

Short Communication

THE THERMAL STABILITIES OF ALKALIMETAL ALKANOATES

PART I.

T. MEISEL, I. LÁNYI and P. FRANZOSINI

*Institute for General and Analytical Chemistry, Technical University of Budapest, Hungary;
"Centro di Studio per la Termodinamica ad Elettrochimica dei sistemi salini fusi e solidi" c/o
Istituto di Chimica Fisica e di Elettrochimica della Università, Pavia, Italy*

(Received January 15, 1979)

Thermal analysis of Li, Na and K isobutyrate, Li and Na isovalerate, and Li and Na isocaproate has been performed between room temperature and 873 K under both inert and oxygen atmospheres. Information has been obtained on the thermostabilities of these salts and the thermal decomposition processes they undergo.

The literature offers a remarkable (although still far from complete) amount of data on the thermal behaviours of alkalimetal linear alkanooates: investigations by many authors through a variety of experimental techniques have provided a picture of the phase relationships in most homologues with n_C (number of carbon atoms) up to 22, and in several cases have revealed their thermal stabilities too.

Branched alkanooates, in contrast have so far received little attention: phase transition enthalpies (ΔH_{tr}): (Joule mole⁻¹) and/or temperatures (T_{tr}) have been determined only for a restricted number of Li, Na and K salts, and as far as we know, information on the pertinent thermal stabilities is completely missing, in spite of its obvious interest in view of possible technical applications.

The present paper deals with the thermal determination in both N₂ and O₂ atmospheres of Li, Na and K isobutyrate (2-methyl-propanoate, hereafter indicated for the sake of brevity as MC_{4,i}, with M = Li, Na, K): Li and Na isovalerate (3-methylbutanoate, MC_{5,i}); and Li and Na isocaproate (4-methylpentanoate, MC_{6,i}). ΔH_{tr} and T_{tr} data were collected in a previous paper [1] where, inter alia, the existence of a mesomorphic anisotropic liquid phase (over a temperature range intermediate between those pertinent to the solid and to the isotropic liquid, respectively) was established for KC_{4,i}, NaC_{5,i} and NaC_{6,i}.

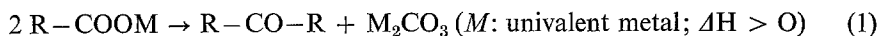
Experimental

Details on the MOM derivatograph are to be found in [2]. Throughout the present work, a heating rate of 10° · min⁻¹ a maximum heating temperature of 600° (873 K), gas flow rates of 15–20 l h⁻¹, a Pt sample holder, and samples weighing between 50 and 100 mg were used.

The materials came from the same batches as those in [1]. Owing to their not negligible hygroscopic natures, each sample (before starting of the decomposition run) was kept at 373 K until its weight became constant, in order to sweep away the moisture it had absorbed during the transfer from the original glass container (sealed under vacuum) into open derivatograph sample holder.

Results and discussion

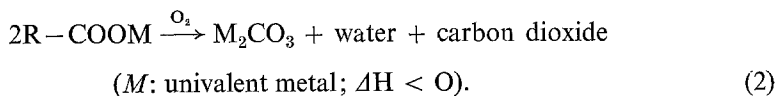
The thermal decomposition of alkalimetal alkanooates under an inert atmosphere is often represented simply as



In fact, however, carbon, CO, H₂, H₂O, organic molecules other than R-CO-R, etc., may also be formed, the yield in R-CO-R actually being affected by the natures of both the anion and the cation and also of the inert gas [3].

A carbonate amount stoichiometrically in agreement with Eq. (1) is to be expected only if (i) the alkanooate does not undergo either sublimation or evaporation; (ii) the carbonate itself does not decompose further; (iii) organic materials are completely removed; and (iv) no formation occurs of crack-carbon (and/or carbides).

Decomposition in an oxygen atmosphere seems to be a rather complicated process too (see below), in spite of the obvious (usually adopted) scheme:



In Table 1 a comparison is made (for the seven isosalts taken into account here) between clearing (T_{Cl}) and fusion (T_F) temperatures, determined either by DSC [1] or by DTA (rounded to the nearest unit, and to the nearest five or ten, respectively): considering the different degrees of accuracy of the two methods, agreement looks satisfactory always. The initial (T_i) and final (T_f) decomposition temperatures are also listed in the same Table, together with the T_m values at which maxima are exhibited by the DTG traces*.

The widest stability range of the melt is apparently that of LiC_{4,i}, for which the ratio, R between T_i and the temperature of isotropic liquid formation (T_F , in this case) is 1.4 in N₂ and 1.1 in O₂ atmosphere.

R is caused to decrease by substituting either Na or K for Li as the cation, or C_{5,i} or C_{6,i} for C_{4,i} as the anion; in nitrogen, however, it never goes below unity, whereas

* Owing to their complicated trends, only "peak temperatures" could be taken on DTG traces recorded in an O₂ atmosphere: for the sake of homogeneity and to allow proper comparison the same manner of taking temperatures was adopted for any DTA and DTG trace recorded with the derivatograph. T_{ir} 's from [1] were in contrast taken in correspondence with the beginning of the deviation from the baseline.

