbon formation, may occur (at least from $n_C = 9$ up), which cause the solid residue to weigh more than expected.

As conclusive remarks, it may first be noted that the $n - C_5, \ldots, n - C_{12}$ alkanoates of both the lithium and potassium series are not capable of stable existence under oxygen at temperatures exceeding T_F. On the other hand, under nitrogen the isotropic liquid obtained through fusion when lithium is the cation is stable from T_F up to a temperature approximately equal to 1.3 T_F, whereas when potassium is the cation the stability range of the isotropic liquid obtained through clearing of the anisotropic one is practically negligible in extent.

References

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