Vapor Pressures and Phase Changes Enthalpy and Gibbs Energy of Three Crystalline Monomethyl Benzenedicarboxylates

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The Knudsen mass-loss effusion technique was used to measure the vapor pressures, between 0.1 Pa and 1 Pa, of the three monomethyl benzenedicarboxylates over the following temperature intervals: monomethyl phthalate, between 335.28 K and 355.28 K; monomethyl isophthalate, between 359.26 K and 379.12 K; monomethyl terephthalate, between 363.16 K and 381.51 K. From the variation of the vapor pressures with temperature, the standard molar enthalpies, entropies, and Gibbs energies of sublimation at $T = 298.15$ K were calculated. The volatility of the studied compounds is compared with the volatilities of the benzene dicarboxylic acids and of the dimethyl benzenedicarboxylates.

Introduction

The vapor pressures of the three crystalline benzenedicarboxylic acids (phthalic, isophthalic, and terephthalic acids) have been recently measured[1] using a new Knudsen effusion apparatus. The Knudsen effusion method was also used to measure the vapor pressures of dimethyl isophthalate and of dimethyl terephthalate.[2] To compare the volatility of the benzenedicarboxylic acids and their dimethyl esters with the volatility of the related monomethyl esters, we decided to measure the vapor pressures at several temperatures of monomethyl phthalate, monomethyl isophthalate, and monomethyl terephthalate using this effusion method. For one of these compounds (monomethyl terephthalate), there are three published values[3−5] for the enthalpy of sublimation, but there is considerable disagreement between them.

Experimental Section

The three compounds were commercially obtained from Aldrich Chemical Company with the following purity certificates: monomethyl phthalate [CAS Registry No. 4376-18-5] 99.3 % (GLC), monomethyl isophthalate [CAS Registry No. 1877-71-0] 98.8 % (GLC), and monomethyl terephthalate [CAS Registry No. 1679-64-7] 101.2 % (NaOH titration). The samples of the three compounds were further purified by repeated sublimation under reduced pressure.

The temperature and the enthalpy of fusion of the purified samples (hermetically sealed in steel crucibles) were measured using a Setaram DSC 141 calorimeter under a heating rate of 3.3×10^{-2} K·s^{-1}. The power scale of the apparatus was calibrated with high-purity indium (mass fraction > 0.99999), and its temperature scale was calibrated by measuring the melting temperature of the following high-purity reference materials:[6] naphthalene, benzoic acid, and indium. From the recorded thermograms, the impurity mass fractions of the samples were computed using a fractional fusion technique.[7] No crystalline transitions were detected between 295 K and the temperature of fusion for each of the studied compounds. At least four independent runs using fresh samples were performed. Mean results of the temperatures (observed at the onset of the calorimetric peaks) and the enthalpies of fusion are presented in Table 1 together with the calculated mass fractions of impurity (x) of the purified samples.

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

	T_{fus}	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$	
	K	kJ·mol^{-1}	$10^3 \cdot x$
monomethyl phthalate	357.50 ± 0.15	21.63 ± 0.48	0.9
monomethyl isophthalate	466.68 ± 0.08	36.50 ± 0.14	1.6
monomethyl terephthalate	492.54 ± 0.04	37.68 ± 0.24	0.7

A new mass-loss Knudsen effusion apparatus (apparatus I),[8] which enables the simultaneous operation of nine effusion cells at three different temperatures, was used to measure the vapor pressure of the purified crystalline samples of monomethyl phthalate and monomethyl isophthalate. As the amount of purified sample of monomethyl terephthalate was not enough for loading all the effusion cells, this compound was studied using our previously reported apparatus (apparatus II),[9] which enables the simultaneous operation of three effusion cells at the same temperature.

The description of the main features of apparatus II, the procedure, the technique, and the results obtained with ferrocene and benzoic acid have been reported.[9] The consistency of the measured vapor pressures has been also checked by comparing the results obtained for benzoic acid and for copper(II) β-diketonates using this apparatus, with the results obtained for the same samples using different experimental apparatuses and different techniques.[10] A few minor changes have been introduced to the original apparatus design and to the lids of the effusion cells, and several other tests have been performed with several other substances including benzophenone, dibenzothiophene, naphthalene, and anthracene.

