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Thermochemical properties of branched alkylsubstituted benzenes

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The standard ($p^{\circ} = 0.1$ MPa) molar enthalpies of formation $\Delta_{\rm f} H_{\rm m}^{\circ}$ (l or cr) at the temperature T = 298.15 K were measured using combustion calorimetry for tert-butylbenzene, 4-methyl-1-tert-butylbenzene, 3,5-dimethyl-1-tert-butylbenzene, 5-methyl-1,3-di-tert-butylbenzene, and 1,4-di-tert-butylbenzene. The standard molar enthalpies of vaporization $\Delta_{\rm f}^{\rm g} H_{\rm m}^{\circ}$, or sublimation $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}$, of these compounds, and also of 3-methyl-1-tert-butylbenzene, 1,3-di-tert-butylbenzene, and 1,3,5-tri-tert-butylbenzene were obtained from the temperature function of the vapour pressure measured in a flow system. Enthalpies of fusion $\Delta_{\rm cr}^{\rm l} H_{\rm m}^{\circ}$ of solid compounds were measured by d.s.c. Strain enthalpies of branched alkylbenzenes were derived from the measured enthalpies of formation of the gaseous compounds. These experimental results, together with the data available from the literature, provided a quantitative understanding of the interrelations of structure and energetics of alkylbenzenes, and a further improvement on the group-contribution methodology for estimation of thermodynamic properties of organic compounds. \circledast 1998 Academic Press

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1. Introduction

Traditionally, relatively little characterization has been done on branched molecules in each class of organic compounds. Recently, systematic investigations have been done in the Thermochemical Laboratory of the University of Freiburg with measurements on branched ethers,⁽¹⁾ esters,⁽²⁾ nitriles,⁽³⁾ ketones,⁽⁴⁾ and hydrocarbons.⁽⁵⁾ This paper follows this course and is concerned with the investigation of branched alkylbenzenes with tert-butyl substituents. There is a paucity of thermochemical data for such compounds in the literature.⁽⁶⁾ Substituted branched alkylbenzenes are represented only by tert-butylbenzenes⁽⁷⁾ and tritertbutylbenzenes.⁽⁸⁾ This set of thermochemical information is too limited to provide a reliable concept for the prediction of enthalpies of formation of polyalkylsubstituted benzenes. We report here a systematic study of the thermochemical properties of a series of tert-butylbenzenes (figure 1). The resulting standard molar enthalpies of formation in the gas phase $\Delta_f H_m^{\circ}(g)$ of branched alkylbenzenes were

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FIGURE 1. Structures of alkylbenzenes: 1a, tert-butylbenzene; 1b, 3-methyl-1-tert-butylbenzene; 1c, 4-methyl-1-tert-butylbenzene; 1d, 3,5-dimethyl-1-tert-butylbenzene; 2a, 1,3-di-tert-butylbenzene; 2b, 5-methyl-1,3-di-tert-butylbenzene; 2c, 1,4-di-tert-butylbenzene; 2d, 1,3,5-tri-tert-butylbenzene.

obtained from calorimetrically measured enthalpies of combustion and enthalpies of sublimation, or vaporization by a transpiration method. These experimental results, together with the data available from the literature, provide a quantitative understanding of the relation between structure and properties of alkylbenznes. The results of the study also could be aimed at an improvement of the Benson group-contribution methodology.

2. Experimental

Pure Aldrich, Acros, and Merck products (figure 1), each with a mass fraction purity of about 0.99, were purified by repeated distillation under reduced pressure. The solid samples were purified by recrystallization from ethanol and petroleum ether and then sublimed at reduced pressure to remove any traces of solvent. Only 3-methyl-1-tert-butylbenzene was synthesized. This was done via isomerization of 4-methyl-1-tert-butylbenzene with a catalytic amount of AlCl₃ at room temperature. The degree of purity was determined by g.l.c. For all solid compounds, mass fraction purities of 0.9999 were additionally established by d.s.c. measurements of the melting process.⁽⁹⁾ No impurities (greater than mass fraction $1 \cdot 10^{-4}$) could be detected in tert-butylbenzenes (figure 1) by either method. The following equipment was used: g.l.c. (Carlo Erba Fraktometer Vega Series GC 6000), Hewlett Packard Integrator 3390A, N₂-flow of 0.333 cm³·s⁻¹, SE-30 capillary column of length 25 m. The standard temperature programme of the g.c. was T = 313 K for 5 min followed

	1a	1c	1d	2b	2c
$m(\text{substance})/g^b$	0.471137	0.593995	0.378116	0.371088	0.333575
$m'(\text{cotton})/g^b$	0.001074	0.001107	0.000867	0.000845	0.000909
m'' (polyethene)/g ^b	0.034480 ^e	0.271660	0.268297		
$\Delta T_{\rm c}/{\rm K}^c$	0.85202	1.53859	1.15803	0.65653	0.58914
$(\varepsilon_{\text{calor}}) \cdot (-\Delta T_{\text{c}})/\text{J}$	-21357.40	-38638.05	-29081.12	-16487.16	-14785.51
$(\varepsilon_{\rm cont.}) \cdot (-\Delta T_{\rm c})/{\rm J}$	-12.00	-20.91	-15.59	-8.33	-7.75
$\Delta u_{\rm corr.}/{\bf J}^d$	9.04	16.01	10.77	5.90	5.28
$-m' \cdot \Delta_{c} u' / \mathbf{J}^{d}$	18.20	18.75	14.68	14.31	15.40
$-m'' \cdot \Delta_{c} u'' / \mathbf{J}^{d}$	788.06	12594.41	12438.50		
$\Delta_{\rm c} u^{\circ}({\rm sub})/({\rm J} \cdot {\rm g}^{-1})$	-43623.6	-43819.1	-43984.6	-44393.3	-44281.3

