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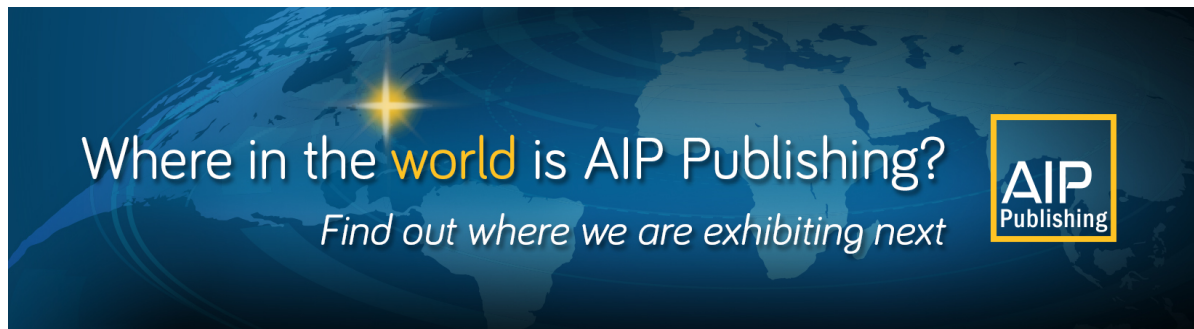
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Critical Evaluation of Thermodynamic Properties for Halobenzoic Acids Through Consistency Analyses for Results from Experiment and Computational Chemistry

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Thermodynamic properties of the twelve monohalobenzoic acids are critically evaluated through the application of computational chemistry methods for the ideal-gas phase and thermodynamic consistency assessment of properties determined experimentally and reported in the literature, including enthalpies of combustion, enthalpies of sublimation, and enthalpies of fusion. The compounds of interest are the 2-, 3-, and 4-halo isomers of fluoro-, chloro-, bromo-, and iodobenzoic acids. Computations were validated by comparison with critically evaluated entropies and heat capacities in the ideal-gas state for benzoic acid, benzene, and some halobenzenes. Experimental enthalpies of formation for 2- and 3-bromobenzoic acids, measured by well-established research groups, are mutually inconsistent and further, are shown to be inconsistent with the computations and assessment in this work. Origins of the discrepancies are unknown, and recommended values for these compounds are based on computations and enthalpies of sublimation validated, in part, by a structure-property (i.e., group-additivity) analysis. Lesser, but significant, inconsistencies between experimental and computed results are demonstrated also for 3- and 4-iodobenzoic acids. The comparison of enthalpies of formation based on the experiment and computation for the ideal-gas state of 1- and 2-chloro-, bromo-, and iodonaphthalenes provides additional support for the findings for halobenzoic acids and also reveals some anomalous results in the experimental literature for chloronaphthalenes. Computations are discussed in detail to demonstrate the approach required to obtain optimal results with modern quantum chemical methods. © *2017 AIP Publishing LLC for the National Institute of Standards and Technology.* [http://dx.doi.org/10.1063/1.4983656]

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1. Introduction

The critical evaluation of thermodynamic properties involves a demonstration of consistency among properties for a given compound based on enforced thermodynamic identities and well-established correlations (cf. the series of articles describing the National Institute of Standards and Technology (NIST) ThermoData Engine[1–8]). In addition, evaluation involves the assessment of trends in property values within families of related compounds, such as trends in properties for homologous series, such as normal alkanes, which have remained a topic of interest to the research community for decades (cf. Refs. [9–11]).

In recent years, the methods of modern computational chemistry have been increasingly applied in the critical

evaluation process, as these provide pathways to properties for the ideal-gas state (specifically, standard entropies and enthalpies of formation) that are independent of calorimetric methods (cf. Refs. 12–14). The demonstration of consistency between the computations and experiment provides a mutual validation of the two methods, together with an increase in confidence in the overall critical evaluation. Simultaneous application of the two methods to families of compounds provides an important path for the validation and quantification of uncertainties for the computational methods. These, in turn, can be used with confidence to resolve discrepancies in the experimental literature or provide essential data that are, otherwise, unobtainable, such as those for materials of extreme expense, high toxicity, low chemical stability, or that cannot be synthesized in adequate quantity or purity for experimental investigation.

