CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Standard Enthalpies of Formation of 4-Methylbiphenyl and 4,4'-Dimethylbiphenyl

S. M. Pimenova^a, L. L. Pashchenko^a, E. A. Miroshnichenko^b, and I. A. Nesterov^c

^a Department of Chemistry, Moscow State University, Moscow, 119991 Russia
 ^b Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia
 ^c Samara State Technical University, Samara, 443100 Russia

e-mail: smpimenova@yandex.ru Received April 17, 2013

Abstract—The energies of combustion of 4-methylbiphenyl and 4,4'-dimethylbiphenyl in the crystal state were measured in a precision calorimeter equipped with a self-sealing bomb at 298.15 K. The enthalpies of vaporization of these substances were measured in an isothermal heat-conducting Calvet microcalorimeter. Standard enthalpies of formation were calculated for 4-methylbiphenyl and 4,4'-dimethylbiphenyl in the crystal, liquid, and gas states.

Keywords: calorimeter, bomb, enthalpies of combustion, enthalpies of formation, enthalpies of vaporization, alkylbiphenyls.

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INTRODUCTION

The data collected to date for the enthalpies of formation of alkylbiphenyls and a number of their functional derivatives are insufficient and too contradictory for correctly predicting the enthalpies of formation of these compounds, or for creating systems of practical value in calculating the thermodynamic properties of these substances [1, 2].

We recently measured the enthalpies of combustion for 4-tert-butyl- and 4,4'-di-tert-butylbiphenyls [3] and 4,4'-dinitrobiphenyl ether [4] and calculated the enthalpies of their formation from the existing data. In this work, the standard enthalpies of combustion $(\Delta_{\rm c} H_{\rm m}^{\rm o})$ and formation $(\Delta_{\rm f} H_{\rm m}^{\rm o})$ were determined for 4methylbiphenyl (4-MBP) and 4,4'-dimethylbiphenyl (4,4'-DMBP), and the enthalpies of vaporization of these substances $(\Delta_{liq}^g H_m^\circ)$ were measured via calorimetry. In the literature, the results from thermochemical studies of the investigated compounds can be found in [2, 5] (Table 1). In both works, the enthalpies of combustion were determined for 4-MBP and 4,4'-DMBP; in [5], the error in measuring $\Delta_{\rm f} H_{\rm m}^{\rm o}$ for these substances was high: 7.1-7.5 kJ/mol. The enthalpies of sublimation were measured for both substances in [2-8]. The enthalpy of vaporization for 4-MBP was measured in [6]. In this work, we determine the enthalpy of vaporization of 4-MBP and the energies of combustion of 4-MBP and 4,4'-DMBP in order to refine the existing literature data.

EXPERIMENTAL

The investigated substances were synthesized at the Chair of Organic and Petrochemical Synthesis Technology, Samara State Technical University. The sample of 4-MBP was prepared via the dehydrogenation of 4-cyclohexyltoluene. The synthesis procedure was described in detail in [6]. The sample was purified by rectification under vacuum ($p_{residual} = 0.8-1.0$ kPa) and subsequent five-fold recrystallization from ethanol. The purity of 4-MBP was 99.67 wt % according to data from GLC analysis, and 99.45 mol % according to the depression of the melting point in measuring heat capacity.

Two-step synthesis was used to prepare 4,4'-dimethylbiphenyl. This included preparation of 4-iodotoluene and its Ullmann condensation [9]. 4-Iodotoluene was prepared by iodination of toluene using nitric acid as the oxidizing agent for hydrogen iodide:



4-Iodotoluene was isolated from the washed and dried organic layer by distillation with Vigreux column under atmospheric pressure, followed by recrystallization from ethanol.

Our 4,4'-DMBP was synthesized by condensing 4-iodotoluene according to the recommendations in [9]:

$$CH_{3} - \swarrow I \xrightarrow{-I_{2}} CH_{3} - \swarrow CH_{3}$$

4,4'-DMBP was isolated by fractionating the reaction mixture with Vigreux column under vacuum