TABLE 1. Results from typical combustion experiments at T = 298.15 K ($p^{\circ} = 0.1 \text{ MPa}$), where 1a = tert-butylbenzene, 1c = 4-methyl-1-tert-butylbenzene, 1d = 3,5-dimethyl-1-tert-butylbenzene, 2b = 5-methyl-1,3-di-tert-butylbenzene, and 2c = 1,4-di-tert-butylbenzene^{*a*}

^{*a*} For the definition of the symbols see reference 11: $T_{\rm h} = 298.15 \,\text{K}$; $V_{\rm bomb} = 0.2664 \,\text{dm}^3$; $p^{\rm i}(\text{gas}) = 3.04 \,\text{MPa}$; $m^{\rm i}(\text{H}_2\text{O}) = 0.78 \,\text{g}$; $\Delta U_{\rm ign} = 1.46 \,\text{J}$; $m(\text{Pt}) = 8.61 \,\text{g}$.

^b Masses obtained from apparent masses.

^c $\Delta T_c = T^{\rm f} - T^{\rm i} + \Delta T_{\rm corr}; \quad \varepsilon_{\rm calor} = (25066.7 \pm 1.8) \, {\rm J} \cdot {\rm K}^{-1}$ for substance 1a; $\varepsilon_{\rm calor} = (25112.6 \pm 1.9) \, {\rm J} \cdot {\rm K}^{-1}$ for substances 1c, 1d, and 2b; and $\varepsilon_{\rm calor} = (25096.64 \pm 0.54) \, {\rm J} \cdot {\rm K}^{-1}$ for substance 2c. $\varepsilon_{\rm cont} \cdot (-\Delta T_c) = (\varepsilon_{\rm cont}^{\rm i}) \cdot (T^{\rm i} - 298.15 \, {\rm K}) + (\varepsilon_{\rm cont}^{\rm f}) \cdot (298.15 \, {\rm K} - T^{\rm f} + \Delta T_{\rm corr}).$

 $^d\Delta u_{\rm corr},$ the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference 11.

^e Combustion in Mylar.

by a heating rate of $0.167 \text{ K} \cdot \text{s}^{-1}$ to T = 523 K. Melting temperatures and enthalpies of fusion were determined with a Perkin-Elmer DSC-2C.

For meausurements of the energies of combustion of tert-butylbenzenes, an isoperibolic macrocalorimeter with a static bomb and a stirred water-bath was used. The substances were placed in polyethene capsules or pressed into pellets of mass $\approx 400 \text{ mg}$ and were burned in oxygen at p = 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.^(2,10) 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 1) 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⁽¹¹⁾ were used. The atomic weights used were those recommended by the IUPAC Commission.⁽¹²⁾ The densities of the commercially available liquid compounds were taken from the Aldrich catalogue. The densities of solid substances were determined by submerging tablets of the substances in water in a calibrated 10 cm³ pycnometer. The massic heat capacities were measured with the d.s.c. The summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass is given in table 2.

The enthalpies of vaporization of tert-butylbenzene, 3-methyl-1-tert-butylbenzene, 4-methyl-1-tert-butylbenzene, 3,5-dimethyl-1-tert-butylbenzene, and 1,3-

	$\frac{T_{\rm fus}}{\rm K}^a$	$\frac{\Delta_{\rm cr}^{\rm l} H_{\rm m}^{\circ}}{{\rm kJ} \cdot {\rm mol}^{-1}}^{a}$	$\frac{\rho}{\mathbf{g} \cdot \mathbf{cm}^{-3}}^{b}$	$\frac{c_p}{\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{g}^{-1}}^a$	$\frac{10^{-6} \cdot (\partial v / \delta T)_p}{\mathrm{dm}^3 \cdot \mathrm{K}^{-1}}^c$
Tert-butylbenzene			0.867	1.73	1.0
4-Methyl-1-tert- butylbenzene 3 5 Dimethyl 1 tert			0.853	1.32	1.0
5. Methyl 1.3 di tert			0.867	1.48	1.0
butvlbenzene	307.55	18.43	0.922	1.28	0.1
1,4-Di-tert-butylbenzene	350.45	21.76	0.943	1.52	0.1
1,3,5-Tri-tert-butylbenzene	343.15	11.92			
Cotton ^d			1.500	1.67	0.1
Polyethene ^e			0.920	2.53	0.1
Mylar ^f			1.38	1.32	0.1

