

# Thermodynamic Study on the Sublimation of 2-Phenylacetic, 4-Phenylbutyric, and 5-Phenylvaleric Acid

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The Knudsen mass-loss effusion technique was used to measure the vapor pressures as a function of temperatures of the following crystalline carboxylic acids: 2-phenylacetic acid, between 305.17 K and 321.16 K; 2-phenylbutyric acid, between 309.16 K and 323.16 K; and 5-phenylvaleric acid, between 315.15 K and 327.18 K. From the temperature dependence of the vapor pressure of the crystalline samples, the standard molar enthalpies of sublimation at the mean temperature of the experimental range were derived by using the Clausius–Clapeyron equation. From these results the standard molar enthalpies, entropies, and Gibbs functions of sublimation at  $T = 298.15$  K were calculated. A correlation between the enthalpies of sublimation and the temperature of sublimation at a reference pressure ( $p = 10^5$  Pa) for some carboxylic acids and other organic compounds is presented.

## Introduction

From thermodynamic studies of the sublimation of several organic compounds, correlations between enthalpies of sublimation and the temperature of sublimation at a reference pressure ( $p = 0.5$  Pa) were derived before.<sup>1–3</sup> The sublimation results of several heterocyclic organic compounds yield eq 1, where  $\{T(p = 0.5 \text{ Pa})\}$  is the

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}\{T(p = 0.5 \text{ Pa})\} / \text{kJ} \cdot \text{mol}^{-1} = (0.330 \pm 0.009)\{T(p = 0.5 \text{ Pa}) / \text{K}\} - (10.5 \pm 3.2) \quad (1)$$

temperature at which the vapor pressure of the crystals of those compounds is  $p = 0.5$  Pa, which can be used for estimations of vapor pressure–temperature data from calorimetric or estimated values of enthalpies of sublimation for a large number of organic compounds.<sup>3</sup>

However, for linear molecules such as the dicarboxylic acids  $\text{COOH}(\text{CH}_2)_n\text{COOH}$ , strong deviations from those correlations were observed for the respective sublimation results.<sup>2</sup>

To investigate if the sublimation results of other long-chain carboxylic acids also deviate in a similar way from eq 1, we decided to study the sublimation of some members of the series  $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{COOH}$ . Using the Knudsen effusion method, vapor pressures of crystalline samples of 2-phenylacetic acid, 4-phenylbutyric acid, and 5-phenylvaleric acid were measured over a temperature range to derive their standard molar enthalpies and entropies of sublimation. The sublimation of the second member of this series, 3-phenylpropionic acid, had been reported recently.<sup>4</sup>

## Experimental Section

The compounds studied were obtained from Aldrich Chemical Co. with the assessed minimum purity of 0.99 (mass fraction). Prior to the measurements the compounds were purified by repeated sublimation under reduced pressure, and their final purity was assessed by DSC

**Table 1. Temperatures of Fusion,  $T_{\text{fus}}$ /K, Enthalpies of Fusion,  $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\circ}(T_{\text{fus}})$ , and Mass Fraction of Impurities,  $w$ , of the Compounds Studied**

	$T_{\text{fus}}$	$\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\circ}(T_{\text{fus}})$	$10^3 w$
	K	$\text{kJ} \cdot \text{mol}^{-1}$	
2-phenylacetic acid	$350.75 \pm 0.13$	$16.51 \pm 0.23$	5.8
4-phenylbutyric acid	$324.19 \pm 0.12$	$19.54 \pm 0.22$	2.0
5-phenylvaleric acid	$331.98 \pm 0.10$	$23.40 \pm 0.19$	3.0

analysis using a fractional fusion technique.<sup>5</sup> Enthalpies and temperatures of fusion were also derived from the DSC experiments and are presented in Table 1, together with the calculated mass fraction of the impurities of the samples. The uncertainties assigned to the results are twice the standard deviation of the mean of at least five independent runs. DSC experiments were performed on a Setaram DSC 141 calorimeter using a heating rate of  $3.33 \times 10^{-2} \text{ K} \cdot \text{s}^{-1}$ . The temperature scale of the calorimeter was calibrated by measuring the melting temperature of three high-purity reference materials (naphthalene, benzoic acid, and indium),<sup>6</sup> and its power scale was calibrated with high-purity indium (mass fraction  $> 0.99999$ ). The recorded thermograms did not show any phase transitions between 298 K and the melting temperature of the samples contained in sealed aluminum crucibles.

