J. Phys. Chem. A **2005,** *109,* 4375−4380

Enthalpies of Formation and Strain of Chlorobenzoic Acids from Thermochemical Measurements and from ab Initio Calculations

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Received: September 14, 2004; In Final Form: March 24, 2005

Molar enthalpies of sublimation of 2-chloro-, 3-chloro-, and 4-chlorobenzoic acids were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. Thermochemical investigations of chlorobenzoic acids available in the literature were collected and combined with own experimental results to obtain their reliable standard molar enthalpies of formation at $T = 298.15$ K in the gaseous state. Ab initio calculations of chlorobenzoic acids have been performed using the G3(MP2) theory, and results from the homodesmic reactions are in excellent agreement with experiment. New results help us to resolve the uncertainty in the available thermochemical data on chlorobenzoic acids. The strain enthalpies of chlorobenzoic acids have been assessed using an isodesmic reaction procedure.

Introduction

Derivatives of benzoic acid are compounds of considerable industrial and environmental significance. However, thermochemical data on substituted benzoic acids are apparently in a state of disarray.[1] Although experimental values of the enthalpies of formation in the crystalline state, $\Delta_f H^\circ_m$(cr), of 2-chloro-, 3-chloro-, and 4-chlorobenzoic acids, available from the literature,[2−4,7] are in close agreement with each other, the range of enthalpy values of sublimation, $\Delta_{cr}^{g} H_m$, for each of these compounds differ over 20.0 kJ mol^{-1} (see Table 1). Thus, additional experiments on chlorobenzoic acids are necessary in order to validate available experimental data on sublimation enthalpies and to obtain reliable enthalpies of formation $\Delta_f H^\circ_m(g) = \Delta_f H^\circ_m(cr) + \Delta_{cr}^{g} H_m$. It is for this reason that measurement of $\Delta_{cr}^{g} H_m$ of three chlorobenzoic acids using transpiration method have been made, and these are complemented with high level ab initio calculations.

Experimental Section

The 2-chloro-, 3-chloro-, and 4-chlorobenzoic acids and 4-*tert*-butylbenzoic acid supplied by Aldrich and Fluka with a mass-fraction purity of about 0.99 were further purified by repeated sublimation in a vacuum. GLC analysis of the samples used for vapor pressure measurements on a capillary column, SE-30 of 25 m length, failed to show the presence of any impurities (greater than 0.01 mass percent).

Vapor pressures and enthalpies of sublimation, $\Delta_{cr}^{g} H_m$, of substituted benzoic acids were determined using the method of transference in a saturated stream of nitrogen. The method has been described in detail before[12,13] and has proven to give results in agreement with other established techniques. The temperature dependence of the vapor pressures was used to determine the enthalpies of vaporization of the pure substances. A sample of approximately 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 10 cm and diameter 0.5 cm. Preheated nitrogen stream was passed through the U-tube at constant temperature (±0.1 K). The flow rate of the nitrogen stream was measured using a soap film bubble flow meter (±0.2−0.3%) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow, below which, the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus the contribution due to diffusion was negligible at flow rates down to 0.5 dm^3·h^{-1}. The upper limit for our apparatus was a flow rate of 7.5 dm^3·h^{-1}. Thus, we carried out the experiments in the using flow rates ranging from 4 to 5 dm^3·h^{-1} which ensured that transporting gas was in saturated equilibrium with the coexisting solid phase in the saturation tube. The material transported was condensed in a cold trap. The amount of condensed product was determined by weighing (±0.0001 g).

The saturated vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures when applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{sat} = m_i R T_a / V M_i; \quad V = V_{N_2} + V_i \quad (V_{N_2} \gg V_i) \qquad (1)$$

where R = 8.31447 J·K^{-1}·mol^{-1}; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas and T_a is the temperature of the soap film bubble flow meter. The volume of transporting gas V_{N_2} was determined from the flow rate and time measurements.

