Thermochemistry of Halogen-Substituted Methylbenzenes

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S Supporting Information

ABSTRACT: Experimental vapor pressures, vaporization, fusion, and sublimation enthalpies of a number of bromo- and iodo-substituted methylbenzenes have been studied by transpiration method in order to evaluate a series of experimental measurements that appear to be internally self-consistent. The compounds studied in this regard include bromobenzene, iodobenzene, 1-bromo-2-methylbenzene, 1-bromo-3-methylbenzene, 1-bromo-4-methylbenzene, 1-iodo-2-methylbenzene, 1-iodo-3-methylbenzene, 1-iodo-4-methylbenzene, 1-bromo-2,6-dimethylbenzene, 1-iodo-2,6-dimethylbenzene, and 1-iodo-2,4-dimethylbenzene. Gas-phase enthalpies of formation of halogen-substituted methylbenzenes were calculated by using quantum-chemical methods. Simple group-additivity procedures were developed for estimation of vaporization enthalpies and gas-phase and liquid-phase enthalpies of formation of halogen-substituted methylbenzenes.

R₁ = F, Cl, Br, I   R₂ = H, CH₃
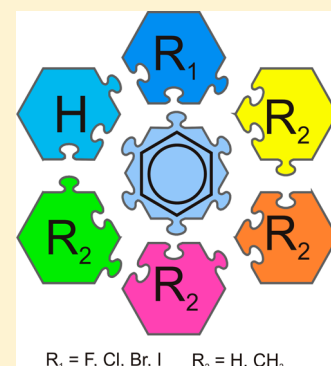
1. INTRODUCTION

Accurate thermodynamic properties for chemicals are needed for the assessment of the feasibility of chemical processes and for design of new and more efficient synthetic routes, as well as for the assessment of the fate of chemicals in the environment. As a rule, two approaches are common to obtain values of thermodynamic properties: experimental and predictive. The experimental approach is associated with higher costs, but it yields more accurate values. In the predictive approach a practical model is developed using certain degree of available empirical observations. A most practical model for simple predictions seems to be the group-additivity approach.[1] However, application of this approach for cyclic and large molecules is restricted.[2] In recent decades, a modern computational chemistry based on high-level quantum-chemical methods has been also successfully used to predict the thermodynamics of chemicals.[3] In the current study, we consider combination of experimental, group-additivity, and quantum-chemical approaches as a reasonable tool to collect a reliable and consistent data set for halogenated benzenes in order to understand general regularities in structure–property relations for this environmentally important class of organic compounds. The focus of the current work is vapor pressures temperature dependence studies, leading to the molar vaporization enthalpies, $\Delta_l^g H_m$, combined with the high-level computational chemistry methods to predict molar enthalpies of formations of halogen-substituted benzenes. Halogenated benzenes are dangerous pollutants appearing in the atmosphere as decomposition products of polyhalogenated biphenyls, dioxins, and so on. The fate and transport of pollutants in the atmosphere are governed by vapor pressures, vaporization enthalpies, and enthalpies of formation. As a part of our systematic studies on the thermochemistry of halogen organic compounds,[4−6] in this work we present new vapor pressure data for 12 halogen-substituted benzenes and methylbenzenes: vapor pressures of bromobenzene, iodobenzene, 1-bromo-2-, 3-, and 4-methylbenzenes, 1-iodo-2-, 3-, and 4-methylbenzenes, as well as of 1-bromo-2,6-dimethylbenzene, 1-iodo-2,6-dimethylbenzene, and 1-iodo-2,4-dimethylbenzene were measured by the transpiration method. Molar standard enthalpies of vaporization, $\Delta_l^g H_m$, for these compounds were calculated from temperature dependences of vapor pressures. These data together with data for halo-methylbenzenes collected from the literature were used to develop a group-additivity procedure for mono- and dihalogen-substituted benzenes. This procedure allowed evaluation of the available $\Delta_l^g H_m$ data set. The evaluated vaporization enthalpies were combined with G4 calculated gaseous enthalpies of formation, $\Delta_f H_m^\circ(g)$, in order to derive molar enthalpies of formation, $\Delta_f H_m^\circ(\text{liq})$, of the halogen-benzenes in the liquid phase absent in the literature.

2. EXPERIMENTAL SECTION

2.1. Materials. All samples used in this work were of commercial origin (see Table 1). Prior to experiments the samples were purified by repeated vacuum fractional distillation

Table 1. Provenance and Purity of the Materials

material	CAS RN	source	initial mass fraction purity	final mole fraction purity[a]
bromobenzene	108-86-1	Sigma-Aldrich	0.99	0.999
iodoobenzene	591-50-4	Sigma-Aldrich	0.98	0.999
1-bromo-2-methylbenzene	95-46-5	Sigma-Aldrich	0.99	0.999
1-bromo-3-methylbenezene	591-17-3	Sigma-Aldrich	0.99	0.999
1-bromo-4-methylbenzene	106-38-7	Sigma-Aldrich	0.99	0.999
1-iodo-2-methylbenzene	615-37-2	Sigma-Aldrich	0.97	0.999
1-iodo-3-methylbenzene	625-95-6	Sigma-Aldrich	0.99	0.999
1-iodo-4-methylbenzene	624-31-7	Sigma-Aldrich	0.99	0.999
1-bromo-2,6-dimethylbenzene	576-22-7	Sigma-Aldrich	0.97	0.998
1-iodo-2,6-dimethylbenzene	608-28-6	Sigma-Aldrich	0.97	0.999
1-iodo-2,4-dimethylbenzene	4214-28-2	Sigma-Aldrich	0.97	0.999

[a]Purity after fractional distillation under reduced pressure measured by gas−liquid chromatograpy.

with the Teflon spinning-band column under reduced pressure. The sample purity was determined by using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector. The carrier gas (nitrogen) flow was 12.1 cm^3·s^{-1}. A capillary column HP-5 (stationary phase cross-linked 5 % phenyl methyl silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was T = 333.15 K for 180 s followed by a heating rate of 0.167 K·s^{-1} to T = 523.15 K. No impurities (greater than mass fraction 0.002) could be detected in the samples used for the thermochemical measurements (see Table 1).

2.2. Transpiration Method and Uncertainties. *2.2.1. Experimental Setup.* The transpiration method has been successfully used in our laboratory for measurements of relatively low vapor pressures of around 500 Pa and downward.[7−9] This method is often used at the temperatures around 298 K, where the data are especially relevant for textbooks and compilations. An experimental setup used in this work is given in Figure 1. About (0.5 to 1) g of the pure sample was mixed
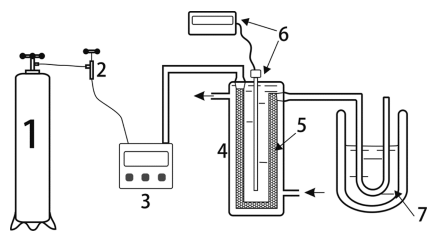

Figure 1. Schematic diagram of the transpiration apparatus: (1) carrier gas cylinder; (2) flow valve; (3) flow meter; (4) equilibrium cell; (5) U-shaped tube filled with the sample; (6) thermometer; (7) cooling trap at 243 K.

with glass beads and placed in a U-shaped saturator having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide a sufficient surface for establishment of vapor−liquid equilibration, as well as they are necessary to avoid hydraulic resistance and to keep the pressure along the saturation tube equal to the atmospheric pressure. At a constant temperature (± 0.1 K), a nitrogen stream was passed through the saturator at an appropriate flow rate, which was selected to be sufficient for saturation of the stream with the sample. An exact defined nitrogen stream was passed through the saturator within a certain time, and the transported material was trapped at 243 K. The mass of the condensed sample was derived by GC using the external standard method.

2.2.2. Vapor Pressure Measurements. The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period of time assuming the validity of the ideal gas law as well as the validity of the Daltoǹs law applied to the nitrogen stream saturated with the substance i:

$$p_i = m_i RT_a/VM_i; \qquad V = V_{N_2} + V_i \quad (V_{N_2} \gg V_i) \tag{1}$$

where R = 8.314472 J·K^{-1}·mol^{-1}; m_i is the mass of the condensed compound, M_i is the molar mass of compound i, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of the carrier gas, and T_a is the temperature of the flow rate sensor. The volume of the carrier gas V_{N_2} was determined by the digital flow rate sensor from integration with a microcontroller.

The transpiration experiment consists usually of the following steps:[8] (1) preconditioning of the sample in saturation tube before the experiment in order to withdraw volatile impurities and water; (2) selection of the flow rate at each temperature of the experiment in order to get saturation of the stream with the sample; (3) determination of saturated vapor pressures by collecting of the certain sample mass in the cold trap at various temperatures.

2.2.3. Uncertainties of Vapor Pressure Measurements. The experimental quantities measured to obtain the vapor pressures and enthalpies of vaporization are as follows.

(a) The mass, m_i, was measured of the compound collected in the cold trap. This amount was determined by gas chromatography (GC) analysis using an external standard. This GC procedure consists of two steps: calibration of the flame ionization detector (FID) using two reference solutions and injecting of the mixture of the transported sample with the well-defined amount of the standard solution. For the first step, about 0.03 g of sample was weighed in a 5 mL calibrated pycnometer, and about 0.05 g of the standard compound (hydrocarbon n-C$_n$H$_{2n+2}$) was weighed in a 10 mL calibrated pycnometer. We used KERN ACJ 220-4m balances with the resolution of ± 0.0001 g. Both pycnometers were filled with acetonitrile with uncertainty ± 0.01 mL. Mixtures for the FID calibration were prepared using the Hamilton syringes of the Gastight 1700 series with (100 and 250) μL volume. Calibration mixtures were analyzed by GC with the repeatability within (1 to 2) %. For the mass determination the cold trap was charged with 200 μL of the standard solution from the 10 mL pycnometer using the syringe of 250 μL nominal volume, and the mixture was analyzed by GC with the same reproducibility.

(b) The volume of the carrier gas V_{N_2} was measuered. For the transpiration experiments with duration over a few hours the

value of V_{N_2} was directly measured by Honeywell S&C HAFBLF0200C2AX5 digital flow rate sensor with uncertainty at the level of 2.5%. For the shorter experiments the carrier gas flow rate was measured with the HP Agilent soap film flow meter (model 0101-0113). The value of V_{N_2} was calculated from the gas-flow and time measurements with uncertainty of 1 %.

(c) The temperature of the saturator was kept constant within ± 0.2 K using a circulating thermostat. The accurate measurement of temperature is done by using a calibrated Pt-100 thermometer with resolution of 0.2 K.

(d) The ambient temperature T_a of the volume V_{N_2} measurements was measured using the calibrated Pt-100 with uncertainty ± 0.2 K.

(e) The atmospheric pressure was measured using a digital pressure indicator with uncertainty ± 2 hPa absolute.

