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The thermal behaviour of dicarboxylic acids in various atmospheres

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Abstract

The thermal decomposition of anhydrous dicarboxylic acids was studied systematically in atmospheres of Ar, CO_2 and air by means of thermogravimetry (TG) and differential thermal analysis (DTA). For all the acids, it was shown that CO_2 has an inhibiting effect on the decomposition, whereas air has an accelerating effect, with respect to the behaviour in Ar. Except for oxalic acid, plots of the initial decomposition temperatures T_i and the DTA peak temperatures T_m versus the number of CH_2 groups in the acids have a saw-tooth or periodic pattern. It is assumed that their properties depend on the zig-zag structures of the dicarboxylic acids.

INTRODUCTION

The thermal reactions of organic and inorganic compounds in the solid state depend on their interatomic relations and in the characteristic cohesive forces acting between their crystals. Organic compounds are characterized by molecular lattices in which the molecules are arranged in some close-packed form in the crystals. It is known that the thermal breakdown of crystalline organic compounds is both a physical and chemical process.

The characteristic chemical behaviour of carboxylic acids is determined by their function groups, e.g. the carbonyl or hydroxyl group. Certain chemical reactions of dicarboxylic acids lead to unusual results as compared with those of monocarboxylic acids because there are two carboxyl groups in each molecule. Furthermore, the thermal behaviour of dicarboxylic acids, such as malonic acid and sebacic acid, may be expected to differ from that of monocarboxylic acids such as formic acid and acetic acid, because of

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the separation of the two carboxylic acid groups by a CH_2 group, which reduces the spatial restriction in bonding. Maleic and fumaric acids are known as geometrical isomers, i.e. the cis and trans isomers. In addition, the acids have a double bond between the carbon atoms. In the cis isomer, the carboxylic groups are sufficiently close to cause crowding; in the trans isomer, however, the carboxyl groups are well separated. Therefore, the cis isomer is expected to be less stable than the trans isomer, and the geometric isomers should have different physical properties. Indeed, the differences in the structures of maleic and fumaric acids are reflected in their thermal behaviours.

The available literature information on the thermal decomposition of dicarboxylic acids is rather scanty [1], and is mostly of a preliminary nature. Thermogravimetric analysis has become widely applied in the rapid assessment of the thermal stability of various substances. In the present research, the thermal behaviour of dicarboxylic acids was studied systematically using TG, DTA (differential thermal analysis) and gas chromatography.

EXPERIMENTAL

Materials and measurements

The recrystallization of dicarboxylic acids, the apparatus and the procedures used were as described in ref. 2. The TG–DTA curves were recorded simultaneously at a heating rate of 10°C min^{-1} in air, Ar, or CO_2 flowing at 200 ml min^{-1}. In each measurement, about 30 mg of powder sample was placed in a Pt pan (7 mm diam., 70 μl volume). The evolved gases were analysed by a conductometric detector at a heating rate of 10°C min^{-1} in a helium atmosphere (60 ml min^{-1}), using a Shimazu GC-3BT gas chromatograph and a Shimazu PYR-2A pyrolyser.

A column (2 m long) packed with 60–80 mesh active carbon was used for the analysis of non-polar gases. The evolved gases were separated in the column which was maintained at 100°C.

RESULTS AND DISCUSSION

The TG and DTA curves of dicarboxylic acids heated from room temperature to 350°C in flowing air are shown in Fig. 1. The solid lines denote the TG curves and the broken lines represent the DTA curves. The temperature range of the successive decompositions, the peak temperatures of the DTA curves T_m, and the weight losses ΔW are listed in Table 1. In all