Ab Initio Calculations. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 Rev.04 series of programs.[14] Energies were obtained at the G3(MP2) level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart based on ab initio molecular orbital theory. A modification of G3 theory that uses reduced orders of Møller−

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10.1021/jp045852q CCC: $30.25

TABLE 1: Compilation of Data on Enthalpies of Sublimation $\Delta_{cr}^{g}H_m$ of Benzoic Acids Derivatives

	technique[a]	temp range/K	$\Delta_{cr}^{g}H_m(T)$/kJ·mol^{-1}	$\Delta_{cr}^{g}H_m$ (298 K)[b]/kJ·mol^{-1}	ref
p-tert-butylbenzoic acid	K	325.4−342.8	103.8 ± 0.4	105.2 ± 0.4	6
	T	373.0−402.5	102.1 ± 0.7	105.4 ± 0.7	this work
2-chlorobenzoic acid	TE	333.2	79.5 ± 1.7	80.4 ± 1.7	8
	DC	413	72.4[c]	101.5	9
	DSC	>414	90.7 ± 0.5[c]	119.9 ± 0.6	10
	C	323.1	100.0 ± 0.5	100.6 ± 0.5	11
	K	320.2−339.2	105.1 ± 0.4	105.8 ± 0.4	29
	T	338.1−402.6	99.91 ± 0.36	101.5 ± 0.4	this work
3-chlorobenzoic acid	TE	328.2	80.8 ± 1.7	81.6 ± 1.7	8
	DC	414	99.6	102.2	9
	C	323.1	100.5 ± 0.4	101.1 ± 0.4	11
	K	320.1−340.1	101.2 ± 0.4	101.9 ± 0.4	29
	T	348.5−404.1	98.8 ± 0.8	100.6 ± 0.8	this work
4-chlorobenzoic acid	TE	333.2	87.9 ± 1.7	88.8 ± 1.7	8
	DC	413	101.9	105.0	9
	C	363.1	99.3 ± 0.4	101.0 ± 0.4	11
	K	333.2−356.1	103.3 ± 0.5	104.5 ± 0.5	29
	T	358.4−398.3	105.7 ± 0.8	107.9 ± 0.8	this work

[a] Techniques: T = transpiration; K = mass loss Knudsen method; C = Calvet calorimetry with Knudsen cell; DC = drop Calvet microcalorimetry; TE = torsion-effusion method. DSC = differential scanning calorimetry. [b] Original vapor pressure available in the literature were treated using eqs 2 and 3 in order to evaluate enthalpy of sublimation at 298.15 K in the same way as our own results in Table 2. [c] Enthalpy of vaporization.

Plesset perturbation theory is G3(MP2) theory.[15,16] This method saves considerable computational time compared to G3 theory with limited loss in accuracy, but it is much more accurate that G2(MP2) theory. G3(MP2) theory uses geometries from second-order perturbation theory and scaled zero-point energies from Hartree−Fock theory followed by a series of single-point energy calculations at the MP2(Full)/6-31G(d), QCISD(T)/6-31G(d) and MP2/GTMP2Large levels of theory (for details see ref 15). The enthalpy value of studied compounds at $T = 298$ K was evaluated according to standard thermodynamic procedures.[17]

Results and Discussion

Vapor Pressure Measurements. Experimental vapor pressures of alkyl carbamides have been measured by using the transpiration method in the broad temperature range over 50 K. In each case the measurements have been performed possibly close to the reference temperature 298.15 K. The following equation

$$R \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_{cr}^{g}C_p \ln\left(\frac{T}{T_0}\right) \qquad (2)$$

was fitted to the experimental p, T data using a and b as adjustable parameters. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which in this case is 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at temperature T is

$$\Delta_{cr}^{g}H_m(T) = -b + \Delta_{cr}^{g}C_pT \qquad (3)$$

Values of $\Delta_{cr}^{g}C_p$ have been derived from the experimental isobaric molar heat capacities of solid chlorobenzoic acids,[18] C_p^{cr}, and isobaric molar heat capacities of gaseous chlorobenzoic acids, C_p^{g}, were calculated using ab initio methods (see Supporting Information). Experimental results and parameters a and b are listed in Table 2.

To establish the validity of the transpiration method for benzoic acid derivatives, the admittedly reliable enthalpy of sublimation of 4-*tert*-butylbenzoic acid[6] was measured in this work. The vapor pressures and enthalpy of sublimation $\Delta_{cr}^{g}H_m$ from this work were in a very good agreement with the literature data[6] (see Table 1).

