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THERMAL DECOMPOSITION OF ALKALI METAL MALONATE ANHYDRIDES IN VARIOUS ATMOSPHERES

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ABSTRACT

The thermal decomposition of malonic acid and alkali metal malonate anhydrides has been studied using TG–DTA and IR spectroscopy. Malonic acid is anhydrous and its decomposition in a nitrogen atmosphere takes place in a single step. In the same atmosphere, the thermal decomposition of Li malonate occurs in four stages and that of other alkali metal malonates occurs in three stages. A comparison of the initial decomposition temperature values leads to the stability order: Cs > Rb > K > Li > Na. DTA was used to follow the process of melting and the decomposition of the malonates. The DTA curves of K, Rb, and Cs malonates indicate a complicated behaviour with the appearance of many small exothermic peaks between 340 and 400, 385 and 410, and 370 and 450 °C, respectively. The activation energy values decrease regularly in Group I of the periodic system from Li to Cs. It was shown that CO_2 has an inhibiting effect on the decomposition whereas the oxidising atmospheres O_2 and air have an accelerating effect, compared with N_2. In fact it was not possible to obtain the thermograms in static air for Na and K malonates because they decomposed explosively above 298 and 295 °C, respectively.

INTRODUCTION

In a continuation of our previous study on the thermal behaviour of metal carboxylates, we have investigated the thermal dehydration of alkali metal malonate hydrates [1]. These studies have been useful in understanding the thermal dehydration behaviour of these compounds with respect to the nature of the metal–OH bonds.

Although numerous references have reported the results of kinetic and mechanistic investigations of the decomposition reactions of metal carboxylates, particularly the formates and oxalates, there is little agreement about the parameters which determine the reactivity of these compounds; and the reversibility of the decarboxylation and carboxylation steps has yet to be established. Relatively few papers have been published on the thermal decomposition of alkali metal malonates [2]. The present paper is a report on the thermal decomposition of alkali metal malonate anhydrides in

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flowing nitrogen and static air atmospheres using thermogravimetry (TG) and differential thermal analysis (DTA). In addition, the kinetics of their main decomposition stage are discussed in order to understand the mechanisms of the decomposition and the nature of the decomposition products.

EXPERIMENTAL

The details regarding the preparations of the metal malonates and the instruments used were described in a preceding paper [1]. All the alkali metal malonates prepared, except Li malonate anhydride, were hydrates and the number of water molecules varied from 1 to 6. The water molecules of alkali metal malonate hydrates heated at a rate of 5°C min^{-1} in an atmosphere of nitrogen flowing at 60 ml min^{-1}, were lost at 100, 140, 200 and 210°C for Na, K, Rb and Cs, respectively. Other experimental details were similar to those previously described.

RESULTS AND DISCUSSION

Decomposition of malonic acid and anhydrous malonates

The TG–DTA curves of malonic acid and alkali metal malonates in flowing nitrogen and static air atmospheres are shown in Figs. 1 and 2, respectively. The TG and DTA curves obtained simultaneously for Li malonate anhydride in various atmospheres are shown in Fig. 3. Table 1 lists the number of decomposition stages (n), the initial decomposition temperature (T_i), the DTA peak temperature (T_m), the weight-loss values at each decomposition step (ΔW), the DTA peak corresponding to melting of malonic acid and alkali metal carbonates in various atmospheres and the decomposition products. The TG curves in a nitrogen atmosphere, given in Fig. 1, show that the thermal decomposition pathways of alkali metal malonate anhydrides proceed via 2–4 stages; the number of stages depends on the nature of the alkali metal involved. The decomposition stages from room temperature to 1000°C in an inert atmosphere can be classified into the three types: (i) formation of $Li_2CO_3 + Li_2O$ from Li malonate, an anhydrous compound; (ii) formation of Na_2CO_3 and K_2CO_3 from Na and K malonates; and (iii) formation of Rb_2CO_3 and Cs_2CO_3, from Rb and Cs malonates; at higher temperatures the carbonates decompose without any detectable formation of Rb_2O and Cs_2O. The TG curve for malonic acid in flowing nitrogen indicates that its thermal decomposition begins at 127°C and ends at 189°C with almost total elimination of the sample. The DTA curve of malonic acid has a small endothermic peak at 97°C followed by a sharp endothermic peak at 136°C due to melting. The acid then decom-