The performance of the apparatus I was checked by measuring the vapor pressures under 1 Pa, over approximately 20 K temperature intervals, of benzoic acid,

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phenanthrene, benzanthrone, anthracene, and 1,3,5-triphenylbenzene. Both the measured vapor pressures of these compounds and the calculated enthalpies of sublimation are in excellent agreement with literature results.[8]

The cylindrical effusion cells used in both apparatus are made in aluminum. The internal dimensions of the closed cells are diameter 20 mm and height 23 mm. Besides the number of effusion cells used in each effusion run, the main differences between the two experimental apparatuses are concerned with the temperature control and measurement. The thermostatic oil bath and the mercury thermometers used in apparatus II were replaced in apparatus I, respectively, by three independently temperature-controlled aluminum blocks and by a platinum resistance thermometers Pt-100. The accuracy of the temperature measurements is estimated to be $\pm\ 1{\cdot}10^{-2}$ K for the platinum resistance thermometers used in apparatus I and $\pm\ 2{\cdot}10^{-2}$ K for the calibrated Amarell mercury thermometers used in apparatus II.

In a typical effusion run, the crystalline sample was placed and pressed at the bottom of each cylindrical cell and kept at a constant temperature, and the vapor (assumed to be monomeric and in equilibrium with the crystalline phase) was allowed to effuse through a small orifice located at the top of the cell into an evacuated space. At the temperature T, the mass m of the sample sublimed from the effusion cell, which is obtained by weighing the cell to within ± 0.01 mg before and after the effusion time period t, is related to the vapor pressure of the crystalline compound by eq 1:

$$p = (m/A_o w_o t){\cdot}(2\pi RT/M)^{1/2} \tag{1}$$

where M is the molar mass of the effusing vapor, R is the gas constant, A_o is the area of the effusion orifice, and w_o is the transmission probability factor that is usually calculated by means of eq 2 or of eq 3 where l is the length of the effusion orifice and r is its radius:

$$w_o = \{1 + (3l/8r)\}^{-1} \tag{2}$$

$$w_o = \{1 + (l/2r)\}^{-1} \tag{3}$$

The accuracy of the measured pressure is estimated to be ± 0.01 Pa.

Apparatus II has been widely used by our research group for measuring the vapor pressures of several compounds under 1 Pa, using three effusion cells for each experimental run. For most of the compounds studied, the vapor pressures calculated at each temperature for each effusion cell are equal within experimental error. For some compounds, however, a systematic decrease of the calculated pressure with an increase in size of the effusion orifice has been observed, indicating that the results may be affected by a low condensation coefficient value or by a self-cooling effect.[11,12] In these cases, the equilibrium pressure at each temperature may be derived by plotting p against (pw_oA_o), to obtain the intercept of the straight line derived at zero area as the equilibrium pressure, according to the equation developed by Whitman[13] and Motzfeldt.[14]