Values kJ/mol	4-1	MBP	4,4' -DMBP		
	this work	literature data	this work	literature data	
$-\Delta_{\rm c} U_{\rm m}^{\rm o}$ (cr)	6883.9 ± 0.7	6881.2 ± 1.8 [2]	7510.0 ± 1.7	7517.4 ± 2.3 [2]	
		6878.6 ± 7.1 [5]		7515.4 ± 7.5 [5]	
$-\Delta_{\rm c} H_{\rm m}^{\rm o}$ (cr)	6891.3 ± 0.9	6888.6 ± 1.8 [2]	7518.7 ± 1.9	7526.1 ± 2.3 [2]	
		6886.0 ± 7.1 [5]		7524.1 ± 7.5 [5]	
$\Delta_{\rm f} H_{\rm m}^{\circ}$ (cr)	60.7 ± 1.0	55.4 ± 7.1 [5]	8.7 ± 2.0	14.1 ± 7.5 [5]	
		58.0 ± 2.5 [2]		16.2 ± 2.9 [2]	
$\Delta_{\rm f} H_{ m m}^{ m o}$ (g)	141.7 ± 1.2	138.2 ± 2.9 [2]	103.9 ± 2.3	111.3 ± 3.6 [2]	
$\Delta_{ m cr}^{ m lig} H_{ m m}^{\circ}$		11.6 ± 0.2 [6]			
$\Delta^{ m g}_{ m lig} H^{ m o}_{ m m}$	69.8 ± 0.8	69.0 ± 0.7 [6]	79.1 ± 0.9		
$\Delta^{\rm g}_{ m cr} H^{ m o}_{ m m}$		80.2 ± 1.4 [2]		95.1 ± 2.0 [2]	
		80.6 ± 0.8 [6]		95.2 ± 1.5 [7]	
		82.7 ± 1.3 [7]		95.2 ± 0.6 [8]	

Table 1. Standard thermodynamic values for 4-methylbiphenyl and 4,4'-dimethylbiphenyl

 $(p_{\text{residual}} = 1-1.5 \text{ kPa})$ and purified by recrystallization from ethanol with subsequent distillation. The yield of 4,4'-DMBP was 50% on the initial 4-iodotoluene.

According to the data from GLC analysis, the purity of 4,4'-DMBP was 99.99 wt %. According to the data from differential scanning calorimetry, the purity of 4,4'-DMBP sample was 100.0 wt % (the error of measurement, estimated from a reference sample, was ± 0.9 wt %).

The synthesized substances were nonhygroscopic and nonvolatile white crystals. The physicochemical characteristics of our 4-MBP and 4,4'-DMBP samples were M = 168.23438 and 182.26096 g/mol (standard atomic weights were used on the recommendation of a 2005 IUPAC Communication [10]), $T_{\text{fusion}} =$ 320.33 ± 0.02 K and 394.1 ± 0.4 K [6, 11]; $\rho =$ 1.02 g/cm³, and $(\partial u/\partial p)_T = -0.2$ J/(g MPa) for both substances [2].

A precision liquid calorimeter equipped with an isothermal shell and a stationary self-sealing bomb with an internal volume of 0.270 dm³ were used to measure the energy of combustion of 4-MBP and 4,4'-DMBP. The rise in temperature was measured by a copper resistance thermometer with a sensitivity of 5×10^{-5} K connected into bridge circuit. The calorimeter energy equivalent ($W = 54258.5 \pm 5.0 \text{ J/}\Omega$) was determined through the combustion of the reference benzoic acid, the energy of combustion of which under certificate conditions was $\Delta_b u(b.a.) = -26432.3 \pm$ 1.9 J/g; and, under our experimental conditions, $\Delta_b u(b.a.) = -26431.2 \pm 1.9 \text{ J/g}$ with allowance for the Jessup correction [12]. The errors of measurement for all values in this work were calculated as ts, where t is Student's coefficient for a 95% confidence interval and s is the standard deviation of the mean value. In calculating our final results for $\Delta_c H_m^\circ$ and $\Delta_f H_m^\circ$, the errors of measurement were considered for all of the values that were used (e.g., the heat of the calorimeter and the energy of combustion for benzoic acid).

The substances were pressed into 240-250 mg pellets and then weighed on Mettler scales (sensitivity, 2×10^{-6} g). Prior to each experiment, 1 mL of water was introduced into the bomb. A pellet was placed in a platinum crucible and burned in the calorimetric bomb filled up to 3.04 MPa pressure with oxygen purified from flammable impurities. The initial temperature of each experiment was 298.15 \pm 0.03 K. The samples were ignited with an electric charge passed from a capacitor through a platinum wire (d = 0.01 mm).

