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Vapor Pressures and Enthalpies of Combustion of the Dihydroxybenzoic Acid Isomers

Manuel J. S. Monte,* Mariana V. Gonçalves, and Maria D. M. C. Ribeiro da Silva

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

The Knudsen mass-loss effusion technique was used to measure the vapor pressures at different temperatures of the following dihydroxybenzoic acids: 2,3-dihydroxybenzoic acid, between (345.22 and 363.18) K; 2,4-dihydroxybenzoic acid, between (376.22 and 392.11) K; 2,5-dihydroxybenzoic acid, between (372.14 and 388.92) K; 2,6-dihydroxybenzoic acid, between (347.14 and 365.17) K; 3,4-dihydroxybenzoic acid, between (387.12 and 403.26) K; and 3,5-dihydroxybenzoic acid, between (345.22 and 363.18) K. From the temperature dependences of the vapor pressure of the crystalline compounds, the standard ($p^0 = 10^5$ Pa) molar enthalpies and Gibbs energies of sublimation, at $T = 298.15$ K, were derived. For each of the six isomers the standard ($p^0 = 0.1$ MPa) molar enthalpy of formation in the crystalline phase was derived from the experimental standard molar energy of combustion, in oxygen, measured by static-bomb combustion calorimetry at $T = 298.15$ K. The combination of the standard molar enthalpy of formation in the crystalline phase with the standard enthalpy of sublimation yields the standard molar enthalpy of formation in the gaseous phase of the studied compounds.

Introduction

Our research group has been investigating the volatility of differently substituted benzoic acids[1−8] through vapor pressure measurements at different temperatures. For some of these compounds enthalpies of combustion were also measured,[1,9,10] enabling the determination of the enthalpy of formation in the crystalline and gaseous phases. This work continues the studies of volatility and enthalpies of formation of substituted benzoic acids.

A decade ago Price et al. published results of the enthalpy of sublimation of the present studied compounds using thermogravimetry.[11] Their main aim was to investigate if there is any relationship between the volatility of the different isomers of dihydroxybenzoic acid and their performance as matrices for MALDI (matrix assisted laser desorption ionization).[11] Their results present large uncertainties even for the test of the experimental apparatus using benzoic acid where $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}} = (89 \pm 6)\ \mathrm{kJ\cdot mol^{-1}}$ (temperature not defined). So we decided to perform a thermodynamic study on the sublimation of the six isomers of the dihydroxybenzoic acid, measuring their vapor pressure at different temperatures. Furthermore, as there were no results of their enthalpies of formation, we decided to measure the enthalpies of combustion of these compounds to determine their standard enthalpies of formation in the gaseous phase.

Experimental Section

Materials. All of the studied compounds were commercially obtained from Aldrich Chemical Co. with the following assessed molar fraction purities (HPLC grade): 2,3-dihydroxybenzoic acid (2,3-DHBA), 0.994; 2,5-dihydroxybenzoic acid (2,5-DHBA), 0.997; 2,6-dihydroxybenzoic acid (2,6-DHBA), 0.988; 3,4-dihydroxybenzoic acid (3,4-DHBA), 0.997; and 3,5-dihydroxybenzoic acid (3,5-DHBA), 0.996. For 2,4-dihydroxybenzoic acid (2,4-DHBA) elemental analysis yields % C, 54.53, and % H, 4.01. All of the samples were further purified using sublimation under reduced pressure. The average ratios, μ, of the mass of CO_2 recovered in the combustion experiments to that calculated from the mass of sample, assuming the density $\rho = 1.0\ \mathrm{g\cdot cm^{-3}}$ for the three compounds, were the following: for 2,3-DHBA, $\mu = (1.0000 \pm 0.0003)$; for 2,4-DHBA, $\mu = (1.0001 \pm 0.0002)$; for 2,5-DHBA, $\mu = (0.9999 \pm 0.0003)$; for 2,6-DHBA, $\mu = (0.9988 \pm 0.0008)$; for 3,4-DHBA, $\mu = (0.9996 \pm 0.0004)$; and for 3,5-DHBA, $\mu = (0.9987 \pm 0.0005)$. The presented uncertainties are the standard deviations of the mean of those ratios.