TABLE 2. Temperature of fusion $T_{\rm fus}$, standard molar enthalpy of fusion $\Delta_{\rm cr}^{\rm l} H_{\rm m}^{\circ}$, density ρ (T = 293 K), massic heat capacity c_p (T = 298.15 K), and expansion coefficients ($\delta v / \delta T$)_p of the materials used in the present study

^{*a*} From d.s.c. measurements; the usual error bars of $\Delta_{cr}^{l} H_{m}^{\circ}$ measurements are $\pm 0.21 \text{ kJ} \cdot \text{mol}^{-1}$. ^{*b*} Measured with a pycnometer. ^{*c*} Estimated. ^{*d*} From 10 combustion experiments, $\Delta_{c} u^{\circ} (\text{CH}_{1,774} \text{O}_{0.887}) = -(16945.2 \pm 4.2) \text{ J} \cdot \text{g}^{-1}$, where $\Delta_{c} u^{\circ}$ denotes standard massic energy of combustion. ^{*c*} From 11 combustion experiments, $\Delta_{c} u^{\circ} (\text{CH}_{1,930}) = -(46361.0 \pm 3.1) \text{ J} \cdot \text{g}^{-1}$. ^{*f*} From seven combusion experiments, $\Delta_{c} u^{\circ} (\text{CH}_{1,930}) = -(46361.0 \pm 3.1) \text{ J} \cdot \text{g}^{-1}$. ^{*f*} From seven combusion experiments, $\Delta_{c} u^{\circ} (\text{CH}_{1,930}) = -(46361.0 \pm 3.1) \text{ J} \cdot \text{g}^{-1}$. ^{*f*} From seven combusion experiments, $\Delta_{c} u^{\circ} (\text{Cm}_{1,930}) = -(22838.8 \pm 4.8) \text{ J} \cdot \text{g}^{-1}$. Calculation of mass of the dry mylar film using the dependence of mass on humidity: $m_{dry} = m_{moist}(1 - 4.64 \cdot 10^{-5} r_{H})$, where r_{H} denotes relative humidity.

di-tert-butylbenzene, and enthalpies of sublimation of 5-methyl-1,3-di-tertbutylbenzene, 1,4-di-tert-butylbenzene, and 1,3,5-tri-tert-butylbenzene were determined with the method of transference in a saturated N₂ stream^(5,10,13) using the Clausius–Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted 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 to 0.56) cm³·s⁻¹ of the nitrogen stream was optimised in order to reach the equilibrium of saturation of the transporting gas at each temperature of the investigation. The amount of condensed substance was determined by g.c. analysis using an internal standard (hydrocarbons, C₁₁H₂₄ or C₁₃H₂₈). 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 $p \cdot V = n \cdot R \cdot T$:

$$p = m \cdot R \cdot T / \{ V(\mathbf{N}_2) \cdot M \}, \tag{1}$$

where $R = 8.31451 \,\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$; *m* is the mass of transported compound; $V(\mathrm{N}_2)$ is the volume of transporting gas; *M* is the molar mass of the compound; and *T* is 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 $0.8) \,\mathrm{cm}^3 \cdot \mathrm{s}^{-1}$, which proved that the transporting gas was saturated with the compound. The vapour pressure *p* was corrected for the residual vapour pressure

