Thermochemical properties of iso-propylbenzenes

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Abstract

The standard ($p^0 = 0.1$ MPa) molar enthalpies of formation $\Delta_f H_m^0$ (l) at the temperature $T = 298.15$ K were measured using combustion calorimetry for 1,3-di-iso-propylbenzene, 1,4-di-iso-propylbenzene, and 1,3,5-tri-iso-propylbenzene. The standard molar enthalpies of vaporization $\Delta_l^g H_m^0$ of these compounds were obtained from the temperature function of the vapour pressure measured in a flow system. Values of the small (1–2 kJ mol^{-1}) stabilized interactions of iso-propyl substituents were derived from the enthalpies of formation in the gas phase of the iso-propylbenzenes studied. © 1998 Elsevier Science B.V.

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1. Introduction

Iso-propylbenzenes are important industrial organic chemicals. The major use for them is hydroperoxidation to dihydroxybenzenes. The uses for hydroquinone are as an antioxidant and antiozonant in rubber manufacture and in chemical formulation for the development of photographic films. Resorcinol is used in the formulation of high-performance adhesives, compounding and plastics additives, dyes, and specialty thermosetting resins. 1,3,5-Tri-iso-propylbenzene is widely used in pharmaceutical, diagnostic, fine chemical, textile and pigment industries. Knowledge of the thermochemical properties of iso-propylbenzenes is useful for working out technological processes of synthesis and purification of dihydroxybenzenes, searching for energy-saving variants of the realization of these processes.

The thermochemistry of substituted benzenes has been of interest to us for a long time [1–3]. The resulting interactions of phenyl substituents in *m*-terphenyl, *p*-terphenyl and 1,3,5-tri-phenylbenzene leads to a weak stabilization of the molecules due to conjugation of phenyls [3]. What is the interaction energy among two and three iso-propyl groups in the iso-propylbenzenes? To answer these questions, the standard molar enthalpies of formation in the gas phase were obtained from calorimetrically measured molar enthalpies of combustion and molar enthalpies of vaporization determined by a transpiration method.

2. Experimental

2.1. Materials

Pure Aldrich products each with a mass-fraction purity of ca. 0.97 were purified by repeated distillation

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Table 1
Purity, density $\rho_{(293\ K)}$, specific heat capacity $c_{p(298.15\ K)}$, and expansion coefficient of the materials

	Purity	$\rho_{(293\ K)}$ [a]/g cm^{-3}	$c_{p(298.15\ K)}$ [b]/J K^{-1} g^{-1}	$10^{-6}(\delta V_m/\delta T)_p$ [c]/dm^3 K^{-1}
1,3-di-iso-propylbenzene	0.9930	0.856	1.48	1.0
1,4-di-iso-propylbenzene	0.9992	0.857	1.30	1.0
1,3,5-tri-iso-propylbenzene	0.9989	0.845	0.96	1.0
Cotton [e]		1.500	1.67	0.1
Polyethene [f]		0.920	2.53	0.1

[a] From Aldrich catalog.
[b] From DSC-measurements.
[c] Estimated.
[d] $CH_{1.93}$, $\Delta_c u^0_{(polyethene)} = -46361.0 \pm 3.1$ J g^{-1}.
[e] $CH_{1.774} O_{0.887}$, $\Delta_c u^0_{(cotton)} = -16945.2 \pm 4.2$ J g^{-1}.

under reduced pressure. The purity of the samples was determined by g.l.c. (Table 1). In case of *meta*- and *para*-di-iso-propylbenzenes, it was the traces of each of the appropriate positional isomer. In case of 1,3,5-tri-iso-propylbenzene, the detected impurity was found very close to the main peak. No corrections by estimations of enthalpies of combustion were applied.

We used the following equipment: g.l.c., Carlo Erba Fraktometer Vega Series GC 6000, Hewlett–Packard Integrator 3390A, N$_2$-flow 0.333 cm^3 s^{-1}, SE-30 capillary column of length 25 m. Standard temperature program of the g.l.c. was 313 K for 5 min with 0.167 K s^{-1} up to T=523 K. Specific heat capacities were determined with a Perkin–Elmer DSC-2C.

2.2. Combustion calorimetry

For measurements of the enthalpies of combustion of iso-propylbenzenes an isoperibolic macrocalorimeter with a static bomb and a stirred water bath was used. The substances were placed in polyethene capsules and were burned in oxygen at 3.04 MPa pressure. To ensure equilibrium in the final state, 0.78 g of water was added to the bomb. The detailed procedure has been described previously [4,5]. The combustion products were examined for carbon monoxide (Draeger tube) and unburnt carbon but neither was detected. The energy of ignition was determined to be 1.46 J. The energy equivalent of the calorimeter ε_{calor} (see Table 3) was determined with a standard reference sample of benzoic acid (sample SRM 39i,

N.I.S.T.). For the reduction of the data to standard conditions, conventional procedures [6] were used. The atomic weights used were those recommended by the IUPAC Commission [7,8]. The densities of the commercially available liquid compounds were taken from the Aldrich catalog. The summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass is given in Table 1.