Apparatus I enables the simultaneous operation of nine effusion cells, which may be controlled at three different temperatures, during one effusion run. By keeping the same temperature for each group of three effusion cells with different orifice areas, deviation of results from the equilibrium pressures at three different temperatures may be checked simultaneously. So, in one experimental run the equilibrium pressures at three different temperatures can be determined. Each effusion cell is contained in one of the three cylindrical holes inside the aluminum blocks. The three aluminum blocks are contained inside a sublimation chamber consisting of a glass bell jar ($\phi_i = 296$ mm, $h = 360$ mm, $l = 5$ mm) with a cylindrical aluminum lid. Each block contains three cylindrical holes of dimensions similar to the effusion cells and is connected to a sliding aluminum platform by three ceramic elements. The glass connection between the pumping system and the sublimation camera includes a glass coldfinger for liquid nitrogen connected to the lid of the sublimation camera. Each aluminum block may be heated to the desired temperature by two circular heating elements. The temperature of each block is kept constant by a PID (proportional, integral, and differential). The temperature of each block is measured by a platinum resistance thermometer Pt-100 (class 1/10) calibrated against a SPRT (25 Ω; Tinsley, 5187A) temperature probe, using an ASL bridge model F26 in accordance to ITS-90. Each sensor is located at the center of the block near the basis of the holes containing the effusion cells. The signals of the thermometer sensors are received by an acquisition system, Agilent model 34970A, connected to a PC that continuously displays, with a resolution of 10^{-3} K, the temperature of the effusion cells which are assumed to be in thermal equilibrium with each aluminum block. The pumping system enables the achievement of a pressure lower than $5{\cdot}10^{-4}$ Pa in less than 1 min and an ultimate pressure of $5{\cdot}10^{-5}$ Pa.

Table 2. Areas and Transmission Probability Factors of the Effusion Orifices

	orifice number	A_0/mm^2	w_0
small orifices	A1	0.502	0.988
	A2	0.499	0.988
	A3	0.497	0.988
	D1	0.663	0.990
medium orifices	B4	0.774	0.991
	B5	0.783	0.991
	B6	0.773	0.991
	D2	0.785	0.991
large orifices	C7	1.116	0.992
	C8	1.125	0.992
	C9	1.150	0.992
	D3	0.996	0.992

The Clausing factors of the effusion orifices used, each precision drilled in platinum foil of 0.0125 mm thickness, were calculated using eq 2 and are reported in Table 2 together with their areas. For the experiments performed with apparatus I, three series of effusion orifices were used (A1 to A3, small orifices; B4 to B6, medium orifices; C7 to C9, large orifices). The orifices of each of these series are similar in area. For apparatus II, only three different effusion orifices were used (D1, small; D2, medium; D3, large).

Results and Discussion

Table 3 presents the experimental results obtained from each effusion cell at each studied temperature for the compounds studied.

Table 4 presents the detailed parameters of the Clausius−Clapeyron equation, together with the calculated standard deviations, and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T = \langle T\rangle$ for the small, medium, and large effusion orifices and for the global treatment of all the (p, T) points obtained for each studied compound (except for monomethyl isophthalate). The equilibrium pressure at the mean temperature $p(\langle T\rangle)$ and the entropies of sublimation at equilib-

Table 3. Effusion Results for the Compounds Studied[a]