The vapor pressures of the purified crystalline samples were measured at several temperatures using a mass-loss Knudsen effusion apparatus enabling the simultaneous operation of three Knudsen cells, with three different effusion orifices. A detailed description of the apparatus, procedure, and technique and the results obtained with two test substances (benzoic acid and ferrocene) have been reported.<sup>7</sup> The consistency of the measured vapor pressure was checked by comparing the results obtained for benzoic acid and for copper(II)  $\beta$ -diketonates using this apparatus with the results obtained for these compounds using different experimental apparatuses and different techniques.<sup>8</sup> Several other tests have been performed with other reference substances such as benzophenone, dibenzothio-phenone, and naphthalene.

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**Table 2. Knudsen Effusion Results for the Compounds Studied<sup>a</sup>**

2-Phenylacetic Acid						
T/K	p/Pa			100 Δ ln(p/Pa)		
	hole 4	hole 5	hole 6	hole 4	hole 5	hole 6
305.17	0.171	0.172	0.168	0.9	0.3	0.5
307.17	0.215	0.220	0.215	-1.6	-0.4	-0.1
309.16	0.279	0.281	0.275	-0.4	-0.8	-0.4
311.17	0.363	0.364	0.353	1.0	0.2	-0.2
313.18	0.459	0.465	0.452	0.0	0.3	0.1
315.16	0.578	0.582	0.566	-0.8	-1.1	-1.2
317.15	0.741	0.749	0.737	0.4	0.5	1.6
319.18	0.930	0.930	0.913	-0.8	-1.7	-0.8
321.16	1.18	1.20	1.16	0.1	0.9	0.3
4-Phenylbutyric Acid						
T/K	p/Pa			100 Δ ln(p/Pa)		
	hole 1	hole 2	hole 3	hole 1	hole 2	hole 3
309.16	0.0747	0.0724	0.0705	1.1	-0.4	-2.9
311.16	0.0983	0.0970	0.0992	0.6	0.8	2.9
313.16	0.127	0.127	0.128	-1.5		0.5
315.15	0.166	0.166	0.168	-1.9	-0.3	0.2
317.16	0.222	0.218	0.221	0.1	-0.1	0.3
319.16	0.291	0.288	0.289	0.5	1.1	0.2
321.16	0.378	0.372	0.378	0.4	0.4	0.5
323.16	0.489	0.478	0.483	0.2	-0.5	-1.2
5-Phenylvaleric Acid						
T/K	p/Pa			100 Δ ln(p/Pa)		
	hole 1	hole 2	hole 3	hole 1	hole 2	hole 3
315.15	0.0443	0.0425	0.0455	0.4	-1.6	0.6
316.18	0.0499	0.0499	0.0513		-0.4	-2.0
317.15	0.0609	0.0589	0.0603	3.6	2.3	0.6
319.16	0.0764	0.0761	0.0794	-2.1	-0.6	0.2
321.17	0.103	0.0999	0.101	-0.2	-1.6	-3.3
323.16	0.134	0.134	0.134	-1.3	0.2	-2.0
325.16	0.178	0.175	0.179	-0.1	-0.5	0.1
326.17	0.207	0.202	0.204	1.4	0.2	-0.2
327.18	0.238	0.230	0.234	1.9	-0.4	0.2

<sup>a</sup> The vapor pressures obtained from each hole are denoted  $p$ , and the deviations of the experimental results from those given by the Clausius–Clapeyron equations are denoted  $\Delta \ln(p/\text{Pa})$ .