2.3. Transpiration method

The enthalpies of vaporization of iso-propylbenzenes were determined with the method of transference in a saturated N$_2$-stream [5,9,10] using Clausius–Clapeyron equation. A sample of ca. 0.5 g was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. At constant temperature (± 0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of material was collected in a cold trap. The flow region, 0.28–0.56 cm^3 s^{-1}, of the nitrogen stream was optimal in order to reach the equilibrium of saturation of transporting gas at each temperature of investigation. The amount of condensed substance was determined by g.l.c. analysis using an internal standard (hydrocarbons $C_{11}H_{24}$ or $C_{13}H_{28}$). The vapour pressure p at each saturation temperature was calculated from the amount of product collected within a definite time period with the help of the ideal gas equation $pV=nRT$:

$$p = mRT/V(N_2)M$$

where $R=8.31451$ J K^{-1} mol^{-1}, m is the mass of transported compound; V(N$_2$) the volume of transporting gas; M the molar mass of compound; and T the saturation temperature. The measured value of the vapour pressure, p, at each temperature was independent of the gas flow in the broad range from 0.1 to 0.8 cm^3 s^{-1}, which has proved the saturation of the transport gas with the compound. The vapour pressure p was corrected for the residual vapour pressure at the condensation temperature. The latter was calculated from a linear correlation between ln p and T^{-1} obtained by iteration. The molar enthalpies of vaporization were calculated from the slope of the linear Clausius–Clapeyron correlation $\Delta_l^g H_m^0 = -R(\mathrm{d}\ln p/\mathrm{d}T^{-1})$. The observed enthalpies of vaporization $\Delta_l^g H_m^0$ (T) at the temperature T obtained by this procedure are listed in Table 2.

3. Results and discussion

The thermochemical properties of *meta*-, and *para*-di-isopropylbenzene, and 1,3,5- tri-isopropylbenzene were determined for the first time.

3.1. Combustion calorimetry

The results for a typical combustion experiment on each compound are given in Table 3. The individual values of the standard specific energy of combustion $\Delta_c u^0$, together with the mean and its standard deviation, are given in Table 4. To derive $\Delta_f H_m^0$ (g) from $\Delta_c H_m^0$, the following molar enthalpies of formation were used [7]: for H$_2$O(l): $-(285.83\pm0.04)$ kJ mol^{-1}, and for CO$_2$(g): $-(393.51\pm0.13)$ kJ mol^{-1}. Table 5 lists the derived standard molar

Table 2
Results from measurements of the vapour pressure p with the transpiration method

T/K [a]	m/mg [b]	$V_{(N_2)}$/dm^3 [c]	p/Pa [d]	T/K [a]	m/mg [b]	$V_{(N_2)}$/dm^3 [c]	p/Pa [d]
1,3-di-iso-propylbenzene							
283.5	2.89	3.304	13.82	303.5	4.90	1.051	71.56
288.4	4.01	3.000	20.88	308.6	5.41	0.821	101.0
293.5	5.13	2.445	32.53	313.5	5.50	0.611	137.9
298.3	4.69	1.567	46.18	318.5	5.26	0.439	183.5

$\Delta_l^g H_m^0$ (301.0 K)=(56.00$\pm$0.82) kJ mol^{-1}
$\Delta_l^g H_m^0$ (298.15 K)=(56.17$\pm$0.82) kJ mol^{-1}

1,4-di-iso-propylbenzene							
283.7	2.01	2.940	10.77	303.6	3.08	0.917	51.68
288.4	2.38	2.340	15.86	308.2	3.51	0.732	73.49
293.4	2.48	1.610	23.90	313.5	2.82	0.413	104.5
298.3	4.16	1.880	34.13	318.3	3.44	0.367	143.3

$\Delta_l^g H_m^0$ (301.0 K)=(56.32$\pm$0.27) kJ mol^{-1}
$\Delta_l^g H_m^0$ (298.15 K)=(56.49$\pm$0.27) kJ mol^{-1}

1,3,5-tri-iso-propylbenzene							
283.6	1.19	9.75	1.492	308.5	2.74	2.480	13.42
288.5	2.94	16.15	2.223	313.4	2.78	1.720	19.59
293.2	1.58	5.13	3.761	318.6	3.37	1.380	29.65
298.4	2.09	4.58	5.550	323.3	3.28	0.960	41.48
303.4	2.49	3.45	8.760				

$\Delta_l^g H_m^0$ (303.4 K)=(64.28$\pm$0.32) kJ mol^{-1}
$\Delta_l^g H_m^0$ (298.15 K)=(64.60$\pm$0.32) kJ mol^{-1}

[a] Temperature of saturation, N$_2$ gas flow (0.26–0.52) cm^3 s^{-1}.
[b] Mass of transferred sample condensed at T=243 K.
[c] Volume of nitrogen used to transfer sample.
[d] Vapour pressure at temperature T of experiment; corrections were made for residual vapour pressure at T=243 K.