The molar masses used for the elements were those recommended by the IUPAC Commission in 2005.[12]

Differential Scanning Calorimetry (DSC). DSC was used mainly to investigate if any phase transitions occur between 298 K and the maximum temperature of the measured vapor pressures. A power compensated differential scanning calorimeter Setaram DSC 141 was used, and all of the experiments were performed under a heating rate of $3.3\cdot10^{-2}\ \mathrm{K\cdot s^{-1}}$ using steel crucibles wherein the samples were hermetically sealed. The power scale of the calorimeter 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:[13] naphthalene, benzoic acid, and indium. For three of the studied compounds (isomers 2,3, 2,5, and 3,5), temperature (observed at the onset of the calorimetric peaks) and enthalpy of fusion could be derived from the thermograms and are presented in Table 1, together with literature values for the temperature of fusion.[11,14,15] The thermograms of the other three isomers indicate decomposition occurring during fusion and the existence of phase transitions starting at $T = 405.0$ K for 2,4-DHBA, $T = 301.7$ K for 2,6-DHBA, and $T = 404.2$ K for 3,4-DHBA. The nature

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* Corresponding author. E-mail: mjmonte@fc.up.pt.

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Table 1. DSC Results for the Temperature and Enthalpy of Fusion Measured in This Work and Temperatures of Fusion Published in Literature

	T_{fusion}	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$
compound	K	$\mathrm{kJ \cdot mol^{-1}}$
2,3-DHBA	(476.4 ± 0.6)[a] 479.5[b] 478.7[c] 477 to 479[d]	(31.9 ± 0.5)
2,4-DHBA	dec[a] 501.7[b] 499 (dec)[c] 481 to 484 (dec)[d]	
2,5-DHBA	(476.2 ± 0.2)[a,e] 478.9[b] 472.7[c] 477 to 481[d]	(20.8 ± 1.7)
2,6-DHBA	dec[a] 443.7[b] 440 (dec)[c] 438 (dec)[d]	
3,4-DHBA	dec[a] 474.9[b] 474 (dec)[c] 470 to 473 (dec)[d]	
3,5-DHBA	(508.3 ± 0.2)[a] 508.9[b] 512[c] 509 to 511 (dec)[d]	(38.3 ± 0.4)

[a] This work (the measured temperatures are the onset temperatures of the calorimetric peaks). [b] Ref[a] 11. [c] Ref[a] 14. [d] Ref[a] 15. [e] A phase transition seems to occur immediately followed by fusion.