			m/mg			p/Pa		
T/K	t/s	orifices	M_S	M_M	M_L	P_S	P_M	P_L
			Monomethyl Phthalate					
335.28	20742	A3-B6-C9	3.66	5.99	8.74	0.112	0.118	0.115
337.26	20742	A2-B5-C8	5.03	7.62	11.05	0.154	0.148	0.149
339.12	20742	A1-B4-C7	5.82	8.89	13.49			
339.28	11115	A3-B6-C9	3.33	5.41	7.95			
339.20[b]						0.184[b]	0.187[b]	0.190[b]
341.24	11115	A2-B5-C8	4.24	6.55	9.60	0.243	0.239	0.243
343.11	11115	A1-B4-C7	5.22	8.27	11.74	0.298	0.306	0.301
345.27	14300	A3-B6-C9	8.61	13.36	20.00	0.388	0.386	0.388
347.24	14300	A2-B5-C8	10.47	16.78	23.57	0.471	0.480	0.468
349.12	14300	A1-B4-C7	12.93	19.80	29.52	0.579	0.575	0.593
351.06	9013	A1-B4-C7	10.42	15.87	23.49	0.743	0.733	0.751
353.23	9013	A2-B5-C8	13.64	21.06	29.81	0.981	0.964	0.948
355.28	9013	A3-B6-C9	16.99	26.71	39.77	1.233	1.242	1.242
			Monomethyl Isophthalate					
359.26	17457	A3-B6-C9	3.56	5.61	8.29	0.134	0.136	0.134
361.24	17457	A2-B5-C8	4.57	7.06	10.17	0.172	0.169	0.169
363.28	25802	A3-B6-C9	8.22	12.75	18.27	0.211	0.210	0.202
365.26	25802	A2-B5-C8	10.33	15.77	22.27	0.264	0.256	0.252
367.13	25802	A1-B4	12.29	18.84		0.313	0.311	
369.28	14549	A3-B6-C9	8.66	13.57	19.39	0.397	0.399	0.382
371.24	14549	A2-B5-C8	10.93	16.77	23.48	0.499	0.487	0.474
373.12	14549	A1-B4-C7	12.91	19.87	27.87	0.588	0.586	0.569
375.27	11212	A3-B6-C9	12.89	19.75	28.74	0.773	0.759	0.741
377.24	11212	A2-B5-C8	15.94	24.41	34.71	0.953	0.928	0.917
379.12	11212	A1-B4	18.84	28.78		1.122	1.111	
			Monomethyl Terephthalate					
363.16	24670	D1-D2		8.23	10.48		0.139	0.140
365.15	23659	D1-D2-D3	8.05	9.67	11.99	0.169	0.171	0.167
367.19	22438	D1-D2-D3	9.57	11.18	14.17	0.212	0.209	0.209
370.18	18318	D1-D2-D3	10.80	12.44	15.88	0.294	0.286	0.289
372.17	16166	D1-D2-D3	11.65	13.89	17.19	0.361	0.363	0.354
374.20	14681	D1-D2-D3	13.21	15.41	19.31	0.452	0.449	0.439
377.37	11826	D1-D2-D3	14.78	17.28	21.88	0.630	0.621	0.620
379.26	10158	D1-D2-D3	15.43	17.72	22.36	0.768	0.743	0.739
381.51	10143	D1-D2-D3	18.81	22.10	27.90	0.940	0.931	0.926

[a] Results related to the small (A1, A2, A3, D1), medium (B4, B5, B6, D2), and large (C7, C8, C9, D3) effusion orifices are denoted, respectively, by the subscripts S, M, and L. [b] Mean of the two previous runs.

Table 4. Experimental Results for the Compounds Studied Where *a* and *b* Are from Clausius−Clapeyron Equation ln (p/Pa) = $a - b\cdot$(K/T), and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(<T>)/R$; $R = 8.3145\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

effusion orifices	a	b	$\frac{<T>}{\mathrm{K}}$	$\frac{p(<T>)}{\mathrm{Pa}}$	$\frac{\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(<T>)}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{cr}}^{\mathrm{g}}S_m\{<T>, p(<T>)\}}{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}}$
			Monomethyl Phthalate			
A	39.65 ± 0.46	14018 ± 158		0.388	116.6 ± 1.3	
B	39.29 ± 0.37	13894 ± 128		0.388	115.5 ± 1.1	
C	39.36 ± 0.31	13918 ± 107		0.388	115.7 ± 0.9	
global	39.43 ± 0.22	13943 ± 77	345.3	0.388	115.9 ± 0.6	335.6 ± 1.7
			Monomethyl Isophthalate			
A	38.58 ± 0.35	14582 ± 127		0.400	121.2 ± 1.1	
B	38.33 ± 0.25	14495 ± 93		0.394	120.5 ± 0.8	
C	38.00 ± 0.50	14380 ± 183		0.387	119.6 ± 1.5	
mean	38.30 ± 0.22	14486 ± 80	369.2		120.4 ± 0.7	326.1 ± 1.9
zero area	39.05 ± 0.22	14745 ± 80	369.2	0.412	122.6 ± 0.7	332.1 ± 1.9
			Monomethyl Terephthalate			
D1	38.53 ± 0.22	14718 ± 82		0.367	122.4 ± 0.7	
D2	37.88 ± 0.26	14479 ± 98		0.364	120.4 ± 0.8	
D3	37.81 ± 0.29	14454 ± 107		0.363	120.2 ± 0.9	
global	38.07 ± 0.17	14550 ± 65	372.3	0.364	121.0 ± 0.5	325.0 ± 1.3