In the present work, thermodynamic properties of monohalobenzoic acids are critically evaluated, including the 2-, 3-, and 4- isomers (i.e., ortho, meta, and para isomers) of fluoro-, chloro-, bromo-, and iodobenzoic acids. Properties for many of these compounds have been reported by multiple independent research groups with low uncertainty and good consistency between the reported values, thus providing a check on the quality of the computed values. Conversely, for some compounds—particularly the bromo derivatives—consistency of experimental results in the literature is poor, and the computations provide essential information to distinguish reliable and anomalous results. In addition to the demonstration of consistency for ideal-gas properties, a trend analysis for condensed phase properties (specifically, enthalpies of vaporization estimated from experimental enthalpies of fusion and sublimation) is used to lend additional confidence to the evaluations.

2. Thermodynamic Relationships Used in the Evaluation Process

The key thermodynamic identity used in the present work is

$$\Delta_f H_m^o(cr, 298.15 \text{ K}) + \Delta_{cr}^g H_m^o(298.15 \text{ K}) = \Delta_f H_m^o(g, 298.15 \text{ K}), \qquad (1)$$

where $\Delta_f H_m^o$ (cr) and $\Delta_f H_m^o$ (g) are the standard molar enthalpies of formation of the crystal and gas, respectively, and $\Delta_{cr}^g H_m^o$ is the enthalpy of sublimation. The reference temperature $T = 298.15$ K is that chosen for nearly all experimental determinations of the enthalpy of formation for condensed states, and the reference pressure is 100 kPa.

Experimental determination of $\Delta_f H_m^o$ (cr, 298.15 K) involves a measurement of the enthalpy of combustion of the compound of interest in oxygen and algebraic combination of the results with well established enthalpies of formation for the combustion products: water, carbon dioxide, and other combustion products specific to the combusted compound. For halobenzoic acids, additional products are HF(aq), HCl (aq), HBr(aq), and I_2(cr).

For substances that are solid near the reference temperature $T = 298.15$ K, enthalpies of sublimation have been determined by direct calorimetry and through the measurement of the temperature dependence of the sublimation pressure and application of the Clausius-Clapeyron equation

$$\frac{d \ln p}{dT} = \frac{\Delta_{cr}^g H_m}{RT^2}, \qquad (2)$$

where p is the sublimation pressure, T is the temperature, and R is the gas constant. In this formulation, it is assumed that the vapor is ideal, which is valid at the low pressures considered here for halobenzoic acids.

Values of enthalpies of formation for compounds in the ideal-gas state have been reported for decades based on the results of computational chemistry, though early results had large uncertainties (cf. Refs. 15 and 16). The quality of such computations has improved such that uncertainties for some modern computations on selected systems are comparable to the best experimental results, and these can be used as a check on experimentally derived values of $\Delta_f H_m^o$ (g),[12] and this approach is used in the present work with application to the twelve monohalogenated (F, Cl, Br, and I) benzoic acids. Direct computation of thermodynamic properties in condensed states is an active area of research today, but has not reached the threshold of uncertainty necessary for use in the critical evaluation of experimental results.

