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Enthalpimetric measurements in solid–solid interactions: The reaction of dicarboxylic acids with amino acids. Part 1

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Abstract

The ability of dicarboxylic acids to interact with amino acids to form monomeric or polymeric products has been observed by means of DSC and TG techniques.

The solid–solid reactions have been carried out, the associated ΔH values evaluated, and the reaction mechanism elucidated. In the solid state phthalic acid interacts with amino acid to form the monomeric product *N*-phthalylaminoacid, by losing two water molecules. The product formed has been characterized from its IR and NMR spectra.

INTRODUCTION

Previously we have studied the possibility of obtaining thermodynamic and kinetic parameters of solid–solid interactions from thermoanalytical curves when reactant molecules were properly chosen [1–12]. The reaction was carried out directly in a thermoanalytical apparatus (DSC, TG) by introducing stoichiometric mixtures of reactants into the pans.

We note that,

(1) *N*-phthalylaminoacids have been prepared in the solid state by melting a mixture of α-amino acid with phthalic acid or anhydride;

(2) the mechanism of the reaction has been described as a mechanism occurring in two steps: (a) partial condensation with formation of the intermediate phthalamic acid; (b) ring closure and formation of *N*-phthalylaminoacid;

(3) this mechanism was proposed and supported by kinetic and DTA measurements [1], but no direct evidence was found for the actual formation of the intermediate product.

In this paper we extend our previous research in order to isolate the intermediate, if it exists, or correctly elucidate the mechanism of reaction.

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The synthesis attempted, using solid reactants, was

Phthalic acid + DL-α-Alanine = *N*-Phthalyl-DL-alanine

EXPERIMENTAL

DSC measurements

All measurements were performed using a Mettler 20 S DSC calorimeter, in aluminium covered pans, in a dynamic nitrogen atmosphere ($5\,\mathrm{l\,h^{-1}}$) and at heating rate of $4°\mathrm{C\,min^{-1}}$ or under isothermal conditions. The reference was an empty closed aluminium pan.

The reactions were performed by introducing finely powdered stoichiometric mixtures of the reactants into the pan, the total mass of the system being about 6–8 mg.

ΔH of the reaction was evaluated by using the ΔH_{melt} value of indium ($6.79\,\mathrm{cal\,g^{-1}}$) as standard.

This same system was also observed in a Koffler apparatus to observe melting or decomposition during the reaction.

TG measurements

All measurements were performed by a Mettler TA model 50 thermoanalyser, in a dynamic nitrogen atmosphere ($3.6\,\mathrm{l\,h^{-1}}$) by using open alumina crucibles and at heating rate of $4°\mathrm{C\,min^{-1}}$ or under isothermal conditions. The solid–solid interactions were carried out using a method similar to that for DSC measurements.

IR spectra

The IR spectra were obtained from KBr pellets, using a Perkin-Elmer 457 spectrophotometer ($4000–250\,\mathrm{cm^{-1}}$).

^1H NMR spectra

The NMR spectra were taken on a Bruker W.P. 80 instrument with $CDCl_3$ solutions at the probe temperature; chemical shifts (δ) are given in ppm from internal tetramethylsilane (TMS).

RESULTS AND DISCUSSION

Thermal behaviour of phthalic acid

DSC measurements

Two endothermic peaks were observed for this compound at a heating rate of $4°\mathrm{C\,min^{-1}}$, (Fig. 1(a)), the first one beginning at 193°C with T_{max} at 202°C and the second being verified in the range 219–258°C. Under isothermal conditions (T_{start}, 198°C; mass 6.682 mg) only one endothermic