rium conditions, $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{<T>,\ p(<T>)\} = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}\ (<T>)/<T>$, are also presented. For monomethyl isophthalate a slight systematic decrease of the vapor pressure with increasing orifice size was observed. So, the equilibrium vapor pressure at each experimental temperature was calculated as the intercept of the plot of p_i against ($p_i w_o A_o$) for each effusion temperature, where p_i represents the pressures calculated through the Clausius−Clapeyron equations presented in this Table IV for each group of effusion cells. According to the Whitman−Motzfeldt model,[13,14] the calculated equilibrium pressures are assumed to represent the vapor pressures that would be obtained using hypothetical effusion orifices of zero area.

The plots of ln $p = f(1/T)$ for each compound studied are presented in Figure 1. The standard molar sublimation enthalpies at the temperature 298.15 K were derived from

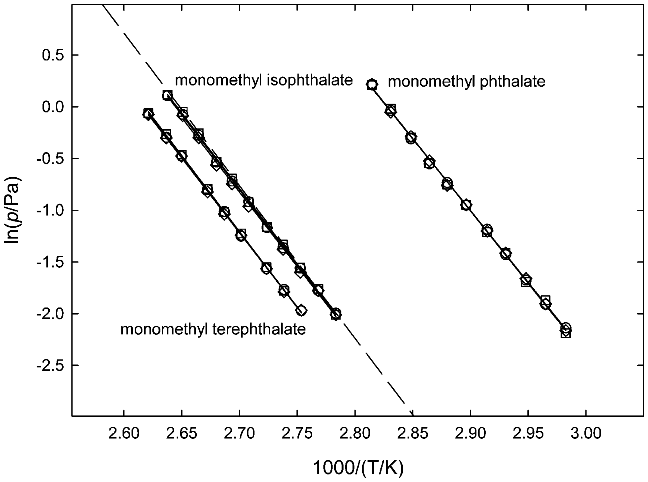

Figure 1. Plots of ln p against $1/T$ for the compounds studied. □, small effusion orifices; ○, medium effusion orifices; ◇, large effusion orifices. The dashed line represents the linear regression on the equilibrium vapor pressures (zero area) for monomethyl isophthalate.

the sublimation enthalpies calculated at the mean temperature $<T>$ of the experiments by

$$\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 298.15\ {\rm K}) = \Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(<T>) + \Delta_{\rm cr}^{\rm g}C_{p,{\rm m}}^{\rm o}(298.15\ {\rm K} - <T>) \quad (4)$$

where $\Delta_{\rm cr}^{\rm g}C_{p,{\rm m}}^{\rm o}$ represents the mean value of the difference between the heat capacities of, respectively, the gas and crystalline phases over the temperature interval 298.15 K and $<T>$. This value was estimated as $\Delta_{\rm cr}^{\rm g}C_{p,{\rm m}}^{\rm o} = -(42 \pm 11)$ J·mol^{-1}·K^{-1}, for all the three isomers, using group contribution values derived by Domalski and Hearing[15] for the gas phase and by Benson[16] for the crystalline phase and considering the value $\Delta_{\rm cr}^{\rm g}C_{p,{\rm m}}^{\rm o}(298.15\ {\rm K}) = -44.4$ J·mol^{-1}·K^{-1} for benzoic acid calculated from the values of the heat capacity of the crystalline phase presented by Furukawa et al.[17] and from the values presented by Stull[18] for the gaseous phase.