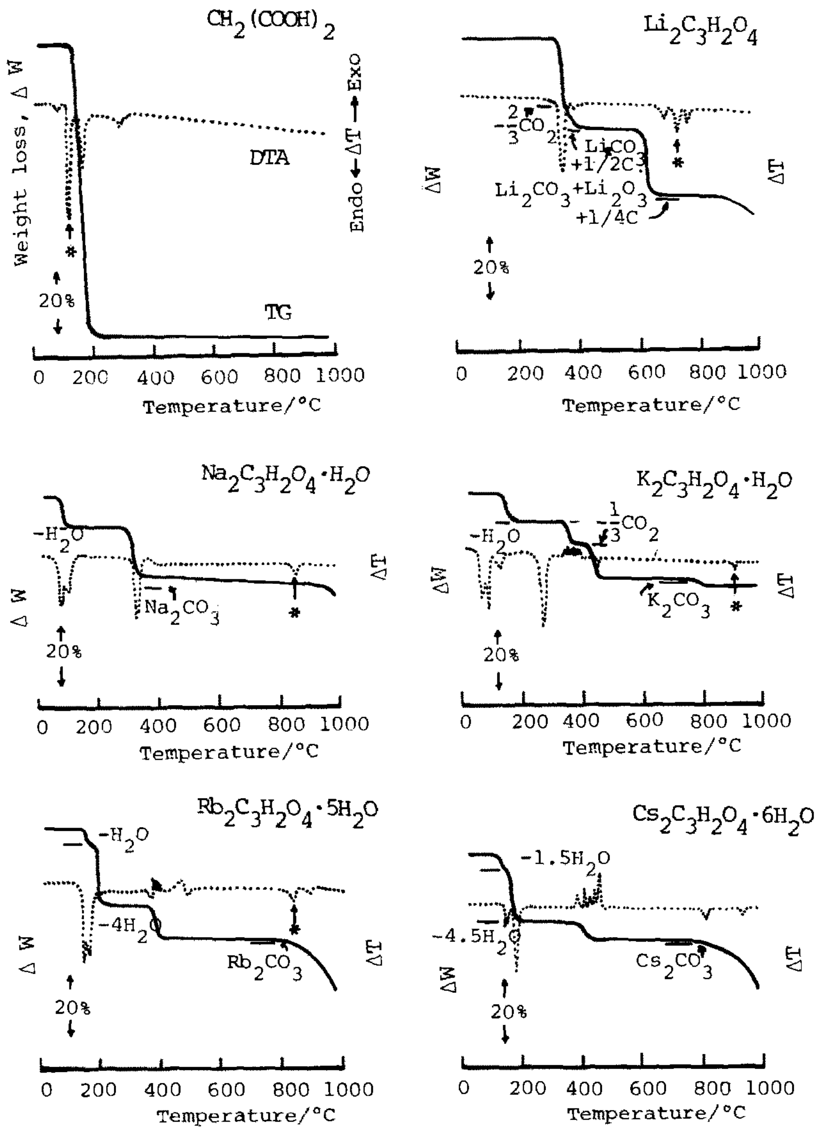

Fig. 1. TG–DTA curves of malonic acid and alkali metal malonates in a flowing nitrogen atmosphere.

posed rapidly with a broad endothermic peak at 175 °C. In the thermal decomposition processes of K, Rb and Cs malonates, the complex features appearing on the DTA curves following formation of the carbonates are presumed to be the multi-stage processes of the decomposition reaction. DTA has been used to explain the melting phenomena in Li alkanoates [3], transition metal isonicotinic hydrazide complexes [4], Mn^{II}, Ni^{II} and Co^{II} cyclotetraphosphates [5], Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} maleates [6] and K_2CO_3 [7]. The sharp, medium endothermic peaks for all malonates indi-

