

Standard Enthalpies of Formation of Some Methyl Esters of Benzene Carboxylic Acids

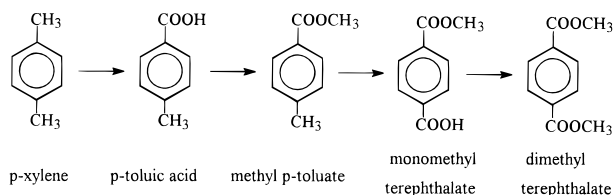
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Enthalpies of combustion of methyl benzoate (I), methyl *o*-toluate (II), methyl *m*-toluate (III), methyl *p*-toluate (IV), monomethyl terephthalate (V), dimethyl phthalate (VI), and trimethyl 1,2,4-benzenetricarboxylate (VII) have been determined using bomb calorimetry. Enthalpies of evaporation of these substances (I–VII), and also of dimethyl terephthalate (VIII) and dimethyl isophthalate (IX), have been measured calorimetrically. Standard molar enthalpies of formation in the gas phase have been calculated (in kJ·mol⁻¹): (I) (–277.7 ± 1.3), (II) (–301.5 ± 1.9), (III) (–309.6 ± 1.6), (IV) (–308.7 ± 1.6), (V) (–648.7 ± 2.3), (VI) (–606.2 ± 2.6), (VII) (–963.3 ± 2.9), (VIII) (–627.4 ± 1.1), and (IX) (–627.1 ± 1.1). Values of additive constants have been obtained to calculate enthalpies of formation of methyl esters of benzene carboxylic acids in the crystal and gas states.

Introduction

Industrial synthesis of dimethyl terephthalate is based on liquid-phase oxidation of *p*-xylene and esterification of acids by methanol by the following scheme:



A number of byproducts are formed beside these acids and esters. The most important byproducts are methyl benzoate, dimethyl isophthalate, dimethyl phthalate, and trimethyl 1,2,4-benzenetricarboxylate.

Modern technology requires a detailed thermodynamic analysis of all stages of industrial processes to elaborate optimal conditions of production procedures. This fact encouraged measurements of combustion and evaporation enthalpies of MEBCA (Table 1). Experimental values of $\Delta_f H_m^\circ$ and $\Delta_{\text{sub(vap)}} H_m^\circ$ for some important substances of that class are absent. Table 1 shows discrepancies among thermodynamic values. There is no good correlation of enthalpies of sublimation for monomethyl and dimethyl terephthalates and enthalpies of vaporization for dimethyl phthalate and trimethyl 1,2,4-benzenetricarboxylate. The data for enthalpy of vaporization for methyl benzoate requires critical analysis in order to recommend the most reliable value.

Experimental measurements of enthalpies of combustion and evaporation for methyl benzoate (I), methyl *o*-toluate (II), methyl *m*-toluate (III), methyl *p*-toluate (IV), monomethyl terephthalate (V), dimethyl phthalate (VI), and trimethyl 1,2,4-benzenetricarboxylate (VII) and enthalpies of sublimation for dimethyl terephthalate (VIII) and dimethyl isophthalate (IX) were made. The method of addi-

tive calculation of enthalpies of formation for compounds of this class is proposed.

Experimental Section

All substances were synthesized and purified in the Scientific and Technical Center of Industrial Association "Khimvolokno" (Mogilev). The purity of the samples determined by chromatographic analysis was 99.9%, except for trimethyl 1,2,4-benzenetricarboxylate, which was 99.5%.

Enthalpies of combustion were determined in two bomb calorimeters with isothermal shields. The accuracy of measurements of combustion energy is ± 0.02% (Frenkel et al., 1992). The calorimeters were calibrated with benzoic acid (trade K-1) with a combustion energy (–26 434.6 ± 4.5) J·g⁻¹.

Substances in the form of tablets pressed in air (V) and with terylene (I–IV) or polyethylene (VI, VII) ampules were burned in a platinum crucible. Energies of combustion of terylene and polyethylene determined in a separate series of measurements were (–22 879.7 ± 11.0) J·g⁻¹ and (–46 435.1 ± 6.8) J·g⁻¹, respectively.

Doubly distilled water (1 cm³) was placed in the calorimetric bomb. The bomb was flushed and filled with oxygen free of organic impurities, CO₂, and water under a pressure of 3.04 MPa. The samples were ignited by discharge from a capacitor battery with a capacity of 0.01 F through a platinum wire (diameter 0.05 mm). The temperature in the calorimetric vessel was measured by a 100-Ω platinum resistance thermometer. The completeness of burning was checked by gravimetric analysis of combustion products using the Rossini (1956) method, and the average was (99.96 ± 0.05)%. The Washburn corrections were calculated by the Prosen (1956) method using recommendations by the Alexandrov et al. (1971)

The experimental results on the energy of combustion of the substances (I–VII) are given in Table 2. These data were used to calculate standard enthalpies of combustion and formation using $\Delta_f H_m^\circ(\text{CO}_2, \text{g}, 298.15 \text{ K}) = (-393.514 \pm 0.130) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{g}, 298.15 \text{ K}) = (-285.830 \pm 0.042) \text{ kJ}\cdot\text{mol}^{-1}$.