Uncertainties resulting from correlations are reported as standard deviations (u). Uncertainties associated with combined results were evaluated as follows:

for the mass of the reference sample:

$$u(P)/P = (0.0001/0.05) = 0.0040 \times 100 = 0.20\%$$

for the mass of the sample under study:

$$u(P)/P = (0.0001/0.03) = 0.0067 \times 100 = 0.67\%$$

for the volumes of calibrated pycnometers:

$$u(P)/P = (0.01/5) + (0.01/10) = 0.0030 \times 100 = 0.30\%$$

for the volume of the standard solution:

$$u(P)/P = (0.25/200) + (0.1/100) = 0.0022 \times 100 = 0.22\%$$

for GC injections (calibration + determination):

$$u(P)/P = (0.02/2) + (0.02/2) = 0.02 \times 100 = 2.0\%$$

for the volume of the tranporting gas:

$$u(P)/P = (0.01/2) = 0.005 \times 100 = 0.5\%$$

for T-measurements (saturator + ambient):

$$u(P)/P = (0.2/323) + (0.2/298) = 0.00129 \times 100 = 0.13\%$$

for ambient atmospheric pressure:

$$u(P)/P = (2/1000) = 0.002 \times 100 = 0.20\%$$

combined uncertainties:

$$u(P)/P = (u_1^2 + u_2^2 + ...)^{0.5} \times 100 = \textbf{2.1\%}$$

It has turned out that the accuracy of vapor pressures measured by transpiration method is governed mostly by the reproducibility of the GC analysis as well as by V_{N_2} determination. For validation of our uncertainty estimations we measured vapor pressures for a series of n-alkanols,[7] where reliable data from different methods were available. It has turned out that vapor pressures of n-alkanols derived from the transpiration method were comparable with available high-precision data within (1 to 3) % in agreement with our estimations.

2.2.4. Vaporization Enthalpy. The saturated vapor pressures p_i measured at different temperatures were fitted with the following:

$$R \ln p_i = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \tag{2}$$

where a and b are adjustable parameters and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phases, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, vaporization enthalpy at temperature T was indirectly derived from the temperature dependence of vapor pressures using eq 3:

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \tag{3}$$

Values of $\Delta_l^g C_p$ have been calculated from isobaric molar heat capacities of liquid halogen-benzenes, C_p^l, according to a procedure developed by Chickos et al.[10] Values of C_p^l were either available from the literature or they were calculated by the group-contribution procedure developed by Chickos and Acree[11] (see Table S1, Supporting Information (SI)). Equations 1 to 3 are also valid for the study of the solid samples. For this case, the enthalpy of sublimation was derived from eq 3 by using the appropriate values of C_p^{cr} and $\Delta_{cr}^g C_p$ derived in the same way as for liquid samples. Primary experimental results and the parameters a and b, as well as $\Delta_l^g C_p$ are listed in Table 1.

2.2.5. Uncertainties of Vaporization Enthalpy. Uncertainties of vapor pressures measured by transpiration method have to affect the accuracy of the vaporization enthalpy. Having established this uncertainty at the level of 2 %, we are able now to evaluate the uncertainty of vaporization enthalpy by using the Clausius−Clapeyron equation:

$$\Delta_l^g H_m = (d \ln p/dT)RT^2 \tag{4}$$

As a rule, vapor pressures should be measured over the range of at least 60 K. Assuming the average temperature of the transpiration experiment with halogen-substituted benzenes of about 300 K and temperature interval equal to 60 K (see Table 2) the uncertainty of the enthalpy of vaporization can be calculated as follows:

$$\begin{aligned} \Delta(\Delta_l^g H_m) &= \Delta(d \ln p/\Delta T)RT^2 \\ &= (0.02/60) \times 8.314462 \times 300^2 \\ &= 250 \text{ J·mol}^{-1} \end{aligned} \tag{5}$$

Assuming the average values of vaporization enthalpies of halogen-benzenes measured in this work of 50 kJ·mol^{-1}, the uncertainty of vaporization enthalpy due to the inaccuracy of vapor pressure was calculated to be

$$u_1(\Delta_l^g H_m) = 0.25/50 = 0.005 \times 100 = 0.5\% \tag{6}$$

An additional contribution to uncertainties of the vaporization enthalpy appears from the inaccuracy of the saturation temperature measured by the platinum resistance thermometer Pt100 Burster 42510 (class A with four-wire connection) with uncertainty of $\Delta T = \pm 0.2$ K according to DIN EN 60751 for A class specification. The effect of this uncertainty can be also derived from the Clausius−Clapeyron equation:

$$\Delta(\Delta_l^g H_m) = (d \ln p/\Delta T)RT(2\Delta T) \tag{7}$$

Relating this result to the vaporization enthalpy, $\Delta_l^g H_m$:

$$\Delta(\Delta_l^g H_m) = (\Delta_l^g H_m/T)(2\Delta T) \tag{8}$$

Assuming the average temperature of the transpiration experiment of 300 K,

$$\Delta(\Delta_l^g H_m)/\Delta_l^g H_m = 2\Delta T/T \tag{9}$$

$$u_2(\Delta_l^g H_m) = (2 \times 0.2)/300 = 0.0013 \times 100 = 0.13\% \tag{10}$$

Table 2. Results from Measurements of the Vapor Pressure p of Halogen-benzenes Using the Transpiration Method

T^a	m^b	$V_{N_2}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})^e$	$\Delta_f^g H_m$
K	mg	dm³	(dm³/h)	Pa	Pa	(kJ·mol⁻¹)

Bromobenzene

$$\Delta_f^g H_m(298.15K) = (44.30 \pm 0.37) \text{ kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{251.76}{R} - \frac{59416.65}{R(T/K)} - \frac{50.7}{R}\ln\left(\frac{T/K}{298.15}\right)$$

276.4	9.43	1.180	2.36	134.5	2.4	45.41
278.3	9.23	1.003	2.36	153.4	2.3	45.31
282.2	9.36	0.787	2.36	195.7	−2.3	45.11
283.1	30.76	2.410	2.41	209.2	−1.3	45.07
285.4	9.02	0.590	2.36	248.7	3.1	44.95
286.2	25.01	1.607	2.41	253.2	−5.7	44.91
288.3	8.98	0.492	2.36	295.4	−1.7	44.80
289.3	24.38	1.225	2.41	321.1	4.3	44.75
291.4	8.68	0.393	2.36	354.9	−7.3	44.65
292.4	18.98	0.803	2.41	379.4	−6.4	44.59
293.2	15.20	0.603	2.41	404.6	−1.0	44.55
294.4	8.68	0.315	2.36	441.3	4.4	44.49
295.5	18.47	0.643	2.41	459.6	−8.0	44.44
297.4	7.73	0.236	2.36	522.5	−2.3	44.34
300.4	7.93	0.197	2.36	640.7	13.2	44.19
303.4	9.43	0.197	2.36	760.4	13.1	44.04

1-Bromo-2-methylbenzene

$$\Delta_f^g H_m(298.15K) = (47.66 \pm 0.17) \text{ kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{261.30}{R} - \frac{65345.27}{R(T/K)} - \frac{59.3}{R}\ln\left(\frac{T/K}{298.15}\right)$$

281.2	3.54	1.073	2.01	49.46	0.47	48.67
284.2	3.55	0.871	2.01	60.67	−0.35	48.50
285.2	2.19	0.494	1.21	65.68	0.12	48.44
287.2	3.44	0.670	2.01	75.92	0.34	48.32
287.2	2.05	0.403	1.21	75.26	−0.31	48.32
290.2	3.79	0.603	2.01	92.38	−0.75	48.14
293.2	3.88	0.503	2.01	113.1	−1.1	47.96
296.2	4.12	0.436	2.01	138.1	−1.2	47.78
299.2	3.88	0.335	2.01	168.4	−0.8	47.61
302.2	3.79	0.268	2.01	205.3	0.8	47.43
305.2	3.18	0.184	2.01	250.0	3.9	47.25
308.2	10.17	0.486	2.01	303.1	8.1	47.07
308.2	9.75	0.469	2.01	300.8	5.8	47.07
308.2	9.94	0.486	2.01	296.2	1.2	47.07
308.2	3.41	0.168	2.01	294.4	−0.6	47.07
313.1	28.05	1.039	2.01	390.3	−2.6	46.78
313.1	14.20	0.520	2.01	395.3	2.3	46.78
313.1	15.97	0.587	2.01	393.6	0.7	46.78
313.1	13.01	0.486	2.01	387.2	−5.7	46.78
313.1	28.23	1.056	2.01	386.5	−6.4	46.78
313.1	24.74	0.922	2.01	388.0	−4.9	46.78

1-Bromo-3-methylbenzene

$$\Delta_f^g H_m(298.15K) = (48.39 \pm 0.23) \text{ kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{260.92}{R} - \frac{66065.60}{R(T/K)} - \frac{59.3}{R}\ln\left(\frac{T/K}{298.15}\right)$$

274.2	2.90	2.236	3.12	20.06	0.05	49.81
276.2	3.10	2.028	3.12	23.40	−0.03	49.69
278.2	1.69	0.933	1.75	27.48	0.11	49.57
278.3	2.86	1.560	3.12	27.76	0.17	49.57
279.2	3.90	2.040	3.60	28.90	−0.65	49.51
280.3	3.04	1.404	3.12	32.59	0.45	49.45

Table 2. continued

T^a	m^b	$V_{N_2}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})^e$	$\Delta_f^g H_m$
K	mg	dm³	(dm³/h)	Pa	Pa	(kJ·mol⁻¹)

$$\ln(p/\text{Pa}) = \frac{260.92}{R} - \frac{66065.60}{R(T/K)} - \frac{59.3}{R}\ln\left(\frac{T/K}{298.15}\right)$$

281.3	1.81	0.773	1.75	35.10	0.45	49.39
282.2	4.95	2.010	3.60	36.86	−0.20	49.33
282.5	3.33	1.300	3.12	38.33	0.42	49.32
284.2	1.71	0.613	1.75	41.71	−1.27	49.22
284.2	3.38	1.196	3.12	42.10	−0.87	49.22
287.2	1.88	0.525	1.75	52.99	−0.41	49.04
287.3	3.33	0.936	3.12	52.60	−1.18	49.03
290.2	2.42	0.540	1.75	66.11	0.10	48.86
290.4	3.70	0.806	3.12	67.61	0.67	48.85
293.2	2.52	0.438	1.75	84.32	3.14	48.68
293.6	4.41	0.754	3.12	85.69	2.27	48.66
296.2	2.52	0.379	1.75	97.18	−2.17	48.50
296.7	4.99	0.702	3.12	103.9	1.2	48.47
299.2	2.40	0.292	1.75	119.9	−1.0	48.33
299.8	4.56	0.520	3.12	127.9	2.1	48.29
302.2	1.78	0.175	1.75	147.8	1.1	48.15
302.8	3.59	0.338	3.12	154.8	2.4	48.11
305.2	1.81	0.146	1.75	180.0	2.9	47.97
308.2	6.28	0.438	1.75	208.4	−4.4	47.79
308.2	8.07	0.554	1.75	211.5	−1.2	47.79
308.2	6.23	0.438	1.75	206.8	−6.0	47.79

1-Bromo-4-methylbenzene (Liquid)

$$\Delta_f^g H_m(298.15K) = (47.31 \pm 0.25) \text{ kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{259.00}{R} - \frac{64988.66}{R(T/K)} - \frac{59.3}{R}\ln\left(\frac{T/K}{298.15}\right)$$