T/\mathbf{K}^{a}	m/mg^b	$V(N_2)/dm^{3 c}$	p/\mathbf{Pa}^d	T/\mathbf{K}^{a}	m/mg^b	$V(N_2)/dm^{3 c}$	p/\mathbf{Pa}^d
			tert-butylbe	nzene (1a)	2		
278.1	6.12	1.739	69.70	293.1	8.91	0.844	199.6
281.7	2.92	0.644	88.51	296.7	3.96	0.303	246.2
283.0	5.86	1.146	99.12	298.1	11.8	0.782	283.4
286.9	3.73	0.555	129.0	303.1	8.11	0.404	375.1
288.1	6.70	0.881	145.1	306.7	7.25	0.280	482.9
291.7	3.95	0.414	181.2	308.2	9.15	0.328	519.7
Δ_1^{g}	$^{5}H_{\rm m}^{\circ}(293.1~{\rm K}$	(47.80 ± 0.36)	$kJ \cdot mol^{-1};$	$\Delta_1^{\rm g} H_{\rm m}^{\circ}$ (298.	15 K) = (47.	50 ± 0.36 kJ·mol	 −1
		1-tert-	-butyl-3-met	hylbenzene	e (1b) ^e		
278.7	0.893	1.784	8.954	298.3	1.10	0.471	39.72
283.5	0.958	1.313	12.78	303.3	1.08	0.337	54.40
288.6	1.13	1.044	18.72	308.4	1.08	0.236	77.43
293.4	1.03	0.640	27.61	313.5	0.845	0.141	100.8
$\Delta_1^{g} H_m^{\circ}(296.1 \text{ K}) = (51.40 \pm 0.60) \text{ kJ} \cdot \text{mol}^{-1}; \Delta_1^{g} H_m^{\circ}(298.15 \text{ K}) = (51.27 + 0.60) \text{ kJ} \cdot \text{mol}^{-1}$							
•		1-tert-	-butvl-4-met	hvlbenzene	e (1b) ^e		
979 1	1.07	1 612	91.90	208.2	9 97	0.407	07 95
210.4 992 1	1.57	1.013	21.20	202 1	2.07	0.497	125.0
200.4	2.40	1.334	31.82 46.93	303.1	2.24	0.279	106.8
293.4	2.83	0.712	40.23	313.2	1.90	0.125	254.4
Λ ^g	⁵ H° (295.8 K	(52.31 + 0.46)	kJ·mol ^{−1} :	$\Lambda^{g}_{H^{\circ}}(298)$	(15 K) = (52)	17 + 0.46 kJ·mol	-1
-1	11 _m (200.011	$1 \text{ tort } \mathbf{h}$	utvl 3.5 dim	othylbonzo	$10 11)^{e}$	17 <u>+</u> 0.10) is inc.	
		1-1011-0	uty1-5,5-uiii	euryiberize	ne (1u)		
283.6	2.50	3.530	11.20	303.3	4.01	1.120	54.99
288.3	3.46	3.200	16.86	308.4	4.65	0.877	81.25
293.4	4.27	2.610	25.35	313.2	4.59	0.653	107.7
298.1	3.95	1.670	36.49	318.2	4.63	0.469	151.0
Δ_1^{g}	$^{8}H_{\rm m}^{\circ}(300.9{\rm K}$	$) = (56.47 \pm 0.60)$	$kJ \cdot mol^{-1};$	$\Delta_1^{g} H_{m}^{\circ}(298.$	15 K) = (56.	63 ± 0.60) kJ · mol	-1
		1,3-	di-tert-buty	lbenzene (2a) ^e		
288.3	3.58	6.500	7.243	313.4	11.1	2.740	52.91
293.1	4.67	5.440	11.24	318.0	12.0	2.090	74.50
297.9	5.84	4.620	16.53	322.9	14.6	1.760	107.9
303.2	7.29	3.890	24.47	328.0	11.1	1.020	142.2
308.1	11.7	4.060	37.49	333.1	11.3	0.750	197.0

TABLE 3. Results from measurements of the vapour pressure p by the transpiration method

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 sublimation were calculated from the slope of the linear Clausius–Clapeyron correlation $\Delta_{cr}^{g} H_{m}^{\circ} = -R(\operatorname{dln} p/\operatorname{d} T^{-1})$. The observed enthalpies of vaporization $\Delta_{1}^{g} H_{m}^{\circ}(T)$, or sublimation $\Delta_{cr}^{g} H_{m}^{\circ}(T)$, at the temperature T obtained by this procedure are listed in table 3.

 $\Delta_{l}^{g}H_{m}^{\circ}(310.7\,\text{K}) = (58.85\,\pm\,0.48)\,\text{kJ}\cdot\text{mol}^{-1};\, \Delta_{l}^{g}H_{m}^{\circ}(298.15\,\text{K}) = (59.60\,\pm\,0.48)\,\text{kJ}\cdot\text{mol}^{-1};\, \Delta_{l}^{g}H_{m}^{\circ}(298\,\text{K}) = (59.60\,\pm\,0.48$

For the purpose of comparing enthalpies of formation of alkylbenzenes measured by combustion calorimetry with data obtained by another method, results from our previous equilibrium study^(14,15) have been included in this paper. The enthalpies of reactions (figure 2) of isomerization and transalkylation of liquid tert-

T/\mathbf{K}^{a}	m/mg^b	$V(N_2)/dm^{3 c}$	p/\mathbf{Pa}^d	T/\mathbf{K}^{a}	m/mg^b	$V(N_2)/dm^{3 c}$	p/\mathbf{Pa}^d
		1,3-di-te	ert-butyl-5-n	nethylbenz	ene $(2b)^e$		
274.7	2.23	87.82	0.3119	294.3	3.16	10.79	3.556
278.8	1.96	44.44	0.5395	297.5	2.65	6.37	5.046
284.0	2.81	33.52	1.020	301.1	2.18	3.60	7.335
289.1	3.64	23.83	1.858				
$\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}(287.9{\rm K}) = (82.42\pm0.47){\rm kJ}\cdot{\rm mol}^{-1}; \Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}(298.15{\rm K}) = (81.80\pm0.47){\rm kJ}\cdot{\rm mol}^{-1}$							
		1,3-di-te	ert-butyl-5-n	nethylbenz	ene (2b) ^e		
308.9	1.95	1.540	15.39	328.4	2.23	0.430	62.79
313.9	2.43	1.310	22.55	333.4	2.08	0.280	90.03
318.7	2.85	1.050	32.89	338.3	1.57	0.150	126.7
323.6	2.44	0.680	43.58				
Δ_1^{ϵ}	$^{3}H_{\rm m}^{\circ}(323.6{\rm K}$	$) = (61.75 \pm 0.90)$	$kJ \cdot mol^{-1};$	$\Delta_1^{\rm g} H_{\rm m}^{\circ}$ (298	(63.15 K) = (63.15 K)	0.27 ± 0.90 kJ \cdot mo	ol^{-1}
		1,4	-di-tert-buty	benzene	(2c) ^e		
288.2	1.13	20.85	0.7055	313.3	3.53	4.14	11.09
293.2	1.89	18.60	1.324	318.2	5.18	3.78	17.82
298.0	2.32	13.58	2.229	323.1	5.64	2.44	30.09
303.3	2.31	7.52	3.994	328.2	4.80	1.36	45.93
308.2	2.84	5.52	6.706	333.2	4.60	0.800	74.89
$\Delta^{ m g}_{ m cr}$	$H_{\rm m}^{\circ}(310.7{\rm K}$	$) = (82.08 \pm 0.36)$	$kJ \cdot mol^{-1};$	$\Delta^{\rm g}_{\rm cr} H^{\circ}_{\rm m}(29$	8.15 K) = (8)	$2.83 \pm 0.36) \mathrm{kJ} \cdot \mathrm{m}$	ol^{-1}
		1,3,	5-tri-tert-bu	tylbenzene	(2d) ^e		
297.7	2.72	27.20	1.009	323.4	8.33	6.150	13.64
303.3	4.04	22.11	1.841	328.4	11.4	5.450	21.07
308.5	5.14	16.12	3.210	333.4	8.85	2.720	32.76
313.4	6.05	11.71	5.207	338.4	7.11	1.460	49.02
318.3	9.57	11.47	8.402	341.3	6.08	0.970	63.12
$\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}(219.5{\rm K}) = (79.93\pm0.26){\rm kJ}\cdot{\rm mol}^{-1}; \ \Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}(298.15{\rm K}) = (81.21\pm0.26){\rm kJ}\cdot{\rm mol}^{-1}$							