In a typical effusion experiment the samples are assumed to be in thermal equilibrium with a thermostatically controlled (to  $\pm 0.001$  K) silicone oil bath in which the effusion cells are immersed. The loss of mass  $\Delta m$  of the samples during a convenient effusion time period  $t$  is determined by weighing the effusion cells to  $\pm 0.01$  mg

before and after the effusion period in a system evacuated to a pressure near  $1 \times 10^{-4}$  Pa. At the temperature  $T$  of the experiment, the vapor pressure  $p$  is calculated by

$$p = (\Delta m/A_0 w_0 t)(2\pi RT/M)^{1/2} \quad (2)$$

where  $M$  is the molar mass of the effusing vapor,  $R$  is the gas constant,  $A_0$  is the area of the effusion orifice, and  $w_0$  is the respective Clausing factor calculated by eq 3, where  $l$  is the thickness of the orifice and  $r$  its radius:

$$w_0 = \{1 + (3l/8r)\}^{-1} \quad (3)$$

For 2-phenylbutyric acid and 5-phenylvaleric acid the thickness of the effusion orifices (made in a brass foil) was 0.049 mm and their areas and Clausing factors were as follows: hole 1,  $A_0/\text{mm}^2 = 0.596$ ,  $w_0 = 0.959$ ; hole 2,  $A_0/\text{mm}^2 = 0.754$ ,  $w_0 = 0.964$ ; hole 3,  $A_0/\text{mm}^2 = 0.862$ ,  $w_0 = 0.966$ . For 2-phenylacetic acid the effusion orifices were made in a 0.0125 mm platinum foil with the following areas and Clausing factors: hole 4,  $A_0/\text{mm}^2 = 0.452$ ,  $w_0 = 0.988$ ; hole 5,  $A_0/\text{mm}^2 = 0.675$ ,  $w_0 = 0.990$ ; hole 6,  $A_0/\text{mm}^2 = 0.996$ ,  $w_0 = 0.992$ .

## Results and Discussion

Using the integrated form of the Clausius–Clapeyron equation,  $\ln(p/\text{Pa}) = a - b(T/\text{K})^{-1}$ , where  $a$  is a constant and  $b = \Delta_{\text{cr}}^{\text{g}} H_m^{\text{g}}(\langle T \rangle)/R$ , the standard molar enthalpies of sublimation at the mean temperature of the experimental temperature range were derived. The experimental results obtained from each effusion cell for each studied compound, together with the residuals of the Clausius–Clapeyron equation, derived from least squares adjustment, are presented in Table 2.

Table 3 presents the parameters of the Clausius–Clapeyron equation together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature  $\langle T \rangle$  of the experiments for each hole used and for the global results. These results are in agreement within experimental error. The equilibrium pressures at the mean temperature  $p(\langle T \rangle)$  and the entropies of sublimation at equilibrium conditions,  $\Delta_{\text{cr}}^{\text{g}} S_m\{\langle T \rangle, p(\langle T \rangle)\} = \Delta_{\text{cr}}^{\text{g}} H_m^{\text{g}}(\langle T \rangle)/\langle T \rangle$ , are also presented.

The plots of  $\ln p = f(1/T)$  for the global results obtained for each compound are presented in Figure 1.

Sublimation enthalpies at the temperature of 298.15 K were derived from the sublimation enthalpies calculated

**Table 3. Experimental Results for the Compounds Studied, where  $a$  and  $b$  Are from the Clausius–Clapeyron Equation  $\ln(p/\text{Pa}) = a - b(T/\text{K})^{-1}$  and  $b = \Delta_{\text{cr}}^{\text{g}} H_m^{\text{g}}(\langle T \rangle)/R$ ;  $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$** 