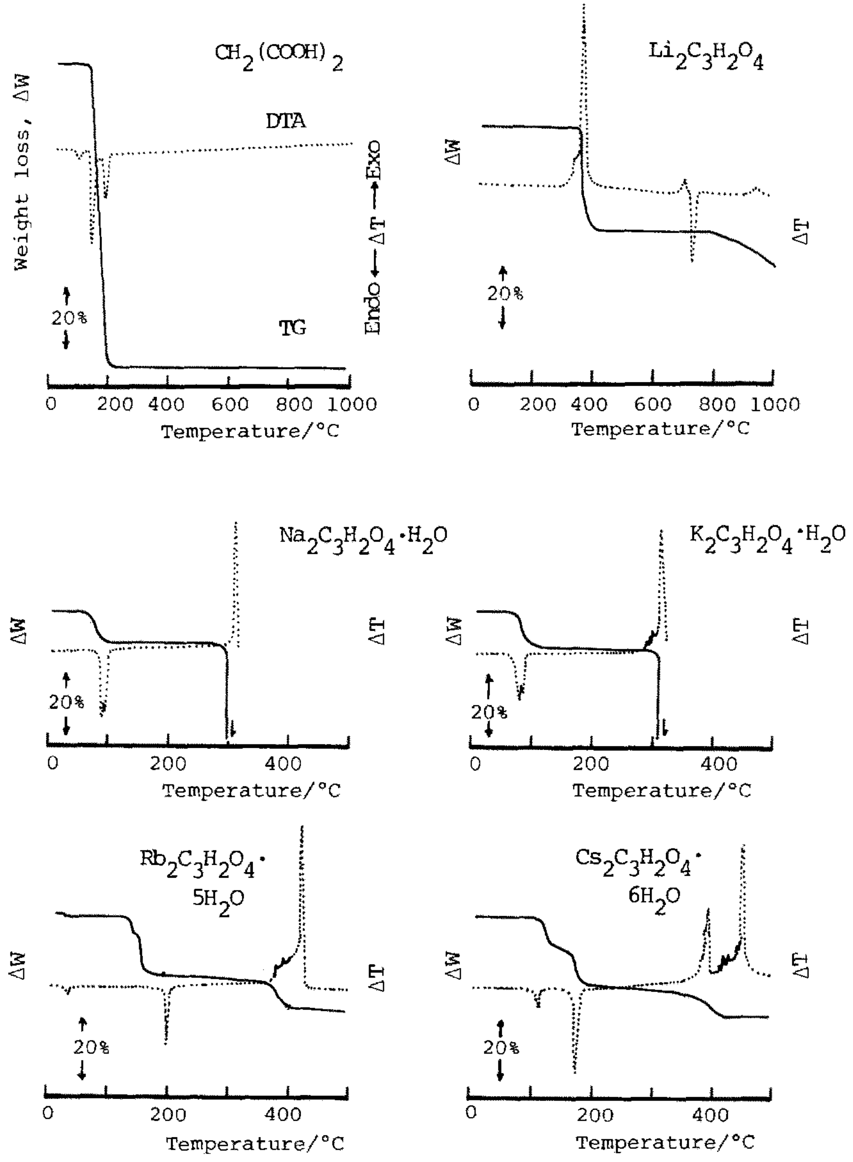

Fig. 2. TG–DTA curves of malonic acid and alkali metal malonates in a static air atmosphere.

cated with arrows and asterisks on the DTA curves in Fig. 1. correspond to the melting point of malonic acid and the carbonates. The DTA peak positions on melting (T_m) for the alkali metal carbonates, together with values obtained by other investigators, are shown in Table 2. The melting points obtained from the DTA curves are in close agreement with the literature values. In flowing CO_2, the thermal decomposition of Li and Na malonates takes place at a higher temperature and proceeds more sluggishly