TABLE 3—continued

^{*a*} Temperature of saturation, N₂ gas flow (0.26 to 0.52) cm³·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, calculated from m and the residual vapour pressure at T = 243 K. ^{*c*} For explanation of number in parenthesis, see figure 1.

butylbenzenes have been determined in our previous work.⁽¹⁴⁾ In order to provide clarity, the methods used here are briefly discussed in this paper. The study was performed in the liquid phase, in glass bulbs, which were at least two-thirds filled with the initial mixture of benzene and tert-butylbenzenes. The catalyst used was AlBr₃ {mole fraction (0.01 to 0.03)}. The bulbs were thermostatted at $T_i \pm 0.2$ K. At the end of each experiment, the glass bulbs were opened in ice water, the organic products were separated, and the compounds dissolved in water and extracted with ether; the organic products were combined with the ether extracts and analysed by g.c. It was established experimentally that the treatment of the samples did not shift the equilibrium. The study was performed in the temperature range (272 to 373) K. At each experimental temperature the equilibrium concentrations of benzene, 1,3- and 1,4-di-tert-butylbenzene, and 1,3,5-tri-tert-butylbenzene varied by



FIGURE 2. Reactions investigated by chemical equilibrium method.

a factor of (4 to 7). The concentration equilibrium constants of reactions (1 to 3) were independent {within (3 to 7) per cent} of the composition of the equilibrium mixtures, and can thus be assumed to be equal to the thermodynamic constants. The experimental data were approximated with the linear equation $\lg K_N = a + b \cdot T^{-1}$, using the method of least squares. The reaction of the positional isomerization of 1-tert-butyl-4-methylbenzene to 1-tert-butyl-3-methylbenzene (figure 2) has been investigated⁽¹⁵⁾ in the same manner.

3. Results and discussion

The results for a typical combustion experiment on each compound are given in table 1. The individual values of the standard massic energy of combustion $\Delta_c u^\circ$, together with the mean and its standard deviation, are given in table 4. To derive $\Delta_f H^\circ_m$ from $\Delta_c H^\circ_m$, the following molar enthalpies of formation were

	2c = 1,4-di-tert-butylbenzene							
1a	1c	1d	2b	2c				
		$-\Delta_{\rm c} u^{\circ}/(\mathbf{J} \cdot \mathbf{g}^{-1})$						
43623.6	43799.7	43984.6	44393.3	44281.3				
43616.9	43810.3	43975.5	44395.0	44283.9				
43640.8	43819.1	43987.8	44386.8	44279.8				
43635.8	43825.0	43974.2	44398.7	44273.9				
43615.3	43821.7	43977.8	44388.2	44274.8				
43631.6		$\langle -\Delta_c u^{\circ} \rangle / (\mathbf{J} \cdot \mathbf{g}^{-1})$						
43627.3	43815.2	43980.0	44392.4	44278.7				
± 4.2	± 4.6	± 2.7	± 2.2	± 0.9				

TABLE 4. Values of standard massic energies of combustion $\Delta_c u^\circ$ at T = 298.15 K ($p^\circ = 0.1$ MPa). $\langle \Delta_c u^\circ \rangle$ denotes mean value. 1a = tert-butylbenzene, 1c = 4-methyl-1-tert-butylbenzene, 1d = 3,5-dimethyl-1-tert-butylbenzene, 2b = 5-methyl-1,3-di-tert-butylbenzene, and 2c = 1.4-di-tert-butylbenzene

used:⁽¹²⁾ for H₂O(l): $-(285.83 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$, and for CO₂(g): $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$. Table 5 lists the derived standard molar enthalpies of combustion and standard molar enthalpies of formation of the compounds in the condensed and gaseous states. The assigned standard deviations of the mean include the uncertainties from calibration and combustion energies of the auxiliary materials. The only previous determination of the standard molar enthalpy of formation $\Delta_{\rm f} H^{\circ}_{\rm m}(l)$ of tert-butylbenzene was made by Prosen *et al.*⁽⁷⁾ using combustion calorimetry. Their value of $-(70.7 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$ is in agreement with our value of $-(71.92 \pm 0.71) \text{ kJ} \cdot \text{mol}^{-1}$ within the bounds of the uncertainties.