301.9	4.57	0.381	0.75	174.6	−0.8	47.09
304.2	10.95	0.800	2.00	198.9	−3.2	46.95
304.9	4.51	0.306	0.75	213.7	2.7	46.91
307.2	5.11	0.306	0.75	242.2	0.0	46.77
310.3	6.14	0.300	0.75	296.4	5.6	46.59
313.2	4.51	0.188	0.75	347.7	4.1	46.42
314.4	6.60	0.260	1.95	367.1	−0.7	46.35
316.3	4.55	0.163	0.75	404.4	−4.6	46.24
317.5	3.97	0.132	0.72	433.5	−3.6	46.16
319.3	5.22	0.156	0.75	482.7	0.2	46.06
320.6	4.64	0.132	0.72	507.0	−10.6	45.98
322.4	5.22	0.131	0.75	574.2	4.4	45.87
325.3	5.80	0.125	0.75	669.6	6.0	45.70
328.2	6.11	0.113	0.75	783.5	13.2	45.53
331.3	8.08	0.131	0.75	887.9	−12.3	45.35
332.3	6.94	0.106	0.75	940.9	−4.9	45.29
335.3	5.25	0.069	0.75	1100	4.9	45.11

1-Bromo-4-methylbenzene (Crystals)

$$\Delta_{cr}^g H_m(298.15K) = (62.37 \pm 0.27) \text{ kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{273.50}{R} - \frac{69583.65}{R(T/K)} - \frac{24.2}{R}\ln\left(\frac{T/K}{298.15}\right)$$

274.5	1.62	1.699	1.80	14.09	0.06	62.94
277.2	3.65	2.901	1.80	18.53	0.17	62.88
278.3	1.67	1.218	1.80	20.13	−0.31	62.85
280.2	4.37	2.622	1.93	24.39	−0.19	62.80
282.2	2.48	1.233	1.80	29.35	−0.41	62.76
283.2	3.64	1.617	1.98	32.80	0.09	62.73
285.5	2.26	0.797	1.80	41.28	0.75	62.68
286.2	4.56	1.512	1.93	43.79	0.55	62.66
288.3	2.41	0.676	1.93	51.78	−0.60	62.61

Table 2. continued

T^a	m^b	$V_{N_2}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})^e$	$\Delta_l^g H_m$
K	mg	dm³	(dm³/h)	Pa	Pa	(kJ·mol⁻¹)

$$\ln(p/\text{Pa}) = \frac{273.50}{R} - \frac{69583.65}{R(T/K)} - \frac{24.2}{R}\ln\left(\frac{T/K}{298.15}\right)$$

289.6	7.61	1.898	1.93	58.09	−0.80	62.58
291.2	2.51	0.522	1.79	69.48	1.54	62.54
294.3	2.03	0.328	1.79	89.57	0.41	62.46
297.3	2.40	0.298	1.79	116.1	0.7	62.39
298.2	2.66	0.313	1.79	122.3	−2.1	62.37
299.2	2.39	0.254	1.79	135.7	0.3	62.34
300.8	2.07	0.194	1.79	154.3	−0.4	62.31

1-Bromo-2,6-dimethylbenzene

$$\Delta_l^g H_m(298.15K) = (52.70 \pm 0.35)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{275.38}{R} - \frac{72590.36}{R(T/K)} - \frac{66.7}{R}\ln\left(\frac{T/K}{298.15}\right)$$

274.2	1.22	2.458	2.95	6.95	−0.07	54.30
276.2	1.37	2.262	2.95	8.40	0.07	54.17
278.3	1.41	1.918	2.95	10.13	0.17	54.03
281.2	3.46	3.693	5.54	12.82	0.15	53.84
284.2	2.04	1.721	2.95	16.10	−0.04	53.64
287.2	2.22	1.450	2.95	20.71	0.25	53.44
290.2	2.70	1.426	2.95	25.51	−0.26	53.24
293.3	1.62	0.688	2.95	31.70	−0.82	53.03
293.3	3.06	1.278	2.95	32.14	−0.38	53.03
293.4	1.78	0.738	2.95	32.44	−0.33	53.02
296.3	3.00	1.008	2.95	39.98	−0.54	52.83
299.3	2.35	0.639	2.95	49.22	−1.00	52.63
302.2	2.21	0.467	2.95	63.13	1.63	52.44
305.3	1.73	0.295	2.95	78.15	2.15	52.23

Iodobenzene

$$\Delta_l^g H_m(298.15K) = (48.53 \pm 0.43)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{255.61}{R} - \frac{63972.26}{R(T/K)} - \frac{51.8}{R}\ln\left(\frac{T/K}{298.15}\right)$$

283.8	12.12	2.864	2.96	52.69	1.53	49.27
286.8	10.19	1.975	2.96	63.86	0.22	49.12
289.9	9.67	1.482	2.96	80.34	1.05	48.96
293.0	7.76	0.988	2.96	96.44	−1.83	48.80
294.0	2.30	0.274	1.09	102.9	−2.3	48.75
296.8	3.76	0.365	1.09	126.1	−0.9	48.60
299.6	10.24	0.840	2.96	148.7	−3.8	48.46
302.6	11.28	0.741	2.96	185.3	0.4	48.30
305.7	9.50	0.519	2.96	222.6	−2.1	48.14
308.7	8.87	0.395	2.96	272.2	2.2	47.98
311.8	6.60	0.247	2.96	323.9	−1.2	47.82
314.6	8.04	0.247	2.96	394.4	11.4	47.68

1-Iodo-2-methylbenzene

$$\Delta_l^g H_m(298.15K) = (52.28 \pm 0.14)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{266.42}{R} - \frac{69724.78}{R(T/K)} - \frac{58.5}{R}\ln\left(\frac{T/K}{298.15}\right)$$

283.2	3.24	2.308	2.77	16.23	−0.04	53.16
288.2	3.37	1.615	2.77	23.87	−0.19	52.87
293.2	3.60	1.154	2.77	35.50	0.48	52.58
301.2	4.94	0.900	2.77	62.12	0.17	52.11
304.2	4.97	0.738	2.77	76.15	0.11	51.93
307.4	5.01	0.600	2.77	94.30	0.17	51.74
310.3	5.32	0.531	2.77	113.1	−0.6	51.58
313.1	5.54	0.462	2.77	135.4	−0.6	51.41
316.2	5.08	0.346	2.77	165.5	0.6	51.23

Table 2. continued

T^a	m^b	$V_{N_2}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})^e$	$\Delta_l^g H_m$
K	mg	dm³	(dm³/h)	Pa	Pa	(kJ·mol⁻¹)

$$\ln(p/\text{Pa}) = \frac{266.42}{R} - \frac{69724.78}{R(T/K)} - \frac{58.5}{R}\ln\left(\frac{T/K}{298.15}\right)$$

319.3	4.87	0.277	2.77	198.3	−0.9	51.05
322.1	4.76	0.231	2.77	232.5	−2.9	50.88
325.1	5.83	0.231	2.77	284.3	3.8	50.71

1-Iodo-3-methylbenzene

$$\Delta_l^g H_m(298.15K) = (54.11 \pm 0.35)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{270.42}{R} - \frac{71549.85}{R(T/K)} - \frac{58.5}{R}\ln\left(\frac{T/K}{298.15}\right)$$

279.3	2.11	2.592	3.11	9.36	0.24	53.97
275.7	2.28	3.704	3.13	7.15	0.39	54.18
283.5	2.16	1.989	3.14	12.41	−0.46	53.72
286.4	2.18	1.575	3.15	15.70	−0.51	53.55
281.9	2.33	2.355	3.14	11.31	0.00	53.82
289.3	2.63	1.527	3.16	19.45	−0.85	53.38
289.3	2.16	1.225	1.05	19.96	−0.42	53.38
293.1	2.14	0.875	1.05	27.57	0.42	53.16
293.2	2.11	0.884	3.12	26.83	−0.53	53.15
298.1	2.15	0.601	1.03	40.30	1.19	52.87
298.2	2.69	0.778	3.11	38.87	−0.38	52.86
308.0	1.98	0.291	1.09	76.65	−0.45	52.29
308.0	2.15	0.312	1.04	77.18	0.09	52.29
302.9	2.25	0.468	1.08	54.24	−0.37	52.59
302.9	2.21	0.438	1.05	56.79	1.99	52.59
313.1	3.00	0.315	1.05	106.5	−0.9	51.99

1-Iodo-4-methylbenzene (Liquid)

$$\Delta_l^g H_m(298.15K) = (52.49 \pm 0.64)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{265.47}{R} - \frac{69930.47}{R\cdot(T/K)} - \frac{58.5}{R}\ln\left(\frac{T/K}{298.15}\right)$$

308.0	3.10	0.429	1.03	81.15	0.54	51.92
311.0	2.25	0.255	1.02	99.22	1.22	51.74
315.0	1.93	0.172	1.03	126.1	−0.2	51.51
319.1	1.45	0.102	1.02	159.9	−2.6	51.27
323.2	1.84	0.102	1.02	202.5	−5.1	51.03
328.1	2.53	0.102	1.02	277.6	2.2	50.74
332.9	2.78	0.085	1.02	366.5	5.6	50.46

1-Iodo-4-methylbenzene (Crystals)

$$\Delta_{cr}^g H_m(298.15K) = (68.00 \pm 0.67)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{280.38}{R} - \frac{74861.75}{R(T/K)} - \frac{23.0}{R}\ln\left(\frac{T/K}{298.15}\right)$$

279.5	2.03	4.253	3.19	5.37	0.00	68.43
283.3	1.89	2.658	3.19	8.00	−0.02	68.35
286.3	1.61	1.643	3.18	11.01	0.15	68.28
289.4	1.30	1.001	3.16	14.56	−0.13	68.21
293.2	1.35	0.737	3.16	20.50	−0.71	68.12
293.2	1.32	0.685	3.16	21.83	0.61	68.12
298.1	1.57	0.527	3.16	33.50	−0.08	68.01
303.0	1.74	0.370	3.17	52.60	0.28	67.89

1-Iodo-2,6-dimethylbenzene

$$\Delta_l^g H_m(298.15K) = (57.59 \pm 0.14)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{283.77}{R} - \frac{77802.55}{R(T/K)} - \frac{67.8}{R}\ln\left(\frac{T/K}{298.15}\right)$$

284.5	5.04	10.88	8.59	5.00	−0.04	58.52
288.4	4.67	7.073	8.66	7.09	0.05	58.25
291.6	4.24	4.908	8.66	9.25	0.07	58.04

Table 2. continued

T^a	m^b	$V_{N_2}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})^e$	$\Delta_l^g H_m$
K	mg	dm^3	(dm^3/h)	Pa	Pa	(kJ·mol^{-1})

$$\ln(p/\text{Pa}) = \frac{283.77}{R} - \frac{77802.55}{R(T/\text{K})} - \frac{67.8}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$$

296.5	4.52	3.444	8.61	14.00	0.38	57.70
298.4	1.20	0.816	3.06	15.72	−0.08	57.57
299.5	4.57	2.870	8.61	16.96	−0.25	57.50
301.5	3.99	2.153	8.61	19.72	−0.33	57.36
303.3	1.88	0.867	3.06	23.03	0.05	57.24
306.4	5.58	2.068	8.27	28.67	−0.22	57.03
308.3	2.35	0.765	3.06	32.67	−0.49	56.90
311.4	5.07	1.275	3.06	42.22	0.87	56.69
313.6	3.48	0.765	3.06	48.35	0.14	56.54
316.4	5.59	1.020	3.06	58.18	−0.22	56.35
318.4	4.80	0.765	3.06	66.57	−0.23	56.22
321.2	5.79	0.765	3.06	80.28	−0.09	56.03
323.4	6.66	0.765	3.06	92.28	−0.40	55.88
326.3	9.17	0.867	3.06	112.3	0.8	55.68
328.5	9.21	0.765	3.06	127.7	−0.2	55.53
331.3	11.01	0.765	3.06	152.6	0.8	55.34
333.4	12.41	0.765	3.06	172.1	−0.2	55.20