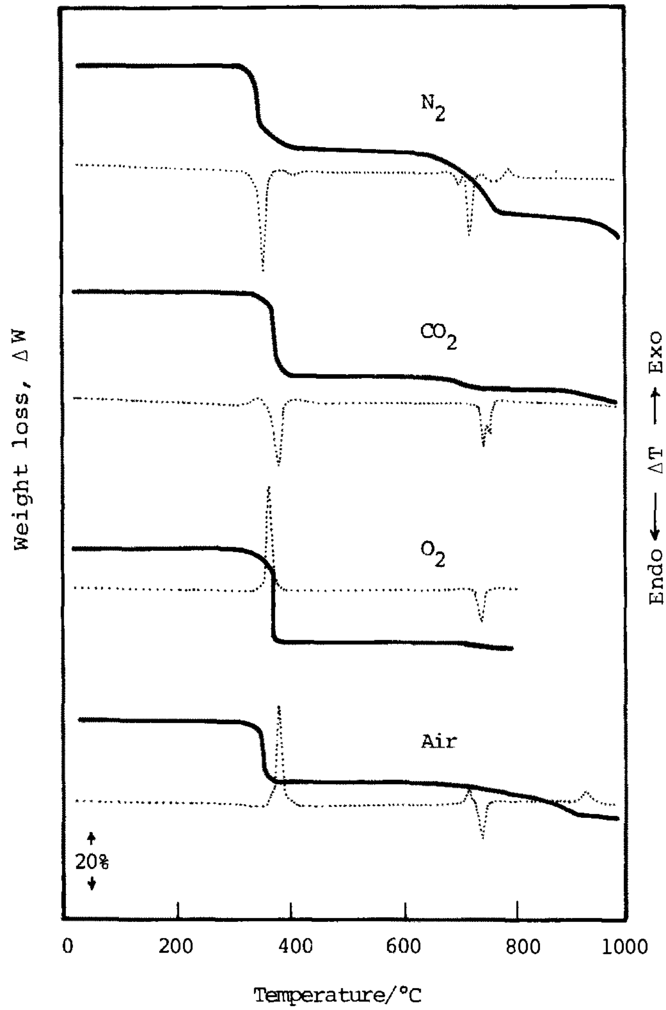

Fig. 3. TG–DTA curves of $Li_2C_3H_2O_4$ in various atmospheres.

compared with that in nitrogen and oxidising atmospheres. The TG curves of Na and K malonates in a static air atmosphere are shown in Fig. 2. The results show that the malonates react with the oxygen in an air atmosphere before decomposing and that the reaction proceeds rapidly above about 310 °C. Furthermore, in an oxidising atmosphere such as air or oxygen, the thermal decomposition of Na and K malonates proceeds with effervescence to form a carbon film at 313 and 315 °C, with an almost 100% weight loss indicated in TG and a sharp exothermic peak due to oxidation of the organic portion.

The IR spectra of heat-treated Li malonate anhydride at different temperatures are shown in Fig. 4. Spectrum b at 390 °C indicates the disappearance of the ν_{CH} bands at 3000 and 2920 cm^{-1} and the appearance of the

TABLE 1

Thermal decomposition data of malonic acid ($C_3H_4O_4$) and alkali metal malonate anhydrides in various atmospheres: n, the number of decomposition stages; T_i, initial decomposition temperature; T_m, DTA peak temperature; ΔW, weight-loss value at each decomposition step; * and **, DTA peaks corresponding to melting points of malonic acid (**) and alkali metal carbonates (*)