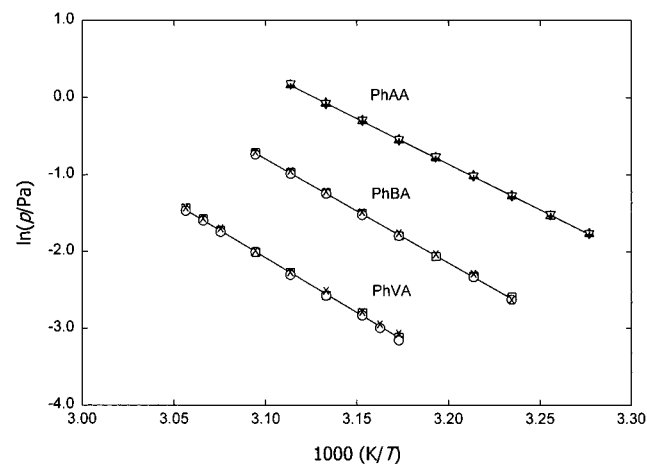
hole	$a$	$b$	$\langle T \rangle$ K	$p(\langle T \rangle)$ Pa	$\Delta_{\text{cr}}^{\text{g}} H_m^{\text{g}}(\langle T \rangle)$ kJ·mol <sup>-1</sup>	$\Delta_{\text{cr}}^{\text{g}} S_m\{\langle T \rangle, p(\langle T \rangle)\}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
2-Phenylacetic Acid						
4	37.15 ± 0.18	11880 ± 57			98.8 ± 0.5	
5	37.13 ± 0.18	11869 ± 57			98.7 ± 0.5	
6	37.06 ± 0.17	11857 ± 54			98.6 ± 0.5	
global	37.12 ± 0.15	11869 ± 48	313.17	0.459	98.6 ± 0.4	315 ± 1
4-Phenylbutyric Acid						
1	40.99 ± 0.28	13478 ± 87			112.0 ± 0.7	
2	40.97 ± 0.17	13478 ± 55			112.0 ± 0.5	
3	41.39 ± 0.44	13607 ± 138			113.1 ± 1.1	
global	41.11 ± 0.19	13517 ± 61	316.16	0.193	112.4 ± 0.8	356 ± 2
5-Phenylvaleric Acid						
1	42.21 ± 0.54	14286 ± 174			118.8 ± 1.4	
2	42.48 ± 0.32	14378 ± 100			119.5 ± 0.8	
3	41.54 ± 0.38	14067 ± 123			117.0 ± 1.0	
global	42.10 ± 0.29	14250 ± 94	321.17	0.103	118.5 ± 0.8	369 ± 2

**Table 4.** Calculated Values of the Heat Capacity of the Crystalline Compounds,  $C_{p,m}^{\circ}(\text{cr})$ , the Heat Capacity Differences between the Gaseous and the Crystalline Phases,  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}$ , and of the Standard ( $p^{\circ} = 0.1 \text{ MPa}$ ) Molar Enthalpies,  $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$ , Entropies,  $\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}$ , and Gibbs Functions,  $\Delta_{\text{cr}}^{\text{g}}G_m^{\circ}$ , of Sublimation at  $T = 298.15 \text{ K}$ 

compound	$C_{p,m}^{\circ}(\text{cr})$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}G_m^{\circ}$ $\text{kJ}\cdot\text{mol}^{-1}$
2-phenylacetic acid	176	$27 \pm 33$	$99.0 \pm 0.6$	$214 \pm 3$	$35.2 \pm 1.1$
3-phenylpropionic acid <sup>a</sup>	203	$31 \pm 33$	$102.4 \pm 0.8$	$223 \pm 3$	$35.9 \pm 1.2$
4-phenylbutyric acid	230	$35 \pm 33$	$113.0 \pm 1.0$	$249 \pm 4$	$38.8 \pm 1.6$
5-phenylvaleric acid	257	$39 \pm 33$	$119.4 \pm 1.1$	$257 \pm 5$	$42.8 \pm 1.9$