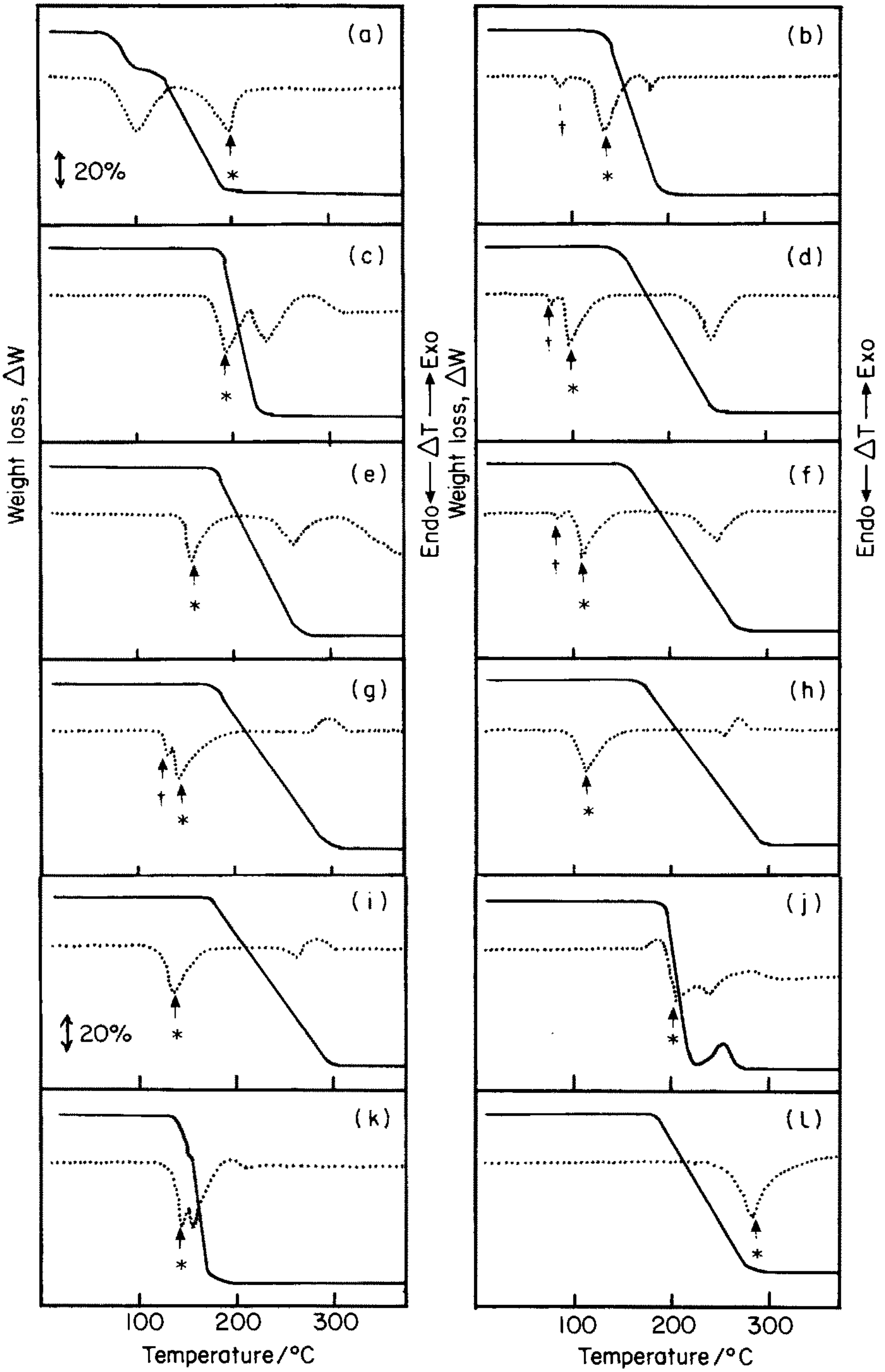

Fig. 1. TG–DTA curves of dicarboxylic acids in flowing air: (a) oxalic acid; (b) malonic acid; (c) succinic acid; (d) glutaric acid; (e) adipic acid; (f) pimelic acid; (g) suberic acid; (h) azelaic acid; (i) sebacic acid; (j) *o*-phthalic acid; (k) maleic acid; (l) fumaric acid.