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Table 1. Literature Data on Enthalpies of Formation and Evaporation for Some Methyl Esters of Benzene Carboxylic Acids

compounds	<i>T</i> /K	$\Delta_{\text{vap}}H_m^{\text{P}}(\Delta_{\text{sub}}H_m^{\text{P}})$ (<i>T</i>)/(kJ·mol ⁻¹)	$\Delta_f H_m^{\text{O}}(\text{cond.}, 298 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_f H_m^{\text{P}}(\text{g}, 298 \text{ K})$ (kJ·mol ⁻¹)
monomethyl terephthalate	473	(86.4) { <i>P</i> = <i>f</i> (<i>T</i>)} ^a		
	476	(77.5) { <i>P</i> = <i>f</i> (<i>T</i>)} ^b		
dimethyl terephthalate	393	(94.0) { <i>P</i> = <i>f</i> (<i>T</i>)} ^a	-732.62 ± 1.00 (cr.) ^c	
	298	53.65 ± 0.54 { <i>P</i> = <i>f</i> (<i>T</i>)} ^d		
methyl benzoate	298	55.57 ± 0.04 {calor.} ^e		
	335	52.84 ± 0.53 { <i>P</i> = <i>f</i> (<i>T</i>)} ^f		
	381	50.00 ± 0.20 { <i>P</i> = <i>f</i> (<i>T</i>)} ^g		
	387	47.29 ± 4.43 { <i>P</i> = <i>f</i> (<i>T</i>)} ^h	-343.55 ± 2.60 (liq.) ^h	-288.09 ± 5.14 ^h
	453	43.41 ± 0.43 { <i>P</i> = <i>f</i> (<i>T</i>)} ^e	-342.59 (liq.) ⁱ	
methyl <i>m</i> -toluate	388	53.5 { <i>P</i> = <i>f</i> (<i>T</i>)} ^j		
dimethyl isophthalate			-730.90 ± 1.00 (cr.) ^c	
dimethyl phthalate	480	60.5 { <i>P</i> = <i>f</i> (<i>T</i>)} ^b		
trimethyl 1,2,4-benzenetricarboxylate	473	60.4 { <i>P</i> = <i>f</i> (<i>T</i>)} ^a		

^a Calculated from the data of Kraus et al. (1962). ^b Calculated from the data of Olevsky et al. (1958). ^c Colomina et al. (1972). ^d Ravdel and Danilov (1968). ^e Kusano and Wadsö (1971). ^f Nickolsky (1966). ^g Katayama (1988). ^h Calculated from the data of Hall and Baldt (1971). ⁱ Auer (1961). ^j Calculated from the data of Murogova et al. (1974).

The enthalpies of sublimation and vaporization were determined in a differential heat-conducting microcalorimeter of Calvet type using special calorimetric cells. A detailed description of the cells was given earlier (Sevruck et al., 1990). The investigated samples were put into hermetic sealed ampules made from stainless steel supplied with an aluminum membrane. After a preliminary thermostating of the calorimeter, the membrane was pierced by a special demountable rod and the heating flux needed for evaporation was recorded. The calorimeter was calibrated by sublimation of benzoic acid (trade K-1) and by vaporization of decane and doubly distilled water. It was found that the reproducibility of enthalpy of evaporation measurements is ±0.5%.

The enthalpy change, ΔH , of specimens and the molar enthalpies of evaporation ΔH_m^{P} were calculated from the expressions

$$\Delta H = K^{-1} \cdot \int_{\tau=0}^{\tau=\tau_2} \Delta E d\tau \quad (1)$$

$$\Delta H_m^{\text{P}} = \Delta H \cdot M \cdot m^{-1} \quad (2)$$

where K is the cell constant, ΔE is the thermocouple potential difference corresponding to the temperature imbalance between cell and calorimeter thermostat at time τ , τ_2 is the experiment duration, m is the mass of a specimen in a vacuum, and M is molar mass.

Experimental results on enthalpies of evaporation of substances (I–IX) are represented in Table 3.

Temperatures and enthalpies of fusion for substances (I–IV) were measured in a vacuum adiabatic calorimeter TAU-1, described in our earlier publication (Kabo et al., 1992).

Results and Discussion

Enthalpies of evaporation and formation of benzene carboxylic acids (MEBCA) in different phases obtained from calorimetric measurements are summarized in Table 4. This table includes the most reliable literature data taken from Table 1. Experimental values of vaporization and sublimation enthalpies were reduced to the base temperature 298.15 K taking into consideration the heat capacities of condensed and gas phases.

Values of $\Delta_f H_m^{\text{P}}$ for MEBCA in the gas state can be represented as a sum of terms based on the principles described earlier (Kabo et al., 1995; Isaev and Isaeva, 1981). The property value P may be represented as

$$P = P_B + \sum n_i P_i + \sum n_{jk} P_{jk} \quad (3)$$

where P is a physical or chemical property of MEBCA or methylbenzenes (MB), P_B is a physical or chemical property of benzene, P_i is a property corresponding to H atom replacement in the benzene ring by COOCH₃ or CH₃ group, n_i ($i = 1, 2$) is a number of these replacements, P_{jk} ($k = 2, 3, 4$) is a property corresponding to 1–2, 1–3, 1–4 interactions of COOCH₃ and CH₃ groups in the benzene ring, and n_{jk} ($j = 1, 2, 3$) is a number of possible pair, COOCH₃–COOCH₃, CH₃–CH₃, COOCH₃–CH₃, interactions.

