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STANDARD ENTHALPIES OF FORMATION FOR SOME SEMI-PRODUCTS AT THE SYNTHESIS OF POLY(ETHYLENE) TEREPHTHALATE

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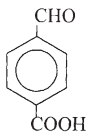
Abstract

The enthalpies of combustion for 4-formylbenzoic acid (I), 4-methylbenzyl alcohol (II), and trimethyl 1,2,4-benzenetricarboxylate (III) were determined by the bomb calorimetry method. Enthalpies of sublimation for I and II were measured with a calorimeter. The contributions of different substituents to the standard enthalpies of formation for benzene derivatives in the gas state were derived.

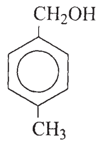
Keywords: enthalpy of combustion, enthalpy of formation, enthalpy of sublimation, 4-formylbenzoic acid, 4-methylbenzyl alcohol, trimethyl 1,2,4-benzenetricarboxylate

Introduction

Terephthalic acid and its dimethyl ester are the starting monomers for poly(ethylene) terephthalate production. Industrial synthesis of these compounds is accompanied by the formation of considerable quantities of by-products and intermediates, which are mostly monoaromatic oxygen-containing compounds [1]. Investigation of the thermodynamic properties of formed individual substances is important to evaluate the efficiency of technological processes and to calculate heat effects of reactions. Standard enthalpies of formation and enthalpies of vaporisation (sublimation) for benzene carboxylic acids and their methyl esters were measured earlier [2–4]. Results of calorimetric studies of the



I



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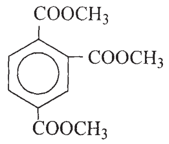

III

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same characteristics for 4-formylbenzoic acid (I), 4-methylbenzyl alcohol (II), and trimethyl 1,2,4-benzenetricarboxylate (III) are presented in this paper.

Experimental

Samples of I (Merck, 97%) and of III (Aldrich, 98%) were purified by series of consecutive recrystallizations from (water–ethanol mixture, bidistilled water) and (methanol, water–methanol mixture), respectively. Filtered sediments of both compounds were dried in a vacuum (residual pressure 1–2 Pa) to constant mass. Sample II was synthesized by hydrolysis from methyl ester of 4-methylbenzene alcohol (separated from industrial 'methyl benzoate' fraction). Structure of the obtained substance was confirmed by ^{1}H NMR spectrum. The sample was purified by recrystallizations from water–methanol mixture and from toluene, and by fractional sublimation at T=320–325 K and P=0.2 kPa. Purity of I (0.9987±0.0005 – mass) was assessed by the results of gravimetric analysis of combustion products. Purities of II and III (each of 0.999) were determined by g.l.c.

The substances were checked on hydroscopicity. Prior to use, the samples were kept in a desiccator over P_2O_5. All measurements were carried out with freshly prepared samples. Densities of the crystals (I – 1.460 g cm^{-3} at 291 K, II – 1.138 g cm^{-3} at 294 K, III – 1.401 g cm^{-3} at 295 K) were determined by the picnometric method using water as a reference liquid.

The combustion enthalpy was measured in two static bomb calorimeters (A and B) with isothermal shields [5]. The accuracy of measurements of combustion energy is ±0.02%. Energy equivalents W_{A}=14939.4±6.5 J K^{-1} and W_{B}=14892.0±5.6 J K^{-1} were found in experiments with a reference sample of benzoic acid (trade mark K-1, $\Delta_{\mathrm{c}}U_{\mathrm{B}}$=—26434.4±0.6 J g^{-1} based on mass in a vacuum). The compounds were burnt in the form of tablets pressed in air. In some experiments the tables were placed in terylene bags. The energy of combustion of terylene determined in separate measurements was –22879.7±11.0 J g^{-1}. A detail description of the equipment and procedures was published earlier [6].

The enthalpies of sublimation were determined in a differential heat-conducting microcalorimeter of Calvet type with special calorimetric cells [7]. The method of measurements was described elsewhere [6]. The calorimeter was calibrated by sublimation of benzoic acid (K-1). The calorimetric constants are K_{A}=222.78 mV s J^{-1} and K_{B}= 211.62 mV s J^{-1} for cells A and B, respectively. The estimated error of measurements does not exceed 0.5%. The enthalpy of sublimation $\Delta_{\mathrm{sub}}H^0_{\mathrm{m}}$ was calculated from the expressions:

$$\Delta_{\mathrm{sub}}H^0_{\mathrm{m}}=\Delta HMm^{-1}$$

$$\Delta H=K^{-1}\int_{\tau=0}^{\tau=\tau_2}\Delta E\,\mathrm{d}\tau$$

where ΔH is the heat effect of the experiment, m is the sample mass corrected to vacuum, M is the molar mass, K is the calorimetric constant, ΔE is the thermocouple e.m.f. corresponding to the heat flow from the thermostated furnace to the cell at the time τ, τ_2 is the experiment duration, T is the temperature of the calorimeter.