3. Thermodynamic Properties for the Ideal-Gas State by Computation

3.1. Overview of the computational methods

The initial conformer mappings, molecular geometries, and vibrational frequencies for halobenzoic acids were evaluated using the hybrid density functional theory (DFT) B3LYP methods and the density-fitted (sometimes also referred to as ''Resolution-of-Identity,'' RI) approximation of the second-order Møller-Plesset perturbation theory, DF-MP2. B3LYP calculations for conformers, rotational barriers, and vibrational frequencies were performed with Gaussian 09.[17] Rotational potentials at the B3LYP level and vibrational frequencies at the DF-MP2 level for the fluoro-, chloro-, and bromo-compounds were computed with the Psi4 package[18] v1.0, taking advantage of its efficient density-fitted implementations. For iodine-containing compounds, the canonical B3LYP implementation in Gaussian 09[17] was used. Thermodynamic functions for the COOH torsion were obtained with the one-dimensional hindered rotor approximation by a direct numerical solution of the Schrödinger equation.[19] Reduced rotational constants for the torsion were evaluated with the model of Pitzer.[20] The Karlsruhe ''def2'' basis sets[21] of quadruple-zeta quality (def2-QZVP and def2-QZVPP) and their augmented versions[22] (def2-QZVPD) were used in these calculations. The Karlsruhe basis sets support all elements considered in this study with the relativistic effects for iodine being accounted for using the effective core potentials. It should also be noted that def2-QZVP and def2-QZVPP are equivalent for all elements considered except bromine and iodine. Atomic

masses for the most abundant isotope were utilized (Gaussian 09 default settings).

High-level single-point energy calculations were performed with the recently proposed Domain Based Local Pair-Natural Orbital Coupled Cluster with Single, Double, and perturbative Triple excitations, DLPNO-CCSD(T), approach.[23] DF-MP2 and DLPNO-CCSD(T) calculations for energy minima and rotational barriers were carried out with ORCA[24] v3.03. For comparison, energy calculations with G4 theory[25] that approximates the CCSD(T) result with the triple-zeta quality basis set were carried out for the fluorine-, chlorine-, and bromine-containing compounds. Iodine-containing compounds are unsupported in G4, so no comparison computations could be made. G4 calculations were performed with the Gaussian 09 package.[17]

3.2. Validation of computations for benzoic acid

3.2.1. Benchmark thermodynamic properties for benzoic acid from experiment

Thermodynamic properties of benzoic acid have been reported extensively in the literature, as the compound is the calibration standard for the measurement of enthalpies of combustion, and it is a reference material for the measurement of condensed-phase heat capacities for temperatures below $T = 400$ K and the measurement of sublimation pressures for the range $[298.15 < (T/\text{K}) < 383]$.[26] The enthalpy of combustion for benzoic acid has been determined by multiple national metrology laboratories with electrically calibrated combustion calorimeters (Table 1).[27–32] Enthalpies of formation for the crystal phase from these sources were

TABLE 1. Benchmark thermodynamic properties of benzoic acid from the experiment: the enthalpy of combustion $\Delta_c H_m^o$(cr, 298.15 K) and enthalpy of formation $\Delta_f H_m^o$ (cr, 298.15 K) for the crystal, standard entropies for the crystal S^o(cr, 298.15 K and 375 K), enthalpies of sublimation $\Delta_{cr}^g H_m^o$(298.15 K and 375 K), and the derived standard enthalpy of formation for the ideal gas $\Delta_f H_m^o$ (g, 298.15 K) and standard entropies for the ideal gas S^o(g, 298.15 K and 375 K)[a]

Authors	Year	$\Delta_c H_m^o$(cr)	$\Delta_f H_m^o$(cr)
Jessup[28]	1942	-3227.1 ± 0.2	-385.0 ± 0.9
Coops et al.[31]	1956	-3227.2 ± 0.5	-384.9 ± 1.1
Challoner et al.[30]	1955	-3227.3 ± 0.3	-384.7 ± 1.0
Prosen and Rossini[29]	1944	-3227.2 ± 0.3	-384.9 ± 1.0
Gundry and Meetham[32]	1958	-3227.4 ± 0.3	-384.6 ± 1.0
Weighted average		-3227.2 ± 0.3	-384.8 ± 0.9