The order in sequence of replacements leading from benzene to the compounds represented by P is not important; only the sum is significant. For example, eq 3 for trimethyl 1,2,4-benzenetricarboxylate is expressed as

$$P(1,2,4\text{-C}_6\text{H}_3(\text{COOCH}_3)_3) = P_B(\text{C}_6\text{H}_6) + 3P_1(\text{COOCH}_3) + P_{12}(\text{COOCH}_3\text{-COOCH}_3) + P_{13}(\text{COOCH}_3\text{-COOCH}_3) + P_{14}(\text{COOCH}_3\text{-COOCH}_3)$$

To calculate enthalpies of formation, $P = \Delta_f H_m^{\text{P}}(\text{g}, 298.15 \text{ K})$ and $P_B = \Delta_f H_m^{\text{P}}(\text{C}_6\text{H}_6, \text{g}, 298.15 \text{ K}) = (82.6 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ (Pedley, 1994) were used.

The parameters, P_i and P_{jk} , for enthalpies of formation of gaseous MEBCA and MB were obtained by the least-squares method. But the values $P_{13}(\text{COOCH}_3\text{-COOCH}_3) = (-2.0 \pm 1.5)$, $P_{23}(\text{CH}_3\text{-CH}_3) = (1.6 \pm 1.3)$, $P_{14}(\text{COOCH}_3\text{-COOCH}_3) = (0.4 \pm 3.1)$, and $P_{24}(\text{CH}_3\text{-CH}_3) = (0.3 \pm 2.1)$ are comparable with the error of their determination. This result implies a weak interaction of COOCH₃ and CH₃ groups in the 1–3 and in the 1–4 position. Therefore the 1–3 and 1–4 interactions of COOCH₃ and CH₃ groups in benzene ring can be ignored. The calculation formula for benzene derivatives with COOCH₃ and CH₃ groups becomes

$$P = P_B(\text{C}_6\text{H}_6) + n_1 P_1(\text{COOCH}_3) + n_2 P_2(\text{CH}_3) + n_{12} P_{12}(\text{COOCH}_3\text{-COOCH}_3) + n_{22} P_{22}(\text{CH}_3\text{-CH}_3) + n_{32} P_{32}(\text{COOCH}_3\text{-CH}_3) \quad (4)$$

and for the trimethyl 1,2,4-benzenetricarboxylate

$$P(1,2,4\text{-C}_6\text{H}_3(\text{COOCH}_3)_3) = P_B(\text{C}_6\text{H}_6) + 3P_1(\text{COOCH}_3) + P_{12}(\text{COOCH}_3\text{-COOCH}_3)$$

The matrix of coefficients n_i and n_{jk} according to eq 4 is represented in Table 5. The following values of additive

Table 2. Energy of Combustion $\Delta_c U^P$ for Some Methyl Esters of Benzene Carboxylic Acids at $T = 298.15 \text{ K}^a$