Malonate	Atmosphere	n	Decomposition				
			T_i (°C)	T_m (°C)	ΔW Obs. (%)	ΔW Calc. (%)	Product
$C_3H_4O_4$	N_2	1	127	97			
				136 **			
				175	97.6		
	Air	1	126	96			
				135 **			
				175	99.8		
$Li_2C_3H_2O_4$	N_2	4	335	357	22.6	25.3	$-\frac{2}{3}CO_2$
			365	–	30.3	31.1	$Li_2CO_3+\frac{1}{2}C$
			612	721 *	53.1	52.7	$Li_2CO_3+Li_2O+\frac{1}{4}C$
			830	–	–	–	–
	CO_2	3	350	380	28.7	25.3	$-\frac{2}{3}CO_2$
			670	740 *	34.0	33.7	$Li_2CO_3+\frac{1}{4}C$
			870	–	–	–	–
	O_2	2	329	361	33.6	33.7	$Li_2CO_3+\frac{1}{4}C$
			720	735 *	–	–	–
	Air	3	348	390	24.3	25.3	$-\frac{2}{3}CO_2$
			369	–	32.4	33.7	$Li_2CO_3+\frac{1}{4}C$
			720	737 *	44.0	–	–
$Na_2C_3H_2O_4$	N_2	3	305	–	16.4	17.7	$-\frac{2}{3}CO_2$
			311	313	23.3	25.3	Na_2CO_3
			768	854 *			
	CO_2	3	310	314	16.7	17.7	$-\frac{2}{3}CO_2$
			675	679	25.1	25.3	Na_2CO_3
			–	869 *			
	O_2	–	290	307			
			Effervescence				
	Air	–	298	312			
			Effervescence				
$K_2C_3H_2O_4$	N_2	3	338	360	7.0	7.4	$-\frac{1}{3}CO_2$
			406	483	20.1	21.2	K_2CO_3
			784	902 *			
	Air	–	295	330			
			Effervescence				
$Rb_2C_3H_2O_4$	N_2	3	373	378	11.3	11.5	Rb_2CO_3
			785	–	19.4	17.6	$Rb_2CO_3+Rb_2O$
			863	831 *			
	Air	–	350	–	10.3	11.5	Rb_2CO_3
			–	426			

TABLE 1 (continued)

Malonate	Atmosphere	n	Decomposition				
			T_i (°C)	T_m (°C)	ΔW Obs. (%)	ΔW Calc. (%)	Product
$Cs_2C_3H_2O_4$	N_2	3	388	420	6.8	8.8	Cs_2CO_3
			789	817	17.4	18.1	Cs_2O
			925	934			
	Air	–	352	392	7.6	8.8	Cs_2CO_3
			–	452			

carbonate bands at around 1080 and 845 cm^{-1} at 390 °C. On further heating, the merging of the bands in spectrum c of the 480 °C sample are attributed to the amorphous nature of the solid products resulting in a broad band. The bands at 1268, 1174, 972, 946, 821 and 663 cm^{-1} are due to CH_2-wag, $\nu_{as}CC$, ν_sCC, CH_2-rock, OCO-wag and $\delta_{as}CCO$, which disap-

TABLE 2

Melting points (°C) of alkali metal carbonates

Carbonate	Atmosphere [a]	T_m (°C) [b] This work	Melting points from literature references
Li_2CO_3	u		720[8] [c], 714[8] [d], 726[9], 735[10], 723[11]
	N_2	721	
	CO_2	740	
	O_2	735	
	Air	737	
Na_2CO_3	u		850[12,13], 856 ± 2[14], 851[11]
	N_2	854	
	CO_2	868	
K_2CO_3	u		901 ± [15], 898 ± 2[14], 901[13], 891[8,11]
	N_2	902	
Rb_2CO_3	u		873 ± 1[8] [c], 864 ± 1[8] [d], 870[16], 840[13], 837[11]
	N_2	831	
Cs_2CO_3	u		792 ± 1[8], 800[17]
	N_2	803	

[a] u, Unknown.

[b] T_m, DTA peak positions on melting.

[c] In an atmosphere of CO_2.

[d] Absence of CO_2 atmosphere.