The experimental enthalpies of vaporization $\Delta_1^g H_m^\circ$, or sublimation $\Delta_{cr}^g H_m^\circ$, at T = 298.15 K are recorded in table 3. Because of the deviations from T = 298.15 K of the average temperatures of measurements by the transpiration method, the observed values of the enthalpies of vaporization, or sublimation of alkylbenzenes (see table 3) had to be corrected to this reference temperature. The corrections were estimated with help of the "Sidgwick correction":

$$\{\Delta_{1}^{g}H_{m}^{\circ}(\langle T \rangle) - \Delta_{1}^{g}H_{m}^{\circ}(298.15 \text{ K})\}/(\text{kJ}\cdot\text{mol}^{-1}) = -6\cdot10^{-2}\cdot\{(\langle T \rangle/\text{K}) - 298.15\},\$$
(2)

following the recommendation of Chickos *et al.*⁽¹⁶⁾ With these corrections and the measured values of $\Delta_1^g H_m^{\circ}(T)$ and $\Delta_{cr}^g H_m^{\circ}(T)$ from table 3, the standard molar enthalpies of vaporization or sublimation at T = 298.15 K were calculated (tables 3 and 5).

Determinations of the enthalpies of vaporization and of sublimation of alkylbenzenes have been made by a number of groups in recent years. The values are very consistent with this research as can be seen by reference to table 6. The observed values of $\Delta_{cr}^g H_m^o(T)$ for 1,4,-di-tert-butylbenzene⁽¹⁷⁾ and 1,3,5-tri-tert-butylbenzene⁽¹⁸⁾ were extrapolated to T = 298.15 K in the same manner as our results, using the "Sidgwick correction". The enthalpy of sublimation at T = 298.15 K of 1,4,-di-tert-butylbenzene, derived from ebulliometry and d.s.c. measurements recently,⁽¹⁹⁾ is in a good agreement with this work within the boundaries of the experimental uncertainties.

	$\Delta_{ m c} {H_{ m m}^\circ}^{~a}$	$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}(\mathrm{l, or \ cr})$	$\Delta_1^g H_m^{\circ} ^b$	$\Delta_{\rm f} H^{\circ}_{ m m}({ m g})({ m expt})$	$\Delta_{ m f} H^{\circ}_{ m m}({ m g})({ m calc})^c$	$\Delta H_{\rm m}(strain)^d$	а е
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
Tert-butylbenzene (l)	-5863.96 ± 0.71	-71.92 ± 0.71	47.50 ± 0.36	-24.42 ± 0.80	-35.30	10.88	
3-Methyl-1-tert-butylbenzene (l)		-109.74 ± 0.87	51.27 ± 0.60	-58.5 ± 1.1	-67.56	9.1	-1.8
4-Methyl-1-tert-butylbenzene (l)	-6506.52 ± 0.86	-109.72 ± 0.86	52.17 ± 0.46	-57.55 ± 0.98	-67.56	10.01	-0.9
3,5-Dimethyl-1-tert-butylbenzene (1)	-7148.10 ± 0.72	-146.48 ± 0.72	56.63 ± 0.50	-89.85 ± 0.88	-99.82	9.97	-0.9
1,3-Di-tert-butylbenzene (l)		-188.75 ± 0.57	59.60 ± 0.48	-129.15 ± 0.75	-152.92	23.77	2.0
5-Methyl-1,3-di-tert-butylbenzene (cr)	-9086.84 ± 0.83	-245.76 ± 0.83	81.80 ± 0.47^{f}	-163.96 ± 0.95	-185.18	21.22	-0.5
1,4-Di-tert-butylbenzene (cr)	-8441.27 ± 0.41	-211.99 ± 0.41	82.83 ± 0.36^{f}	-129.16 ± 0.55	-152.92	23.76	2.0
1,3,5-Tri-tert-butylbenzene (cr)		-320.0 ± 1.4	81.21 ± 0.26^{f}	-238.8 ± 1.4	-270.54	31.7	-0.9
^{<i>a</i>} Calculated from the massic energie	es of combustion in	table 4. ^b Calcul	ated from the m	easurements of vap	our pressure at diffe	erent temperature	s from table 2
using the Clausius-Clapeyron equat	tion. ^c Calculated	as the sum of s	strain-free incre	ments (see text).	^d Strain enthalpy	$\Delta H_{\rm m}({\rm strain}) = \Delta_{\rm f}$	$H_m^{\circ}(g)(expt) -$
$\Delta_{\epsilon} H^{\circ}_{m}(g)(calc)$. ^e The sum of resultin	ug interactions of al	lkvl substituents ir	n alkvlbenzenes:	$\Delta = \Delta H_{\rm m}({\rm strain})(a$	lkvl-benzene) – $n\{\Delta$	A H(strain)(tert-b)	utvl-benzene)}.