m_1/g	m_2/g	$-\delta/K$	$k \cdot 10^3$	$\Delta T/K$	q_i/J	q_{HNO_3}/J	q_2/J	$\Sigma q_W/J$	cal. ^b	$\Delta_c U^P/(J \cdot g^{-1})$
Methyl <i>p</i> -Toluuate (cr)										
0.591 22	0.028 33	0.024 53	1.31	1.250 57	2.0	10.1	648.2	10.9	A	30 463.5
0.624 91	0.028 13	0.031 69	1.13	1.319 61	2.0	11.3	643.6	11.5	A	30 475.7
0.582 35	0.027 15	0.010 87	1.21	1.230 83	2.0	9.8	621.2	10.7	A	30 468.2
0.548 29	0.021 44	0.036 23	1.19	1.152 17	2.0	10.1	490.5	9.9	A	30 457.0
0.623 19	0.021 09	0.023 91	1.11	1.304 79	2.0	10.1	482.5	11.4	A	30 465.4
0.624 73	0.025 72	0.023 24	1.14	1.314 86	2.0	11.1	588.5	11.5	A	30 459.7
average value: 30 464.9 \pm 6.9										
$\Delta_c U_m^P(\text{cr}, 298.15 \text{ K}) = -(4575.12 \pm 1.04)$										
$\Delta_c H_m^P(\text{cr}, 298.15 \text{ K}) = -(4578.84 \pm 1.04)$										
Monomethyl Terephthalate (cr)										
0.410 65		0.038 06	1.03	0.597 04	2.0	4.4		6.7	A	21 687.0
0.552 10		0.035 44	1.10	0.802 66	2.0	5.6		9.4	A	21 687.3
0.459 38		0.045 12	1.06	0.667 68	2.0	4.9		7.6	A	21 680.6
0.480 82		0.047 09	1.03	0.698 31	2.0	5.7		8.0	A	21 662.9
0.421 22		0.071 59	0.96	0.614 01	2.0	4.8		6.9	B	21 672.4
0.632 38		0.070 26	0.99	0.922 54	2.0	7.5		10.9	B	21 689.5
average value: 21 680.0 \pm 10.9										
$\Delta_c U_m^P(\text{cr}, 298.15 \text{ K}) = -(3905.86 \pm 1.96)$										
$\Delta_c H_m^P(\text{cr}, 298.15 \text{ K}) = -(3905.86 \pm 1.96)$										
Methyl Benzoate (liq.)										
0.590 33	0.068 24	0.033 07	1.14	1.254 03	2.0	11.3	1561.3	12.0	A	29 046.2
0.632 21	0.022 99	0.034 67	1.12	1.265 83	2.0	9.8	526.0	11.9	A	29 040.9
0.377 20	0.022 15	0.039 98	1.07	0.768 22	2.0	6.6	506.8	6.8	A	29 040.5
0.650 52	0.027 75	0.030 62	1.16	1.309 28	2.0	10.7	634.9	12.4	A	29 051.5
0.599 16	0.022 27	0.035 85	1.18	1.200 75	2.0	10.7	509.5	11.2	A	29 047.5
0.567 42	0.022 94	0.038 21	1.06	1.139 87	2.0	9.4	524.9	10.6	A	29 045.8
average value: 29 045.4 \pm 4.4										
$\Delta_c U_m^P(\text{l}, 298.15 \text{ K}) = -(3954.53 \pm 0.60)$										
$\Delta_c H_m^P(\text{l}, 298.15 \text{ K}) = -(3957.01 \pm 0.60)$										
Methyl <i>m</i> -Toluuate (liq.)										
0.525 96	0.027 87	0.021 83	1.14	1.121 97	2.0	6.3	637.7	9.6	A	30 620.7
0.393 35	0.023 99	0.037 13	1.17	0.843 57	2.0	4.5	548.9	6.9	A	30 607.8
0.493 84	0.024 98	0.028 05	1.12	1.051 25	2.0	6.0	571.5	8.9	A	30 609.2
0.615 23	0.026 41	0.025 41	1.17	1.302 59	2.0	6.6	604.3	11.3	A	30 614.4
0.555 75	0.024 33	0.031 90	1.13	1.177 20	2.0	5.7	556.7	10.1	A	30 609.8
average value: 30612.4 \pm 6.6										
$\Delta_c U_m^P(\text{l}, 298.15 \text{ K}) = -(4597.27 \pm 1.00)$										
$\Delta_c H_m^P(\text{l}, 298.15 \text{ K}) = -(4600.99 \pm 1.00)$										
Methyl <i>o</i> -Toluuate (liq.)										
0.321 77	0.017 88	0.054 28	1.10	0.688 02	2.0	6.6	409.1	5.5	A	30 684.4
0.568 31	0.022 85	0.040 01	1.15	1.204 38	2.0	10.1	545.2	10.3	A	30 699.0
0.482 39	0.021 16	0.038 47	1.09	1.024 43	2.0	8.7	484.1	8.6	A	30 680.9
0.548 52	0.024 69	0.033 00	1.12	1.165 80	2.0	9.7	564.9	10.0	A	30 680.6
0.547 06	0.026 36	0.049 68	1.04	1.169 62	2.0	9.5	602.7	10.0	B	30 692.9
average value: 30 687.6 \pm 10.0										
$\Delta_c U_m^P(\text{l}, 298.15 \text{ K}) = -(4608.56 \pm 1.50)$										
$\Delta_c H_m^P(\text{l}, 298.15 \text{ K}) = -(4612.28 \pm 1.50)$										
Trimethyl 1,2,4-Benzenetricarboxylate (liq.)										
0.981 74	0.065 52	0.032 09	1.12	1.607 31	2.0	6.8	3047.1	18.3	A	21 326.2
0.601 29	0.044 30	0.046 86	1.13	0.997 74	2.0	4.8	2057.1	10.5	A	21 338.4
0.677 88	0.048 61	0.033 30	1.15	1.120 60	2.0	5.4	2257.2	12.0	A	21 336.6
0.537 76	0.038 50	0.042 44	1.08	0.889 25	2.0	4.3	1787.8	9.2	A	21 349.5
0.701 55	0.052 14	0.044 19	1.03	1.170 61	2.0	6.3	2421.1	12.5	B	21 344.2
average value: 21 337.2 \pm 9.4										
$\Delta_c U_m^P(\text{l}, 298.15 \text{ K}) = -(5381.74 \pm 2.36)$										
$\Delta_c H_m^P(\text{l}, 298.15 \text{ K}) = -(5381.74 \pm 2.36)$										
Dimethyl Phthalate (liq.)										
0.830 52	0.055 06	0.018 38	1.12	1.512 76	2.0	6.6	2556.7	15.6	A	24 102.5
0.617 16	0.053 84	0.041 48	1.00	1.168 12	2.0	6.3	2500.1	11.3	B	24 100.0
0.684 93	0.056 43	0.039 65	1.02	1.285 15	2.0	6.3	2620.3	12.7	B	24 082.0
0.679 06	0.050 68	0.022 73	1.12	1.254 07	2.0	6.6	2353.3	12.5	A	24 091.6
0.614 89	0.032 28	0.028 39	1.21	1.093 01	2.0	5.7	1499.4	10.9	A	24 085.8
0.607 11	0.041 38	0.018 57	1.15	1.109 43	2.0	5.7	1921.5	10.9	A	24 103.3
average value: 24 094.2 \pm 9.5										
$\Delta_c U_m^P(\text{l}, 298.15 \text{ K}) = -(4678.77 \pm 1.85)$										
$\Delta_c H_m^P(\text{l}, 298.15 \text{ K}) = -(4680.01 \pm 1.85)$										

^a m_1 , mass of the substance; m_2 , mass of auxiliary substance; δ , correction for the heat exchange between the calorimeter vessel and surroundings; k , cooling constant of the calorimeter; ΔT , corrected temperature rise; q_i , correction for ignition; q_{HNO_3} , correction for nitric acid formation; q_2 , correction for auxiliary substances combustion; Σq_W , sum of the Washburn corrections. ^b Calorimeters with energetic equivalents $W(A) = (14\,938.6 \pm 6.4) \text{ J} \cdot \text{K}^{-1}$, $W(B) = (14\,889.9 \pm 5.6) \text{ J} \cdot \text{K}^{-1}$.