The experimental results of calorimetric determination of the standard energies of combustion of 4-MBP and 4,4'-DMBP ($-\Delta_c u^\circ$) are given in Table 2. The following designations are used in the table: $m_{\rm substance}$ is the mass of the investigated substance in a vacuum; ΔR_c is the rise in the experimental temperature, corrected for heat exchange in a calorimeter equipped with a shell; $\Delta R_c W'$ is total amount of heat evolved in the experiment ($W' = W + \delta$ is the calorimeter energy equivalent, corrected for the difference between the heat capacities (δ) of the products of combustion for benzoic acid and the investigated substance since the δ value was $-0.6 \text{ J}/\Omega$ for 4-MBP and $-0.4 \text{ J}/\Omega$ for 4,4'-DMBP, both of which are less than the error of measurement for W, W' = W was used in our calculations); $q_{\rm HNO_3}$ is the correction to the energy of formation for 0.1 N solutions of nitric acid produced from nitrogen, oxygen, and water $(\Delta_{\rm f} H^{\circ}_{\rm m}({\rm HNO}_3, 0.1 \text{ N solution}) = -59.8 \text{ kJ/mol [13]});$

Experiment	m _{sub} , g	$\Delta R_{\rm c}, \Omega$	$\Delta R_{\rm c} W'$	$q_{ m NHO_3}$	<i>q</i> _{S.S.}	$-\Delta_{c}u^{\circ},$	
			J			J/g	
4-MBP							
1	0.261214	0.196960	10686.8	0.6	5.3	40889.5	
2	0.261378	0.197086	10693.6	0.6	5.3	40890.0	
3	0.261061	0.196858	10681.2	1.2	5.3	40889.7	
4	0.261480	0.197200	10699.8	1.2	5.3	40895.2	
5	0.260224	0.196263	10648.9	0.7	5.3	40899.0	
6	0.260667	0.196571	10655.6	0.7	5.3	40893.6	
4.4'-DMBP							
1	0.256965	0.195299	10596.6	2.1	4.9	41210.3	
2	0.253511	0.192703	10455.8	1.5	4.9	41218.7	
3	0.258152	0.196185	10644.7	0.9	5.1	41211.0	
4	0.255470	0.194118	10532.6	0.9	5.0	41205.2	
5	0.256499	0.194834	10571.4	0.9	5.0	41191.2	
6	0.258645	0.196528	10663.3	0.9	5.1	41204.4	
7	0.256300	0.194692	10563.7	0.9	5.0	41 193.1	

Table 2. Results of calorimetric measurement of the energies of combustion of 4-methylbiphenyl and 4,4'-dimethylbiphenyl at 298.15 K

Note: For 4-MBP, $(\Delta_c u^{\circ}) = -40.892.8 \pm 4.1 \text{ J/g and, for 4,4'-DMBP, } (\Delta_c u^{\circ}) = -41.204.8 \pm 9.1 \text{ J/g.}$

 $q_{\text{S.S}}$ is the correction for reducing a system to the standard state calculated according to the recommendations in [12]; and $-\Delta_c u^\circ$ is the standard specific energy of combustion for 4-MBP and 4,4'-DMBP, obtained in each experiment and calculated using the equation: $-\Delta_c u^\circ = (W'\Delta R_c - q_{\text{HNO}_3} - q_{\text{S.S}})/(m_{\text{substance}}).$

After each combustion, the $CO_2(g)$ content was measured in the gas products of combustion via Rossini gravimetric method [12] with a precision of $\pm 4 \times 10^{-4}$ g, and the absence of CO in the combustion products was confirmed using indicator tubes (TU.12.43.20-76). The sensitivity of analysis was 6×10^{-6} g.

For experiments with 4-MBP, the results from gas analysis (ratio of the mass of CO₂ determined experimentally to the mass of CO₂ calculated using equations for the combustion of the substance) was 99.90 ± 0.03 wt %. The deficit of CO₂ at 0.10 wt % was due to the presence of ethanol traces in the sample, the content of which should be 0.23 wt % according to the results from gas analysis. This agrees well with the results from GLC analysis (99.67 wt % for 4-MBP) given above.

The result from CO_2 analysis for 4,4'-DMBP was 99.97 \pm 0.04 wt %, confirming the high purity of the investigated sample and the completeness of its combustion.

In the case of 4-MBP, the correction for the 0.23 wt % ethanol, 25.9 J/g ($\Delta_c u^\circ$ ethanol = -29632.0 ± 6.5 J/g [1]), was included in $\langle \Delta_c u^\circ \rangle = -40892.8 \pm 4.1$ J/g (Table 2). The mean value of the standard spe-

cific energy of combustion for pure samples of 4-MBP was $\langle \Delta_c u_{p,s}^{\circ} \rangle = -40918.7 \pm 4$. J/g; for 4,4'-DMBP, $\langle \Delta_c u^{\circ} \rangle = -41204.8 \pm 9.1$ J/g.