Authors	Year	S^o(cr, 298.15 K)	S^o(cr, 375 K)
Furukawa et al.[33]	1951	167.6 ± 0.2	205.2 ± 0.2
Sklyankin et al.[34]	1960	$(167.2 \pm 0.2)^b$	$(204.9 \pm 0.2)^b$
Tatsumi et al.[35]	1975	167.8 ± 0.2	
Arvidsson et al.[36]	1976	167.5 ± 0.2	
Moriya et al.[37]	1982	167.7 ± 0.2	
Sorai et al.[38]	1992	167.6 ± 0.2	
Kobashi et al.[39]	1998	167.4 ± 0.2	
Blokhin et al.[40]	2006	167.8 ± 0.2	205.4 ± 0.2
Weighted average		167.6 ± 0.1	205.3 ± 0.2

Authors	Year	Range/K	$\Delta_{cr}^g H_m^o$(298.15 K)	$\Delta_{cr}^g H_m^o$(375 K)
Van Ginkel et al.[50]	1975	294–331	93.0 ± 2.4	91.2 ± 2.4
Colomina et al.[51]	1982	293–313	90.4 ± 0.8	88.6 ± 0.8
De Kruif and Blok[52]	1982	316–391	91.1 ± 0.6	89.3 ± 0.6
Ribeiro da Silva and Monte[53]	1990	307–314	88.9 ± 7	87.1 ± 7
Bazyleva et al.[54]	2005	318–333	90.9 ± 1.2	89.0 ± 1.2
Bazyleva et al.[55]	2006	303–338	89.4 ± 1.4	87.6 ± 1.4
Monte et al.[56]	2006	310–362	90.9 ± 0.8	89.1 ± 0.8
Ribeiro da Silva et al.[57]	2006	299–317	90.2 ± 2.6	88.4 ± 2.6
Fonseca et al.[58]	2014	293–317	90.0 ± 0.9	88.2 ± 0.9
Zaitsau et al.[59]	2015	298–339	89.8 ± 0.5	88.0 ± 0.5
Weighted average			90.3 ± 0.3	88.5 ± 0.3

Experimental values	Computed values
$\Delta_f H_m^o$ (g, 298.15 K) $= -294.5 \pm 0.9$ kJ mol^{-1}	
S^o(g, 298.15 K)$^c = 356.5 \pm 0.9$ J K mol^{-1}	S^o(g, 298.15 K)$^c = 356.7$ J K mol^{-1}
S^o(g, 375 K)$^c = 389.0 \pm 0.9$ J K mol^{-1}	S^o(g, 375 K)$^c = 388.9$ J K mol^{-1}

[a]Units are kJ mol^{-1} for all enthalpies and J K mol^{-1} for all entropies. Uncertainties given in the table are the expanded uncertainty with 0.95 level of confidence.
[b]Values reported by Sklyankin et al.[34] were not used in the calculation of the weighted average.
[c]Sublimation pressures p used in the calculation of the entropy of compression to the reference pressure $p^o = 100$ kPa were $p = (0.110 \pm 0.003)$ Pa at $T = 298.15$ K and $p = (186 \pm 3)$ Pa at $T = 375$ K derived from the experimental sublimation pressure data listed in the tables.

reevaluated by Cox and Pilcher, with uncertainties expressed on a consistent basis with 0.95 level of confidence. The value reported by Jessup in 1934[27] was superseded in a later publication from the same laboratory in 1942,[28] so we have included only the latter value in the averaged results. The weighted average for the enthalpy of formation for crystalline benzoic acid $\Delta_f H_m^o$(cr) is given in the top section of Table 1.