Table 3. Enthalpies of Evaporation for Some Methyl Esters of Benzene Carboxylic Acid

<i>m/g</i>	<i>T/K</i>	τ_2/s	$K \cdot \Delta H/$ (mV·s)	type of cell ^e	$\Delta H/J$	$\Delta H_m^F/$ (kJ·mol ⁻¹)	<i>m/g</i>	<i>T/K</i>	τ_2/s	$K \cdot \Delta H/$ (mV·s)	type of cell ^e	$\Delta H/J$	$\Delta H_m^F/$ (kJ·mol ⁻¹)
Sublimation of Methyl <i>p</i> -Toluate ^a (IV) (<i>M</i> = 150.1768)													
0.065 58	301.5	7030	6813.1	A	36.105	82.68	0.083 09	301.4	8585	9088.4	B	46.127	83.37
0.076 12	300.8	8325	7947.3	A	42.116	83.10	0.095 45	300.8	9800	10402.6	B	52.797	83.07
0.058 82	301.0	7370	6157.8	A	32.633	83.32	0.073 10	301.0	8295	7954.0	B	40.370	82.94
0.062 45	300.9	7275	6758.7	B	34.303	82.49							
$\langle \Delta_{\text{sub}} H_m^F(301.1 \text{ K}) \rangle = (83.00 \pm 0.3)$													
Sublimation of Monomethyl Terephthalate ^a (V) (<i>M</i> = 180.1598)													
0.007 03	373.5	7885	905.06	A	4.8954	125.45	0.010 58	373.3	6790	1405.1	B	7.3171	124.60
0.012 50	373.9	7045	1607.8	A	8.6965	125.34	0.013 45	374.0	8055	1780.8	B	9.2736	124.22
0.016 27	374.0	7965	2087.0	A	11.289	125.01	0.012 27	373.7	6265	1630.8	B	8.4920	124.69
$\langle \Delta_{\text{sub}} H_m^F(373.3 \text{ K}) \rangle = (124.89 \pm 0.50)$													
Sublimation of Dimethyl Terephthalate ^b (VIII) (<i>M</i> = 194.1866)													
0.029 65	363.7	5560	2865.8	A	15.408	100.91	0.052 37	363.7	5560	5217.7	B	26.861	99.60
0.054 21	363.7	6215	5189.8	A	27.902	99.95	0.067 43	363.8	5985	6765.7	B	34.830	100.31
0.056 59	363.9	5780	5394.9	A	29.005	99.53	0.055 01	363.6	6015	5533.7	B	28.488	100.56
0.040 31	363.7	5285	4047.3	B	20.835	100.37							
$\langle \Delta_{\text{sub}} H_m^F(363.7 \text{ K}) \rangle = (100.18 \pm 0.50)$													
Vaporization of Methyl Benzoate ^a (I) (<i>M</i> = 136.1500)													
0.060 80	303.0	4210	4812.5	A	25.503	57.11	0.077 17	303.0	5765	6376.1	B	32.361	57.09
0.075 88	303.1	5375	6023.8	A	31.923	57.28	0.074 51	303.3	5315	6149.8	B	31.213	57.03
0.075 23	303.0	5520	5973.3	A	31.655	57.29	0.074 57	303.0	5425	6168.5	B	31.307	57.16
0.059 48	303.0	5315	4922.3	B	24.983	57.19							
$\langle \Delta_{\text{vap}} H_m^F(303.0 \text{ K}) \rangle = (57.16 \pm 0.09)$													
Vaporization of Methyl <i>o</i> -Toluate ^c (II) (<i>M</i> = 150.1768)													
0.086 64	293.2	5842	7458.59	A	32.937	57.09	0.085 85	293.2	7089	7060.64	B	32.842	57.45
0.101 58	293.8	6549	8813.67	A	38.921	57.54	0.098 44	293.9	6845	8097.38	B	37.664	57.46
0.117 35	294.2	6444	10135.01	A	44.756	57.28	0.108 10	294.2	6829	8815.67	B	41.005	56.97
$\langle \Delta_{\text{vap}} H_m^F(293.8 \text{ K}) \rangle = (57.30 \pm 0.24)$													
Vaporization of Methyl <i>m</i> -Toluate ^c (III) (<i>M</i> = 150.1768)													
0.107 03	295.2	7686	9760.96	A	43.104	60.48	0.107 73	295.2	7632	9268.05	B	43.109	60.10
0.110 70	298.0	7229	10066.54	A	44.454	60.31	0.113 72	298.1	8937	9813.12	B	45.645	60.28
0.112 11	295.8	7020	10206.38	A	45.071	60.38	0.113 77	296.0	7869	9790.62	B	45.540	60.11
$\langle \Delta_{\text{vap}} H_m^F(296.4 \text{ K}) \rangle = (60.28 \pm 0.16)$													
Sublimation of Dimethyl Isophthalate ^c (IX) (<i>M</i> = 194.1866)													
0.151 23	334.3	17127	17792.6	A	78.572	100.89	0.151 50	334.3	16658	16854.8	B	78.398	100.49
0.085 13	333.7	12284	10061.2	A	44.430	101.35	0.095 01	334.0	13047	10568.2	B	49.157	100.47
0.078 72	334.7	10268	9244.0	A	40.822	100.70	0.084 70	335.0	9920	9408.9	B	43.765	100.34
$\langle \Delta_{\text{sub}} H_m^F(334.3 \text{ K}) \rangle = (100.71 \pm 0.39)$													
Vaporization of Trimethyl 1,2,4-Benzenetricarboxylate ^d (VII) (<i>M</i> = 252.2232)													
0.082 10	398.1	7851	5735.4	A	25.499	78.34	0.089 04	400.4	5627	5920.0	B	27.643	78.30
0.089 23	398.2	6168	5966.6	B	27.860	78.85	0.105 65	400.8	6087	7052.5	B	32.931	78.62
$\langle \Delta_{\text{vap}} H_m^F(399.4 \text{ K}) \rangle = (78.53 \pm 0.41)$													
Vaporization of Dimethyl Phthalate ^d (VI) (<i>M</i> = 194.1866)													
0.138 56	364.9	6434	11142.5	A	49.537	69.43	0.111 52	364.8	5810	8538.3	B	39.869	69.42
0.108 73	344.7	6596	9148.0	A	40.670	72.64	0.112 32	344.5	7756	9034.9	B	42.188	72.94
0.132 88	343.6	7173	11096.2	A	49.332	72.09	0.132 70	343.5	6279	10562.1	B	49.319	72.17
0.096 29	327.0	7981	8310.9	A	36.949	74.51	0.110 32	326.9	9612	9044.2	B	42.231	74.34
0.118 61	324.3	10903	10223.1	A	45.450	74.41	0.147 44	324.0	12336	12146.5	B	56.717	74.70
0.096 97	325.4	6883	8332.8	A	37.046	74.19	0.101 22	325.3	8139	8372.7	B	39.095	75.00
$\langle \Delta_{\text{sub}} H_m^F(364.9 \text{ K}) \rangle = (69.43 \pm 0.09)$													
$\langle \Delta_{\text{sub}} H_m^F(344.1 \text{ K}) \rangle = (72.46 \pm 0.64)$													
$\langle \Delta_{\text{sub}} H_m^F(325.5 \text{ K}) \rangle = (74.53 \pm 0.30)$													