Enthalpies of Sublimation. $\Delta_{cr}^{g}H_m$. The temperature dependencies of vapor pressures of chlorobenzoic acids have been reported in the literature recently.[29] Also enthalpies of sublimation for these compounds were measured at elevated temperatures with the help of a Tian-Cavet calorimeter equipped with the Knudsen effusion cell[11] or by using the "drop-method" (a sample was dropped into the hot zone of the calorimeter)[9] and have been reported. The authors of these works adjusted their measured values of $\Delta_{cr}^{g}H_m$ to the reference temperature, $T = 298.15$ K, by different and ill-defined methods. It is for this reason that in this work the original published experimental results[9,11] were readjusted to the reference temperature $T = 298.15$ K in the same manner as our own results (using the experimental isobaric molar heat capacities of solid chlorobenzoic acids,[18] C_p^{cr}, and gaseous isobaric heat capacities, C_p^{g}, from ab initio calculations), and new $\Delta_{cr}^{g}H_m$ (298.15 K) values were calculated in order to make a more reliable comparison with results from this work (see Table 1).

The value of $\Delta_{cr}^{g}H_m$(298.15 K) for 2-chlorobenzoic acid obtained in this work is in very good agreement with those from Adedeji et al.[9] as well as those from Sabbah and Hirtz.[11] However, it should be noted that Adedeji et al.[9] measured the vaporization enthalpy $\Delta_{l}^{g}H_m$ for this compound. To calculate sublimation enthalpy, $\Delta_{cr}^{g}H_m$(298.15 K), the value of the enthalpy of fusion, $\Delta_{cr}^{l}H_m$ (298.15 K), for 2-chlorobenzoic acid is required. The experimental enthalpy of fusion, $\Delta_{cr}^{l}H_m(T_{fus}) = 26.29 \pm 0.28$ kJ·mol^{-1} of 2-chlorobenzoic acid was measured at a melting temperature of 414.10 K,[11] and due to the deviation of the melting temperature from $T = 298.15$ the observed value of the enthalpy of fusion of 2-chlorobenzoic acid had to be adjusted to the reference temperature of 298.15 K. The adjustment was calculated using the equation[19,20]

$$\begin{aligned}\{\Delta_{cr}^{l}H_m(T_{fus}/\text{K}) - \Delta_{cr}^{l}H_m^{\circ}(298.15\ \text{K})\}/(\text{J·mol}^{-1}) = \\ \{(0.75 + 0.15C_p^{cr})[(T_{fus}/\text{K}) - 298.15]\} - \\ \{(10.58 + 0.26C_p^{l})\,[(T_{fus}/\text{K}) - 298.15]\}\end{aligned} \qquad (4)$$

where the value of $\Delta_{cr}^{l}C_p$ has been derived from the isobaric molar heat capacities of liquid chlorobenzoic acids, $C_p^{l} = 236.0$ J·mol^{-1}·K^{-1} calculated according to procedure developed by Chickos.[21] The isobaric molar heat capacities of the solid

TABLE 2: Results from Measurements of the Vapor Pressure *p* of Benzoic Acid Derivatives Using the Transpiration Method