TABLE 1

Thermal decomposition data of dicarboxylic acids in various atmospheres

Dicarboxylic acid	Purity/%	Temp. range/°C			T_m/°C [a]			ΔW/% [b]		
		Ar	CO_2	Air	Ar	CO_2	Air	Ar	CO_2	Air
Oxalic acid (*n* = 0)	98.7	53–106	57–107	55–107						
		125–203	124–219	123–197	192	193	190	98.7	98.8	98.8
Malonic acid (*n* = 1)	99.5	134–198	135–198	133–195	138	137	136	98.3	98.2	98.6
Succinic acid (*n* = 2)	99.2	188–251	189–253	186–250	188	190	187	98.7	98.3	98.9
Glutaric acid (*n* = 3)	98.6	144–249	146–258	142–255	98	99	98	98.4	98.2	98.5
Adipic acid (*n* = 4)	99.0	181–285	182–287	179–276	153	154	153	98.8	98.6	98.8
Pimelic acid (*n* = 5)	98.5	151–287	153–290	152–285	105	106	105	98.3	97.9	98.6
Suberic acid (*n* = 6)	98.3	174–298	173–302	174–296	142	143	143	98.1	98.0	98.3
Azelaic acid (*n* = 7)	98.1	162–300	163–301	162–300	109	110	108	97.9	97.7	98.0
Sebacic acid (*n* = 8)	98.0	171–306	170–304	169–300	134	135	133	98.2	98.0	98.4
Maleic acid	99.2	146–179	148–180	145–177	143	145	144	98.2	98.1	98.3
Furamic acid	99.5	175–275	182–286	187–284	283	285	282	98.5	98.2	98.6
Phthalic acid	98.9	192–243	193–245	190–241	212	213	210	98.5	98.3	98.7

[a] DTA peak temperatures. [b] Weight loss values.

the acids examined, the major features of the TG–DTA curves in air, Ar and CO_2 atmospheres were found to be similar to each other. The TG curves of the acids in the various atmospheres show evidence of only one decomposition stage, except for oxalic acid which shows two stages, with almost total elimination of the samples. In Ar, CO_2 and air, a gray residue was produced, due to dispersed carbon. Decomposition is CO_2 takes place at a somewhat higher temperature and proceeds more sluggishly than in Ar and air atmospheres.

The DTA curves of malonic, glutaric, pimelic and suberic acids show a small endothermic peak at 91, 79, 84 and 133°C, respectively, which represents the transition due to the absorption of heat energy by the molecules at these temperatures. A medium-sized exothermic peak at the end of decomposition process is a characteristic feature in suberic, azelaic and sebacic acids. Except for malonic, fumaric and phthalic acids which show a broad endotherm, the DTA curves of dicarboxylic acids indicate sharp, medium endothermic peaks due to melting; these are indicated with arrows and asterisks on the DTA curves in Fig. 1. Thus this series of dicarboxylic acids begins to melt before decomposition. The melting and the decomposition processes occur within a 10°C range in malonic and

TABLE 2

Melting points (°C) of dicarboxylic acids in flowing air atmosphere

Dicarboxylic acid	Melting points from literature references					
	[3]	[4]	[5]	[6]	[7]	This work
Oxalic acid	189.5	189.5				
Malonic acid	135.6	135.6	135.0–137.0	135[a]	135.6	136.0
Succinic acid	184–185	188	187–190	187–190	188	187.7
Glutaric acid	97–98	99	95.0–96.0	97.5	99	98.5
Adipic acid	153	153	152.0–154.0	152	153	153.4
Pimelic acid	104–105	105–106	103–105	105.8	106	105.0
Suberic acid	144			140–144	144	143.3
Azelaic acid	106.5		103–104	106.5	106.5	108.1
Sebacic acid	134.5		131–134	134.5	134.5	133.1
Maleic acid	138–139	139–140	134.0–136.0	138–139	139–140	144.0
Fumaric acid	286–287	300–302	299.0–300.0	287	300–302	282.6
Phthalic acid	234	210[a]	210[a]	206–208	191	210.2

[a] Decomposition.

succinic acids. The DTA melting peaks for the dicarboxylic acids T_m in the various atmospheres are shown in Table 2 together with the literature values. The melting points (m.p.) obtained from the DTA curves are in close agreement with the literature values.

Many recent investigations have studied the melting of various compounds; including: the calculation of the thermal properties of the m.p. and the crystal lattice energies of a series of inorganic and organic substances by bond group contribution methods [8]; a new relation between the melting points of organic solids and their reactivity $\xi = -k \log(\mathrm{m.p.}) + C$ where ξ is the thickness of the coloured boundary and C a constant [9]; a simple DTA technique for determining the pressure dependence of solid–liquid and solid–solid transition temperatures [10]; the interpretation of the stability of crystals using a model which includes atomic vibration and the thermal creation of vacancies [11]; and thermodynamic studies on the melting of aliphatic dicarboxylic acids [12]. Consequently, the melting process can be described as the change that takes place when a temperature is reached at which the thermal energy of the molecules in the crystalline lattice is great enough to overcome the intracrystalline forces that hold them in position.