^a $K_A = 188.70 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$, $K_B = 197.03 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$. ^b $K_A = 186.00 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$, $K_B = 194.25 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$. After modernization of measurements scheme of the calorimeter. ^c $K_A = 226.45 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$, $K_B = 214.99 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$. ^d $K_A = 224.93 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$, $K_B = 214.16 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$. ^e A and B are two different cells of the differential calorimeter.

Table 4. Enthalpies of Evaporation and Formation of Some Methyl Esters of Benzene Carboxylic Acids

compounds	process	$\Delta_{\text{process}} H_m^F(T)/$ (kJ·mol ⁻¹)	$\Delta_{\text{process}} H_m^F(298.15)$ K)/(kJ·mol ⁻¹)	$\Delta_f H_m^F(\text{cond.},$ 298.15 K)/(kJ·mol ⁻¹)	$\Delta_f H_m^F(\text{g},$ 298.15 K)/(kJ·mol ⁻¹)
methyl <i>p</i> -toluate	sub.	83.00 ± 0.30 (301.1 K)	83.25 ± 0.30	-391.94 ± 1.58 (cr)	-308.69 ± 1.61
monomethyl terephthalate	sub.	124.89 ± 0.50 (373.3 K)	130.41 ± 0.50	-779.09 ± 2.29 (cr)	-648.68 ± 2.34
dimethyl terephthalate	sub.	101.18 ± 0.50 (363.7 K)	105.20 ± 0.50	-732.62 ± 1.00a (cr)	-627.42 ± 1.12
methyl benzoate	vap.	57.16 ± 0.09 (303.0 K)	56.68 ± 0.30b	-334.42 ± 1.21 (liq)	-277.74 ± 1.25
dimethyl isophthalate	sub.	100.71 ± 0.39 (334.3 K)	103.79 ± 0.39	-730.90 ± 1.00a (cr)	-627.11 ± 1.07
methyl <i>o</i> -toluate	vap.	57.30 ± 0.24 (293.8 K)	57.00 ± 0.24	-358.50 ± 1.91 (liq.)	-301.50 ± 1.93
methyl <i>m</i> -toluate	vap.	60.28 ± 0.16 (296.4 K)	60.22 ± 0.16	-369.79 ± 1.55 (liq.)	-309.57 ± 1.56
dimethyl phthalate	vap.	69.43 ± 0.09 (364.9 K)	78.04 ± 0.71	-684.28 ± 2.48 (liq.)	-606.24 ± 2.58
		72.46 ± 0.46 (344.1 K)			
		74.53 ± 0.30 (325.5 K)			
trimethyl 1,2,4-benzenetricarboxylate	vap.	78.53 ± 0.41 (399.4 K)	92.08 ± 0.41	-1055.41 ± 2.84 (liq.)	-963.33 ± 2.87

^a Colomina et al. (1972). ^b Weight-averaged value (Nickolsky, 1966; Katayama, 1988; Kusano and Wadso, 1971; this work), calculated with consideration of statistical weight of each value.