T^a/K	m^b/mg	$V_{N_2}{}^c$/dm^3	gas flow/(dm^3/h)	p^d/Pa	($p_{expt} - p_{calcd}$)/Pa	$\Delta_{cr}^{g}H_m$/kJ·mol^{-1}
4-*tert*-Butylbenzoic acid; $\Delta_{cr}^{g}H_m$(298.15 K) = (105.40 ± 0.69)kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{337.64}{R} - \frac{116576.59}{R(T,\mathrm{K})} - \frac{37.5}{R}\ln\left(\frac{T,\mathrm{K}}{298.15}\right)$						
373.0	35.0	65.76	4.79	7.49	0.1	102.59
383.0	13.1	10.39	4.79	17.63	0.1	102.22
387.9	12.5	6.79	4.79	25.79	−0.6	102.03
392.6	13.2	4.79	4.79	38.46	0.0	101.86
397.6	8.7	2.16	4.79	56.58	−0.4	101.67
402.5	28.7	4.79	4.79	84.08	1.3	101.48
2-Chlorobenzoic acid; $\Delta_{cr}{}^{g}H_m$(298.15 K) = (101.50 ± 0.36)kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{321.2}{R} - \frac{108153.2}{R(T,\mathrm{K})} - \frac{22.3}{R}\ln\left(\frac{T,\mathrm{K}}{298.15}\right)$						
338.1	13.2	249.83	5.37	0.85	0.0	100.71
344.0	8.0	85.84	5.37	1.50	0.0	100.56
348.0	14.0	98.81	5.37	2.26	0.0	100.46
352.9	18.7	78.75	5.35	3.80	0.1	100.33
362.8	11.9	19.72	5.38	9.59	0.1	100.08
369.9	13.2	11.55	5.41	18.15	0.2	99.91
376.1	13.2	6.77	5.41	30.95	0.3	99.75
382.8	12.7	3.83	5.35	52.89	−0.6	99.58
387.8	27.9	5.43	5.35	81.76	1.7	99.45
392.7	14.0	1.97	5.37	112.7	−5.4	99.33
397.7	20.1	1.88	5.37	170.6	−1.9	99.20
402.6	129.5	7.96	5.37	258.1	8.6	99.08
402.6	26.3	1.70	4.85	246.4	−2.2	99.08
3-Chlorobenzoic acid; $\Delta_{cr}^{g}H_m$(298.15 K) = (100.58 ± 0.78)kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{318.5}{R} - \frac{107316.8}{R(T,\mathrm{K})} - \frac{22.6}{R}\ln\left(\frac{T,\mathrm{K}}{298.15}\right)$						
348.5	15.8	111.35	5.14	2.25	−0.1	99.51
353.6	16.4	66.60	5.14	3.91	0.1	99.38
363.6	5.0	8.57	5.14	9.23	−0.4	99.13
368.7	13.4	13.80	5.14	15.30	0.2	99.00
374.1	18.8	12.17	5.14	24.46	0.4	98.87
379.1	26.7	10.80	5.14	39.02	2.5	98.74
384.1	17.8	5.14	5.14	54.81	−0.1	98.61
389.1	12.4	2.57	5.14	76.10	−5.5	98.49
394.1	16.7	2.23	5.14	119.1	−1.1	98.36
399.1	14.2	1.29	5.14	174.3	−0.7	98.23
404.1	21.0	1.29	5.14	257.7	5.3	98.11
4-Chlorobenzoic acid; $\Delta_{cr}^{g}H_m$(298.15 K) = (107.87 ± 0.80)kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{329.4}{R} - \frac{115891.6}{R(T,\mathrm{K})} - \frac{26.9}{R}\ln\left(\frac{T,\mathrm{K}}{298.15}\right)$						
358.4	24.2	334.21	5.46	1.15	0.02	106.23
363.2	13.4	116.77	5.52	1.82	0.01	106.11
367.7	22.9	135.51	5.46	2.67	−0.12	105.99
368.2	14.4	77.09	5.50	3.00	0.07	105.98
373.2	19.6	68.12	5.05	4.61	−0.04	105.85
378.3	13.3	29.69	5.05	7.12	−0.27	105.71
382.5	14.2	20.18	5.05	11.19	0.54	105.61
384.3	11.3	14.29	5.50	12.48	−0.02	105.56
388.3	12.9	11.46	5.50	17.96	0.47	105.46
393.3	11.9	7.33	5.50	25.88	−0.59	105.33
398.1	11.5	4.58	5.50	39.93	0.89	105.20
398.3	12.8	5.22	5.50	38.69	−0.98	105.20

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at T = 299 K. [c] Volume of nitrogen, used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at the cooling temperature T = 299 K.