The mean standard molar enthalpies of combustion $\Delta_c U_m^{\circ}$ given in Table 1 were calculated from values obtained using equations

$$C_{13}H_{12}(cr) + 16O_{2}(gas) = 13CO_{2}(gas) + 6H_{2}O(liq),$$
(1)

$$C_{14}H_{14}(cr) + 17.5O_{2}(gas) = 14CO_{2}(gas) + 7H_{2}O(liq),$$
(2)

for the reactions of combustion, with allowance for the molecular masses of the substances.

The standard molar enthalpies of combustion for 4-MBP and 4,4'-DMBP were calculated using ΔnRT for reactions (1) and (2), -7.4 kJ/mol and -8.7 kJ/mol, respectively. We can see from Table 1 that our $\Delta_{c} H^{\circ}_{m}(4-MBP)$ is in good agreement with the same value from [2], while the data diverge for $\Delta_c H_m^{\circ}(4,4'-$ DMBP). The reason for this divergence is hard to explain. Two things should be noted: From the data in [2], the question of whether we can determine the mass of burned substance using only the results from gas analysis of the final products of combustion for the content of CO_2 (g) remains unclear. When a substance burns completely and the amount of CO₂ formed during the combustion of the cotton thread used to ignite the substance introduces an additional error in measuring the mass of burnt substance, it is more precise to

Sample	<i>m</i> , g	$K_{1, 2} = (p/g) \times 10^6,$ J/(cm s)	<i>S</i> , cm s	<i>Q</i> , J	$\Delta_{ m lig}^{ m g} H_{ m m}^{ m o}$, kJ/mol	<i>Т</i> , К
4-MBP	0.020463	1322.1	6180	8.1684	67.2	321.1
4,4'-DMBP	0.016553	1246.8	5055	6.3003	69.4	398.2

Table 3. Results of typical experiments to measure the enthalpies of vaporization of 4-methylbiphenyl and 4,4'-dimethyl

 biphenyl at different temperatures

Note: *m* is the mass of a sample under vacuum; $K_{1, 2}$ are constants of calorimeter cell sensitivity; *S* is area of the thermogram; *Q* is the total heat effect of the experiment, including the energy of breaking ampoules (0.0024 J) (Q = (KS + 0.0024)); *T* is the experimental temperature; and $\Delta_{iig}^{g} H_{m}^{o} = (Q/m)M$ is the molar enthalpy of vaporization at the temperature of the experiment, where *M* is the molecular mass of the substance [10].

use the results from weighing the investigated sample in our calculations (or at least to compare the results from weighing the sample prior to combustion and the mass determined from the results of gas analysis). In addition, it is insufficient to characterize the purity of initial substances using only the results from the elemental microanalysis for carbon; it is desirable to study the purity of samples by other means as well.

The standard enthalpies of formation $\Delta_{\rm f} H_{\rm m}^{\rm o}$ for 4-MBP and 4,4'-DMBP in the crystal state were calculated from the experimental values of the enthalpies of combustion of 4-MBP and 4,4'-DMBP (Table 1) using the key values $\Delta_{\rm f} H_{\rm m}^{\rm o}({\rm H_2O},{\rm liq}) = -285.83 \pm 0.04$ kJ/mol and $\Delta_{\rm f} H_{\rm m}^{\rm o}({\rm CO_2},{\rm g}) = -393.51 \pm 0.13$ kJ/mol recommended by CODATA [14]. The mean weighted values of the enthalpies of sublimation ($\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$) taken from the data [2, 6, 7] for 4-MBP and from the data [2, 7, 8] for 4,4'-DMBP (Table 1), since the results for each compound coincide within the range of measurement error. Ultimately, we obtained the values $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}(4.4'-DMBP) = 95.2 \pm 1.1$ kJ/mol. Then this values were used to calculate the enthalpies of formation for the investigated

The enthalpies of vaporization $(\Delta_{liq}^{g}H_{m}^{\circ})$ for liquid samples of 4-MBP at T = 321.1 K and 4,4'-DMBP at T = 398.2 K were determined by means of calorimetry on an isothermal heat-conducting differential calorimeter using two cells and an evacuated glass ampoule into which 20 to 30 mg of the investigated substance were placed [15]. The calorimeter and vacuum system allowed us to measure the enthalpies of vaporization and sublimation of substances with saturation vapor pressures of 1×10^{-4} kPa to 2 kPa in the 293 to 473 K range of temperatures. The calorimeter was calibrated using an electric current. The error of our potentiometric circuit was <0.01%. The error of calibrating each cell was 0.1%. The constants of the calorimeter cells' sensitivity (*K*) were found to be $K_1 = (1322.1 \pm 1.3) \times 10^{-6}$ and $K_2 = (1246.8 \pm 1.2) \times 10^{-6}$ J/(cm s).

compounds in gas state.