Table 5 presents the calculated values, at the temperature $T = 298.15$ K, of the standard molar enthalpies of sublimation, the standard molar entropies of sublimation calculated by eq 5 (where $p^0 = 10^5$ Pa), and the standard molar Gibbs energies of sublimation:

$$\Delta_{\rm cr}^{\rm g}S_{\rm m}^{\rm o}(T = 298.15\ {\rm K}) = \Delta_{\rm cr}^{\rm g}S_{\rm m}\{<T>, p(<T>)\} + \Delta_{\rm cr}^{\rm g}C_{p,{\rm m}}^{\rm o}\ln(298.15\ {\rm K}/<T>) - R\ln\{p°/p(<T>)\} \quad (5)$$

For comparison reasons, the enthalpy of sublimation of dimethyl phthalate at $T = 298.15$ K, which is a liquid at this temperature, was estimated from the enthalpy of fusion at the triple point, $\Delta_{\rm cr}^{\rm l}H_{\rm m}(T = 274.18\ {\rm K}) = 16.94$ kJ·mol^{-1},[19] and from the enthalpy of vaporization, $\Delta_{\rm l}^{\rm g}H_{\rm m} = 78.6$ kJ·mol^{-1},[20] derived from vapor pressure measurements (temperature not defined) as $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 298.15\ {\rm K}) = 95.5$ kJ·mol^{-1}. Heat capacity corrections for this estimation were neglected.

Table 5. Standard (p^0 = 0.1 MPa) Molar Enthalpies ($\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}$), Entropies ($\Delta_{\rm cr}^{\rm g}S_{\rm m}^{\rm o}$), and Gibbs Energies ($\Delta_{\rm cr}^{\rm g}G_{\rm m}^{\rm o}$) of Sublimation at T = 298.15 K for Benzene Dicarboxylic Acids and Methyl and Dimethyl Esters

	$\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}$	$\Delta_{\rm cr}^{\rm g}S_{\rm m}^{\rm o}$	$\Delta_{\rm cr}^{\rm g}G_{\rm m}^{\rm o}$
	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	kJ·mol^{-1}
phthalic acid[a]	143.3 ± 1.5	248.4 ± 4.1	69.2 ± 1.9
monomethyl phthalate[b]	117.9 ± 0.8	238.2 ± 1.7	46.9 ± 1.0
dimethyl phthalate[c]	(95.5)		
isophthalic acid[a]	143.4 ± 1.7	234.3 ± 4.5	73.5 ± 2.2
monomethyl isophthalate[b]	125.6 ± 1.0	238.0 ± 3.0	54.6 ± 1.3
dimethyl isophthalate[d]	100.9 ± 0.2	224.6 ± 0.7	33.9
terephthalic acid[a]	152.2 ± 1.7	237.2 ± 4.8	81.5 ± 2.2
monomethyl terephthalate[b]	124.1 ± 1.0	230.2 ± 3.5	55.5 ± 3.5
dimethyl terephthalate[d]	104.6 ± 0.3	217.0	39.9

[a] Results from ref 1. [b] Present work. [c] Result estimated in this work from literature values of $\Delta_{\rm cr}^{\rm l}H_{\rm m}$ [19] and of $\Delta_{\rm l}^{\rm g}H_{\rm m}$.[20] [d] Sublimation enthalpy results from ref 2 (the values of $\Delta_{\rm cr}^{\rm g}S_{\rm m}^{\rm o}$ and $\Delta_{\rm cr}^{\rm g}G_{\rm m}^{\rm o}$ were calculated in the present work from the experimental data presented in this reference).