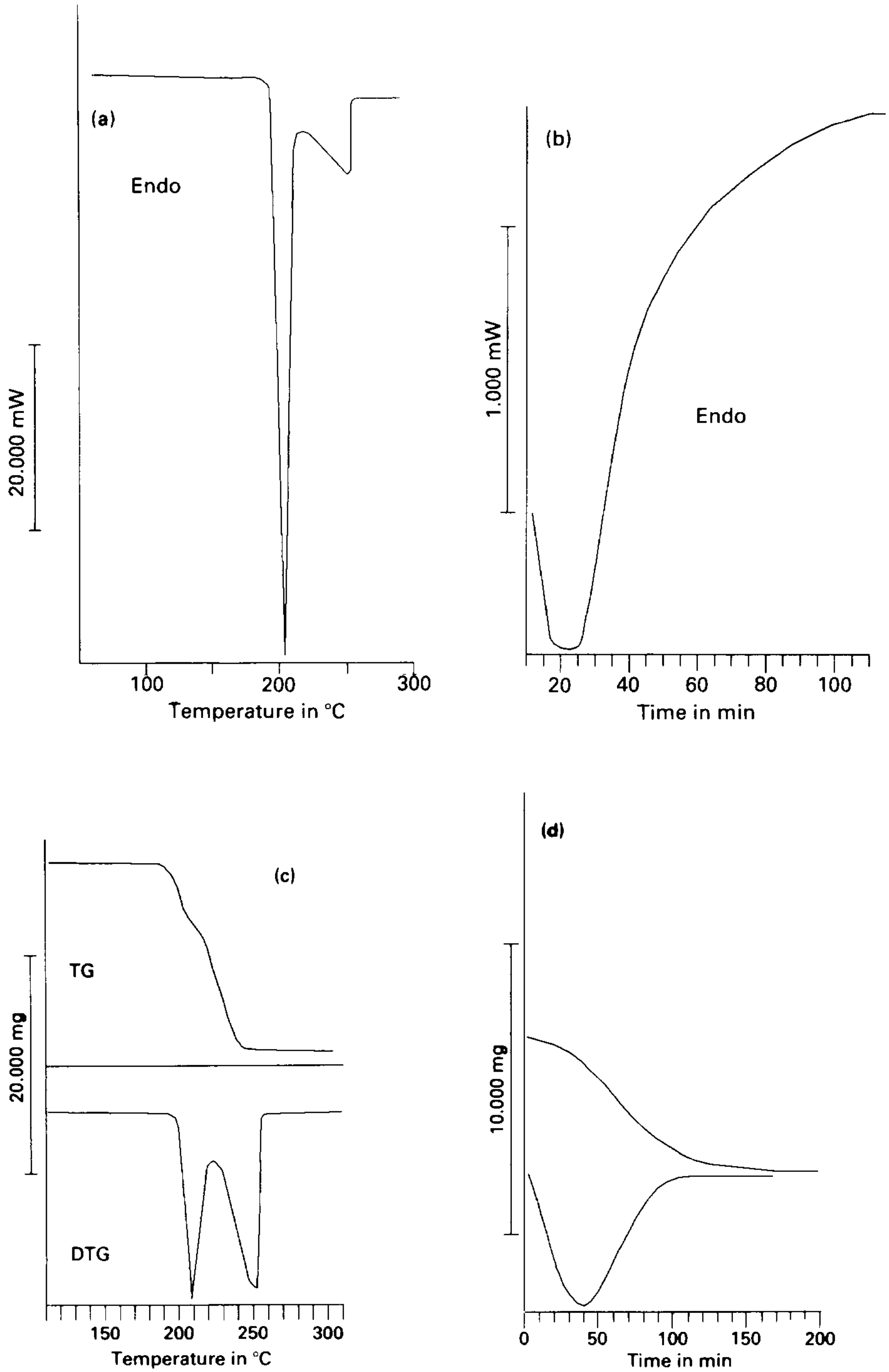

Fig. 1. Thermal behaviour of phthalic acid: (a) DSC curve obtained under dynamic conditions; (b) DSC curve obtained under isothermal conditions; (c) TG and DTG curves obtained under dynamic conditions; (d) TG curves obtained under isothermal conditions.

process was observed that is complete in 115 min (Fig. 1(b)). The enthalpic values associated with these processes are reported in Table 1.

TG measurements

Two consecutive steps were observe at a heating rate of 4°C min^{-1}. The first process began at 179.6°C and corresponds to a mass loss of 30%; the second process began at 218.0°C and corresponds to a mass loss of 70% (Fig. 1(c)).