The results from a typical experiment to measure calorimetrically the enthalpies of vaporization at given temperature are presented as an example in Table 3. Six measurements were performed to determine the enthalpy of vaporization for 4-MBP and five measurements for 4,4'-DMBP. The mean value of the standard enthalpy of vaporization at the experimental temperature was thus $\Delta_{\text{lig}}^{\text{g}} H_{\text{m}}^{\circ}(4\text{-MBP}) = 67.7 \pm 0.8 \text{ kJ/mol}$ and

$\Delta_{\text{lig}}^{\text{g}} H_{\text{m}}^{\circ}(4,4'\text{-DMBP}) = 69.1 \pm 0.9 \text{ kJ/mol.}$

Corrections to bring the experimental enthalpies of vaporization to the standard temperature of 298.15 K were calculated using the Kirchhoff equation and the experimental values for the heat capacities of the liquid phases of 4-MBP and 4,4'-DMBP and the heat capacities of the gas phases of these substances given in [6, 11]. The corrections for 4-MBP and 4,4'-DMBP were 2.1 and 10.0 kJ/mol, respectively. The standard enthalpies of vaporization (Table 1) were determined for 4,4'-DMBP for the first time; for 4-MBP, they coincided within the range of measurement error with the results from [6], obtained from data on vapor pressure acquired from the transfer of mass in a flow of inert gas.

CONCLUSIONS

The results of this work allowed us to estimate the contribution of the [CH₃-] group to the enthalpies of formation for methylbiphenyls. Contributions Δ_1 and Δ_2 of the [CH₃-] group were calculated according to the difference between $\Delta_f H^{\circ}_m(4-MBP, g)$ or $\Delta_f H^{\circ}_m(4,4'-DMBP, g)$ and $\Delta_f H^{\circ}_m(biphenyl, g)$: $\Delta_1 = 36.7 \pm 2.8$ and (1/2) $\Delta_2 = 37.3 \pm 3.8$ kJ/mol. In our calculations, we used $\Delta_f H^{\circ}_m(biphenyl, g) = 178.4 \pm 2.6$ kJ/mol from [16], in which precise literature data were analyzed. In addition, the contribution of the [CH₃-] group (Δ_3) can be also estimated according to the difference between the $\Delta_f H^{\circ}_m(4-MBP, g)$ and $\Delta_f H^{\circ}_m(4,4'-DMBP, g)$ values obtained in this work: $\Delta_3 = 37.8 \pm 2.5$ kJ/mol. All values of the contributions of the [CH₃-] group,

i.e., Δ_1, Δ_2 , and Δ_3 , thus agree with one another quite well:



Similar estimates were performed using the enthalpies of formation for compounds 4-MBP and 4,4'-DMBP obtained in [2]. Values of the contributions of the [CH₃-] group were $\Delta_1 = 40.2 \pm 3.9$, $(1/2)\Delta_2 =$ 33.6 ± 4.4 , and $\Delta_3 = 26.9 \pm 4.6$ kJ/mol. It can be seen that the values of the contributions in [2] differ considerably. These differences were presumably due to the same reasons (see above) for the $\Delta_c H_m^o(4,4'-DMBP,$ cr) obtained in this work differing from the one determined in [2].

The contributions of the [CH₃-] group for methylsubstituted benzenes were calculated in a similar manner in order to compare them to the contribution of methyl group in a series of biphenyls. They were found to be virtually identical: $\Delta_4 = 32.2 \pm 0.9$; $(1/2)\Delta_5 = 32.3 \pm$ 1.2, and $\Delta_6 = 32.4 \pm 1.2$ kJ/mol (where Δ_6 is the difference between the enthalpies of formation for toluene and *p*-xylene). The following parameters were used in our calculations: $\Delta_f H^o(C_6H_6, g) = 82.6 \pm 0.7$ kJ/mol [1], $\Delta_f H^o(C_7H_8, g) = 50.4 \pm 0.6$ kJ/mol [1], and $\Delta_f H^o(C_8H_{10}, g) = 18.0 \pm 1.0$ kJ/mol [1]



It was thus found that the mean value for the contribution of the $[CH_3-]$ group to biphenyls (37.2 kJ/mol) exceeds the mean value for the contribution of the $[CH_3-]$ group to benzenes (32.3 kJ/mol) by ~5 kJ/mol.

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