TABLE 5. Thermochemical results for alkylbenzenes at $T = 298.15 \text{ K} (p^\circ = 0.1 \text{ MPa})$

nuty1-1 √^m ⊔ ∇ 1 ł = dikyi 5 mult ulle $\Delta_{\rm f} H_{\rm m}^{\rm M}$ (g)(carc). The sum of the f Enthalpy of sublimation $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}$.

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	$\frac{\Delta_l^g H_m^\circ}{kJ\!\cdot\!mol^{-1}}$	$\frac{\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}}{\rm kJ} \cdot {\rm mol}^{-1}}$	Reference
Tert-butylbenzene	48.1 ± 0.2		7
	47.7 ± 0.2		23
	47.5 ± 0.4		24
	47.5 ± 0.4		This work
1,-4-Di-tert-butylbenzene	63.0 ± 0.6	83.2 ^{<i>a</i>}	17
U U		$84.5~\pm~0.8$	19
		82.8 ± 0.4	This work
1,3,5-Tri-tert-butylbenzene		79.5 ± 0.4^b	18
		81.2 ± 0.3	This work

TABLE 6. Comparison at T = 298.15 K with earlier values of enthalpy of vaporization or sublimation

^{*a*} The observed value ($\langle T \rangle$ = 305 K) 82.8 kJ·mol⁻¹ was extrapolated to T = 298.15 K. ^{*b*} The observed value ($\langle T \rangle$ = 294 K) 79.7 kJ·mol⁻¹ was extrapolated to T = 298.15 K.

The following results⁽¹⁴⁾ were obtained from the study of the equilibria of reactions (1 to 3) (see figure 2): $\lg K_{\rm N} = 0.3268 - 77.3 \cdot (T/{\rm K})^{-1}$, $\Delta_{\rm r} H_{\rm m} = (1.48 \pm 0.33) \, \text{kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\rm r} S_{\rm m} = (6.26 \pm 0.73) \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for reaction (1); $\lg K_{\rm N} = 0.5436 + 157.5 \cdot (T/{\rm K})^{-1}$, $\Delta_{\rm r} H_{\rm m} = -(3.02 \pm 0.72) \, \text{kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\rm r} S_{\rm m} = (10.41 \pm 1.66) \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for reaction (2); and $\lg K_{\rm N} = 0.5752 - 52.3 \cdot (T/{\rm K})^{-1}$, $\Delta_{\rm r} H_{\rm m} = (1.00 \pm 1.08) \, \text{kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\rm r} S_{\rm m} = (11.01 \pm 3.62) \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for reaction (3).

The values of the enthalpies $\Delta_r H_m$ and entropies $\Delta_r S_m$ of reactions (1 to 3) were derived for the average temperature 313 K. In further calculations it was assumed that the enthalpies of the reaction hardly change on passing from the average temperature of the experimental range to T = 298.15 K.

Reaction (4) was investigated in the liquid phase and in the temperature range (293 to 383) K. The following experimental results were derived⁽¹⁵⁾ for the average temperature 338 K by this study: $\lg K_{\rm N} = 0.3291 - 1.04 \cdot (T/{\rm K})^{-1}$, $\Delta_{\rm r} H_{\rm m} = (0.02 \pm 0.13) \, \rm kJ \cdot mol^{-1}$, and $\Delta_{\rm r} S_{\rm m} = (6.30 \pm 0.40) \, \rm J \cdot {\rm K}^{-1} \cdot mol^{-1}$. The errors in the thermodynamic functions are given by the uncertainty for the meaningful level 0.05. They were derived in accordance with the requirements of the IUPAC Commission and include the errors in the equilibrium constants K_N as well as deviations of K_N from linear dependence $\lg K_N = a + b \cdot (T/K)^{-1}$. Using the experimental enthalpy of reaction (1), and the enthalpy of formation

of liquid 1,4-di-tert-butylbenzene, $\Delta_f H_m^{\circ}(l) = \Delta_f H_m^{\circ}(cr) + \Delta_{cr}^l H_m^{\circ} = -190.23$ kJ·mol⁻¹ (from tables 2 and 5), the enthalpy of formation in the liquid phase of 1,3-di-tert-butylbenzene was calculated to be $\Delta_f H_m^{\circ}(l) = -(188.75 \pm$ 0.57) kJ·mol⁻¹. The valuable check of the experimental data for mutual consistency allows the calculation of $\Delta_{\rm f} H^{\circ}_{\rm m}(l)$ of 1,3-di-tert-butylbenzene from the experimental enthalpy of reaction (2) and the enthalpies of formation of benzene $\Delta_f H_m^{\circ}(l) = (49.0 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1(6)}$ and tert-butylbenzene (see table 5). Calculated in this way, the value $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm l})$ of 1,3-di-tert-butylbenzene $-(189.8 \pm 1.2) \, \rm kJ \cdot mol^{-1}$ is in a very good agreement with the calculation from data for reaction (1).