Under isothermal conditions ($T_{\text{start}} = 180°\text{C}$) we observe a continuous mass loss in a single step corresponding to the release of the total amount of the initial mass (Fig. 1(c)).

In order to elucidate the thermal behaviour of phthalic acid we suppose that the process registered under non-isothermal conditions can be attributed to the following reactions: the first process is due to the decarboxylation of the phthalic acid to form benzoic acid and simultaneously to the melting of the product formed (first DSC peak; first TG step); the second process can be attributed to the liquid–vapour transition of the benzoic acid (second DSC peak; second TG step).

The single step, recorded under isothermal conditions, can be interpreted as the sum of all the indicated processes.

To verify the supposed thermal behaviour of the phthalic acid we have also performed DSC and TG analyses of the benzoic acid, as described below.

Thermal behaviour of benzoic acid

DSC measurements

At a heating rate of 4°C, the melting point at 123°C (first endothermic process) and the subsequent liquid–vapor transition in the temperature range 133–212°C (second broad endothermic peak) were observed (Fig. 2(a)). Enthalpic and kinetic data are reported in Table 1.

TG measurements

A continuous mass loss in a single step, was observed at a heating rate of 4°C min^{-1} in the temperature range 106–218°C, (Fig. 2(b)).

Thermal behaviour of DL-*α-alanine*

DSC measurements

At heating rate of 4°C min^{-1} a continuous endothermic effect was observed in the temperature range 197–309°C with $T_{\text{max}} = 289°\text{C}$ (Fig. 3(a)). The associated value of ΔH was 87.22 kJ mol^{-1}.

TABLE 1

Thermoanalytical data

Compound	First process			Reaction	Second process			Transition
	T_{start}/°C	T_{peak}/°C	ΔH/ kJ mol^{-1}		T_{start}/°C	T_{peak}/°C	ΔH/ kJ mol^{-1}	
Phthalic acid								
DSC dyn	193	02	100	Decarb., melting	219	253	55.8	l–v
TG dyn	179	213		Decarb.	218	250		l–v
Benzoic acid								
DSC dyn	119	123	16.7	Melting	133	206	55.1	l–v
TG dyn					106	212		l–v
DL-Alanine								
DSC dyn	197	289	87.22	Sublim.				
TG dyn	221	294		Sublim.				
N-Phthalyl-alanine								
DSC dyn	115	161	24.92	Melting	191	313	98.38	Decomp.
TG dyn					211			Decomp.
1:1 mixture								
DSC dyn	144	158	136	Interac., dehydr., melting	241	342	94.3	Decomp.
TG dyn	138	153		Dehydr.	195	329		Decomp.
	153	195						