chlorobenzoic acids, C_p^{cr}, were sourced from ref 18. The standard enthalpy of fusion at T = 298.15 K, $\Delta_{cr}^{l}H_m$(298.15 K) = 20.87 ± 0.28 kJ·mol^{-1} was calculated (see Table 3) with this adjustment (the uncertainty of the correlation was not taken into account). The latter value was used to calculate the enthalpy of sublimation, $\Delta_{cr}^{g}H_m$(298.15 K), of the solid 2-chlorobenzoic acid from the data in ref 9 (see Table 1). The vaporization enthalpy of 2-chlorobenzoic acid measured by Holdiness[10] has also been adjusted to the reference temperature in the same way, but his value of sublimation enthalpy is about 20 kJ·mol^{-1} large than other values, and we have no explanation for this discrepancy because of the lack of detail in the experimental procedure reported in the original publication.[10] Thus, for 2-chlorobenzoic acid we now have three consistent values of sublimation enthalpy which are all are very close to a value of 101 kJ·mol^{-1} (see Table 1). Recently, new data on the vapor pressures of a series of chlorobenzoic acids have been measured using the Knudsen method.[29] Surprisingly, this recent result for

TABLE 3: Compilation of Experimental Data on Enthalpies of Fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$, Enthalpies of Sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$, and Calculated Enthalpies of Vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ of Methyl- and Chlorobenzoic Acids

compound	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ at T_{fus}/kJ·mol^{-1}	T_{fus}/K	$\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H_{\mathrm{m}}{}^{a}$ at 298.15 K/kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ at 298.15 K/kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}{}^{b}$ at 298.15 K/kJ·mol^{-1}
2-methylbenzoic acid	20.17[18]	376.9	16.55	95.9 ± 0.1[5]	79.3 ± 0.1
3-methylbenzoic acid	15.73[18]	381.9	11.73	97.0 ± 0.3[5]	85.3 ± 0.3
4-methylbenzoic acid	22.72[18]	452.8	15.47	98.8 ± 0.3[5]	83.3 ± 0.3
2-chlorobenzoic acid	26.29 ± 0.28[11]	414.10	20.87 ± 0.28	101.5 ± 0.4	80.6 ± 0.5
3-chlorobenzoic acid	22.00 ± 0.33[11]	427.83	15.95 ± 0.33	100.6 ± 0.8	84.7 ± 0.8
4-chlorobenzoic acid	34.26 ± 0.17[11]	513.53	24.35 ± 0.17	107.9 ± 0.8	83.6 ± 0.8

[a] The experimental enthalpies of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ measured at T_{fus} and adjusted to 298.15 K (see text). [b] The enthalpy of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$, calculated as the difference $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (from column 5) and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ (from column 4).

2-chlorobenzoic acid $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) = = 105.8 ± 0.4 kJ·mol^{-1} (see Table 1) is in substantial disagreement with the average of 101 kJ·mol^{-1} discussed above. We compared the data for the temperature dependence of vapor pressure derived in this work with those measured in ref 29. High-temperature ranges of the both studies are almost overlapping, and the vapor pressures in this region are in very good agreement. However, the vapor pressures at lower temperatures from ref 29 have a different trend, which is the cause of the disagreement in the sublimation enthalpies. Taking into account, that vapor measurements from this work covers temperature range which is three times larger than that in ref 29, our value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) for 2-chlorobenzoic acid seems to be more reliable. Furthermore, the measurements in this work are in good agreement with the two other values reported in the literature.[9,11]

The value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) for 3-chlorobenzoic acid obtained in this work is in good agreement with those from Adedeji et al.[9] and those from Sabbah and Hirtz,[11] and Ribeiro da Silva et al.[29] (see Table 1).

The values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) for 4-chlorobenzoic acid is not in very good agreement with the data reported by Adedeji et al.[9] and Ribeiro da Silva et al.[29] but are still within acceptable limits. The disagreement of our result with those from Sabbah and Hirtz[11] is over 5 kJ·mol^{-1} and cannot be explained.

Experimental measurement of the sublimation enthalpies of the three isomeric chlorobenzoic acids are reported by Wolf and Weghofer[8] from the torsion−effusion method. As can be seen in Table 1, their values are generally 20 kJ·mol^{-1} lower than data from other sources. This method is considered the most reliable for vapor pressure measurements, hence we postulate that in fact the vaporization enthalpies of chlorobenzoic acids were measured in the work of Wolf and Weghofer and are erroneously denoted sublimation enthalpies. If this suggestion is indeed true, then the values reported by Wolf and Weghofer[8] are in good agreement with the vaporization enthalpies of chlorobenzoic acids reported in this work (Table 3, column 6).