Table 2. Effusion Results for the Studied Compounds

T	t		m/mg			p/Pa	
K	s	m_1	m_2	m_3	p_1	p_2	p_3
			2,3-DHBA				
345.22	26115	7.93	9.42	11.86	0.158	0.159	0.157
347.21	24283	9.34	10.82	13.78	0.201	0.196	0.197
349.23	21597	10.29	12.12	15.26	0.250	0.248	0.246
351.19	17696	10.42	12.31	15.62	0.310	0.308	0.308
353.21	14404	10.38	12.21	15.51	0.380	0.377	0.377
355.17	12635	11.18	13.19	16.84	0.468	0.466	0.468
357.20	10835	11.62	13.69	17.35	0.569	0.565	0.564
359.20	10083	13.57	15.93	20.30	0.716	0.708	0.711
361.21	9210	14.97	17.55	22.39	0.867	0.857	0.861
363.18	10804	20.98	24.65	31.29	1.039	1.029	1.029
			2,4-DHBA				
376.22	25257	9.19	10.58	13.64	0.198	0.192	0.195
377.32	21743	8.93	10.25	13.23	0.224	0.217	0.220
379.13	21221	10.44	11.97	15.44	0.269	0.260	0.264
381.15	19551	11.85	13.32	17.12	0.332	0.315	0.319
383.13	16208	11.78	13.56	17.32	0.399	0.388	0.390
385.12	10537	9.58	11.09	14.20	0.501	0.489	0.493
387.17	13547	15.03	17.2	21.89	0.613	0.591	0.593
389.35	10821	14.88	16.96	21.81	0.762	0.732	0.741
391.30	9096	25.00	17.18	22.03	0.916	0.884	0.893
392.11	9009	16.02	18.47	23.30	0.988	0.961	0.955
			2,5-DHBA				
372.14	21625	6.00	6.93	8.74	0.150	0.146	0.145
374.13	18050	6.37	7.16	9.18	0.192	0.182	0.183
376.19	15022	6.37	7.24		0.231	0.221	
378.15	11493	6.30	7.11	9.09	0.299	0.285	0.287
380.30	11033	7.51	8.52	11.04	0.373	0.356	0.364
382.22	10841	8.89			0.450		
384.7	10626		13.09	16.67		0.572	0.574
386.12	9328	11.22	13.01		0.663	0.649	
388.92	10001	16.35	18.66	23.56	0.905	0.871	0.866
			2,6-DHBA				
347.14	25428	6.71	7.57	9.76	0.138	0.131	0.133
349.32	21850		8.47	10.86		0.171	0.173
351.02	21816		10.03	12.97		0.204	0.208
353.26	18523		10.63	13.16		0.255	0.249
355.35	15258	9.68		14.01	0.336		0.323
357.20	16096	12.16	14.08	17.64	0.401	0.391	0.386
359.28	13293	12.26	14.15	18.02	0.491	0.477	0.479
361.38	11918	13.60	15.64	19.70	0.609	0.590	0.586
363.19	12636	16.84	19.38	24.13	0.713	0.692	0.679
365.17	9669	15.89	18.07	22.64	0.881	0.845	0.834
			3,4-DHBA				
387.12	21645	3.48	4.05	5.10	0.089	0.087	0.086
391.31	25272	6.00	7.17	9.12	0.132	0.133	0.133
393.33	21920	6.54	7.64	9.75	0.166	0.164	0.165
395.2	14469	5.22	6.15	7.90	0.201	0.200	0.202
397.32	18911	8.43	10.14	12.71	0.249	0.253	0.250
401.25	14491	9.46	11.23	14.17	0.367	0.367	0.365
403.26	14488	11.60	13.77	17.42	0.451	0.452	0.450
			3,5-DHBA				
407.36	21422	3.70	4.33	5.5	0.098	0.097	0.097
410.25	16696	3.81	4.52	5.72	0.130	0.130	0.129
413.16	12790	3.95	4.75	5.91	0.176	0.179	0.175
416.13	11739	4.56	5.39	6.75	0.238	0.237	0.234
419.21	6863	4.93	5.94	7.56	0.305	0.310	0.311
422.20	7240	4.84	5.77	7.39	0.407	0.409	0.412
425.23	7234	7.01	8.34	10.56	0.561	0.563	0.561

of these transitions could not be identified from the thermograms, and investigating the structure of these phases using other techniques was beyond the purpose of the present study. For all of the studied compounds no phase transitions were detected between the temperature of 298.15 K and the maximum temperature of the measured vapor pressures.

Vapor Pressure Measurements. The vapor pressures of the crystalline phase of each of the six dihydroxybenzoic acids were measured through a convenient temperature range using a mass-loss Knudsen effusion apparatus. This apparatus enables the simultaneous operation of three Knudsen cells with three different effusion orifices and has been described in detail together with the results obtained for benzoic acid and ferrocene.[16] A few changes have been introduced to the original apparatus design and to the lids of the effusion cells since 2001, when the previous effusion orifices made in brass foil were replaced by more precise orifices made in very thin platinum foil. Several other tests have been performed since then using several substances such as benzoic acid, ferrocene, benzophenone, and naphthalene. Results derived using this apparatus are also in excellent agreement with results obtained when using a more recent apparatus constructed in our research group.[17,18]

In a typical effusion experiment the loss of mass Δm of the samples during a convenient effusion time period t is determined by weighing the effusion cells to ± 0.01 mg before and after the effusion period in a system evacuated to a pressure near $1 \cdot 10^{-4}$ Pa. The samples are assumed to be in thermal equilibrium with a thermostatically controlled (to ± 0.001 K) silicone oil bath where the effusion cells are immersed. The temperature of the bath is measured using Amarell mercury thermometers, calibrated by Eichamt Wertheim (Germany), and graduated to 0.01 K. At the temperature T of the experiment, the vapor pressure p is calculated by eq 1:

$$p = (\Delta m / A_{\mathrm{o}} w_{\mathrm{o}} t)(2\pi RT/M)^{1/2} \tag{1}$$

where M is the molar mass of the effusing vapor, R is the gas constant, A_{o} is the area of the effusion hole, and w_{o} is the respective Clausing factor calculated by eq 2 with l being the thickness of the orifice and r its radius:

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

In this work, circular effusion orifices made in platinum foil of 0.0125 mm thickness were used. Their areas and Clausing factors were the following: orifice 1, $A_{\mathrm{o}}/\mathrm{mm}^2 = 0.663$, $w_{\mathrm{o}} = 0.990$; orifice 2, $A_{\mathrm{o}}/\mathrm{mm}^2 = 0.785$, $w_{\mathrm{o}} = 0.991$; and orifice 3,

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

effusion orifices	a	b	$\langle T\rangle$ K	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) kJ·mol^{-1}	R^2
			2,3-DHBA				
1	36.16 ± 0.21	13113 ± 75		109.0 ± 0.6	110.6 ± 0.6	48.07 ± 0.10	0.9998
2	36.11 ± 0.20	13100 ± 71		108.9 ± 0.6	110.5 ± 0.6	48.07 ± 0.09	0.9998
3	36.27 ± 0.24	13155 ± 83		109.4 ± 0.7	110.9 ± 0.7	48.14 ± 0.11	0.9997
mean	36.18 ± 0.25	13123 ± 88	354.20	109.1 ± 0.8	110.7 ± 0.8	48.09 ± 0.12	
			2,4-DHBA				
1	38.11 ± 0.18	14948 ± 68		124.3 ± 0.6	126.7 ± 0.6	58.63 ± 0.13	0.9998
2	38.10 ± 0.23	14956 ± 88		124.4 ± 0.7	126.8 ± 0.7	58.73 ± 0.16	0.9997
3	37.80 ± 0.25	14838 ± 97		123.4 ± 0.8	125.8 ± 0.8	58.49 ± 0.18	0.9997
mean	38.00 ± 0.26	14914 ± 98	384.16	124.0 ± 0.8	126.4 ± 0.8	58.62 ± 0.16	
			2,5-DHBA				
1	39.36 ± 0.43	15348 ± 164		127.6 ± 1.4	129.9 ± 1.3	58.85 ± 0.29	0.9993
2	39.64 ± 0.34	15469 ± 128		128.6 ± 1.1	130.9 ± 1.1	59.16 ± 0.23	0.9996
3	39.50 ± 0.33	15413 ± 124		128.2 ± 1.0	130.5 ± 1.0	59.04 ± 0.22	0.9997
mean	39.50 ± 0.43	15410 ± 161	380.5	128.1 ± 1.4	130.4 ± 1.3	59.02 ± 0.29	
			2,6-DHBA				
1	35.34 ± 0.24	12952 ± 85		107.7 ± 0.7	109.3 ± 0.7	48.76 ± 0.11	0.9997
2	35.47 ± 0.26	13013 ± 92		108.2 ± 0.8	109.8 ± 0.7	48.93 ± 0.12	0.9997
3	34.89 ± 0.37	12807 ± 132		106.5 ± 1.1	108.1 ± 1.1	48.66 ± 0.18	0.9992
mean	35.23 ± 0.34	12924 ± 121	356.16	107.5 ± 1.0	109.1 ± 1.0	48.78 ± 0.16	
			3,4-DHBA				
1	38.37 ± 0.41	15798 ± 161		131.4 ± 1.3	134.1 ± 1.4	65.14 ± 0.34	0.9995
2	38.86 ± 0.30	15993 ± 120		133.0 ± 1.0	135.7 ± 1.0	65.54 ± 0.25	0.9997
3	38.85 ± 0.21	15989 ± 82		132.9 ± 0.7	135.6 ± 0.7	65.54 ± 0.16	0.9999
mean	38.69 ± 0.37	15927 ± 145	395.19	132.3 ± 1.2	135.1 ± 1.2	65.41 ± 0.30	
			3,5-DHBA				
1	38.72 ± 0.52	16717 ± 218		139.0 ± 1.8	142.3 ± 1.8	72.08 ± 0.52	0.9991
2	38.96 ± 0.49	16820 ± 205		139.8 ± 1.7	143.2 ± 1.7	72.31 ± 0.48	0.9993
3	39.20 ± 0.26	16921 ± 108		140.7 ± 0.9	144.0 ± 0.9	72.57 ± 0.26	0.9998
mean	38.96 ± 0.51	16819 ± 212	416.30	139.8 ± 1.8	143.2 ± 1.8	72.32 ± 0.50	