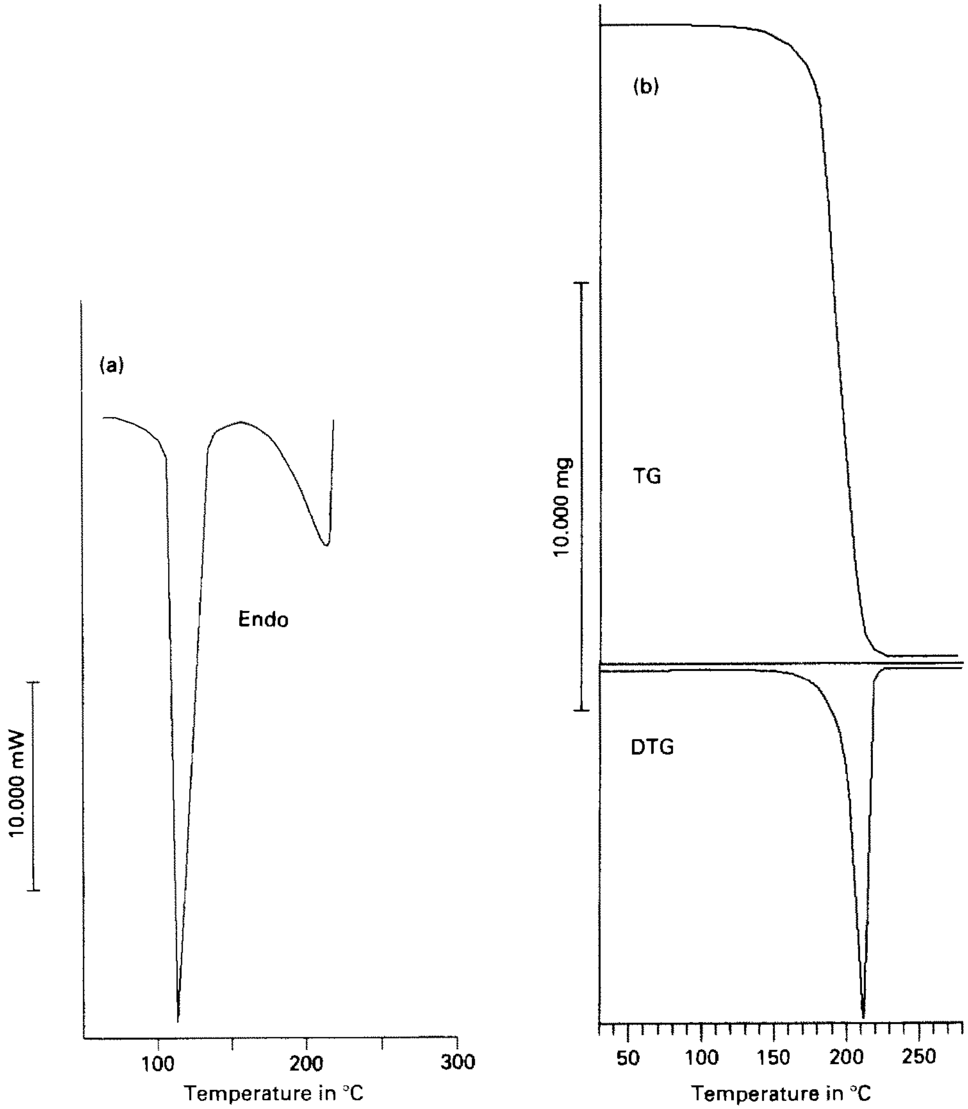

Fig. 2. Thermal behaviour of benzoic acid: (a) DSC curve obtained under dynamic conditions; (b) TG and DTG curves obtained under dynamic conditions.

TG measurements

At a heating rate of 4°C $\min^{-1}$ and in the temperature range 221–373°C we observed a continuous mass loss in a single step due to the sublimation of the amino acid (Fig. 3(b)).

Thermal behaviour of N*-phthaly-*DL*-alanine*

This product, employed as test material, was prepared as described in refs. 1 and 13. The first thermal effect was melting observed by DSC at $T_{\max}$ 161°C, followed by decomposition observed by DSC in the temperature

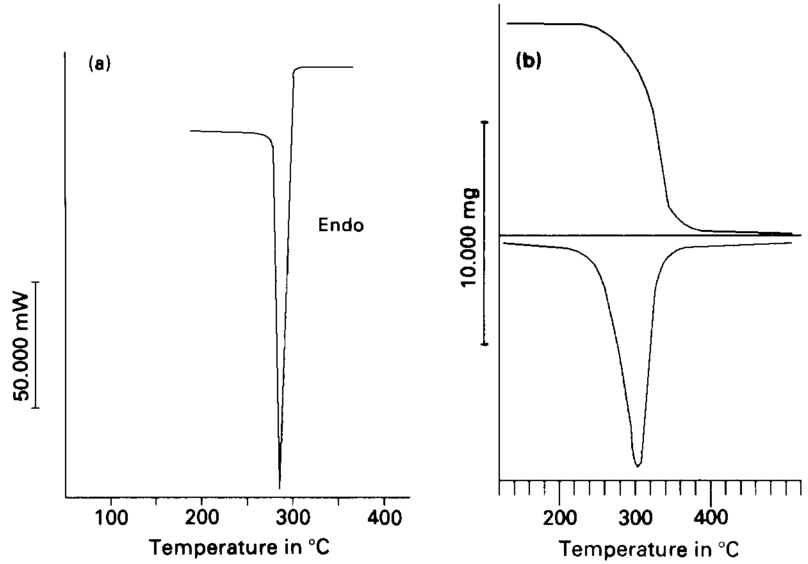

Fig. 3. (a) Thermal behaviour of DL-α-alanine: DSC curve obtained under dynamic conditions. (b) Thermal behaviour of benzoic acid: TG and DTG curves obtained under dynamic conditions.