Table 3
Results from typical combustion experiments at 298.15 K [a]

	1,3-di-iso-propylbenzene	1,4-di-iso-propylbenzene	1,3,5-tri-iso-propylbenzene
m(substance)/g [b]	0.408957	0.648698	0.644806
$m'_{(cotton)}$/g [b]	0.000876	0.001051	0.001291
$m''_{(polyethene)}$/g	0.276087	0.279223	0.263260
ΔT_c/K [c]	1.22769	1.65347	1.62855
$\varepsilon_{calor}(-\Delta T_c)$/J	−30830.53	−41546.58	−40920.46
$\varepsilon_{cont}(-\Delta T_c)$/J	−16.60	−22.78	−22.04
Δu_{corr}/J [d]	11.60	17.34	16.43
$-m'\Delta_c u'$/J	14.84	17.80	21.87
$-m''\Delta_c u''$/J	12799.66	12945.03	12204.99
$\Delta_c u$ (substance)/J g^{-1}	−44062.2	−44069.4	−44506.0

[a] For the definition of the symbols see Ref. [6]: T_h=298.15 K; V(bomb)=0.2664 dm^3; p^i(gas)=3.04 MPa; m^i(H$_2$O)=0.78 g; ΔU(ign)=1.46 J; m(Pt)=8.61 g;
[b] Masses obtained from apparent masses.
[c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; ε_{calor}=(25112.6±1.9) J K^{-1} for 1,3- and 1,4-di-isopropylbenzene, and ε_{calor}=(25126.9±1.9) J K^{-1} for 1,3,5-tri-isopropylbenzene, $(\varepsilon_{cont})(-\Delta T_c)=(\varepsilon^i_{cont})(T^i-298.15$ K$)+(\varepsilon^f_{cont})(298.15$ K$-T^f+\Delta T_{corr}.)$.
[d] Δu_{corr}, the correction to standard states is the sum of items 81 to 85, 87 to 90, 93, and 94 in Ref. [6].

Table 4
Values of specific energies of combustion $-\Delta_c u^0$ in J g^{-1} at T=298.15 K as the results of all combustion experiments

1,3-di-iso-propylbenzene	1,4-di-iso-propylbenzene	1,3,5-tri-iso-propylbenzene
44062.2	44069.4	44535.1
44084.6	44072.6	44506.0
44061.3	44069.3	44512.6
44078.7	44054.1	44526.6
44072.6	44085.5	44532.7
	mean value:	
44071.9±4.6	44070.2±5.0	44522.6±5.7

Table 5
Thermochemical results for iso-propylbenzenes at T=298.15 K (p^0=0.1 MPa) in kJ mol^{-1}

	$-\Delta_c H^0_m$ [a]	$\Delta_f H^0_m$ (l)	$\Delta_l^g H^0_m$ [b]	$\Delta_f H^0_m$ (g) (exp.)	$\Delta_f H^0_m$ (g) [c] (calc.)	H$_s$ [d]	Δ [e]
1,3-di-iso-propylbenzene	−7163.02±0.94	−131.56±0.94	56.17±0.82	−75.4±1.3	−84.4	9.0	−1.1
1,4-di-iso-propylbenzene	−7162.74±0.98	−131.83±0.98	56.49±0.27	−75.3±1.0	−84.4	9.1	−1.0
1,3,5-tri-iso-propylbenzene	−9113.5±1.4	−219.2±1.4	64.60±0.56	−154.6±1.5	−167.7	13.13	−2.0

[a] Calculated from the specific energies of combustion in Table 4. [b] Calculated from the measurements of vapour pressure at different temperatures from Table 2 using the Clausius–Clapeyron equation.
[c] Calculated as the sum of strain-free increments (see text).
[d] Strain enthalpy $H_s = \Delta_f H^0_m$ (g) (exp.)$- \Delta_f H^0_m$ (g) (calc.).
[e] The sum of resulting interactions of iso-propyl substituents in iso-propylbenzenes: $\Delta = H_s$ (di or tri-isopropylbenzene)$- n$ [H$_s$ (iso-propylbenzene)], where n is the number of iso-propyl substituents in a molecule.

enthalpies of combustion, and standard molar enthalpies of formation in the condensed and gaseous states. The given standard deviations of the mean

include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials.