[a] a and b are from Clausius−Clapeyron equation $\ln(p/\mathrm{Pa}) = a - b(\mathrm{K}/T)$ and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)/R$. $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) and $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) were derived from the Clarke−Glew eq 2 considering the reference pressure $p^0 = 0.1$ MPa and the estimated value $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}} = -28$ J·K^{-1}·mol^{-1} for all of the isomers. Experimental uncertainties of the mean values were calculated as twice the standard deviation.

$A_{\mathrm{o}}/\mathrm{mm}^2 = 0.996$, $w_{\mathrm{o}} = 0.992$. The accuracy of the measured pressures is estimated to be better than ± 0.01 Pa.

Static Bomb Combustion Calorimetry. The energies of combustion for all of the studied isomers were measured in a static bomb calorimeter (the bomb with an internal volume of 0.290 dm^3 was equipped with a twin valve system) installed in our laboratory, as it has been previously reported.[19−21]

The energy equivalent of the calorimeter ε(calor) was determined using benzoic acid [CAS RN 65-85-0, standard reference material (SRM 39j) supplied by National Institute of Standards and Technology (NIST)], having a massic energy of combustion, under bomb conditions, of −(26434 ± 3) J·g^{-1}. Eight calibration experiments were made under oxygen at p = 3.04 MPa, with 1.00 cm^3 of water added to the bomb, leading to an energy equivalent of the calorimeter, ε(calor) = (15546.3 ± 1.3) J·K^{-1} (the uncertainty quoted is the standard deviation of the mean), corrected to an energy equivalent ε(calor) corresponding to an average mass of water added to the calorimeter of 2900.0 g.

For the combustion experiments, the crystalline samples were burnt in pellet form. As the compound 2,6-DHBA seems to be hygroscopic and was very difficult to keep in pellet form, it has been sealed in Melinex bags. The massic energy of combustion of dry Melinex was taken as $-\Delta_{\mathrm{c}}u^{\mathrm{o}} = -(22902 \pm 5)$ J·g^{-1}.[22] Also, as the available amount of sample of this compound was small, n-hexadecane (CAS RN 544-76-3, Aldrich Chemical Co., ≥ 99 %) has been used as an auxiliary of the combustion measurements, to achieve a rise in temperature close to that obtained in the calibration experiments. The measured standard massic energy of combustion of n-hexadecane was $-\Delta_{\mathrm{c}}u^{\mathrm{o}}(\mathrm{l}) = (47150.4 \pm 2.4)$ J·g^{-1}.

All of the samples were ignited at $T = (298.150 \pm 0.001)$ K, in oxygen at p = 3.04 MPa, with 1.00 cm^3 of deionized water previously added to the bomb. The electrical energy for ignition ΔU(ign) was determined from the change in potential difference across a 1400 μF capacitor when discharged through the platinum ignition wire. For the cotton thread fuse, of empirical formula $\mathrm{CH_{1.686}O_{0.843}}$, the massic energy of combustion is $\Delta_{\mathrm{c}}u^{\mathrm{o}} = -16250$ J·g^{-1}.[23] The corrections for nitric acid formation, $\Delta U(\mathrm{HNO_3})$, were based on the value of −59.7 kJ·mol^{-1},[24] for the molar energy of formation of 0.1 mol·dm^{-3} $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2}$, $\mathrm{O_2}$, and $\mathrm{H_2O(l)}$. An estimated pressure coefficient of specific energy, $(\partial u/\partial p)_T = -0.2$ J·g^{-1}·MPa^{-1} at T = 298.15 K, a typical value for most organic compounds,[25] was assumed. The mass of the compound, m(cpd), used in each experiment was determined from the total mass of carbon dioxide, $m(\mathrm{CO_2}$, total), produced after allowance for that formed from the combustion of the cotton thread fuse, Melinex, or n-hexadecane. For each compound, the standard massic energy of combustion, $\Delta_{\mathrm{c}}u^{\mathrm{o}}$, was calculated by the procedure given by Hubbard et al.[26]