range 191–335°C at T_{max} 313°C (Fig. 4(a)) and by TG in the temperature range 211–326°C (Fig. 4(b)). In Table 1 we report the enthalpic values for the processes described.

Thermal behaviour of 1:1 *mixture*

DSC measurements

The shape of the DSC curve indicates that the amino acid–phthalic acid mixture (12.36 mg) reacts between 144 and 187°C, which is a lower temperature than that required to convert phthalic acid into benzoic acid and to sublime the amino acid, and shows a first endothermic peak with T_{max} of 158°C (Fig. 5(a)). The associated ΔH value was 136.11 kJ/mol^{-1}.

A second broad endothermic effect was registered in the 241–335°C temperature range. The associated ΔH value was 94.3 kJ mol^{-1}.

TG Measurements

Similarly to DSC, the TG and DTG curves, recorded at a heating rate of 4°C min^{-1}, indicate that the interaction occurs at a lower temperature than that required by each single reactant. However, in contrast to DSC behaviour, we can observe three consecutive processes (Fig. 5(b)). The first occurs in the temperature range 138–153°C with a mass loss of about 1.7%, and the second one occurs in the temperature range 153–195°C with a mass loss of about 13.2%. The total mass loss corresponds to the release of a molecular mass of 38, i.e. to about two water molecules. A third thermal effect was recorded in the temperature range 195–352°C.

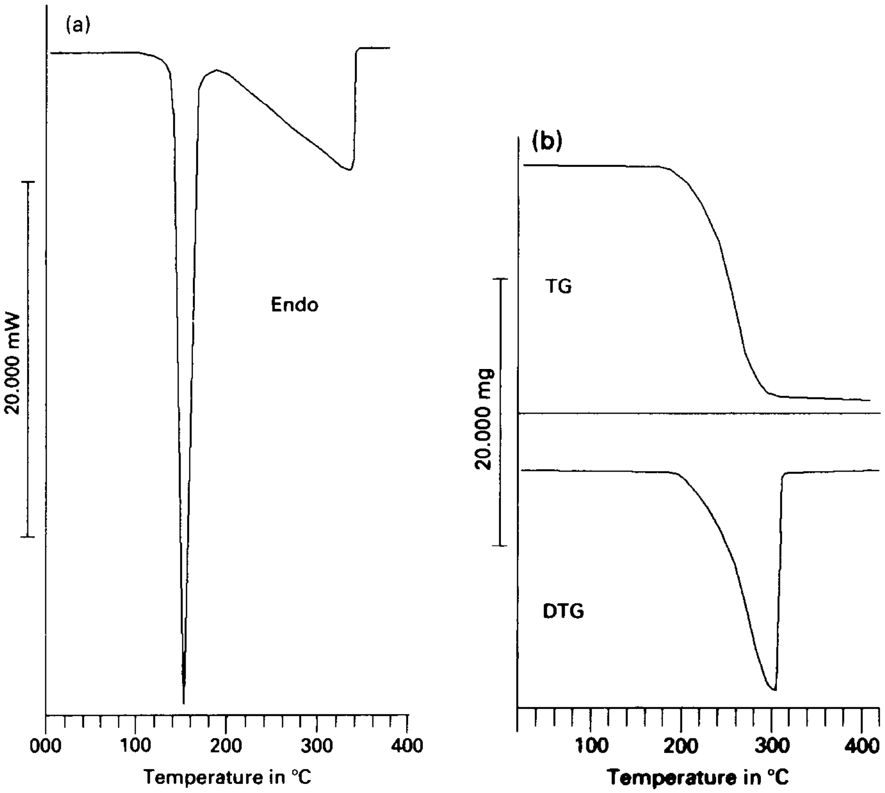

Fig. 4. Thermal behaviour of *N*-phthalyl-DL-alanine: (a) DSC curve obtained under dynamic conditions; (b) TG and DTG curves obtained under dynamic conditions.