1-Iodo-2,4-dimethylbenzene

$$\Delta_l^g H_m(298.15\text{K}) = (57.67 \pm 0.31)\ \text{kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = \frac{283.33}{R} - \frac{77881.36}{R(T/\text{K})} - \frac{67.8}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$$

293.5	2.78	3.063	5.25	9.72	−0.12	57.99
298.4	3.52	2.614	5.23	14.34	−0.18	57.65
301.4	3.74	2.178	5.23	18.27	−0.02	57.45
303.4	1.49	0.731	2.92	21.75	0.48	57.31
306.3	2.96	1.186	2.85	26.54	0.17	57.12
308.3	2.07	0.731	2.92	30.17	−0.33	56.98
311.3	3.79	1.038	2.83	38.76	0.99	56.78
313.3	2.98	0.731	2.92	43.22	−0.22	56.64
316.4	3.72	0.731	2.83	54.07	0.33	56.43
318.6	4.31	0.728	2.91	62.84	0.53	56.28
321.4	4.96	0.708	2.83	74.38	−0.58	56.09
323.4	5.71	0.728	2.91	83.33	−2.01	55.96
326.4	7.05	0.708	2.83	105.8	2.4	55.75
326.4	7.11	0.731	2.83	103.2	−0.1	55.75
328.5	7.94	0.728	2.91	115.8	−2.0	55.61

^{a}Saturation temperature ($u(T) = 0.1$ K). ^{b}Mass of transferred sample m condensed at $T = 243$ K. ^{c}Volume of nitrogen ($u(V) = 0.005$ dm^3) used to transfer m ($u(m) = 0.0001$ g) of the sample. ^{d}Vapor pressure at temperature T calculated from the m and the residual vapor pressure at $T = 243$ K. ^{e}The combined standard uncertainty of vapor pressure measurements estimated to be $u(p)/p = 2.1\%$ (see text), taking into account uncertainties of all variables involved in eq 1. Uncertainties of vaporization enthalpies are expressed in this table as standard deviations $u_3(\Delta_l^g H_m)$ (see text).

Thus, the uncertainty in the enthalpy of vaporization due to the inaccuracy of the temperature measurements corresponds to 0.13 %. Taking into account that the average values of vaporization enthalpies of halogen-benzenes measured in this work are around 50 kJ·mol^{-1}, the contribution from the uncertainty of temperature determination was at the level of 0.06 kJ·mol^{-1}.

Reliable determination of $\Delta_l^g H_m$ requires correct correlation of the experimental vapor pressures. The principle of maximum likelihood provides a basis for an exact approach. In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i) = f(T^{-1})$ according to eq 2 using the method of least-squares. Uncertainties in the enthalpy of vaporization are essentially identical to the average deviation of experimental $\ln(p_i)$ values from the linear fitting.[12] Analysis of primary experimental results on halogen-benzenes listed in Table 1 has revealed that the uncertainties of vaporization enthalpies from least-squares treatment of the linear equation $\ln(p_i) = f(T^{-1})$ do not exceed (0.2 to 0.4) kJ·mol^{-1}. Assuming the average values of vaporization enthalpies of halogen-benzenes measured in this work of 50 kJ·mol^{-1}, the uncertainty of vaporization enthalpy due to the inaccuracy of vapor pressure temperature dependence approximation is equal to

$$u_3(\Delta_l^g H_m) = 0.4/50 = 0.008 \times 100 = 0.8\% \tag{11}$$

Uncertainties associated with the combined impact of factors expressed by eqs 6, 10, and 11 were evaluated as follows:

$$\begin{aligned} u(\Delta_l^g H_m) &= u_1(\Delta_l^g H_m) + u_2(\Delta_l^g H_m) + u_3(\Delta_l^g H_m) \\ &= (0.5^2 + 0.13^2 + 0.8^2)^{0.5} \\ &= 0.95\% \end{aligned} \tag{12}$$

Thus, the combined uncertainties of enthalpies of vaporization $\Delta_l^g H_m(T)$ derived according to eqs 2 and 3 within the experimental temperature range are associated with uncertainties at the level of (1.0 to 1.5) %. This level of uncertainty is sufficient and quite comparable with other well-established thermochemical methods.

In fact, most of the modern thermodynamic databases, handbooks, and compilations obligatorily demand for vaporization enthalpies at the reference temperature $\Delta_l^g H_m(298.15\text{K})$. It means, that enthalpies of vaporization $\Delta_l^g H_m(T)$ derived from vapor pressure measurements have to be adjusted to this reference temperature , $T = 298.15$ K, using eq 3 and $\Delta_l^g C_p$ values. The latter values are also associated with certain uncertainties which have to be taken into account.

2.2.6. Uncertainties of Temperature Adjustments of Vaporization Enthalpy. Uncertainties of the temperature adjustments of $\Delta_l^g H_m$ from the temperature interval where it was measured to the reference temperature are crucially dependent on the length of extrapolation ($\Delta_l^g C_p \times \Delta T$), as well as from the uncertainties of the $\Delta_l^g C_p$ values. Uncertainties in temperature adjustments of vaporization enthalpies were calculated using an assumption that a standard deviation of $\pm$ 16 J·mol^{-1}·K^{-1} of the liquid-phase heat capacity, C_p^l, can be ascribed for a broad range of small organic molecules.[13] This uncertainty was derived for substances with heat capacities C_p^l averaging about (150 to 250) J·mol^{-1}·K^{-1}. Heat capacities of halogen-benzenes studied in this work fit well in this range (see Table S1, SI). As an example, we consider uncertainties of temperature adjustments of vaporization enthalpy for 4-iodo-methylbenzene with $C_p^l = (184.2 \pm 16.0)$ J·mol^{-1}·K^{-1}[10] and $\Delta_l^g C_p = 58.5$ J·mol^{-1}·K^{-1}. The result from transpiration experiment $\Delta_l^g H_m(T_{av}=320.5\text{K}) = (51.21 \pm 0.64)$ kJ·mol^{-1} was measured between (308.0 and 332.9) K (see Table 2). Contribution in eq 3 from temperature adjustment is equal to

$$\begin{aligned} (\Delta_l^g C_p \times \Delta T) &= 58.5 \times (320.5 - 298.2)/1000 \\ &= 1.30\ \text{kJ·mol}^{-1} \end{aligned} \tag{13}$$

Uncertainty of heat capacity $u(C_p^l) = (16.0/184.2) \times 100 = 8.7$ %. With this value the uncertainty of the of vaporization enthalpy due to the temperature adjustment was calculated as follows:

$$\Delta(\Delta_l^g C_p \times \Delta T) = (8.7 \times 1.30)/100 = 0.11 \text{ kJ} \cdot \text{mol}^{-1} \quad (14)$$

Uncertainty in Table 2 assigned for 4-iodo-methylbenzene was expressed as the standard deviation:

$$u_3(\Delta_l^g H_m) = 0.64 \text{ kJ} \cdot \text{mol}^{-1} \quad \text{or} \quad (0.64/51.21) \times 100 = 1.25\% \quad (15)$$

The combined uncertainties for 4-iodo-methylbenzene were calculated as follows

$$\begin{aligned} u(\Delta_l^g H_m) &= u_1(\Delta_l^g H_m) + u_2(\Delta_l^g H_m) + u_3(\Delta_l^g H_m) \\ &= (0.5^2 + 0.13^2 + 1.25^2)^{0.5} \\ &= 1.35\% \end{aligned} \quad (16)$$

For simplicity we keep the values $u_1(\Delta_l^g H_m)$ and $u_2(\Delta_l^g H_m)$ the same as previously described in eq 12. The combined uncertainty for 4-iodo-methylbenzene derived by eq 16 was calculated as follows: $u(\Delta_l^g H_m) = (51.21 \times 1.35)/100 = 0.69$ kJ·mol^{-1}. Taking into account the uncertainty of the vaporization enthalpy due to the temperature adjustment $\Delta(\Delta_l^g C_p \times \Delta T) = 0.11$ kJ·mol^{-1}, the final combined uncertainty for 4-iodo-methylbenzene was calculated:

$$\begin{aligned} u_{\text{final}}(\Delta_l^g H_m) &= u(\Delta_l^g H_m) + \Delta(\Delta_l^g C_p \times \Delta T) \\ &= (0.69^2 + 0.11^2)^{0.5} \\ &= 0.70 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned} \quad (17)$$

These final uncertainties $u_{\text{final}}(\Delta_l^g H_m)$ are given in Table 3.

In order to reduce uncertainties of the vaporization enthalpy, the transpiration experiment is advisable to perform possibly closer to the reference temperature. In the current study on halogen-benzenes we managed to perform the transpiration experiment with liquid samples mostly around the reference temperature (the deviations of the T_{av} from $T = 298.15$ K were not larger than 23 K). In such conditions contributions to the uncertainty of vaporization (or sublimation) enthalpies due to temperature adjustments were on the level of (0.2 to 0.3) kJ·mol^{-1} for halogen-benzenes studied in this work.

2.3. Phase Transitions in the Solid State. DSC Measurements. The thermal behavior of 1-bromo-4-methylbenzene and 1-iodo-4-methylbenzene including melting temperature and enthalpy of fusion was studied with a PerkinElmer DSC-2. The instrument was standardized using indium metal with a mass fraction of 0.9999. The samples were hermetically sealed in 50 μL pans supplied by PerkinElmer. The thermal behavior of the specimen was investigated during heating of the sample with a rate of 10 K·min^{-1}. The differential scanning calorimetry (DSC) measurements were repeated in triplicate, and values agreed within the experimental uncertainties $u(\Delta_{cr}^l H_m) = 0.2$ kJ·mol^{-1} for the enthalpy of fusion and $u(T) = 0.5$ K for the melting temperature. The resulting fusion enthalpies measured for 1-bromo-4-methylbenzene and 1-iodo-4-methylbenzene are reported in Table 4. Uncertainties in the temperature adjustment of fusion enthalpies from T_{fus} to the reference temperature were assumed to amount to 30% of the total adjustment.[13]

2.4. Computational Details. Quantum-chemical calculations were performed with the Gaussian 09 series of programs.[14] The energies of the compounds studied were calculated using the Gaussian-4 (G4) method.[15] The G4 method was chosen as it represents a good compromise between cost and accuracy for substituted benzenes studied in this work. Details on this method have been given in our previous work.[16] The enthalpy values of studied compounds at $T = 298.15$ K were evaluated according to standard thermodynamic procedures.[17]

3. RESULTS AND DISCUSSION

3.1. Vapor Pressure and Vaporization Enthalpies. At a first glance a lot of vapor pressure measurements have been published in the literature. However, collection of experimental data available for bromo- and iodo-substituted methylbenzenes suffered from ambiguity. For example, the comprehensive compilations by Stull[18] and by Stephenson and Malanowski[19] list vapor pressure data for numerous halogen-substituted benzenes over a wide range of temperature. The origin of the data presented there is not clear; methods of measurements and their uncertainties are unknown, as well as purities of compounds are not available. It has turned out that authors of original works have not always derived enthalpies of vaporization from their results or performed these calculations in a different manner. In this context, additional measurements on halogen-substituted methylbenzenes are desired.