Results and Discussion

The vapor pressures of the six compounds calculated at several temperatures through eq 1 are presented in Table 2. Table 3 presents, for the three effusion orifices, the detailed parameters of the Clausius−Clapeyron equation, $\ln(p/\mathrm{Pa}) = a - b(\mathrm{K}/T)$, where a is a constant and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)/R$, and the standard molar enthalpies of sublimation at the mean temperature of the experiments, $T = \langle T\rangle$. The values of the molar standard enthalpy and Gibbs energy of sublimation, at the reference temperature θ = 298.15 K, are also presented in this

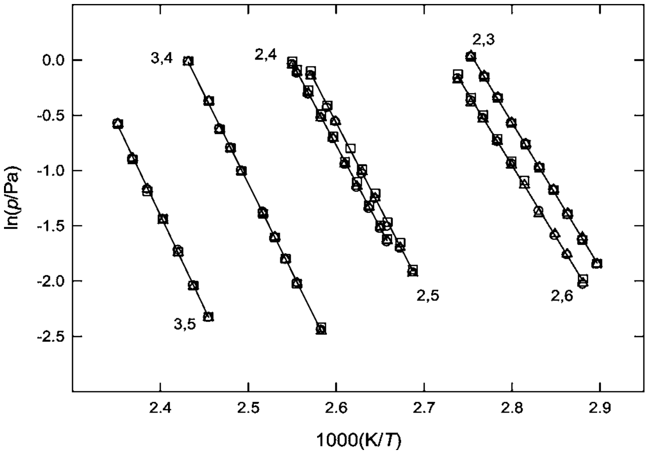

Figure 1. Plots of ln p against $1/T$ for the isomers of dihydroxybenzoic acid. □, small effusion orifices; ○, medium effusion orifices; Δ, large effusion orifices.

table. These values were derived fitting the experimental results of the vapor pressures by the Clarke and Glew eq 3.[27]

$$R\ln\left(\frac{p}{p^0}\right) = -\frac{\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(\theta)}{\theta} + \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (3)$$

where p is the vapor pressure at the temperature T, p^0 is a selected reference pressure ($p^0 = 10^5$ Pa in this work), R is the molar gas constant, and $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)$ is the difference in molar heat capacity at constant pressure between the gaseous and the crystalline phase.

The value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)$ inserted in eq 3 was estimated through eq 4[7] from the gas phase heat capacity, which was also estimated using a group contribution method as $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 153.7$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for all of the studied isomers. Equation 4 is just a rearrangement of eq 5 proposed by Chickos et al.[28] for the estimation of $\{C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) - C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})\}$, at the temperature of 298.15 K, from $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$ values. From the estimated value of $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$, eq 4 yields $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta) = -28$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta) = -\{0.9 + 0.176C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g})\}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} \quad (4)$$

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

The plots of ln(p/Pa) versus $1/T$ for the five studied compounds are presented in Figure 1.

Table 4 presents the results for one typical combustion experiment on each compound, with $\Delta m(\mathrm{H_2O})$ being the deviation of the mass of water added to the calorimeter from 2900.0 g, the mass assigned for ε(calor); the internal energy for the isothermal bomb process, ΔU(IBP), is calculated according to eq 6, where $c_p(\mathrm{H_2O, l})$ is the heat capacity of liquid water, ε_{f} is the energy of the bomb contents after ignition, ΔT_{ad} is the temperature rise corrected for adiabatic conditions, ΔU_{ign} is the energy of ignition, and the ΔU_{Σ} is the correction to the standard state. The remaining terms are as previously described.[26]