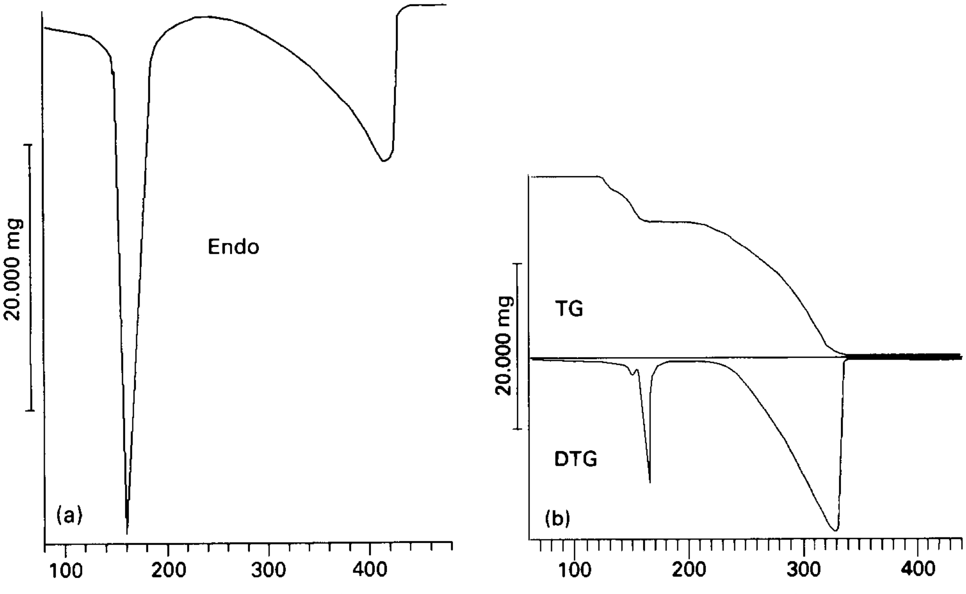

Fig. 5. Thermal behaviour of 1:1 mixture: (a) DSC curve obtained under dynamic conditions; (b) TG and DTG curves obtained under dynamic conditions; (c) TG and DTG curves obtained under isothermal conditions.

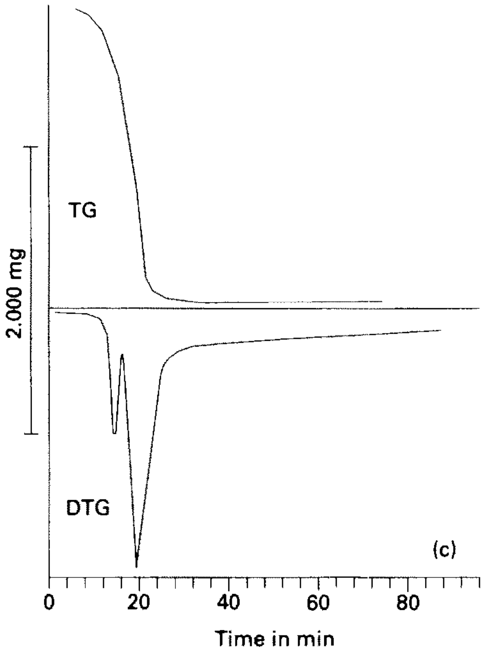

Fig. 5 (continued)

It is worth noting that after the end of the second thermal process, when the obtained product is cooled and then heated again, the thermoanalytical curves (TG, DTG, DSC) show the thermal behaviour of *N*-phthalyl-DL-α-alanine described above.

The TG and DTG curves recorded under isothermal conditions at 140°C exhibit, analogously, two thermal effects, but the total mass loss corresponds to the exact release of two water molecules (Fig. 5(c)).