We collected the available in the literature experimental data and treated these data uniformly in the same way as our own results by using eqs 2 and 3 with $\Delta_l^g C_p$ values listed in Table S1, SI. Enthalpies of vaporization of halogen-benzenes at 298.15 K have been calculated (see Table 3) for the sake of comparison, as well as for the evaluation of the $\Delta_l^g H_m(298.15\text{K})$ aiming their recommendation for further thermochemical calculations.

Absolute vapor pressures of pure compounds are very sensitive for possible systematic errors. Sometimes simple graphical comparison could reveal inconsistency of experimental data. In order to evaluate our new results on the absolute vapor pressures of halogen-substituted benzenes, we compared experimental $p{-}T$ data for fluorobenzene,[6] chlorobenzene,[6] bromobenzene, and iodobenzene (see Figure 2a). From this plot it was apparent even qualitatively that the increasing size of halogen caused a relative reduction of vapor pressures in the series F > Cl > Br > I. The same qualitative trends were observed for halogen-substituted methylbenzenes (see Figure 2b). As can be seen in Figure 2b, vapor pressures of para-isomers in all four series were systematically lower in comparison to ortho-isomers. Vapor pressures of all meta-isomers were in-between, but in most cases very close to those of para-isomers (see Figure 2b). Thus, new vapor pressures of halogen-substituted benzenes measured in this work can be considered as internally consistent and used for calculation vaporization enthalpies according to eqs 2 and 3.

3.1.1. Vaporization Enthalpies of Bromobenzene and Iodobenzene. For the bromobenzene, a remarkably consistent set of vaporization enthalpies measured directly (calorimetric) and indirectly (from vapor pressure temperature dependence) was collected from the literature (see Table 3). We measured vapor pressures for this compound by transpiration method rather in order to collect experiences working with volatile compounds. The transpiration value of $\Delta_l^g H_m(298.15\text{K}) = (44.3 \pm 0.6)$ kJ·mol^{-1} for bromobenzene was in very good agreement with those from the most reliable calorimetric method, as well as with the static and the ebulliometric methods (see Table 3). Such good agreement has encouraged using of the transpiration method for studies of similarly shaped

Table 3. Compilation of Data on Enthalpies of Vaporization, $\Delta_l^g H_m$, of the Halogen-benzenes

| compounds	technique[a]	T-range/K	$\Delta_l^g H_m$/(kJ·mol⁻¹) T_{av}	298.15 K[b]	ref
bromobenzene (liq)	C	427.9	37.88 ± 0.05	44.46 ± 1.67	24
	C	298.15	44.54 ± 0.04	44.54 ± 0.04	25
	n/a	276.1−429.4	42.4	44.9 ± 2.0	18
	n/a	333−463	40.1	45.2 ± 3.0	19
	n/a	429−633	37.2	(49.0 ± 3.0)	19
	E	329.2−427.4	40.92 ± 0.04	44.97 ± 0.49	26
	C	293.0	43.96 ± 0.06	43.71 ± 0.10	27
	S	321.0−429.2	41.00 ± 0.08	44.69 ± 0.49	28
	T	276.4−303.4	44.80 ± 0.38	44.30 ± 0.64	this work
				44.29 ± 0.10[c]	average
1-bromo-2-methylbenzene (liq)	n/a	297.6−455.0	47.6	(51.6 ± 2.0)	18
	S	277−348	47.8	48.5 ± 2.0	23
	n/a	353−518	42.1	(50.3 ± 3.0)	19
	T	281.2−313.1	47.71 ± 0.17	47.66 ± 0.49	this work
				47.71 ± 0.48[c]	average
1-bromo-3-methylbenzene (liq)	n/a	288.0−456.9	44.1	47.8 ± 2.0	
	S	277−348	48.6	49.3 ± 2.0	
	T	274.2−308.2	48.82 ± 0.23	48.39 ± 0.48	this work
				48.41 ± 0.45[c]	average
1-bromo-4-methylbenzene (liq)	n/a	320.7−457.7	44.7	49.5 ± 2.0	18
	S	277−348	42.8	51.3 ± 2.0	23
	T	301.9−335.3	46.22 ± 0.25	47.31 ± 0.58	this work
				47.75 ± 0.54[c]	average
1-bromo-4-methylbenzene (cr)					
	T	274.5−300.8	62.63 ± 0.27	**62.37 ± 0.60**[c]	this work
iodobenzene (liq)		302.5−461.4	46.41 ± 0.70	49.05 ± 0.84	29
	n/a	297.3−461.8	45.9	49.6 ± 2.0	18
	n/a	243−255	43.1	(45.6 ± 3.0)	20
	n/a	358−543	42.4	50.3 ± 3.0	19
	n/a	462−679	40.0	(54.1 ± 3.0)	19
	n/a	273−358	49.4	50.3 ± 3.0	19
	T	283.8−314.6	48.50 ± 0.43	48.53 ± 0.65	this work
				48.86 ± 0.48[c]	average
1-iodo-2-metylbenzene (liq)	n/a	310.4−484.2	47.6	52.7 ± 2.0	18
	T	283.2−325.1	52.02 ± 0.14	52.28 ± 0.40	this work
				52.29 ± 0.28[c]	average
1-iodo-3-metylbenzene (liq)					
	T	279.3−318.0	53.02 ± 0.41	**52.86 ± 0.58**	this work
1-iodo-4-metylbenzene (liq)					
	T	308.0−332.9	51.21 ± 0.64	**52.49 ± 0.70**	this work
1-iodo-4-metylbenzene (cr)					
	T	279.5−303.0	68.17 ± 0.67	**68.00 ± 0.91**	this work
1-bromo-2,6-dimethylbenzene (liq)					
	T	274.2−305.3	53.41 ± 0.35	**52.70 ± 0.58**	this work
1-bromo-2,5-dimethylbenzene (liq)					
	n/a	310.7−429.7	48.6	54.3 ± 2.0	18
1-iodo-2,6-dimethylbenzene (liq)					
	T	284.5−333.4	56.91 ± 0.14	**57.59 ± 0.36**	this work
1-iodo-2,4-dimethylbenzene (liq)					
	T	293.5−328.5	56.83 ± 0.31	**57.67 ± 0.56**	this work
		dibromo-	*benzenes*		
1,2-dibromobenzene (liq)	T	290.3−328.2	53.7 ± 0.3	54.3 ± 0.5	45
1,3-dibromobenzene (liq)	T	276.0−318.0	55.1 ± 0.2	54.9 ± 0.4	45
1,4-dibromobenzene (liq)				54.9 ± 0.5	45

[a]Techniques: C = calorimetry; E = ebulliometry; S = static method; T = transpiration method. [b]Uncertainties of vaporization enthalpies are expressed in this table as standard deviations $u_{final}(\Delta_l^g H_m)$ (see text). Real uncertainties of literature data were evaluated in this work. Values in brackets were not taken into account. [c]Average value calculated using the uncertainty as the weighing factor.

Table 4. Compilation of Experimental Data on Enthalpies of Fusion, $\Delta_{cr}^{l}H_m$, kJ·mol^{-1}

compound	T_{fus}/K	$\Delta_{cr}^{l}H_m$ at T_{fus}	$\Delta_{cr}^{l}H_m{}^a$ at 298.15 K	$\Delta_{cr}^{g}H_m{}^b$ at 298.15 K	$\Delta_{f}^{g}H_m{}^b$ at 298.15 K	$\Delta_{cr}^{l}H_m{}^c$ at 298.15 K
1-bromo-4-methylbenzene	301.2	15.1[46]				
	301.3	14.9 ± 0.3	14.9 ± 0.3	62.37 ± 0.60	47.75 ± 0.54	14.6 ± 0.8
1-iodo-4-methylbenzene	306.7	14.9[47]				
	307.5	15.0 ± 0.3	14.7 ± 0.3	68.00 ± 0.91	52.49 ± 0.70	15.5 ± 1.1

[a]The experimental enthalpies of fusion $\Delta_{cr}^{l}H_m$ measured at T_{fus} and adjusted to 298.15 K (see Supporting Information). [b]Taken from Table 3. [c]Calculated as the difference between $\Delta_{cr}^{g}H_m$ and $\Delta_{f}^{g}H_m$ in this table.
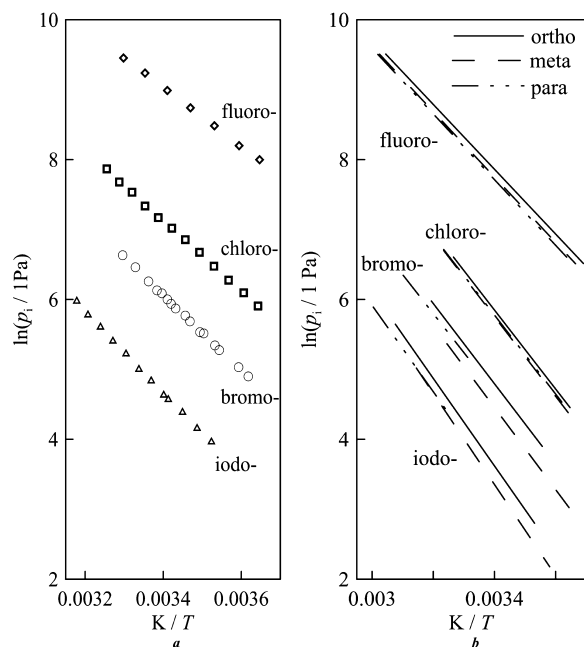
Figure 2. Experimental vapor pressures of halogen-substituted benzenes over liquids: (a) for fluorobenzene,[6] chlorobenzene,[6] bromobenzene, and iodobenzene; (b) for fluoro-methylbenzenes,[6] chloro-methylbenzenes,[6] bromo-methylbenzenes, and iodo-methylbenzenes.

halogen-substituted methylbenezenes, where the available experimental data were found to be less consistent. Indeed, the collected data for the iodobenzene were apparently of a lower quality, coming mostly from ill-defined sources.[18−20] The transpiration value of $\Delta_{f}^{g}H_m(298.15K) = (48.5 \pm 0.6)$ kJ·mol^{-1} derived for iodobenzene was about (1 to 2) kJ·mol^{-1} lower than other results collected for this compound in Table 3. However, it should be mentioned that within the relatively large error bars of (2 to 3) kJ·mol^{-1} the agreement of the new and old results can be considered as acceptable. In order to avoid any ambiguity in $\Delta_{f}^{g}H_m(298.15K)$ of iodobenzene, we decided to check the consistency of the new enthalpy of vaporization of iodobenzene with vaporization enthalpies of other halogen-substituted benzenes. These values were recently evaluated for fluoro- and chlorobenzene.[6] For bromobenzene we can take the value evaluated in this work (see Table 3). It is well-established that vaporization enthalpies correlate well with a surface area[21] and volume[22] of a molecule. We used both of these correlations as for validation of $\Delta_{f}^{g}H_m(298.15K)$ of iodobenzene.