<sup>a</sup> Reference 4.**Table 5.** Experimental and Calculated Values of the Enthalpies of Sublimation,  $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}\{T(p = 0.5 \text{ Pa})\}$ , at the Temperature of Sublimation,  $T(p = 0.5 \text{ Pa})$ , for the Phenylcarboxylic and Dicarboxylic Acids

compound	$T(p = 0.5 \text{ Pa})$ K	$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$ $\{T(p = 0.5 \text{ Pa})\}$ (exptl) $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$ $\{T(p = 0.5 \text{ Pa})\} - 5N_{\text{CH}_2}$ (exptl) $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$ $\{T(p = 0.5 \text{ Pa})\}$ (calcd, eq 1) $\text{kJ}\cdot\text{mol}^{-1}$
2-phenylacetic acid	313.9	$99.0 \pm 0.6$	94.0	93.1
3-phenylpropionic acid <sup>a</sup>	315.4	$101.8 \pm 0.7$	91.8	93.6
4-phenylbutyric acid	323.3	$111.5 \pm 0.8$	96.5	96.2
5-phenylvaleric acid	333.0	$118.0 \pm 0.9$	98.0	99.4
propanedioic acid <sup>b</sup>	351.1	$108.7 \pm 0.7$	103.7	105.4
butanedioic acid <sup>c</sup>	371.8	$118.1 \pm 3.3$	108.1	112.2
pentanedioic acid <sup>b</sup>	355.3	$117.0 \pm 1.2$	102.0	106.7
hexanedioic acid <sup>c</sup>	377.7	$129.6 \pm 1.3$	109.6	114.1
heptanedioic acid <sup>c</sup>	369.2	$136.4 \pm 1.0$	111.4	111.3
octanedioic acid <sup>c</sup>	385.9	$143.4 \pm 3.8$	113.4	116.8
nonanedioic acid <sup>b</sup>	380.1	$155.8 \pm 1.6$	120.8	114.9
decanedioic acid <sup>c</sup>	397.2	$160.5 \pm 2.9$	120.5	120.6

<sup>a</sup> Reference 4. <sup>b</sup> Reference 2. <sup>c</sup> Reference 11.**Figure 1.** Plots of  $\ln p$  against  $1/T$  for 2-phenylacetic acid (PhAA), 4-phenylbutyric acid (PhBA), and 5-phenylvaleric acid (PhVA):  $\square$ , hole 1;  $\circ$ , hole 2;  $\times$ , hole 3;  $\triangle$ , hole 4;  $\nabla$ , hole 5;  $+$ , hole 6.

at the mean temperature  $\langle T \rangle$  of the experiments by using the equation

$$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}}H_m^{\circ}(\langle T \rangle) + \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}(298.15 \text{ K} - \langle T \rangle) \quad (4)$$

The value of  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}$  was estimated within an uncertainty of  $\pm 33 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , for each compound, using eq 5 derived by Chickos et al.<sup>9</sup> after comparison of experimental values of  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}$  with calculated values of  $C_{p,m}^{\circ}(\text{cr})$  for 114 organic solids. The heat capacities of the crystals were calculated using a group additivity method developed by Chickos et al.<sup>10</sup>

$$\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -\{0.75 + 0.15C_{p,m}^{\circ}(\text{cr})\} \quad (5)$$

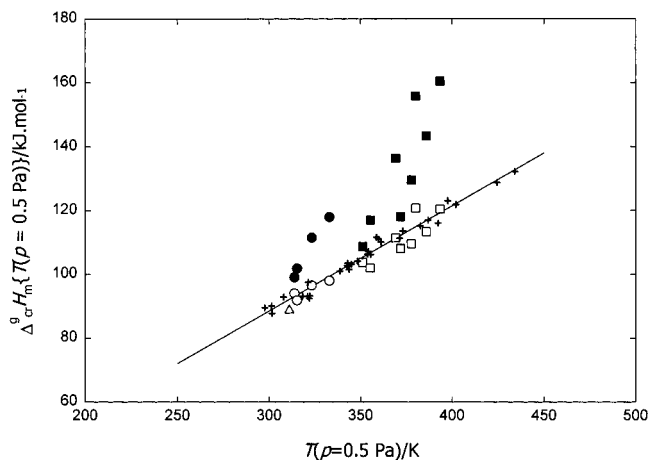
The calculated values of  $C_{p,m}^{\circ}(\text{cr})$  and of  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}$  are presented in Table 4. This table also includes the values, at the temperature  $T = 298.15 \text{ K}$ , of the standard molar enthalpies of sublimation, the standard molar entropies of sublimation calculated by eq 6, where  $p^{\circ} = 10^5 \text{ Pa}$ , and the standard molar Gibbs energies of sublimation.