Table 5. Matrix Coefficients of n_i and n_{jk} Used To Calculate Enthalpies of Formation $\Delta_f H^\circ$ for Some Methyl Esters of Benzene Carboxylic Acids and Methyl Benzenes in the Gas State at $T = 298.15$ K

compounds	n_1	n_2	n_{12}	n_{22}	n_{32}	$\Delta_f H^\circ(\text{exptl})/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta_f H^\circ(\text{calcd})/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta\Delta/(\text{kJ}\cdot\text{mol}^{-1})$
C ₆ H ₅ COOCH ₃	1	0	0	0	0	-277.7	-271.7	6.1
1,2-C ₆ H ₄ (COOCH ₃) ₂	2	0	1	0	0	-606.2	-610.5	-4.3
1,3-C ₆ H ₄ (COOCH ₃) ₂	2	0	0	0	0	-627.1	-625.8	1.2
1,4-C ₆ H ₄ (COOCH ₃) ₂	2	0	0	0	0	-627.4	-625.8	1.6
1,2,3-C ₆ H ₃ (COOCH ₃) ₃	3	0	2	0	0		-949.3	
1,2,4-C ₆ H ₃ (COOCH ₃) ₃	3	0	1	0	0	-963.3	-964.7	-1.4
1,3,5-C ₆ H ₃ (COOCH ₃) ₃	3	0	0	0	0	-982.2 ^a	-980.0	2.2
1,2,3,4-C ₆ H ₂ (COOCH ₃) ₄	4	0	3	0	0		-1288.2	
1,2,3,5-C ₆ H ₂ (COOCH ₃) ₄	4	0	2	0	0		-1303.5	
1,2,4,5-C ₆ H ₂ (COOCH ₃) ₄	4	0	2	0	0	-1296.5 ^b	-1303.5	-7.0
C ₆ H(COOCH ₃) ₅	5	0	4	0	0	-1623.0 ^a	-1627.0	-4.0
C ₆ (COOCH ₃) ₆	6	0	6	0	0	-1956.5 ^a	-1950.6	6.0
2-C ₆ H ₄ CH ₃ (COOCH ₃)	1	1	0	0	1	-301.5	-301.5	0
3-C ₆ H ₄ CH ₃ (COOCH ₃)	1	1	0	0	0	-309.6	-305.7	3.9
4-C ₆ H ₄ CH ₃ (COOCH ₃)	1	1	0	0	0	-308.7	-305.7	3.0
C ₆ H ₅ CH ₃	0	1	0	0	0	50.2 ^c	48.5	-1.7
1,2-C ₆ H ₄ (CH ₃) ₂	0	2	0	1	0	19.1 ^c	21.3	2.2
1,3-C ₆ H ₄ (CH ₃) ₂	0	2	0	0	0	17.3 ^c	14.5	-2.8
1,4-C ₆ H ₄ (CH ₃) ₂	0	2	0	0	0	18.0 ^c	14.5	-3.5
1,2,3-C ₆ H ₃ (CH ₃) ₃	0	3	0	2	0	-9.5 ^c	-6.0	3.5
1,2,4-C ₆ H ₃ (CH ₃) ₃	0	3	0	1	0	-13.8 ^c	-12.9	1.0
1,3,5-C ₆ H ₃ (CH ₃) ₃	0	3	0	0	0	-15.9 ^c	-19.5	-3.6
1,2,3,4-C ₆ H ₂ (CH ₃) ₄	0	4	0	3	0	-33.1 ^c	-33.3	-0.2
1,2,3,5-C ₆ H ₂ (CH ₃) ₄	0	4	0	2	0	-40.5 ^c	-40.1	0.5
1,2,4,5-C ₆ H ₂ (CH ₃) ₄	0	4	0	2	0	-44.6 ^c	-40.1	4.6
C ₆ H(CH ₃) ₅	0	5	0	4	0	-61.2 ^c	-60.6	0.6
C ₆ (CH ₃) ₆	0	6	0	6	0	-77.4 ^d	-81.1	-3.7
								±3.4

^a Jimenez et al. (1995). ^b Calculated from the data of Colomina et al. (1972) and Turrion (1967). ^c TRC p-3200, p-3290, p-3351 (1983). ^d Pedley (1994).

Table 6. Matrix of Coefficients n_i and n_{jk} Used To Calculate Enthalpies of Formation $\Delta_f H^\circ$ for Methyl Esters of Some Benzene Carboxylic Acids and Methyl Benzenes in the Crystalline State at $T = 298.15$ K

compounds	n_1	n_2	n_{12}	n_{22}	n_{32}	$\Delta_f H^\circ(\text{exptl})/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta_f H^\circ(\text{calcd})/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta\Delta/(\text{kJ}\cdot\text{mol}^{-1})$
C ₆ H ₅ COOCH ₃	1	0	0	0	0	-351.1 ^a	-343.5	7.6
1,2-C ₆ H ₄ (COOCH ₃) ₂	2	0	1	0	0	-703.2 ^b	-702.3	1.6
1,3-C ₆ H ₄ (COOCH ₃) ₂	2	0	0	0	0	-730.9 ^c	-726.0	4.9
1,4-C ₆ H ₄ (COOCH ₃) ₂	2	0	0	0	0	-732.6 ^c	-726.0	6.6
1,2,3-C ₆ H ₃ (COOCH ₃) ₃	3	0	2	0	0		-1061.1	
1,2,4-C ₆ H ₃ (COOCH ₃) ₃	3	0	1	0	0		-1084.7	
1,3,5-C ₆ H ₃ (COOCH ₃) ₃	3	0	0	0	0	-1101.1 ^d	-1108.4	-7.3
1,2,3,4-C ₆ H ₂ (COOCH ₃) ₄	4	0	3	0	0		-1419.8	
1,2,3,5-C ₆ H ₂ (COOCH ₃) ₄	4	0	2	0	0		-1443.5	
1,2,4,5-C ₆ H ₂ (COOCH ₃) ₄	4	0	2	0	0	-1432.5 ^d	-1443.5	-11.0
C ₆ H(COOCH ₃) ₅	5	0	4	0	0	-1788.1 ^d	-1778.6	9.5
C ₆ (COOCH ₃) ₆	6	0	6	0	0	-2110.8 ^d	-2113.7	-2.9
2-C ₆ H ₄ CH ₃ (COOCH ₃)	1	1	0	0	1	-373.5 ^e	-373.5	0
3-C ₆ H ₄ CH ₃ (COOCH ₃)	1	1	0	0	0	-392.5 ^f	-391.1	1.4
4-C ₆ H ₄ CH ₃ (COOCH ₃)	1	1	0	0	0	-391.9 ^g	-391.1	0.8
1,2,4,5-C ₆ H ₂ (CH ₃) ₄	0	4	0	2	0	-121.7 ^h	-123.5	-1.8
C ₆ H(CH ₃) ₅	0	5	0	4	0	-144.6 ^h	-143.1	1.5
C ₆ (CH ₃) ₆	0	6	0	6	0	-162.4 ^h	-162.8	-0.4
								±5.4