Table 1 Energies of combustion $\Delta_c U^0$ for substances I–III

m/g	m_{ter}/g	ΔT/K	q_{HNO_3}/J	q_{ter}/J	Σq_w/J	W/J V^{-1}	$-\Delta_c U^0$/J g^{-1}
			I, $C_8H_6O_3$, (M=150.1314)				
0.61070	–	0.95303	7.8	–	11.3	14892.0	23205.4
0.75265	–	1.17133	9.0	–	14.3	14939.4	23216.3
0.60085	–	0.93793	7.2	–	11.1	14892.0	23212.8
0.73773	–	1.14735	9.5	–	14.0	14939.4	23199.8
							23208.6±11.8
			II, $C_8H_{10}O$, (M=122.1644)				
0.46143	–	1.10241	9.4	–	7.6	14939.4	35650.8
0.48653	–	1.16258	9.0	–	8.1	14939.4	35659.2
0.44226	0.02911	1.10100	9.0	666.0	7.8	14939.4	35642.8
0.59147	0.02900	1.45784	11.3	663.5	10.8	14939.4	35659.6
0.30673	0.02897	0.77968	6.0	662.8	5.3	14892.0	35650.2
							35652.5±8.7
			III, $C_{12}H_{12}O_6$, (M=252.2201)				
0.47123	0.02902	0.71749	6.6	664.0	8.1	14892.0	21230.2
0.50974	0.03199	0.77417	6.6	731.9	8.8	14939.4	21219.3
0.68404	–	0.97315	8.4	–	11.4	14939.4	21221.8
0.63002	–	0.89926	8.4	–	10.4	14892.0	21223.3
							21223.7±7.5

m is the sample mass, m_{ter} is the mass of terylene, ΔT is the corrected temperature rise, q_{HNO_3} is the correction for nitric acid formation, q_{ter} is the correction for combustion of terylene, Σq_w is the sum of the Washburn corrections, W is the energetic equivalent of the calorimeter

Results

The measured energies of combustion and enthalpies of sublimation for the studied substances are given in Tables 1 and 2, respectively. The standard enthalpies of formation ($\Delta_f H^0$) in the crystalline state were calculated using the auxiliary values [8]: $\Delta_f H^0$ (CO_2, *g*, 298.15 K)=–393.51±0.13 kJ mol^{-1}, $\Delta_f H^0$ (H_2O, l, 298.15 K)= –285.83±0.04 kJ mol^{-1}. Experimental values of sublimation enthalpies for I and II were reduced to the temperature 298.15 K basing on the differences between the heat capacities of condensed and gas phases. These differences (I – 30, II – 40 J mol^{-1} K^{-1}) were estimated from the characteristics of related compounds (I – benzaldehyde, benzoic and terephthalic acids; II – *n*-alkan-1-ols and phenols). The standard enthalpies of formation in the gas state were calculated as well.

Table 2 Enthalpies of sublimation $\Delta_{sub} H^0$ for I and II

m/g	*T*/K	τ_2/s	*K*Δ*H*/ mV s	Type of cells	$\Delta_{sub}H^0$/ kJ mol^{-1}
		I			
0.04196	385.2	15198	6699.6	A	107.60
0.03168	385.1	14677	5014.8	A	106.58
		$\Delta_{sub}H^0$(385.1 K)=107.09±0.51*			
		II			
0.03780	308.3	8351	5994.2	A	86.96
0.03733	309.1	7648	5904.1	A	86.73
0.03669	308.9	8482	5824.5	A	87.05
0.03282	308.3	7304	4141.3	B	86.92
0.04494	309.2	10255	6793.6	B	87.27
0.04467	308.9	9257	6736.9	B	87.06
		$\Delta_{sub}H^0$(308.8 K)=87.00±0.19			