Enthalpies of Vaporization. $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$. The scatter of the available experimental results on sublimation enthalpies for 2- and 4-chlorobenzoic acids, described above, has made it necessary to analyze the vaporization enthalpies of these compounds in order to further validate results obtained in this work. Indeed, experimental values of sublimation enthalpies, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$, hardly lend themselves for further interpretation or comparison, because each enthalpy of sublimation consists from two contributions: the enthalpy of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$, and enthalpy of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$. In contrast, enthalpies of vaporization, in most cases readily obey the additive rules,[22] or are able to demonstrate some general regularities, especially for ortho-, meta-, and para-substituted benzenes.[23,24] Thus, a valuable test of the consistency of the experimental data presented in this work on sublimation enthalpies of chlorobenzoic acids, is the comparison of their vaporization enthalpies. The latter values were calculated from difference $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ} - \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ and presented in Table 3. We used the experimental enthalpies of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ available in the literature[11] (these values are generally consistent with the earlier measurements reported in the ref 18) and adjusted them to $T = 298.15$ K according to eq 4.

It is obvious, from Table 3, that the vaporization enthalpies of 3- and 4-chlorobenzoic acids are indistinguishable within the boundaries of their experimental uncertainties. Such behavior is typical for most of meta- and para-substituted benzenes.[23] The vaporization enthalpy of *o*-chlorobenzoic acid is about 5 kJ·mol^{-1} lower than those of meta- and para-isomers, and this diminishment is quite apparent because of the lower packing order in the liquids due to the steric hindrance caused by the repulsion between chloro and carboxylic groups. A similar pattern is exhibited by methyl derivatives of benzoic acids, which can be seen from the highly reliable thermodynamic data reported in Table 3.[5] Indeed, the spatial requirements of chloro- and methyl-group are very similar, following enthalpies of vaporization of ortho-, meta-, and para-isomers of chlorobenzoic acids and methylbenzoic acids should be very close. The data on vaporization enthalpies of these benzoic acid derivatives presented in Table 3 validate this hypothesis. Thus, the values for the vaporization enthalpies of benzoic acid derivatives taken for comparison possess internal consistency, subsequently the values of the sublimation enthalpies of chlorobenzoic acids measured in this work (see Table 2) could be used further for the calculation of the standard enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$(g), of these compounds.

Calculation of the Gaseous Enthalpies of Formation. Combustion enthalpies of the chlorobenzoic acids have been reported by numerous investigators.[2−4,7] Most measurements have been performed on 4-chlorobenzoic acid, which is now accepted as a suitable reference compound for the combustion enthalpies of chloro-containing compounds.[4,7] The enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$(cr) at 298.15 K, derived from the combustion results are very consistent and we selected the following recently published values for the calculation of the gaseous enthalpy of formation: 2-chlorobenzoic acid[11] $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$(cr) = (−405.1 ± 0.5) kJ·mol^{-1}; 3-chlorobenzoic acid[11] $\Delta_{\mathrm{f}}H_{\mathrm{m}}{}^{\circ}$(cr) = (−423.2 ± 0.8) kJ·mol^{-1}; and 4-chlorobenzoic acid[4] $\Delta_{\mathrm{f}}H_{\mathrm{m}}{}^{\circ}$(cr) = (−429.9 ± 2.2) kJ·mol^{-1}. Furthermore, for the estimation of the gaseous enthalpy of formation of chlorobenzoic acids, we used values $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) derived in the present study that are listed in Table 2. The calculated values of the standard molar enthalpies of formation $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$(g) of chlorobenzoic acids are given in the last column in Table 5.