The standard entropy for crystalline benzoic acid is determined experimentally through an appropriate integration of heat capacities measured from near $T = 0$ K (typically from below $T = 20$ K) to a temperature between $T = 298.15$ K and the melting temperature ($T_m \approx 395.5$ K). As benzoic acid is a recommended reference material for the testing of adiabatic calorimeters, a large number of high quality data sets have been published.[33–40] A summary of the standard entropies derived from these measurements is given in Table 1, together with the selected average value. Entropy increments between $T = 0$ K and the lowest temperature reported for each study were estimated by assuming a T^3 dependence for the heat capacities in this region, as per the Debye model.[41]

The derivation of properties for the gas phase from the experimental values for the crystal phase requires evaluated enthalpies and entropies of sublimation. For benzoic acid, these values have been reported based on direct calorimetry[42–46] and studies of the temperature dependence of sublimation pressures.[47–59] The calorimetric results are difficult to assess because reported uncertainties are often repeatabilities only (cf. Ref. 42) and as such, are an incomplete representation of the standard uncertainty. We estimate the uncertainties in the direct calorimetric results to be, at minimum, 1% of the measured enthalpy of sublimation, and as such, these would add little to the analysis here. In this work, we have evaluated the enthalpy of sublimation for benzoic acid using only results from studies of sublimation pressure as a function of temperature that are consistent with ~3% in pressure.[50–59] Even this restricted set includes ten independent and consistent determinations.

Enthalpies of sublimation were derived through the application of the Clausius-Clapeyron equation [Eq. (2)]. A straight line was fitted to the experimental data plotted as $\ln(p)$ against $(T/K)^{-1}$. The slope of the line was used to calculate the enthalpy of sublimation for the temperature at the middle of the experimental range. Adjustment of this value to the temperatures $T = 298.15$ and $T = 375$ K was accomplished with heat capacities for the gas computed in this research (Sec. 3.2.2. and listed in Table 23) and heat capacities for the crystals reported by Furukawa *et al.*[33]

Murata *et al.*[43] considered the association of benzoic acid in the gas phase and concluded that the vapor composition was, at least, 99.7% monomer. Any error associated with the failure to consider association in the gas phase was found to be less than 0.2 kJ mol^{-1}.[43] We ignore any contribution from gas-phase association here.

Uncertainties for enthalpies of sublimation derived from the measurement of sublimation pressures are directly related to uncertainties in the slope for plots of $\ln(p)$ against $(T/K)^{-1}$ based Eq. (2). To account for possible systematic errors in pressures, this uncertainty for each data source was calculated as follows: a straight line was fitted to plots of $\ln(p)$ against $(T/K)^{-1}$,

average percent standard deviations for the experimental pressures were calculated, and the expanded uncertainty (0.95 level of confidence) for the slope was taken as the change in the slope, calculated with values at the temperature extremes with pressures fractionally shifted with opposite sign by twice the percent standard deviation of the experimental values from the fit. Uncertainties in the heat capacities for the gas (this research, Sec. 3.2.2.) and crystals[33] used to adjust the enthalpies of sublimation from the mid-temperature of the experimental range to $T = 298.15$ and $T = 375$ K were considered, but their contributions are very small in comparison to those arising from uncertainty in the slope. All uncertainties for enthalpies of sublimation derived from studies of sublimation pressures were calculated with this method, and resulting uncertainties are listed in Table 1.

The standard enthalpy of formation for benzoic acid in the ideal-gas state is calculated as the sum of the standard enthalpy of formation of the crystal $\Delta_f H_m^o$(cr) and the enthalpy of sublimation $\Delta_{cr}^g H_m^o$ at the reference temperature $T = 298.15$ K according to Eq. (1).

The value derived for benzoic acid in this research is given at the bottom of Table 1. The standard entropy S^o(g) for benzoic acid in the ideal-gas state at reference pressure $p^o = 100$ kPa is calculated as the sum of the standard entropy of the crystal, the entropy of vaporization, and the entropy of compression from the saturation pressure to $p^o = 100$ kPa. Because the gas is assumed to be ideal, the entropy of compression is $R \cdot \ln(p/p^o)$, where R is the gas constant. Values for the standard entropy of benzoic acid in the ideal-gas phase S^o(g) for the temperatures $T = 298.15$ and $T = 375$ K are listed at the bottom of Table 1.