*Uncertainty is standard deviation

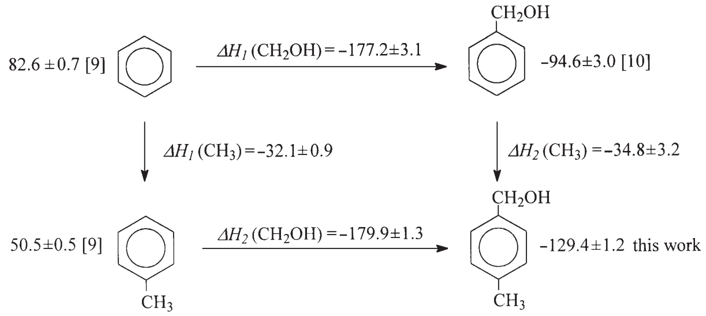
Thermochemical data for all studied substances at *T*=298.15 K are summarized in Table 3.

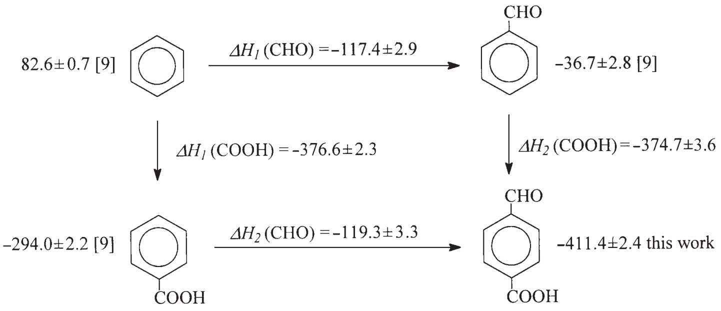
Table 3 Thermodynamic properties of substances I–III at 298.15 K/kJ mol^{-1}

Substance	$-\Delta_c U^0(cr)$	$-\Delta_c H^0$ (*cr*)	$-\Delta_f H^0$ (*cr*)	$\Delta_{sub}H^0$	$-\Delta_f H^0$ (*g*)
I	3484.3±1.8	3484.3±1.8	521.2±1.8	109.8±1.5	411.4±2.4
II	4355.5±1.1	4360.4±1.1	216.8±1.1	87.4±0.4	129.4±1.2
III	5353.0±1.9	5353.0±1.9	1084.1±2.0	123.8±3.5*	960.3±2.9 [3]

*Calculated as difference $\Delta_f H^0$ (*g*)–$\Delta_f H^0$ (*cr*)

The values of contributions ΔH to Δ_fH^0 (g, 298.15 K) corresponding to replacement of H atom in benzene ring by CH_3, CHO, COOH, CH_2OH groups were calculated on the basis of the standard enthalpies of formation according to the scheme:





Mass averaged values of parameters ΔH for each substituent (Table 4) were calculated from the values of ΔH_1 and ΔH_2. The ΔH values for methyl (CH_3) and carboxyl (COOH) groups are in a good accordance with those derived from the additive scheme for 48 compounds by Maksimuk and Trahanov [3]. The according ΔH values obtained by Cohen and Benson [11] are also given in Table 4. The data [11] agree with parameters obtained by other methods, except parameters on COOH and $COOCH_3$ groups. This is probably caused by inexact values of CO–(C_B)(O) Benson's contributions.

Table 4 Contributions of different substituents (ΔH) to Δ_fH^0 (g, 298.15 K) of aromatic compounds

Substituent	ΔH/kJ mol^{-1}		
	this work	[4]	[11]
CH_3	–32.3±0.9	–33.3±0.5	–32.6
COH	–118.2±2.2	–	–120.0
COOH	–376.1±1.9	–376.5±0.6	–394.1
CH_2OH	–179.5±1.2	–	–183.1
$COOCH_3$	–	–355.8±0.6	–373.6

Conclusions

Standard enthalpies of formation for I–III compounds in crystal and gas states were determined from combustion and sublimation experiments. Contributions for COOH, CHO, CH_2OH, CH_3, $COOCH_3$ groups to gaseous standard enthalpies of formation for benzene derivatives were obtained that enable to estimate $\Delta_f H^0$ of aromatic compounds with those substituents (it is not located in *ortho*-position). For example:

$$\Delta_f H^0(4\text{-}CH_3C_6H_4CHO,\ g,\ 298.15\ \text{K})=$$
$$\Delta_f H^0(\text{benzene},\ g,\ 298.15\ \text{K})+\Delta H(CH_3)+\Delta H(CHO)=$$
$$(82.6\pm0.7)+(-33.3\pm0.5)+(-118.2\pm2.2)=-68.9\pm2.4\ \text{kJ mol}^{-1}.$$

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