A cavity surface area, S_c, and a cavity volume, V_c, were calculated by using the B3LYP/3-21G (see Table S2, SI). Correlations of $\Delta_{f}^{g}H_m(298.15K)$ of fluoro-, chloro-, bromo-, and iodobenzene with their surface areas and volumes fitted well to linear dependences as follows:

cavity surface area, S_c/Å^2:

$$\Delta_{f}^{g}H_m(298.15K)/(kJ\cdot mol^{-1}) = 0.483S_c - 37.25 \quad (R^2 = 0.9995)$$
(18)

cavity volume, V_c/Å^3:

$$\Delta_{f}^{g}H_m(298.15K)/(kJ\cdot mol^{-1}) = 0.390V_c - 19.88 \quad (R^2 = 0.9992)$$
(19)

Having correlation coefficients R^2 for both lines very close to unity we could consider the selected values $\Delta_{f}^{g}H_m(298.15K)$ of halogen-benzenes as consistent and recommend them for further thermochemical calculations.

3.1.2. Vaporization Enthalpies of Bromo- and Iodomethylbenzenes. Vapor pressure data available for bromo- and iodo-methylbenzenes are scarce. Enthalpies of vaporization derived from the compilations[18,19] are questionable, because methods and purities of samples are absent. The only traceable results measured for all three bromo-methylbenzenes by static method[23] are in agreement with our new results within the large error bars of 2 kJ·mol^{-1} (see Table 3). According to our new transpiration results, enthalpies of vaporization of 1-bromo-2-, 3-, and 4-methylbenzenes were very similar: their differences do not exceed 1 kJ·mol^{-1}, and they are quite comparable within their boundaries of experimental uncertainties. The same trend was observed for enthalpies of vaporization of 1-iodo-2-, 3-, and 4-methylbenzenes, which showed differences of about 1 kJ·mol^{-1}. In order to establish more confidence, we calculated the average values $\Delta_{f}^{g}H_m(298.15K)$ of halogen-substituted benzenes as the weighted average from the available results (see Table 3), and these new results were recommended for further thermochemical calculations.

3.1.3. Consistency Test of the Vaporization, Sublimation, and Fusion Enthalpies of 1-Bromo-4-methylbenzene and 1-Iodo-4-methylbenzene. According to Table 3 the available in the literature values of $\Delta_{f}^{g}H_m(298.15K)$ for 1-bromo-4-methylbenzene were of (2 to 4) kJ·mol^{-1} higher than our transpiration result. For 4-iodo-4-methylbenzene the literature data were absent. Following, for both compounds an additional prove of our new vapor pressure measurements was desired. For this purpose we deliberately measured vapor pressures of 1-bromo-4-methylbenzene and 1-iodo-4-methylbenzene over the liquid as well as over the solid samples. A valuable test of consistency of the experimental data on sublimation and vaporization enthalpies derived for 1-bromo-4-methylbenzene and 1-iodo-4-methylbenzene (see Tables 2 and 3) provides a comparison with the experimental values of enthalpy of fusion collected in Table 4. For example, in this work the sample of 1-bromo-4-methylbenzene was investigated by the transpiration method in both ranges, above and below its temperature of melting $T_{fus} = 301.3$ K. The value of $\Delta_{cr}^{g}H_m(298K) = (62.37 \pm 0.60)$ kJ·mol^{-1} for 1-bromo-4-methylbenzene was obtained in this work from measurements in the temperature range of (274.5 K to 300.8) K and the vaporization enthalpy for 1-bromo-4-methylbenzene

$\Delta_{cr}^g H_m(298K) = (47.31 \pm 0.58)$ kJ·mol^{-1} from measurements in the temperature range of (301.9 K to 335.3) K. To test the consistency of the experimental data on vaporization and sublimation enthalpies measured in this work for 1-bromo-4-methylbenzene, we compare the enthalpy of fusion calculated as the difference $\Delta_{cr}^l H_m(298.15K) = \Delta_{cr}^g H_m - \Delta_l^g H_m = (14.6 \pm 0.8)$ kJ·mol^{-1} (both values referring to $T = 298$ K) with the $\Delta_{cr}^l H_m(298.15K) = (14.9 \pm 0.3)$ kJ·mol^{-1} of 1-bromo-4-methylbenzene measured by DSC (see Table 3). The enthalpy of fusion $\Delta_{cr}^l H_m$ calculated from the difference $\Delta_{cr}^g H_m - \Delta_l^g H_m$ measured in this work is in excellent agreement with those measured directly by calorimetry (and adjusted to $T = 298.15$ K; see SI). Thus, our new results for vaporization and sublimation enthalpies of 1-bromo-4-methylbenzene have been proven to be consistent. In the same way we tested the experimental results for 1-iodo-4-methylbenzene (see Table 4), which have been found in agreement within the experimental uncertainties. Thus, our addition measurements on vaporization, sublimation, and fusion enthalpies of 1-bromo-4-methylbenzene and 1-iodo-4-methylbenzene have ascertained the thermochemical data for these compounds.

3.1.4. Vaporization Enthalpies of Bromo-dimethylbenzenes and Iodo-dimethylbenzenes.
Experimental results on bromo-dimethylbenzenes and iodo-dimethylbenzenes are absent in the literature except for 1-bromo-2,5-dimethylbenzene mentioned by Stull.[18] In order to contribute to this kind of substitution on the benzene ring and evaluate the available data, we measured enthalpies of vaporization of some commercially available 1-bromo-2,6-dimethylbenzene, 1-iodo-2,6-dimethylbenzene, and 1-iodo-2,4-dimethylbenzene (see Tables 2 and 3). These new data were helpful for developing correlation methods and group-contribution methods as follows.

3.2. Evaluation of $\Delta_l^g H_m(298.15K)$ of Halogen-benzenes.
Compilation of available data on enthalpies of vaporization, $\Delta_l^g H_m(298.15K)$, of the halogen-substituted benzenes is given in Table 3. For each compound the weighted average values have been derived, having the uncertainty as the weighing factor. However, a possible systematic error is not excluded, especially if only a single value is available. In order to avoid an erroneous value, any kind of logical correlations should be applied to the data set under consideration. In this context, correlations of experimental values of $\Delta_l^g H_m(298.15K)$ with the structure-related parameters seem to be a valuable tool for the data evaluation. In this work we are going to discuss two types of correlations: the group-additivity procedure[2] and the correlation of vaporization enthalpies with the gas chromatographic parameters such as Kovat's index.[30] We used these methods in the past to evaluate vaporization enthalpies available for ethers,[31] esters,[32] and aldehydes[33] successfully.

3.2.1. Correlation of $\Delta_l^g H_m(298.15K)$ of Substituted Benzenes with Kovat's Indices.
Kovat's indices measured by gas−liquid chromatography are widely used for identification of molecules,[30] as well as they help to reveal structure−property relations within a series of parent compounds.[32,34] For example, we have already pointed out earlier that evaluated enthalpies of vaporization of 1-bromo-2-, 3-, and 4-methylbenzenes, as well as 1-iodo-2-, 3-, and 4-methylbenzenes were hardly distinguishable in each series within their uncertainties (see Table 3). The same patterns follow Kovat's indices collected for these isomers in Table S3, SI. Following, an inherent qualitative relationship between Kovat's indices and vaporization enthalpies is valid for these halogen-substituted benzenes. In order to get a quantitative relationship, we collected Kovat's indices for

substituted benzenes relevant to this study in Table S3, SI. In our previous study we demonstrated that the vaporization enthalpy $\Delta_l^g H_m(298.15K)$ appears to be a linear function of the Kovat's indices in homologous series of fluoro- and chlorobenzenes.[6] In this study we have shown that the data for $\Delta_l^g H_m(298.15K)$ of bromo- and iodobenzenes also fit very well in the linear correlation. The following empirical equation for the enthalpy of vaporization has been obtained:

$$\Delta_l^g H_m(298.15K)/(\text{kJ·mol}^{-1}) = 10.04 + 0.039 J_x \quad \text{with } (R^2 = 0.991) \tag{20}$$

where J_x is the Kovat's index of a substituted benzene and R^2 is the correlation coefficient. This relationship can be used to estimate enthalpies of vaporization of the parent substituted benzenes provided that their Kovat's indices are known in the same conditions. However, in the context of this work eq 20 should be considered also as the evidence of internal consistency of experimental results on vaporization enthalpies evaluated in Table 3.

3.2.2. Group-Contribution Method for Evaluation of $\Delta_l^g H_m(298.15K)$ of Halobenzenes.
Substituted benzenes are a remarkably suitable series for the group-additivity (GA) procedure. In our previous work we already reported the GA approach for benzenes substituted with chlorine,[35] chlorine and hydroxyl,[35] and CH_3 and F or Cl groups.[6] In this work we extend the GA method for estimation of $\Delta_l^g H_m(298.15K)$ of benzenes substituted with CH_3 and Br or I groups. In short, the difference between $\Delta_l^g H_m(298.15K)$ of bromobenzene and benzene provides the increment $\Delta H(\text{H}\rightarrow\text{Br})$ for substitution of H atom on the benzene ring by Br group. The same procedure is valid for the iodobenzenes with the increment $\Delta H(\text{H}\rightarrow\text{I})$. For the sake of brevity a general definition $\Delta H(\text{H}\rightarrow\text{Hal})$ was used throughout this work. Introduction of the second halogen atom into the benzene ring produces few additional increments, e.g. $o(\text{Br}-\text{Br})$, $p(\text{Br}-\text{Br})$, and $m(\text{Br}-\text{Br})$, taking into account the mutual interactions of substituents on the benzene ring.

The following general formula for calculation of vaporization enthalpy of any polyhalogen-substituted benzene (HalB) at 298.15 K can be suggested:

$$\begin{aligned}\Delta_l^g H_m(\text{HalB}) \\= \Delta_l^g H_m(\text{B}) + n_a \Delta H(\text{H}\rightarrow\text{Hal}) + n_b o(\text{Hal}-\text{Hal}) \\+ n_c p(\text{Hal}-\text{Hal}) + n_d m(\text{Hal}-\text{Hal})\end{aligned} \tag{21}$$

where $\Delta_l^g H_m(\text{B})$ is vaporization enthalpy of benzene; $\Delta H(\text{H}\rightarrow\text{Hal})$ is an increment of H → Hal substitutions on the benzene ring. The mutual interactions of the Hal atoms were taken into account through the three types of corrections in ortho-, para-, and meta-position on the benzene ring. n_a, n_b, n_c, and n_d are the quantities of the corresponding increments and correction. This approach is valid[5,36] for any kind of polysubstitution of the benzene ring (e.g., $\Delta H(\text{H}\rightarrow\text{Hal})$ for Hal = Br and I in this work). The same simple substitution procedure can be applied to the toluene, xylenes, or polymethylbenzenes using the increment $\Delta H(\text{H}\rightarrow\text{CH}_3)$ for methyl substituent and the appropriately modified eq 21 with the pairwise interactions parameters $o(\text{CH}_3-\text{CH}_3)$, $p(\text{CH}_3-\text{CH}_3)$, and $m(\text{CH}_3-\text{CH}_3)$.

We used the experimental enthalpies $\Delta_l^g H_m(298.15 \text{ K})$ from ref 37: for benzene (33.92 ± 0.06) kJ·mol^{-1}, for toluene (38.06 ± 0.04) kJ·mol^{-1}, for 1,2-dimethylbenzene (43.45 ± 0.10) kJ·mol^{-1}, for 1,3-dimethylbenzene (42.68 ± 0.10) kJ·mol^{-1},

and for 1,4-dimethylbenzene (42.42 ± 0.10) kJ·mol⁻¹, available from the literature together with vaporization enthalpies of halogen-substituted benzenes evaluated in Table 3 in order to derive increments $\Delta H(\text{H}\rightarrow\text{Br})$, $\Delta H(\text{H}\rightarrow\text{I})$, and parameters for mutual interactions of substituents on the benzene ring (see Table 5).