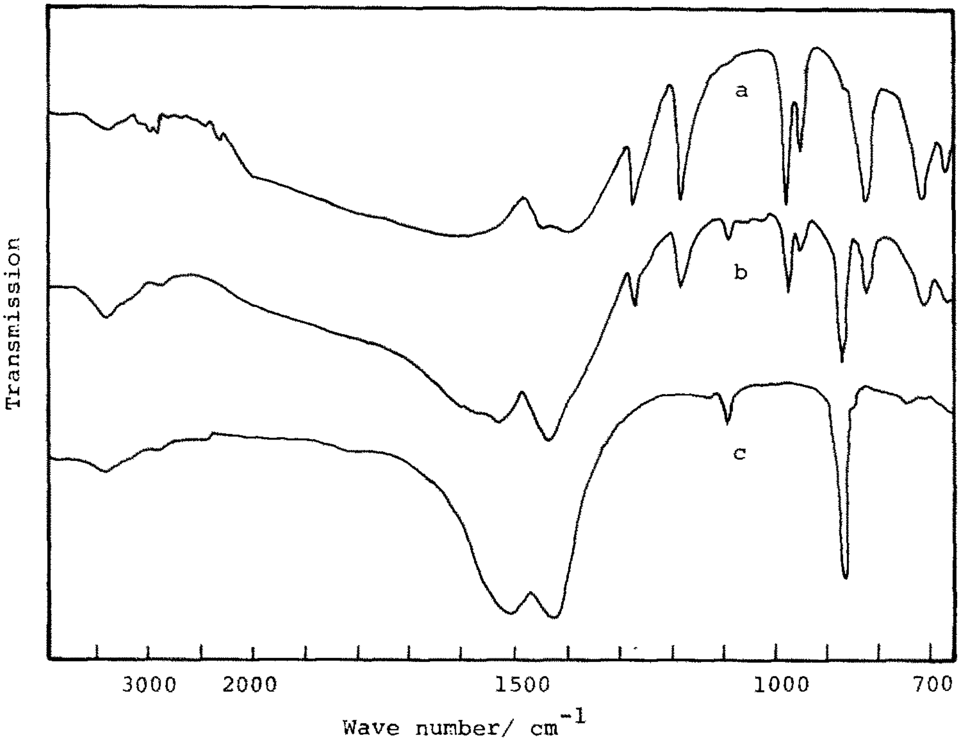

Fig. 4. IR spectra of (a) $Li_2C_3H_2O_4$ and its products at (b) 390 and (c) 480 °C in a flowing nitrogen atmosphere.

peared on heating at 480 °C. Thus spectrum c indicates the absence of malonate ion. Essentially similar data were obtained with the other alkali metal malonates.

TABLE 3

Kinetic parameters for the thermal decomposition of malonic acid ($C_3H_4O_4$) and alkali metal malonate anhydrides ($M_2C_3H_2O_4$) in a flowing nitrogen atmosphere

Compound	Decomposition		
	Stage	E_a (kJ mol^{-1})	A (s^{-1})
$C_3H_4O_4$		170.3	1.2×10^{15}
$Li_2C_3H_2O_4$	1	290.8	4.1×10^{23}
	2	327.6	2.9×10^{24}
$K_2C_3H_2O_4$	1	242.2	2.4×10^{17}
	2	312.9	9.7×10^{23}
$Rb_2C_3H_2O_4$	1	212.5	7.8×10^{16}
	2	256.1	2.9×10^{18}
$Cs_2C_3H_2O_4$	1	177.0	4.7×10^{15}
	2	212.1	8.0×10^{16}

Kinetics

The activation energy and the frequency factor for the decomposition of malonic acid and alkali metal malonate anhydrides in a flowing atmosphere calculated by the Coats–Redfern method [18,19] are shown in Table 3. The reaction order seems to be 2/3 for all the compounds. The decomposition of malonic acid takes place in one step, and the decomposition temperature and activation energy are lower than those of the malonates (Tables 1 and 3). The activation energy values for the second decomposition step of the malonates show higher values than for the first step.

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