Quantum Chemical Calculations for Chlorobenzoic Acids. Results of ab initio molecular orbital methods for calculation of the enthalpy of formation of chlorobenzoic acids have not

TABLE 4: G3(MP2) Total Energies at 0 K and Enthalpies at 298.15 K (in hartree) of the Molecules Studied in This Work

compounds	G3(MP2) $-E_0$	G3(MP2) $-H_{298}$
2-chlorobenzoic acid	879.355008	879.346429
3-chlorobenzoic acid	879.362481	879.353033
4-chlorobenzoic acid	879.363190	879.353741
benzoic acid	420.200783	420.192542
chlorobenzene	690.992623	690.986059
benzene	231.829758	231.824309

TABLE 5: Results of Calculation of the Standard Enthalpy of Formation $\Delta_f H_m^\circ$(g) for ChloroBenzoic Acids in the Gaseous Phase at 298.15 K in kJ·mol^{-1}

compounds	G3(MP2) atomization	G3(MP2) homodesmic	experimental
2-chlorobenzoic acid	−314.6	−303.9	−303.6 ± 0.6
3-chlorobenzoic acid	−331.9	−321.3	−322.6 ± 1.1
4-chlorobenzoic acid	−333.8	−323.2	−322.0 ± 2.3

been yet reported in the literature. In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions.[25] Raghavachari et al.,[26] have proposed the use of a set of isodesmic reactions, the “bond separation reactions”, to derive theoretical enthalpies of formation. Isodesmic reactions conserve the number of types of bonds and should thus be an improvement on simple atomization reactions. Further enhancement in the calculation of enthalpies of formation should be provided by homodesmic reactions, which, in addition to the types of bonds, also conserve the hybridization of the atoms in the bond. We have calculated the enthalpies of formation of chlorobenzoic acids with help from both standard atomization reactions as well as homodesmic reactions. For the latter method, we have chosen the following three reactions:

$$\text{2-chlorobenzoic acid} + \text{benzene} \rightarrow \text{benzoic acid} + \text{chlorobenzene} \quad (5)$$

$$\text{3-chlorobenzoic acid} + \text{benzene} \rightarrow \text{benzoic acid} + \text{chlorobenzene} \quad (6)$$

$$\text{4-chlorobenzoic acid} + \text{benzene} \rightarrow \text{benzoic acid} + \text{chlorobenzene} \quad (7)$$

Using enthalpies of these reactions calculated by G3(MP2) and enthalpies of formation $\Delta_f H_m^\circ$(g), for benzene, chlorobenzene, and benzoic acid recommended by Pedley et al.[24] enthalpies of formation of all three isomeric chlorobenzoic acids have been calculated (see Table 5) and they are in excellent agreement with the experimental values derived in this work. Enthalpies of formation of chlorobenzoic acids derived with help of the atomization procedure are systematically (about 10 kJ·mol^{-1}) more negative than the experimental results.

Strain in Chlorobenzoic acids. Conventional strain-enthalpies could be derived as the differences between the observed enthalpies of formation in the gaseous state and values calculated by application of group-additivity schemes.[27,28] However, especially for the benzene derivatives their strain is more convenient to determine as the enthalpy of a distribution reaction which is in general the same as reactions 5−7 mentioned above. In this case, a sum of bricks (or additive groups) on the left and on the right side of reaction remains constant and the enthalpy of such a reaction expresses only the mutual interaction of substituents on the benzene ring. For instance, from the enthalpy of reaction 5, one can distinguish the strain of 2-chlorobenzoic acid in comparison with benzene, chlorobenzene, and benzoic acid, or in other words, this strain is caused by steric interactions of the chloro and carboxylic substituents. As can be seen in Figure 1, the carboxylic group in 2-chlorobenzoic acid is forced to take a position out of the plane of the benzene ring with a distance of 3.01 Å between chlorine and oxygen atoms. This distance would be only 2.85 Å if there was coplanar positioning of the carboxylic relative to the benzene ring, but during geometry optimization procedures the carboxylic group prefers the out-of plane position in order to avoid steric repulsions. In contrast, (see Figures 2 and 3) the carboxylic group in 3- and 4-chlorobenzoic acid is coplanar with the benzene ring, and such a position is more preferable for the conjugation of π-electrons of benzene ring with electrons of carboxylic group and these two molecules, in the absence of the steric effects, are expected to exhibit only weak destabilization. We calculated the strain in chlorobenzoic acids with help of reactions 5−7 and using experimental enthalpies of formation, $\Delta_f H_m^\circ$(g), of the reaction participants. These calculations (see Table 6) reveal that 2-chlorobenzoic acid is profoundly destabilized by about 20 kJ·mol^{-1} due to steric reasons. A weak destabilization of about 2 kJ·mol^{-1} in 3- and 4-chlorobenzoic acid is apparently due to the electron redistribution in the benzene ring on substitution.