The thermal stabilities which were evaluated from initial decomposition temperatures T_i and the DTA peak temperatures (melting points, T_m) on melting were compared among the dicarboxylic acids. As seen in Fig. 2, the T_i and T_m values of the acids $HOOC(CH_2)_nCOOH$ ($n = 0$, 1–8) with an even or odd number of n, show an alternating succession of values. Acids with even numbers of n have relatively high T_i and T_m values,

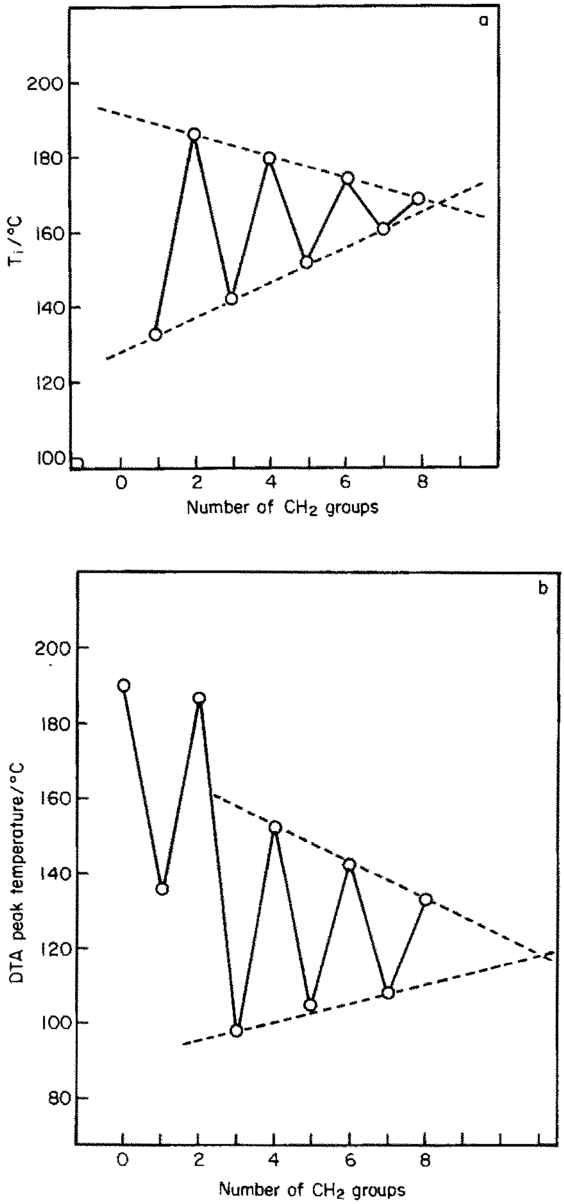

Fig. 2. a. Relationship between the initial decomposition temperatures T_i in flowing air and the number of CH_2 groups n in the dicarboxylic acids [$HOOC(CH_2)_nCOOH$]. b. Relationship between the DTA peak temperatures T_m in flowing air and the number of CH_2 groups in the dicarboxylic acids.

corresponding to more stable crystalline structures [13]. The upper line corresponds to T_i (oxalic acid does not fit) and T_m for even n, and the lower line corresponds to T_i and T_m for odd n acids. Thus, a saw-tooth pattern describes the properties of the acids. The deviation between the T_i and T_m

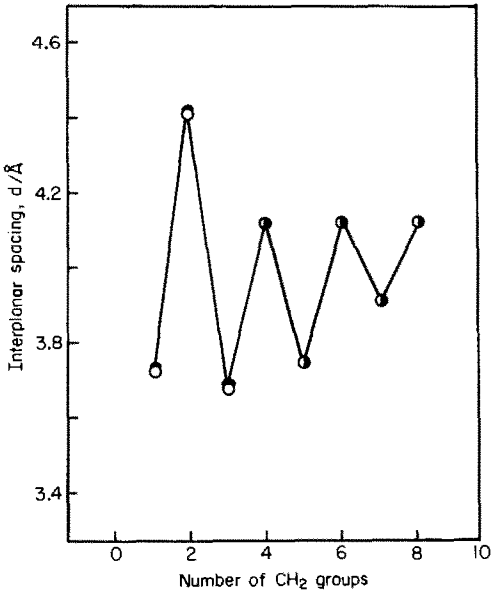

Fig. 3. Relationship between the strongest interplanar spacing and the number of CH_2 groups in the dicarboxylic acids.

values of the odd and even acids are assumed to derive from interactions of the terminal groups: intermolecular hydrogen bonding is more effective for even-membered acids than for the odd-membered acids.