Table 5. Parameters for the Calculation of Enthalpies of Vaporization $\Delta_l^g H_m$ of Halogen-Substituted Benzenes at 298.15 K

groups	$\Delta_l^g H_m/(\text{kJ·mol}^{-1})$
benzene	33.9[37]
$\Delta H(\text{H}\rightarrow\text{F})$	0.8[6]
$\Delta H(\text{H}\rightarrow\text{Cl})$	7.9[6]
$\Delta H(\text{H}\rightarrow\text{Br})$	10.4
$\Delta H(\text{H}\rightarrow\text{I})$	14.9
$\Delta H(\text{H}\rightarrow\text{CH}_3)$	4.2[6]
(F−F)	1.5[6]
(Cl−Cl)	−1.5[6]
(Br−Br)	0.0
halogen−CH$_3$	0.0
$o(\text{CH}_3-\text{CH}_3)$	1.2[6]
$m(\text{CH}_3-\text{CH}_3)$	0.0[6]
$p(\text{CH}_3-\text{CH}_3)$	0.0[6]

Collection of parameters listed in Table 5, column 2 represents a reasonably detailed scheme for estimation vaporization enthalpies of halogen-substituted benzenes. In order to reduce the number of parameters required for estimation of $\Delta_l^g H_m(298.15\text{K})$ of halobenzenes, some minor interactions (having a level below 0.3 kJ·mol⁻¹) were neglected or fixed as structure-independent constants. For example from the three possible (CH$_3$−CH$_3$) interactions on the benzene ring only to the ortho-substitution was assigned the contribution of 1.2 kJ·mol⁻¹. More simple was it to describe (Hal−Hal) interactions on the benzene ring. For all three (F−F) interactions a single parameter of 1.5 kJ·mol⁻¹ was sufficient to reproduce the experimental data. Also for all three (Cl−Cl) interactions a single parameter of −1.5 kJ·mol⁻¹ was assigned. Surprisingly, all three (Br−Br) interactions were close to zero, and even the contribution to $\Delta_l^g H_m$ due to steric repulsions of two large substituents in o(Br−Br) was well below 1 kJ·mol⁻¹.

Comparison of the experimental and estimated by GA vaporization enthalpies is given in Table S5, column 4. As can be seen the average deviation of experimental and calculated $\Delta_l^g H_m(298.15\text{K})$ was at the level of (0.2 to 0.5) kJ·mol⁻¹, and it was quite comparable with the experimental errors of the most entries in Table 3. Following, values of $\Delta_l^g H_m(298.15\text{K})$ for the mono- and dihalogen-substituted benzenes can be predicted with acceptable accuracy using eq 21 with basic increments listed in Table 5. In our previous work on F- and Cl-substituted benzenes, we observed that even the consequent 1,2,3-substitution of the benzene ring with methyl and fluorine or chlorine substituent did not require any increment specific for steric crowding of the benzene ring. New species of this art studied in this work 1-bromo-2,6-dimethylbenzene, 1-iodo-2,6-dimethylbenzene, and 1-iodo-2,4-dimethylbenzene have supported this observation even for larger substituents Br and I. Thus, collection of increments from Table 5 fitted to eq 21 allows prediction of $\Delta_l^g H_m(298.15\text{K})$ for halogen-methylbenzenes even in cases with 1,2,3-positions of substituents on the benzene ring. Some restriction for eq 21 could be expected for the case of

1,2,3,4-substitution, but synthesis of such crowded benzenes is challenging and samples are hardly available for experimental studies. Otherwise, success of prediction with eq 21 could be also considered as the evidence of internal consistency of experimental results on vaporization enthalpies evaluated in Table 3.

3.3. Standard Molar Enthalpies of Formation of Halogen-benzenes. Values of standard enthalpies of formation, $\Delta_f H_m^\circ$, of halogen-benzenes are dramatically scarce in the literature. The main reason for this scarcity is a consistent decay of a sophisticated art of the rotating bomb combustion calorimetry. There are only a few such devices still being kept working over the world.

3.3.1. Experimental Gas-Phase Enthalpies of Formation. Experimental $\Delta_f H_m^\circ(\text{liq},298.15\text{K})$ values (see Table 6, column 2) for fluoro-, chloro-, bromo-, and iodobenzene were revised and adjusted to contemporary standards in the compilation by Pedley et al.[39] Vaporization enthalpies $\Delta_l^g H_m(298.15\text{K})$ for these compounds evaluated in our recent work (see Table 6, column 3) have led to new values of the molar standard enthalpies of formation in the gas state, $\Delta_f H_m^\circ(\text{g},298.15\text{K})$, given in Table 6 (column 4) for these four halogen-benzenes.

A valuable check for internal consistency of these new experimental $\Delta_f H_m^\circ(\text{g},298.15\text{K})$ values for C$_6$H$_5$−Hal derived in this work can be comparison with enthalpies of formation of the similarly shaped aliphatic halides R−Hal (R = CH$_3$ and i-C$_3$H$_7$) available in the literature.[39] This comparison is presented in Figure S1, SI. As can be seen from this figure vaporization enthalpies of aromatic and aliphatic halides are in excellent agreement with the correlation coefficient 0.9999 for both series, and this fact has proved the reliability of the experimental results derived in this work. With respect to careful evaluation and internal consistency of vaporization and formation enthalpies established in this work, our new experimental thermochemical results for C$_6$H$_5$−Hal presented in Table 6 can be now recommended as the benchmark thermochemical properties for these compounds. Now this experimental value $\Delta_f H_m^\circ(\text{g},298.15\text{K})$ can be compared with the results from quantum-chemical calculations.

3.3.2. Quantum-Chemical Calculations of the Gas-Phase Enthalpies of Formation. In contrast to the decay of the experimental thermochemistry, the rapid progress of the quantum chemistry of recent decade promises to shed a light into this troublesome situation. Development of composite methods toward organic molecules with <10 to 15 heavy atoms allowed calculation of enthalpies of formation in the gas-phase $\Delta_f H_m^\circ(\text{g},298.15\text{K})$ with a "chemical accuracy"[40,41] of (2 to 4) kJ·mol⁻¹. Thus, a combination of the quantum-chemistry methods with vaporization (or sublimation) enthalpies evaluated in the current study suggests a rational indirect way to obtain $\Delta_f H_m^\circ(\text{liq},298.15\text{K})$ and $\Delta_f H_m^\circ(\text{cr},298.15\text{K})$ of halogen-benzenes lacking in the thermochemical literature. Accurate values of standard molar enthalpies of formation in condensed phases can be obtained by combining high-level quantum chemistry calculations of gas-phase enthalpies of formation with experimentally determined enthalpies of sublimation or vaporization. The procedure was successfully illustrated for catechol, resorcinol, and hydroquinone just recently.[41]

Isodesmic reactions are conventionally used for converting quantum-chemically calculated energies into enthalpies of formation. Isodesmic reactions as a rule are constructed from the small molecules with well-established properties. Unfortunately, the resulting $\Delta_f H_m^\circ(\text{g})$ values depend strongly on the choice of reference species used.[16,42] To achieve an objective result, one tries to use a reference species with accurate

Table 6. Thermochemical Data at T = 298.15 K ($p°$ = 0.1 MPa) for Halogen-benzenes (kJ·mol⁻¹)ᵃ

compounds	$\Delta_f H°_m$(liq or cr)	$\Delta_l^g H_m$	$\Delta_f H°_m$(g)(exp)	$\Delta_f H°_m$(g)(G4)	$\Delta_f H°_m$(liq)ᵉ
fluorobenzene	−150.8 ± 1.4[48]	35.0 ± 0.3[6]	−115.8 ± 1.4	−112.6	
chlorobenzene	11.0 ± 1.3[39]	41.8 ± 0.3[6]	52.8 ± 1.3	53.6ᵃ	
bromobenzene	60.9 ± 4.1[39]	44.5 ± 0.1ᶜ	105.4 ± 4.1	105.5ᵇ	
iodobenzene	117.2 ± 4.2[39]	48.9 ± 0.5ᶜ	166.1 ± 4.2		
1-fluoro-2-methylbenzene	−155.2[50]	39.3 ± 0.4[6]		−148.3	−187.6
1-fluoro-3-methylbenzene	−	39.0 ± 0.3[6]		−146.5	−185.5
1-fluoro-4-methylbenzene	−186.9 ± 1.1[39]	40.0 ± 0.3[6]	146.9 ± 1.1	−144.7	−184.7
1-chloro-2-methylbenzene	−27.2[49,50]	46.1 ± 0.3[6]		13.1ᵃ	−33.0
1-chloro-3-methylbenzene	−25.1[49,50]	46.8 ± 0.4[6]		16.3ᵃ	−30.5
1-chloro-4-methylbenzene	−20.5[49,50]	46.2 ± 0.3[6]		17.1ᵃ	−29.1
1-bromo-2-methylbenzene		47.7 ± 0.5ᶜ		66.6ᵇ	18.9
1-bromo-3-methylbenezene		48.4 ± 0.4ᶜ		70.0ᵇ	21.6
1-bromo-4-methylbenzene	26.6ᵍ	47.8 ± 0.5ᶜ			22.9
	12.0ᵈ[51]	62.4 ± 0.6ᵈ	74.4	70.7ᵇ	
1-iodo-2-methylbenzene	78.4 ± 4.2[39]	52.3 ± 0.4ᶜ	130.7 ± 4.2	128.9ᶠ	76.6
1-iodo-3-methylbenzene	79.2 ± 4.2[39]	52.9 ± 0.6ᶜ	132.1 ± 4.2	134.9ᶠ	82.0
1-iodo-4-methylbenzene	83.0ᵍ	52.5 ± 0.7ᶜ			80.8
	67.5 ± 4.2ᵈ,[39]	68.0 ± 0.7ᵈ	135.5 ± 4.3	133.3ᶠ	

ᵃCalculated using eq 22 for atomization reaction of Cl-containing molecules. ᵇCalculated using eq 23 for atomization reaction of Br-containing molecules. ᶜEnthalpies of vaporization/sublimation from Table 3. ᵈFor the crystal state, enthalpy of sublimation. ᵉCalculated as the difference of $\Delta_f H°_m$(g)(G4) − $\Delta_l^g H_m$. ᶠCalculated from enthalpy of formation of iodobenzene (this table) and mutual interactions from Table 7. ᵍCalculated from experimental enthalpy of formation $\Delta_f H°_m$(cr) and enthalpy of fusion from Table 4.

experimental enthalpies of formation, as well as design a large number of reactions to compensate for the possible inaccuracy in their values.[43] As an alternative approach to isodesmic reactions, we suggested in our recent works[16] a simple linear correlation based on the atomization reaction enthalpies calculated with a quantum-chemical method (e.g., G4 in this work). We observed the linear-type correlation between experimental enthalpies of formation and those calculated by the standard atomization procedure.[3] In this work we have used the restricted data set collected for eight chlorine-containing compounds (see SI Table S6) and 12 bromine-containing compounds (see SI Table S7), in order to derive the following linear correlations:

for Cl-containing molecules:

$$\Delta_f H°_m(g)(exp)/(kJ \cdot mol^{-1})$$
$$= (1.00 \pm 0.01)\Delta_f H°_m(g,G4) + (0.27 \pm 0.98)$$
$$\text{with } (r = 0.9996) \tag{22}$$

for Br-containing molecules:

$$\Delta_f H°_m(g)(exp)/(kJ \cdot mol^{-1})$$
$$= (1.03 \pm 0.01)\Delta_f H°_m(g,G4) + (2.99 \pm 0.75)$$
$$\text{with } (r = 0.9994) \tag{23}$$

With these correlations derived for the quantum-chemical method, we are able to calculate theoretical enthalpies of formation of halogen-benzenes using the simple atomization procedure (see Table 6). As can be seen from this table the AT "corrected" values are in good agreement with few experimental $\Delta_f H°_m$(gas,298.15K) values evaluated in section 3.3.1. In our opinion, the combination of the quantum-chemical methods with such a "corrected atomization procedure" could be generally recommended for reliable calculations of $\Delta_f H°_m$(gas,298.15K) of organic compounds.