Using the experimental enthalpy of reaction (3) and the enthalpies of formation of tert-butylbenzene, and 1,3- and 1,4-di-tert-butylbenzene (see table 5), the

enthalpy of formation $\Delta_{\rm f} H^{\circ}_{\rm m}(l)$ of 1,3,5-tri-tert-butylbenzene $-(308.1 \pm 1.4) \, \rm kJ \cdot mol^{-1}$ was calculated. By taking into account the enthalpy of fusion $\Delta_{\rm cr}^{\rm l} H^{\circ}_{\rm m} = 11.92 \, \rm kJ \cdot mol^{-1}$ of 1,3,5-tri-tert-butylbenzene (table 2), our value for $\Delta_{\rm f} H^{\circ}_{\rm m}(cr)$ agrees satisfactorily with the value of $-(321.9 \pm 3.8) \, \rm kJ \cdot mol^{-1}$ measured by combustion calorimetry.⁽⁸⁾ The experimental enthalpy of reaction (4) allowed the calculation of $\Delta_{\rm f} H^{\circ}_{\rm m}(l)$ of 3-methyl-1-tert-butylbenzene, $-(109.74 \pm 0.87) \, \rm kJ \cdot mol^{-1}$, from the known (table 5) enthalpy of formation $\Delta_{\rm f} H^{\circ}_{\rm m}(l)$ of 4-methyl-1-tert-butylbenzene. A summary of the standard enthalpies of formation derived in this investigation is given in table 5.

We define the strain of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm g})$ and the calculated sum of the strain-free increments of the Benson type⁽²⁰⁾ for this molecule. The system of strain-free increments is based on the standard enthalpies of formation $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm g})$ of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons⁽²¹⁾ and arenes⁽²²⁾ are well defined. Their advantage with respect to the classic Benson increments⁽²⁰⁾ is the possibility to determine strain enthalpies. All the increments necessary in this work are as follows:^(21,22) $CH_3[\hat{C}] =$ $-42.05 \text{ kJ} \cdot \text{mol}^{-1}$; $CH_2[2C] = -21.46 \text{ kJ} \cdot \text{mol}^{-1}$; $CH[3C] = -9.04 \text{ kJ} \cdot \text{mol}^{-1}$; $C[4C] = -1.26 \text{ kJ} \cdot \text{mol}^{-1}; C_{B}H[2C_{B}] = 13.72 \text{ kJ} \cdot \text{mol}^{-1}; C_{B}[C, 2C_{B}] = 23.51$ $kJ \cdot mol^{-1}$ (where C_B represents the aromatic C atoms). Using these group-additivity parameters and the values of $\Delta_f H_m^{\circ}(g)$ of alkylbenzenes (table 5) derived in this research, the values of strain enthalpies $\Delta H_{\rm m}({\rm strain}) = \{\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g}) - \Sigma \text{ increments}\}$ of alkylsubstituted benzenes have been estimated. These resulting interactions are listed in table 5. All studied tert-butylbenzenes are strained. The value of $\Delta H_{\rm m}({\rm strain}) = 10.88 \, {\rm kJ} \cdot {\rm mol}^{-1}$ for the tert-butylbenzene has been included in each molecule studied. This value describes the intrinsic strain of the tert-butylbenzenes due to steric repulsions of methyl groups and the benzene ring attached to the quaternary carbon atom. The comparison with this strain allowed the derivation of the effects of non-nearest-neighbour interactions of alkyl substituents on the benzene ring directly. We calculated the differences between individual strains for each compound and the strain of tert-butylbenzene (table 5). These values were interpreted as the sum of excess interactions of alkylsubstituents on the benzene ring. The quantities of the pairwise interactions of methyl and tert-butyl substituents indicated a very weak stabilization (about $0.9 \text{ kJ} \cdot \text{mol}^{-1}$ to $1.8 \text{ kJ} \cdot \text{mol}^{-1}$), independent of the type of substitution (meta- or para- position of alkyl substituents) of the benzene ring. The interactions of the two tert-butyl groups led to a weak destabilization $(2.0 \text{ kJ} \cdot \text{mol}^{-1})$ both in the meta- and para- substitution. The resulting weak stabilization (about $0.5 \text{ kJ} \cdot \text{mol}^{-1}$ to $0.9 \text{ kJ} \cdot \text{mol}^{-1}$) was detected by the location of the three alkyl substituents on the benzene ring in the 1,3,5-positions. It is significant that all the effects of interactions for meta- and para- alkyl substituted benzenes (alkyl: methyl and tert-butyl) detected here are not significantly larger than the individual error bars of about $\pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ of the thermochemical measurements, which were performed in this work. The same trend was observed for the methyl-, ethyl-, and propyl-substituted benzenes.⁽²⁵⁾ Because of this, one can be assured that no new group-additivity parameters or correction terms are necessary for the application of the group-contribution

correlation for $\Delta_f H_m^{\circ}(g)$ of the meta-, para-, and 1,3,5-alkylsubstituted (as alkyl: methyl, ethyl, propyl, and tert-butyl) benzenes.

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