3.2. Enthalpies of vaporization

The resulting enthalpies of vaporization $\Delta_l^g H_m^0$ at $T=298.15$ K are recorded in Table 2. Because of the deviations from $T=298.15$ K of the average temperatures of measurement by transpiration method, the observed values of the enthalpies of vaporization of iso-propylbenzenes (see Table 2) had to be corrected to this reference temperature. The corrections were estimated with help of the 'Sidgwick correction':

$$\{\Delta_l^g H_m^0(\langle T\rangle) - \Delta_l^g H_m^0(298.15\,\mathrm{K})\}(\mathrm{kJ\,mol^{-1}})$$
$$= -6\cdot10^{-2}\cdot\{(\langle T\rangle/K) - 298.15\},$$

following the recommendation of Chickos et al. [11]. With these corrections and the measured values of $\Delta_l^g H_m^0$ (T) from Table 2, the standard molar enthalpies at $T=298.15$ K were calculated (Tables 2 and 5).

3.3. Calculation of non-nearest neighbour interactions of iso-propyl substituents

We define the strain of a molecule, as the difference between the experimental standard enthalpy of formation $\Delta_f H_m^0$ (g) and the calculated sum of the strain-free increments of the Benson type [12,13] for this molecule. The system of strain-free increments is based on the standard enthalpies of formation $\Delta_f H_m^0$ (g) of simple homologous ('strainless') molecules. Strain-free group additivity increments for hydrocarbons [14] and arenes [15] are well defined. Their advantage with respect to the classic Benson increments [12] is the possibility to determine strain enthalpies. All the increments necessary in this work are as follows [14,15]: CH$_3$[C]=−42.05 kJ mol^{-1} CH$_2$[2C]=−21.46 kJ mol^{-1}; CH[3C]=−9.04 kJ mol^{-1}; C[4C]=−1.26 kJ mol^{-1}; C$_B$H[2C$_B$]=13.72 kJ mol^{-1}; C$_B$ [C,2C$_B$]=23.51 kJ mol^{-1} (C$_B$ represents the aromatic C atoms). Using the given group-additivity parameters and the values of $\Delta_f H_m^0$ (g) of iso-propylbenzenes (Table 5) derived in this research, the values of strain enthalpies $H_s=(\Delta_f H_m^0$ (g)$-\sum$ increments) of iso-propyl substituted benzenes have been estimated. These resulting interactions are listed in Table 5.

All studied iso-propylbenzenes are strained. Meta- and para-di-isopropylbenzene both have strained enthalpies of 9 kJ mol^{-1}, and 1,3,5- tri-isopropylbenzene has a strain enthalpy of ca. 13 kJ mol^{-1} (Table 5).

The value of $H_s=5.03$ kJ mol^{-1} calculated for the iso-propylbenzene ($\Delta_f H_m^0$ (g)=4.0±1.0 kJ mol^{-1}) [16] has been included in each molecule studied. This value describes the intrinsic strain of the iso-propylbenzenes due to steric repulsions of methyl groups and benzene ring attached to the tertiary carbon atom. The comparison with this strain allowed the derivation of the effects of non-nearest neighbour interactions of iso-propyl substituents on the benzene ring directly. We calculated the differences between individual strains for each compound studied in this work and the strain of iso-propylbenzene (Table 5). These values were interpreted as the sum of excess interactions of iso-propyl substituents on the benzene ring. The quantities of the pairwise interactions of iso-propyl substituents indicated (Table 5) the very weak stabilization (ca. 1 kJ mol^{-1}) independent of the type of substitution (meta- or para- position of iso-propyl substituents) of the benzene ring. The resulting weak stabilization (ca. 2 kJ mol^{-1}) was detected by the location of the three iso-propyl substituents on the benzene ring in 1,3,5-position. It is conspicuous, that all the effects of interaction detected here for meta-, para-, and 1,3,5-iso-propyl substituted benzenes are not significantly larger than the individual error bars of ca. (1.0 kJ mol^{-1}) of the thermochemical measurements, which were performed in this work. The same trend was observed for the methyl, ethyl, and propyl substituted benzenes [17]. Because of this, one can assure that no new group-additivity parameters or correction terms are necessary by the application of group-contribution correlation for $\Delta_f H_m^0$ (g) of the meta-, para-, and 1,3,5-alkylsubstituted (as alkyl: methyl, ethyl, propyl, and iso-propyl) benzenes.

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