^a Calculated with $\Delta_{\text{fus}} H^\circ(260.80 \text{ K}) = (14\,831 \pm 12) \text{ J}\cdot\text{mol}^{-1}$. ^b Calculated with $\Delta_{\text{fus}} H^\circ(274.16 \text{ K}) = (16\,945 \pm 42) \text{ J}\cdot\text{mol}^{-1}$ (Rabinovich et al., 1986). ^c Colomina et al. (1972). ^d Jimenez et al. (1995). ^e Calculated with $\Delta_{\text{fus}} H^\circ(228.77 \text{ K}) = (12\,498 \pm 29) \text{ J}\cdot\text{mol}^{-1}$. ^f Calculated with $\Delta_{\text{fus}} H^\circ(269.93 \text{ K}) = (21\,156 \pm 77) \text{ J}\cdot\text{mol}^{-1}$. ^g Calculated with $\Delta_{\text{fus}} H^\circ(306.5 \text{ K}) = (20\,772 \pm 29) \text{ J}\cdot\text{mol}^{-1}$. ^h Pedley (1994).

constants to calculate the enthalpies of formation of gaseous MEBCA and MB (in $\text{kJ}\cdot\text{mol}^{-1}$, using the Student coefficient for the 95% confidence interval) were obtained by the least-squares method: $P_1(\text{COOCH}_3) = (-354.2 \pm 1.5)$, $P_2(\text{CH}_3) = (-34.1 \pm 1.5)$, $P_{12}(\text{COOCH}_3-\text{COOCH}_3) = (15.4 \pm 2.1)$, $P_{22}(\text{CH}_3-\text{CH}_3) = (6.8 \pm 2.1)$, and $P_{32}(\text{COOCH}_3-\text{CH}_3) = (4.2 \pm 8.3)$. The large uncertainty in the determination of the constant $P_{32}(\text{COOCH}_3-\text{CH}_3)$ is due to the fact that the constant was calculated by only one equation.

Values $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$ for all MEBCA, which contain only the group COOCH_3 , were calculated using the above-mentioned additive constants. The correspondence of experimental and calculated values ($\pm 3.4 \text{ kJ}\cdot\text{mol}^{-1}$) can

be considered satisfactory. The obtained additive constants can be used also to calculate properties of MEBCA with other substitutes in the benzene ring. So, for example, the difference between enthalpy of formation of gaseous monomethyl terephthalate and benzoic acid (Pedley, 1994) is $-354.7 \text{ kJ}\cdot\text{mol}^{-1}$. It is in good agreement with the value $P_1(\text{COOCH}_3) = -354.2 \text{ kJ}\cdot\text{mol}^{-1}$. We expect that our calculated additive constants $P_1(\text{COOCH}_3)$ can be used to calculate $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$ of MEBCA with different substitutes in positions 3 and 4 according to the COOCH_3 groups.

It was previously shown (Kabo et al., 1995; Simirsky et al., 1987) that the additive rules to calculate $\Delta_f H_m^\circ$ are

observed also for substances in the crystalline state. The results of additive calculations for crystalline MEBCA and MB using $\Delta_f H_m^c(C_6H_6, cr, 298.15 K) = (38.9 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$ (calculated from the data of Cox and Pilcher (1970) and Oliver et al. (1948)) and additive constants (in $\text{kJ} \cdot \text{mol}^{-1}$) $P_1(\text{COOCH}_3) = (-382.4 \pm 1.4)$, $P_2(\text{CH}_3) = (-47.6 \pm 2.8)$, $P_{12}(\text{COOCH}_3-\text{COOCH}_3) = (23.7 \pm 1.8)$, $P_{22}(\text{CH}_3-\text{CH}_3) = (14.0 \pm 3.4)$, and $P_{32}(\text{COOCH}_3-\text{CH}_3) = (17.6 \pm 7.4)$, found by the least-squares method, are given in Table 6. The average difference $\{\Delta_f H^c(\text{calcd}) - \Delta_f H^c(\text{exptl})\}$ is $\pm 5.3 \text{ kJ} \cdot \text{mol}^{-1}$. Some diminution of the accuracy of the additive calculations of $\Delta_f H_m^c$ for crystals (35%) is probably connected with the additional specific interactions in the crystals.

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