The saw-tooth or periodic pattern was also observed for the relationship between the most intense XRD signal (Fig. 3) and the dipole moment [14, 15] (Fig. 4), and the number of CH_2 groups in the dicarboxylic acids. It can be assumed that these properties also depend on whether an acid contains an even or odd number of carbon atoms because of the zig-zag patterns observed for the dicarboxylic acids [16].

The effect of the symmetry of the cis and trans configuration on T_i and T_m is apparent in maleic and fumaric acids. In fumaric acid, there is less crowding and less van der Waals strain. The two larger substituents in the trans isomer are located further apart than in the cis isomer; therefore fumaric acid is more stable than maleic acid. It can be presumed that the cis isomer is less stable than the trans isomer. As expected, the T_i and T_m values of fumaric acid are higher than those of malonic acid.

The ratio of CO_2/CO evolved on thermal decomposition in He decreases with increasing number of CH_2 groups in the chain. Furthermore, this relation was observed to vary somewhat periodically with increasing number of CH_2 groups. Except for oxalic acid, the CO_2/CO ratio decreased linearly with the number of CH_2 groups (Fig. 5).

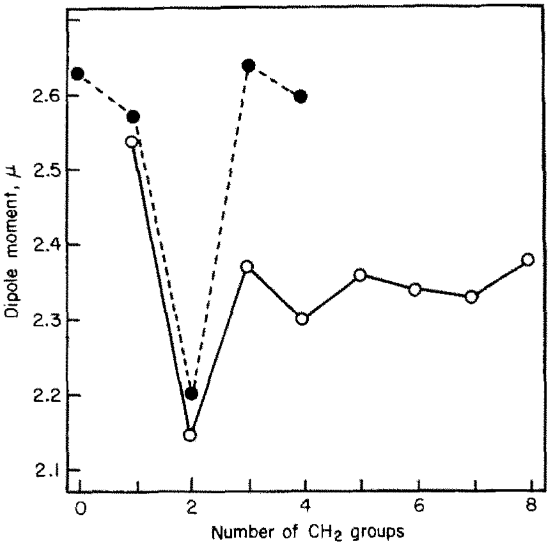

Fig. 4. Relationship between the dipole moment and the number of CH_2 groups in the dicarboxylic acid: ●, ref. 14; ○, ref. 15.

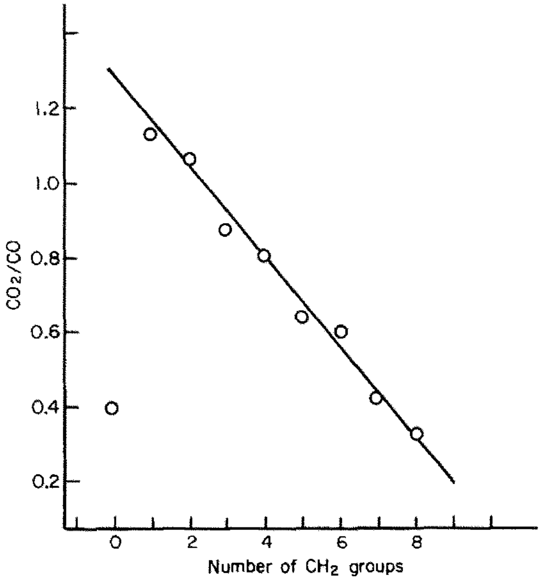

Fig. 5. Plot of the ratio of CO_2/CO evolved during decomposition of the dicarboxylic acids in helium.

From Figs. 2 and 3, it is suggested that the behaviour of oxalic and malonic acids reflects differences in crystal structures. Oxalic and malonic acids, belong to the orthorhombic and triclinic systems, whereas the dicarboxylic acids of the series from succinic acid to sebacic acid ($n = 2$–8), and maleic and fumaric acids, belong to the monoclinic system.

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