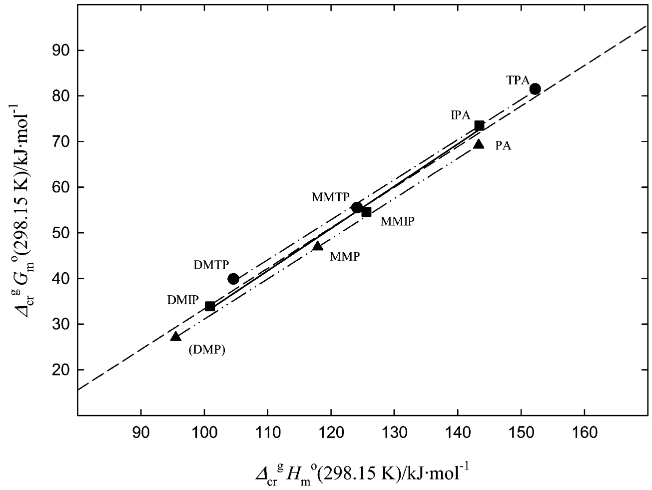

Figure 2. DMP, dimethyl phthalate; DMIP, dimethyl isophthalate; DMTP, dimethyl terephthalate; MMP, monomethyl phthalate; MMIP, monomethyl isophthalate; MMTP, monomethyl terephthalate; PA, phthalic acid; IPA, isophthalic acid; TPA, terephthalic acid. – –, regression line over all results; – · –, regression line over the results of DMTP, MMTP, and TPA; —, regression line over the results of DMIP, MMIP, and IPA; – ·· –, regression line over the results of MMP and PA.

The enthalpy of sublimation of monomethyl terephthalate was determined calorimetrically by Kabo and co-workers[3] as $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 373.3\ {\rm K}) = (124.89 \pm 0.50)$ kJ·mol^{-1}. From the data presented in the literature, these authors calculated the values $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 476\ {\rm K}) = 77.5$ kJ·mol^{-1}, from the data presented by Olevsky et al.,[4] and $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 473\ {\rm K}) = 86.4$ kJ·mol^{-1}, from the data presented by Kraus et al.[5] Using the presently estimated value $\Delta_{\rm cr}^{\rm g}C_{p,{\rm m}}^{\rm o} = -(42 \pm 11)$ J·mol^{-1}·K^{-1} in eq 4, the values of $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 298.15\ {\rm K})$ corresponding to those literature values were calculated as (128.0 ± 0.5) kJ·mol^{-1};[3] 85.0 kJ·mol^{-1};[4] and 93.8 kJ·mol^{-1}.[5] The value determined in the present work $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 298.15\ {\rm K}) = (124.1 \pm 1.0)$ kJ·mol^{-1} is clearly higher than the values determined from the experimental data presented by Olevsky et al.[4] and by Kraus et al.[5] but only slightly lower than the calorimetric value determined by Maksimuk et al.[3]

As expected from the intermolecular hydrogen bonds existing in the crystals of the benzene dicarboxylic acids and (most probably) of their monomethyl esters, the volatility of the crystalline compounds, at $T = 298.15$ K, increases from the acids to the dimethyl esters, with the volatily of the monomethyl esters laying between those two groups of compounds.

Figure 2 represents a plot of $\Delta_{\rm cr}^{\rm g}G_{\rm m}^{\rm o}(T = 298.15\ {\rm K})$ against $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\rm o}(T = 298.15\ {\rm K})$ for the compounds studied and for the literature results for the benzene dicarboxylic acids and their dimethyl esters. The results of the para compounds (terephthalic acid and their methyl terephthalate esters) and of the meta compounds (isophthalic acid and their methyl isophthalate esters) are well-correlated, repectively, by eqs 6 and 7:

$$\text{para:}\ -\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}(T = 298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = -(52.4 \pm 4.4) + (0.878 \pm 0.035) \times \{\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(T = 298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1}\} \quad (6)$$

$$\text{meta:}\ -\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}(T = 298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = -(60.2 \pm 7.7) + (0.926 \pm 0.062) \times \{\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(T = 298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1}\} \quad (7)$$

The value $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}(T = 298.15\ \text{K}) = 27.1\ \text{kJ}\cdot\text{mol}^{-1}$ was estimated, for the virtual sublimation of dimethyl phthalate, inputing the value of $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(T = 298.15\ \text{K})$ presented in Table 5 in eq 8, derived from the results of phthalic acid and monomethyl phthalate. This equation has the same slope as eq 6:

$$\text{ortho:}\ -\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}(T = 298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = -56.7 + 0.878\{\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(T = 298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1}\} \quad (8)$$

The volatilities of the benzene dicarboxylic acids, of the monomethyl esters, and of the dimethyl esters follows the order: para < meta < ortho, although the volatilities of the monomethyl isophthalate and of the monomethyl terephthalate are similar.

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