$$\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}}S_m^{\circ}\{\langle T \rangle, p(\langle T \rangle)\} + \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ} \ln(298.15 \text{ K}/\langle T \rangle) - R \ln\{p^{\circ}/p(\langle T \rangle)\} \quad (6)$$

The uncertainties assigned to  $\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}(298.15 \text{ K})$  were obtained by considering the uncertainties of  $\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}\{\langle T \rangle, p(\langle T \rangle)\}$  and of  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}$  as well as the uncertainties of  $\ln p(\langle T \rangle)$  calculated from the standard deviations of the parameters of the Clausius–Clapeyron equations presented in Table 3.

Table 5 presents the temperatures of sublimation at the pressure  $p = 0.5 \text{ Pa}$  and the enthalpies of sublimation for the studied acids and for the dicarboxylic acids from propanedioic to decanedioic (the higher members of this series seem to be cyclic in the gas phase<sup>2,11</sup>) calculated from the values of  $T(p = 0.5 \text{ Pa})$  through eq 1. The experimental values of the sublimation enthalpies are  $\sim 5 \text{ kJ}\cdot\text{mol}^{-1}$  higher, per methylene group, than those calculated values. Therefore, the correlation that yielded eq 1, which included 30 heterocyclic compounds, was now extended to include the values of  $[\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}\{T(p = 0.5 \text{ Pa})\} - 5N_{\text{CH}_2}]$ , where  $N_{\text{CH}_2}$  is the number of methylene groups present in the structure of the carboxylic acids considered. The linear correlation obtained is shown in Figure 2 (in which the result reported for benzoic acid<sup>7</sup> is also presented) and represented by eq 7, which is identical to eq 1 when  $N_{\text{CH}_2} = 0$ .

$$[\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}\{T(p = 0.5 \text{ Pa})\} - 5N_{\text{CH}_2}]/\text{kJ}\cdot\text{mol}^{-1} = (0.329 \pm 0.010)\{T(p = 0.5 \text{ Pa})/\text{K}\} - (10.4 \pm 3.7) \quad (7)$$



**Figure 2.** Dependence of the enthalpies of sublimation on the temperature of sublimation at  $p = 0.5$  Pa: ●, experimental values of the enthalpies of sublimation of the phenylcarboxylic acids; ○, experimental values of the enthalpies of sublimation minus 5 times the number of methylene groups of the phenylcarboxylic acids; ■, experimental values of the enthalpies of sublimation of the dicarboxylic acids; □, experimental values of the enthalpies of sublimation minus 5 times the number of methylene groups of the dicarboxylic acids; +, experimental values for some substituted quinolines and quinoxalines (ref 3); △, benzoic acid (ref 7).

At present, eq 7 predicts the enthalpies of sublimation of many organic compounds depending on how many methylene groups are present in their structure. We will investigate in future work if this equation holds for other long-chain organic compounds.

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Received for review May 15, 2001. Accepted August 20, 2001. We thank Fundação para a Ciência e Tecnologia, FCT, for financial support through Centro de Investigação em Química da Universidade do Porto (Research Unit 81) and through Faculty of Science of University of Porto (Project PBIC/C/QUI/2193/95). D.M.H. thanks PRAXIS XXI for the award of a research grant (BD/9349/96) under Programa Ciência.

JE010153H