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + \Delta m(\mathrm{H_2O})c_p(\mathrm{H_2O, l}) + \varepsilon_{\mathrm{f}}\}\Delta T_{\mathrm{ad}} + \Delta U(\mathrm{ign}) \quad (6)$$

The individual results of all combustion experiments, together with the mean value and its standard deviation, for each compound, are given in Table 5. The derived standard molar energies and enthalpies of combustion, $\Delta_{\mathrm{c}}U_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$ and $\Delta_{\mathrm{c}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, and the standard molar enthalpies of formation for the compounds in the condensed phase, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, at $T = 298.15$ K, are listed in Table 6. This table also presents the standard molar enthalpies of sublimation and of formation in the gaseous phase at that temperature. The uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities, in accordance with the recommended thermochemical practice.[29]

The values for $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$ were derived from the corresponding values for $\Delta_{\mathrm{c}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, using the standard molar enthalpies of formation of $\mathrm{H_2O(l)}$ and $\mathrm{CO_2(g)}$, at $T = 298.15$ K, $-(285.830 \pm 0.042)$ $\mathrm{kJ\cdot mol^{-1}}$[28] and $-(393.51 \pm 0.13)$ $\mathrm{kJ\cdot mol^{-1}}$,[30] respectively.

According to Price et al.[11] the performance of the isomers of dihydroxybenzoic acids as good MALDI matrices follows the decreasing sequence: (2,3-DHBA, 2,5-DHBA) > 2,6-DHBA >

Table 4. Typical Combustion Experiments, at $T = 298.15$ K[a]

	2,3-DHBA	2,4-DHBA	2,5-DHBA	2,6-DHBA	3,4-DHBA	3,5-DHBA
$m(\mathrm{CO_2}$, total)/g	1.89196	1.88990	1.44954	1.95566	1.99464	1.82364
m(cpd)/g	0.94468	0.94343	0.41154	0.90769	0.99561	0.91038
m(fuse)/g	0.00227	0.00254	0.00231	0.00264	0.00281	0.00242
m(Melinex)/g				0.06241		
m(hexadecane)/g			0.20041			
ΔT_{ad}/K	1.11887	1.11347	1.09610	1.16671	1.17816	1.07537
$\varepsilon_{\mathrm{f}}/(\mathrm{J\cdot K^{-1}})$	14.77	14.76	14.84	14.87	14.85	14.75
$\Delta m(\mathrm{H_2O})$/g	−0.8	−3.7	−1.5	+0.6	−3.8	−0.5
$\Delta U(\mathrm{IBP})^b$/J	17406.37	17308.84	17048.59	18157.48	18314.13	16731.05
ΔU(fuse)/J	36.86	41.25	37.51	42.87	45.63	39.30
$\Delta U(\mathrm{HNO_3})$/J	0.29	6.40	0.46	0.52	7.10	0.36
ΔU(ign)/J	0.70	0.70	1.10	0.82	0.66	0.59
ΔU(Melinex)/J				1429.40		
ΔU(hexadecane)/J			9449.33			
ΔU_{Σ}/J	17.02	17.01	9.53	17.66	18.05	16.33
$-\Delta_{\mathrm{c}}u^{\circ}/(\mathrm{J\cdot g^{-1}})$	18368.34	18278.18	18349.99	18362.03	18323.79	18316.59

[a] $m(\mathrm{CO_2}$, total) is the total mass of $\mathrm{CO_2}$ formed in the experiment; m(cpd) is the mass of compound burnt in the experiment; m(fuse) is the mass of fuse (cotton) used in the experiment; ΔT_{ad} is the corrected temperature rise; ε_{f} is the energy equivalent of contents in the final state; $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 2900.0 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta U(\mathrm{HNO_3})$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for the ignition; ΔU_{Σ} is the energy correction to the standard state; $\Delta_{\mathrm{c}}u^{\circ}$ is the standard massic energy of combustion. [b] ΔU(IBP) includes ΔU(ign).