3.3.3. Combination of Quantum-Chemical Calculations and Evaluated Vaporization Enthalpies for the Liquid-Phase Enthalpies of Formation.

Theoretical enthalpies of formation $\Delta_f H°_m$(g) of halogen-substituted benzenes calculated using quantum-chemical methods are collected in Table 6, column 5. Consistent values of vaporization enthalpies evaluated in this work for thermochemical calculations were taken from Table 3. Using the basic thermodynamic equation

$$\Delta_f H°_m(l) = \Delta_f H°_m(g) - \Delta_l^g H_m \tag{24}$$

which is referred to the reference temperature T = 298.15 K, values of enthalpies of formation of halogen-benzenes in the liquid phase were derived (see Table 6, column 6). These results are in good agreement with data for C₆H₅−Hal evaluated in this work, as well as in acceptable agreement with few experimental $\Delta_f H°_m$(liq,298.15K) values for halogenated methylbenzenes available in the literature, which unfortunately was aggravated with high uncertainties of ± 4.2 in kJ·mol⁻¹ (see Table 6, column 2).

3.3.4. Mutual Interactions of Substituents on the Benzene Ring (Gas Phase, 298.15 K).

Interactions of substituents in the ortho-, meta-, and para-positions on the benzene ring belong to the basics of organic chemistry. Energetics of such interplay of electron-donating and electron-accepting substituents determines as a rule the mechanism of a chemical reaction. Having established a set of quantum-chemical enthalpies H_{298} for halogen-substituted benzenes (see Table S8, SI), we estimated interactions on the benzene ring directly from enthalpies H_{298}. For this purpose the well-balanced distribution reaction

halogen-benzene + methylbenzene

$$= x\text{-halogen-methylbenzene} + \text{benzene} \tag{25}$$
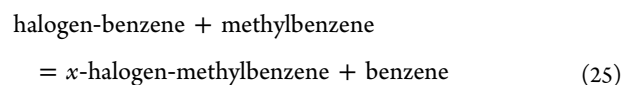
was applied. Enthalpies H_{298} of all reaction participants were calculated in this work by G4 method (Table S8, SI). The enthalpy $\Delta_r H°_m$ of the distribution reaction 25 was calculated

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according to Hess' law. The value of $\Delta_r H_m^\circ$ for this distribution reaction 25 expresses energetics of the mutual interaction of substituents on the benzene ring depending on their ortho-, meta-, or para-position. A significant advantage of the quantum-chemical calculations toward benzene derivatives is that this method allows estimation of substituent effects directly from enthalpies H_{298}, skipping the common step of the calculation of $\Delta_f H_m^\circ(g)$ for the reaction 25 participants by any theoretical or empirical method.

Substituent effects in halogen-substituted methylbenzenes defined by $\Delta_r H_m^\circ$ of reaction 25 are listed in Table 7. It has

Table 7. Mutual Interactions of Substituents, $\Delta_r H_m^\circ$, on the Benzene Ring for Halogen-Substituted Methylbenzenes As Calculated by G4 at 298.15 K

methylbenzene	$\Delta_r H_m^\circ(G4)^a/(kJ\cdot mol^{-1})$
1-fluoro-2-methylbenzene	−2.24
1-fluoro-3-methylbenzene	−0.45
1-fluoro-4-methylbenzene	1.37
1-chloro-2-methylbenzene	−3.99
1-chloro-3-methylbenzene	−0.79
1-chloro-4-methylbenzene	0.02
1-bromo-2-methylbenzene	−4.21
1-bromo-3-methylbenzene	−0.91
1-bromo-4-methylbenzene	−0.19
1-iodo-2-methylbenzene	−5.03^b
1-iodo-3-methylbenzene	1.04^b
1-iodo-4-methylbenzene	−0.56^b

^{a}Calculated using enthalpies H_{298} calculated by G4 (see Table S7) for the following reaction: methylbenzene + halogen-benzene = x-halogen-methylbenzene + benzene. ^{b}Calculated using correlations between $\Delta_r H_m^\circ$(G4) and between $\Delta_r H_m^\circ$(B3LYP6/-311G(d,p))

turned out that o-halogen-substituted methylbenzenes exhibit very weak stabilization due to attraction of substituents, slightly depending on the size of the halogen. The estimated gas-phase quantities of ortho-effects are as follows (kJ·mol^{-1}): F (−2.2) < Cl (−4.0) < Br (−4.2) < I (−5.0). Also for all meta-isomers very weak stabilzations of less than 1 kJ·mol^{-1} were observed, but independent of the size of the halogen with the effects as follows: F, −0.5 kJ·mol^{-1}; Cl, −0.8 kJ·mol^{-1}; Br, −0.9 kJ·mol^{-1}; I, −0.6 kJ·mol^{-1}. For para-isomers, except for F, effects of interactions can be considered as negligible with the following values: F, 1.4 kJ·mol^{-1}; Cl 0.1 kJ·mol^{-1}; Br, −0.2 kJ·mol^{-1}; I, −0.6 kJ·mol^{-1}.

Unfortunately the G4 method has not been parametrized for the I-containing molecules yet. In order to derive mutual interactions of iodine and methyl substituents, we additionally used B3LYP/6-311G(d,p) method[44] where all elements F, Cl, Br, and I are included. Results from density functional theory (DFT) calculation enthalpies $\Delta_r H_m^\circ$ according to reaction 25 for F-, Cl-, Br-, and I-substituted methylbenzenes are given in Tables S9 and S10, SI. Both sets of mutual interactions $\Delta_r H_m^\circ$ derived by G4 and DFT are not comparable directly, but it was possible to establish simple linear correlations separately for o-, m-, and p-halogen-substituted methylbenzenes (see Table S9, SI). With these correlations the missing in Table 7 mutual interactions of iodine and methyl substituents were estimated.

The mutual interactions of substituents on the benzene ring listed in Table 7 can be also utilized for prediction of $\Delta_f H_m^\circ(g,298.15K)$ using the GA method described in this work

Table 8. Parameters for the Calculation of Enthalpies of Formation, $\Delta_f H_m^\circ$, in the Gas and Liquid States of Halogen-Substituted Benzenes at 298.15 K

groups	$\Delta_f H_m^\circ(g)/(kJ\cdot mol^{-1})$	$\Delta_f H_m^\circ(liq)/(kJ\cdot mol^{-1})$
benzene	82.6[39]	49.0[39]
$\Delta H(H{\to}F)$	−198.4	−199.8
$\Delta H(H{\to}Cl)$	−29.8	−38.0
$\Delta H(H{\to}Br)$	22.8	11.9
$\Delta H(H{\to}I)$	83.5	68.2
$\Delta H(H{\to}CH_3)$	−32.2	−36.6
$(CH_3{-}CH_3)$	0.0	0.0
$o(F{-}CH_3)$	−2.2	0.0
$o(Cl{-}CH_3)$	−4.0	−7.0
$o(Br{-}CH_3)$	−4.2	−5.0
$o(I{-}CH_3)$	−5.0	−4.0
$m,p(F{-}CH_3)$	0.0	2.0
$m,p(Cl{-}CH_3)$	0.0	−4.0
$m,p(Br{-}CH_3)$	0.0	−2.0
$m,p(I{-}CH_3)$	0.0	1.0

for vaporization enthalpies. Using $\Delta_f H_m^\circ$(g,298.15K) values for benzene,[39] (82.6 ± 0.6) kJ·mol^{-1}, and methylbenzene,[39] (50.4 ± 0.6) kJ·mol^{-1}, in combination with evaluated enthalpies of formation for C_6H_5−Hal (Table 6, column 4), the appropriate contributions for exchange of H with halogen on the benzene ring (kJ·mol^{-1}) $\Delta H(H{\to}F)$, $\Delta H(H{\to}Cl)$, $\Delta H(H{\to}Br)$, and $\Delta H(H{\to}I)$ have been derived. These increments together with mutual interactions listed in Table 8 can be applied for prediction of $\Delta_f H_m^\circ$(g,298.15K) of halogen-benzenes of different structures using eq 21 adjusted for gaseous enthalpies of formation.

3.3.5. Mutual Interactions of Substituents on the Benzene Ring (Liquid Phase, 298.15 K). Enthalpies of formation in the liquid phase are often required for chemical engineering calculations. We used $\Delta_f H_m^\circ$(liq,298.15K) derived in this work by combination of quantum-chemical calculations with evaluated vaporization enthalpies in order to derive mutual interactions of substituents in halogenated methylbenzenes (see Table 8) according to eq 21 adjusted for liquid enthalpies of formation. Quantities of ortho-, meta-, and para-effects of substituents on the benzene ring in the liquid phase are not large, but they are difficult for interpretation, because, in contrast to the effects in the gas phase, a certain amount of ill-defined additional intermolecular interactions is present in these values. These mutual effects were considered as a set of empiric constants. We deliberately neglected some small effects in order to reduce the number of additive parameters. Increments and interactions listed in Table 8 can be used for estimation of $\Delta_f H_m^\circ$(liq,298.15K) of similarly shaped halogen-benzenes.

4. CONCLUSION

Vapor pressures and vaporization enthalpies of bromo- and iodo-substituted methylbenzenes were measured by transpiration method. These data together with results available in the literature were checked for internal consistency using the correlation GC method as well as GA procedure. Simple group-contribution procedure was developed for calculation enthalpies of vaporization of halogen-substituted benzenes. Gas-phase enthalpies of formation of halogen-substituted methylbenzenes were calculated by using quantum-chemical methods. These data together with evaluated vaporization enthalpies were used for estimation liquid-phase enthalpies of formation of

halogen-substituted methylbenzenes. Mutual interactions of substituents on the benzene ring were derived and utilized for developing of a simple GA method for prediction enthalpies of formation of similarly shaped molecules in the gas as well in the liquid state. Parameters of GA procedures should be transferable for prediction thermochemical properties of halogenated polyaromatic compounds, dibenzodioxins or dibenzofurans.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables listing molar heat capacities, cavity surface areas and volumes, Kovat's indices, correlation of experimental and calculated $\Delta_f H_m^\circ$ values, G4 total energies, interactions of substituents, and electronic and thermal enthalpies, text discussing determination of enthalpies of fusion, and figures showing enthalpy of formation comparisons. This material is available free of charge via the Internet at http://pubs.acs.org.

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