Heat capacities for the gas phase of benzoic acid were determined by Santos *et al.*[60] with the "vacuum sublimation/vaporization Calvet microcalorimetry drop method." This method requires knowledge of the enthalpy of sublimation to convert the measured quantities to heat capacities. We have recalculated the results of Santos *et al.*,[60] using the enthalpy of sublimation for benzoic acid at $T = 298.15$ K determined in this work (Table 1), and have included the uncertainty in this value in the calculations. Values are 3% lower than those reported by Santos *et al.*[60] In addition, the expanded uncertainty (0.95 level of confidence) is ~8 J K^{-1} mol^{-1}, rather than 5 J K^{-1} mol^{-1}, as reported by Santos *et al.*,[60] who chose to ignore the uncertainty in the enthalpy of sublimation.

3.2.2. Comparisons of computations with benchmark thermodynamic properties

To select the best model for the computation of thermodynamic properties for the systems considered here, a range of methods (B3LYP, B3LYP with empirical dispersion correction,[61] and DF-MP2) with the def2-QZVPD basis set were tested. In addition, treatment of the COOH torsion was addressed both as a regular vibration and as a hindered one-dimensional quantum rotor. In the latter case, the rotational potentials and reduced rotational constants computed at the corresponding levels of theory were used, and the potentials were scaled to match the barriers computed at the
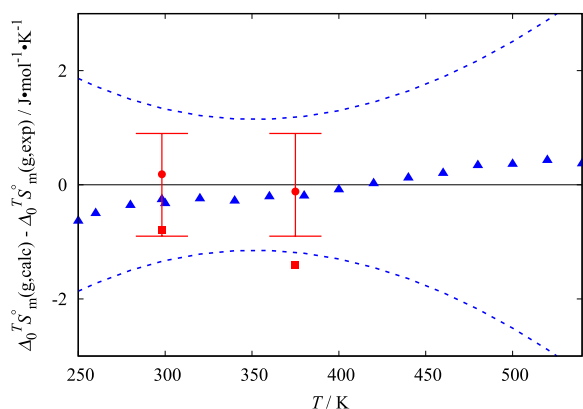
FIG. 1. Difference plot of experimental and computed ideal-gas entropies S_m^o for benzene and benzoic acid. Computations were performed with the model (B3LYP/def2-QZVPD, with the low-frequency scaling factor of 0.9689) optimized for benzoic acid and benzene. The dashed curves represent the expanded uncertainty (0.95 level of confidence) for $\Delta_0^T S_m^o$ (g,exp) for benzene.[62] Vertical solid lines represent the expanded uncertainty for $\Delta_0^T S_m^o$ (g,exp) for benzoic acid derived in this work. Circles and triangles represent differences calculated with $\Delta_0^T S_m^o$ (g,calc) derived with the optimized scaling factor (0.9689) for benzoic acid and benzene, respectively. Squares represent differences between $\Delta_0^T S_m^o$ (g,exp) for benzoic acid (Table 1) and values of $\Delta_0^T S_m^o$ (g,calc) reported by Santos et al.[60]

DLPNO-CCSD(T)/def2-QZVP//DF-MP2/def2-QZVP level of theory. In each case, the scaling factors for vibrational frequencies were optimized against the ideal-gas entropy derived from the experimental data for benzoic acid (given in Sec. 3.2.1.) and for benzene as evaluated by Chirico and Steele.[62] Consideration of benzene was included to better constrain the optimization procedure due to the limited experimental data available for benzoic acid. Experimental uncertainties were used as weights in the optimization procedure. The combination of B3LYP/def2-QZVPD with the hindered rotor treatment of the COOH torsion yielded the lowest root-mean-square deviation (RMSD) from the experimental ideal-gas entropies. This observation is consistent with prior reports on the B3LYP performance

with the basis sets augmented to optimize the prediction of electrical properties.[63] The optimal vibrational frequency scaling factor was found to be 0.9689 ± 0.0070, consistent with results reported for basis sets of similar sizes.[64] The deviations between the gas-phase entropies derived from the experiment and those computed with the optimal model are shown in Fig. 1. This model was adopted for the computation of the thermodynamic properties for all molecules considered in this research.