Table 1
Clearing, fusion and decomposition temperature, K

Anion	Cation	DSC [1]		Derivatograph (present work)									
		T_{Cl}	T_F	N ₂ atm.		O ₂ atm.		N ₂ atm.			O ₂ atm.		
				T_{Cl}	T_F	T_{Cl}	T_F	T_i	T_m	T_f	T_i	T_m	T_f
C _{4,i}	Li	—	503	—	500	—	500	710	800	820	550	620	760
	Na	—	527	—	525	—	(525)	660	790	840	520	670	825
	K	626	554	620	550	d	(550)	695	780	820	535	730	780
C _{5,i}	Li	—	534	—	540	—	d	695	760	785	515	595	775
	Na	559	462	555	465	d	d	675	775	810	460	640	795
												750	
C _{6,i}	Li	—	500	—	495	—	(495)	635	735	795	485	475	795
	Na	626	534	625	530	d	(530)	625	735	785	525	610	745
												665	
												685	
												725	

d: decomposition
in brackets: T_{tr} value which could be detected even if decomposition had already started

in oxygen it does for all salts other than LiC_{4,i}. In particular, the anisotropic liquid phases look stable in nitrogen atmosphere (although for NaC_{6,i} decomposition starts just in correspondence with T_{Cl}), whereas not even the lower limits of their existence fields can be reached in the presence of oxygen.

As a specimen of the results obtained, the thermal curves pertinent to KC_{4,i} are shown in Fig. 1.

It may be stressed that: (i) in either atmosphere the solid state transition detected by DSC at 424 ± 3 K gives rise (at about 425 K) to DTA peaks completely overlapping; (ii) the fusion (as well as the clearing) peak can be fully recorded in nitrogen atmosphere only, since decomposition in oxygen apparently starts as soon as the crystal lattice begins to collapse; (iii) according to the DTG traces, the weight loss process proves to be much more complicated in O₂ than in N₂, although the single peak recorded in the latter case lies close to the highest temperature peak

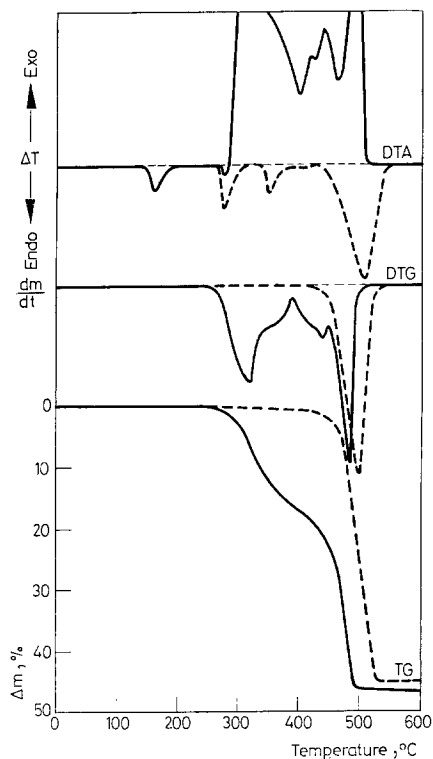


Fig. 1. Thermal curves of $KC_{4,i}$ obtained with a derivatograph. — in O_2 atmosphere; ---- in N_2 atmosphere

Table 2
Thermogravimetric data

Anion	Cation	$(\Delta m, \%)_{\text{calc}}$	O_2 atmosphere		N_2 atmosphere	
			$(\Delta m, \%)_e$	Δ	$(\Delta m, \%)_e$	Δ
$C_{4,i}$	Li	61	62	+2	58	-5
	Na	52	54	+4	53	+2
	K	45	46.5	+3	45	± 0
$C_{5,i}$	Li	66	62	-6	73	+11
	Na	57	57	± 0	57	± 0
$C_{6,i}$	Li	70	69	-1	65	-7
	Na	62	60	-3	62.5	+1

$(\Delta m, \%)_c$: calculated weight loss, %

$(\Delta m, \%)_e$: experimental weight loss, %

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

recorded in the former one. This peculiarity is common to all the investigated salts except $\text{LiC}_{4,1}$.

In Table 2 the calculated and experimental % weight losses are compared. Taking into account that with TG measurements an accuracy of $\pm 3-5\%$ is routine, it may be said that schemes (1) and (2) are reasonably obeyed whenever Na and K salts are concerned (Δ values ranging between -3 and $+4$; mean Δ value: ± 1.6). In contrast, should Li be present, some of the disturbing factors listed above probably play a not negligible role (values ranging between -7 and $+11$; mean Δ value: ± 5.3).

*

One of us (P. F.) gratefully acknowledges a financial contribution jointly supplied by the Hungarian Academy of Sciences and the Italian National Research Council.

References

1. P. FERLONI, M. SANESI, P. L. TONELLI and P. FRANZOSINI, *Z. Naturforsch.*, 33a (1978) 240.
2. F. PAULIK, J. PAULIK and L. ERDEY, *Talanta*, 13 (1966) 1405.
3. T. MEISEL and Z. HALMOS, *Hung. Sci. Instr.*, 28 (1973) 7.