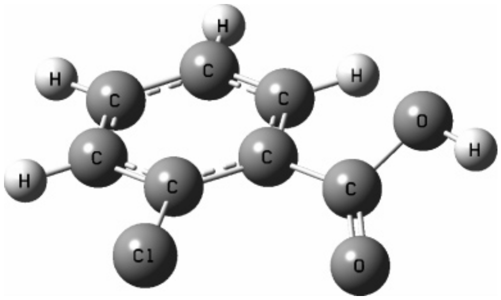

Figure 1. Optimimized structure of 2-chlorobenzoic acid.

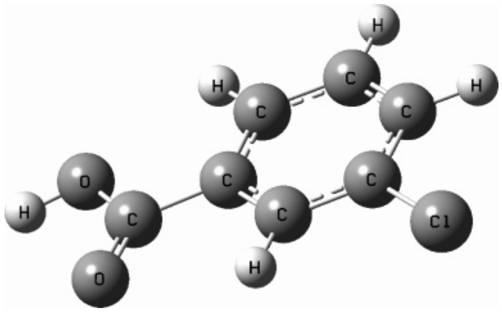

Figure 2. Optimimized structure of 3-chlorobenzoic acid.

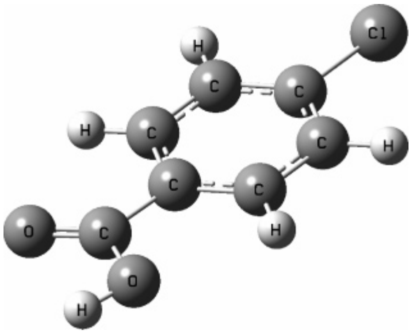

Figure 3. Optimimized structure of 4-chlorobenzoic acid.

A substantial advantage of ab initio calculations toward benzene derivatives is that this method allows for the calculations of such interactions (or strain) directly from enthal-

TABLE 6: Results of Calculation of the Standard Enthalpies of Reactions, $\Delta_r H^\circ_m$ for Reactions Involving Chlorobenzoic Acids in the Gaseous Phase at 298.15 K in kJ·mol^{-1}

	$-\Delta_r H^\circ_m$/kJ·mol^{-1}	
reaction	G3(MP2)	experimental
2-chlorobenzoic acid (eq 5)	20.6	21.4
3-chlorobenzoic acid (eq 6)	3.3	2.4
4-chlorobenzoic acid (eq 7)	1.4	2.6

pies H_{298} (see Table 5) skipping the step of the calculation of $\Delta_f H^\circ_m$(g) by any method. This advantage becomes more apparent if one takes into consideration the substantial differences in enthalpies of formation calculated from atomization and from bond separation methods as it is shown in the Table 5.

We have also derived the strain in chlorobenzoic acids simple with the help of reactions 5−7) and using only ab initio values of enthalpies H_{298} of the reaction participants from Table 4. For comparison, the same procedure has been carried out by applying selected experimental $\Delta_f H^\circ_m$(g) of reaction participants. Results are presented in Table 6 and they show that the strain calculated by G3(MP2) and determined by experiment for chlorobenzoic acids are in excellent agreement.

Conclusions

This investigation was undertaken to establish a consistent set of experimental thermochemical quantities for isomeric chlorobenzoic acids. Our own results together with a large number of the experimental results from the literature, have been used to derive reliable values for the enthalpy of formation of the chlorobenzoic acids at the reference temperature 298.15 K. This collection, which includes the literature data and results from this work, helps to resolve previous contradictions in the experimental thermochemistry of chlorobenzoic acids.

Acknowledgment. V.N.E., from Mogilev Technologicale Institute, Belarus, acknowledges gratefully a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst). A.S., from Warsaw University of Technology, Poland, acknowledges gratefully financial support from the ERASMUS−SOKRATES Program.

Supporting Information Available: Table 1 giving values of frequencies of normal vibrations and moments of inertia and Table 2, giving rotation constants and moments of inertia of chlorobenzoic acids. This material is available free of charge via the Internet at http://pubs.acs.org.

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