Molecular vibrations at high frequencies, corresponding to highly localized hydrogen stretches, have essentially no influence on the thermodynamic properties at practical temperatures and therefore, were effectively not considered in the model optimization. Nonetheless, these vibrational modes do affect the zero-point vibrational energy (ZPVE) needed in the calculation of the enthalpies of formation. Therefore, the dual scaling factor approach was adopted, with the vibrational frequencies corresponding to C–H and O–H stretches scaled with the factor (0.9601 ± 0.0038) obtained from the fits to experimentally measured vibration frequencies for benzoic acid[65] and benzene.[66]

Heat capacities, standard entropies, and enthalpy increments for benzoic acid in the ideal gas state, computed with the adopted model, are given in Table 23 of the Appendix. The heat capacities for the ideal gas are in agreement with those derived recently with isodesmic reaction schemas by Santos et al.[60] A graphical comparison is shown in Fig. 5 of the Appendix. This result supports the conclusion by Santos et al.[60] that several often-used sources of ideal-gas heat capacities for benzoic acid[67,68] are in error by ~20 J K^{-1} mol^{-1} between $T = 300$ and $T = 1000$ K, which corresponds to 6–18% of the heat capacity. Burcat and Ruscic[69] maintain a database[70] of ideal-gas and condensed-phase thermodynamic properties for species involved in combustion processes that is used extensively within the combustion research community. Heat capacities for benzoic acid in the ideal-gas state given there are ~5% lower than those evaluated in this research. Differences are also shown in Fig. 5 of the Appendix.

TABLE 2. Comparison of experimental and computed ideal-gas entropies S_m^o and heat capacities $C_{p,m}^o$ for fluorobenzene and the ideal-gas entropies S_m^o at temperature $T = 298.15$ K for bromobenzene ($p^o = 100$ kPa)[a]

	S_m^o (J K^{-1} mol^{-1})			$C_{p,m}^o$ (J K^{-1} mol^{-1})	
T (K)	Experiment	Computed	T (K)	Experiment	Computed
Fluorobenzene[b]					
318.4	309.7 ± 0.6	309.8	343.2	108.7 ± 0.4	109.2
336.8	315.5 ± 0.6	315.6	364.2	115.1 ± 0.5	115.6
357.9	322.1 ± 0.6	322.3	389.2	122.3 ± 0.5	122.8
382.4	329.5 ± 0.6	330.1	426.2	132.5 ± 0.5	133.0
			463.2	142.2 ± 0.6	142.4
			500.2	150.9 ± 0.6	151.0
Bromobenzene[c]					
298.15	325.7 ± 1.8	327.0			

[a]Computations were performed with the model optimized for benzoic acid and benzene (B3LYP/def2-QZVPD, with the low-frequency scaling factor of 0.9689).
[b]Experimental values are based entirely on the work of Scott et al.,[71] who measured heat capacities by adiabatic calorimetry, vapor pressures by comparative ebulliometry, and enthalpies of vaporization by vapor-flow calorimetry.
[c]The experimental value is based on heat capacities determined with adiabatic calorimetry by Masi and Scott,[72] the enthalpy of vaporization measured by direct calorimetry by Wadsö,[73] and vapor pressures measured with the transpiration method by Verevkin et al.[74] Vapor pressures were used to derive the entropy of compression from the saturation pressure to the reference pressure $p^o = 100$ kPa.