In Table 1 we report the values associated with the thermal processes of phthalic and benzoic acids, DL-α-alanine, *N*-phthalyl-DL-α-alanine, and the 1:1 mixture.

IR and NMR spectra

IR and NMR spectra obtained on cooling the product obtained at 25°C from the 1:1 mixture after dehydration were compared with the IR and NMR spectra of *N*-phthalyl-DL-alanine prepared as test material; no differences were observed.

All DSC, TG and DTG measurements performed and the data reported in Table 1, suggest the following may be considered.

(i) DL-α-Alanine is thermally stable up to 289°C and then sublimes.

(ii) Phthalic acid decomposes, on heating, as shown below.

First thermal effect

$$C_6H_4(COOH)_2(s) = CO_2(g) + C_6H_5(COOH)(s) \qquad 83.3\ \mathrm{kJ\ mol^{-1}}$$

and simultaneously

$C_6H_5(COOH)(s) = C_6H_5(COOH)(l)$ 16.7 kJ mol^{-1}

Second thermal effect

$C_6H_5(COOH)(l) = C_6H_5(COOH)(v)$ 55.8 kJ mol^{-1}

(iii) Benzoic acid is thermally stable up to 123°C and then melts and vaporizes

$C_6H_5(COOH)(s) = C_6H_5(COOH)(l)$ s–l 16.7 kJ mol^{-1}

$C_6H_5(COOH)(l) = C_6H_5(COOH)(v)$ l–v 55.1 kJ mol^{-1}

(iv) *N*-Phthalyl-DL-alanine melts at 161°C and then vaporizes.

(v) 1:1 mixtures interact in the solid state to form *N*-phthalyl-DL-alanine as described below. On considering the DSC curve the first thermal process is

$C_6H_4(COOH)_2(s)$ + DL-α-alanine(s) = *N*-Phthalyl-DL-alanine(s)
+ $2H_2O(v)$ 111.2 kJ mol^{-1}

and, simultaneously

N-Phthalyl-DL-alanine(s) = *N*-Phthalyl-DL-alanine(l) 24.91 kJ mol^{-1}

and the second thermal process is

N-Phthalyl-DL-alanine(l) = *N*-Phthalyl-DL-alanine(v) 94.3 kJ mol^{-1}

On considering the TG curve the first step is due to the formation of a small quantity of *N*-phthalyl-DL-alanine. A second step is indicated because the newly formed product begins to melt and for this absorbs the relative quantity of heat which slows formation of the remaining product. The third step is due to the vaporization of the *N*-phthalyl-DL-alanine formed.

As reported in Table 1, the ΔH value associated with the first DSC process for phthalic acid is 100 kJ mol^{-1}. The ΔH value for the second process can assume different values, according to whether the thermal effect is referred to the relative molecular mass of phthalic acid ($\Delta H = 76.01$ kJ mol^{-1}) or that of the supposedly formed benzoic acid ($\Delta H = 55.8$ kJ mol). Effectively this last ΔH value is quite similar to the ΔH value obtained for the liquid–vapor transition and this is the suggested decomposition mechanism of phthalic acid. Moreover, considering that ΔH_{melt} of benzoic acid is 16.7 kJ mol^{-1}, it is possible to calculate the contribution of the decarboxylation process to the first thermal effect for phthalic acid

$$\Delta H_{\text{decarboxylation}} = \Delta H_1 - \Delta H_{\text{melting}} = 100.0 - 16.7 = 83.3 \text{ kJ mol}^{-1}$$

For the 1:1 mixture the ΔH data reported in Table 1 also allow the determination of the different steps of the reactions as described above. In particular, the curves evaluated for the second thermal effect of the product, obtained from the solid–solid interaction, are the same shape (and have the same enthalpic value) as the curves for the thermal effects of *N*-phthalyl-DL-alanine prepared as test material, thus confirming the interaction. It is thus possible to interpret the first thermal effect as being due to the sum of dehydration, consequent upon the interaction and melting of the *N*-phthalyl-DL-alanine formed.

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