Table 5. Individual Values of the Massic Energy of Combustion, $\Delta_c u^\circ$, at $T = 298.15$ K

2,3-DHBA	2,4-DHBA	2,5-DHBA	2,6-DHBA	3,4-DHBA	3,5-DHBA
18353.58	18277.15	18343.77	18321.09	18311.86	18353.78
18355.27	18278.18	18349.99	18370.45	18315.95	18322.76
18368.34	18273.16	18348.87	18375.47	18318.74	18332.39
18356.93	18276.20	18341.21	18360.62	18348.81	18326.75
18381.87	18258.05	18335.69	18362.03	18372.70	18316.59
18364.32	18252.58	18331.99	18334.58	18323.79	18355.12
	18249.56		18342.21	18309.16	18369.01
			18348.87		
$-\langle\Delta_c u^\circ\rangle/(\mathrm{J\cdot g^{-1}})$					
18363.4 ± 4.4	18266.4 ± 4.7	18341.9 ± 2.9	18351.9 ± 6.6	18328.7 ± 8.8	18339.5 ± 7.5

Table 6. Derived Standard ($p^0 = 0.1$ MPa) Molar Values in Condensed and Gaseous Phases, at $T = 298.15$ K

compound	$-\Delta_c U_m^o$ / kJ·mol^{-1}	$-\Delta_c H_m^o$ / kJ·mol^{-1}	$\Delta_f H_m^o$(cr) / kJ·mol^{-1}	$\Delta_{cr}^{g} H_m^o$ / kJ·mol^{-1}	$\Delta_f H_m^o$(g) / kJ·mol^{-1}
2,3-DHBA	2830.1 ± 1.5	2828.9 ± 1.5	−783.2 ± 1.8	110.7 ± 0.8	−672.5 ± 2.0
2,4-DHBA	2815.3 ± 1.6	2814.1 ± 1.6	−798.0 ± 1.8	126.4 ± 0.8	−671.6 ± 2.1
2,5-DHBA	2826.9 ± 1.1	2825.7 ± 1.1	−786.4 ± 1.4	130.4 ± 1.3	−656.0 ± 1.9
2,6-DHBA	2828.4 ± 2.1	2827.2 ± 2.1	−784.9 ± 2.3	109.1 ± 1.0	−675.8 ± 2.5
3,4 DHBA	2824.9 ± 2.8	2823.7 ± 2.8	−788.3 ± 2.9	135.1 ± 1.2	−653.2 ± 3.1
3,5 DHBA	2826.5 ± 2.4	2825.3 ± 2.4	−786.9 ± 2.6	143.2 ± 1.8	−643.7 ± 3.2

Table 7. Performance as a MALDI Matrix and Thermodynamic Parameters of Sublimation of the Isomers of Dihydroxybenzoic Acid

performance as MALDI matrix[a]	2,3-DHBA	2,5-DHBA	2,6-DHBA	3,5-DHBA	3,4-DHBA	2,4-DHBA
$\Delta_{cr}^{g} H_m^o$[b]	116 ± 4	109 ± 3	111 ± 7	135 ± 6	153 ± 9	126 ± 6
$\Delta_{cr}^{g} H_m^o$ (298.15 K)[c]	110.7 ± 0.8	130.4 ± 1.3	109.1 ± 1.0	143.2 ± 1.8	134.1 ± 1.4	126.4 ± 0.8
$\Delta_{cr}^{g} G_m^o$ (298.15 K)[c]	48.09 ± 0.12	59.02 ± 0.29	48.78 ± 0.16	72.32 ± 0.50	65.14 ± 0.34	58.62 ± 0.16

[a] Decreasing order in performance: (2,3-DHBA, 2,5-DHBA) > 2,6-DHBA > (3,5-DHBA, 3,4-DHBA) > 2,4-DHBA. [b] Ref 11 (temperature not defined). [c] This work.

(3,5-DHBA, 3,4-DHBA) > 2,4-DHBA. Price et al. concluded that there was no connection between that performance and the enthalpies of sublimation derived by them, as shown in Table 7. Despite the large uncertainties of those results, our results strongly deviate from the enthalpies of sublimation presented by Price et al. for the 2,5- and 3,4-isomers, but there is also no trend on the present measured enthalpies of sublimation and the stated MALDI performance of the isomers of dihydroxybenzoic acid. Furthermore, there is also no connection between that performance and the volatility of these compounds measured as $\Delta_{cr}^{g} G_m^o$ (298.15 K).

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