Finally, additional validations were performed against experimental ideal-gas properties for fluorobenzene[71] (S_m^o and $C_{p,m}^o$) and bromobenzene[72–74] (S_m^o), as the optimization procedure did not include halogenated compounds which are the main subject of this study. Comparisons with the experimental values are given in Table 2. Uncertainties for the experimental values are very small, yet excellent agreement between the experimental and computed values is obtained. Experimental molecular rotational constants can be obtained from the molecular geometry reported by Aarset *et al.*[75] for benzoic acid and direct measurements by Daly *et al.*[76] for 2-, 3-, and 4-fluorobenzoic acids. A comparison of experimental and computed molecular rotational constants is provided in the Appendix (Table 24).

3.3. Computation of thermodynamic properties for the halobenzoic acids in the ideal-gas state

As noted earlier, the initial conformer mapping for halobenzoic acids was performed at the B3LYP/def2-QZVPD level. 4-Halobenzoic acids exhibit the same symmetry as the parent compound (benzoic acid) with two distinct conformers (syn and anti), due to the rotation of the C–O bond (Fig. 2).

Conformers of 4-halobenzoic acids

| syn | anti |
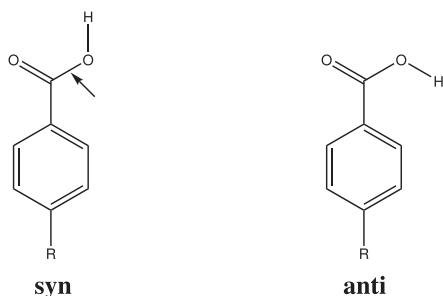
Conformers of 2- and 3-halobenzoic acids

| anti-syn | syn-syn |

| anti-anti | syn-anti |
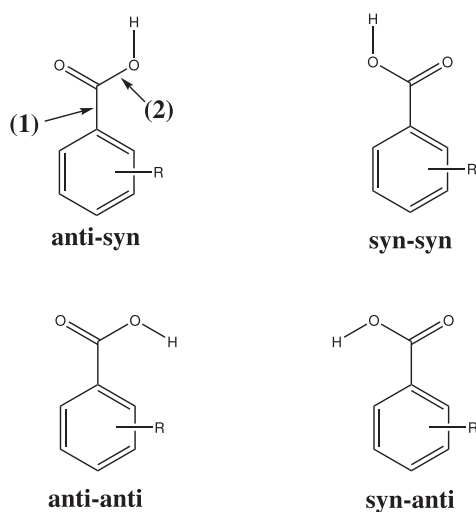
FIG. 2. Conformers of halobenzoic acids, where R represents the halogen. Arrows indicate the bonds for which the substituents are specified as "syn" or "anti." For 2- and 3-halobenzoic acids, substituent orientations for two bonds must be specified, and the numbered arrows indicate the naming order. For example, "anti-syn" implies that bond (1) is in the "anti" orientation and bond (2) is "syn."

The conformer energies, computed at several levels of theory, are given in Table 3. The anti conformer was computed to be ∼27 kJ mol^{-1} higher in energy than the syn counterpart for all of the 4-halobenzoic acids and was ignored in further analysis. The barrier to internal COOH rotation that connects syn conformations was computed to be 27.9 kJ mol^{-1} for 4-fluorobenzoic acid at the highest level of theory: DLPNO-CCSD (T)/def2-QZVPP//DF-MP2/def2-QZVPP. The barrier decreases slightly with the size of the halogen, reaching 26.3 kJ mol^{-1} for 4-iodobenzoic acid. All conformations for 4-halobenzoic acids were predicted to have planar (Cs) structures.

For 3- and 2-halobenzoic acids, four distinct conformations exist, due to the rotation of both the COOH and OH groups (Fig. 2). The computed conformer energies and barriers for COOH internal rotation are given in Tables 4 and 5 for 3- and 2-halobenzoic acids, respectively. For 3-halobenzoic acids, the anti-syn conformer was generally computed to have the lowest energy (Table 4). For 3-chloro-, 3-bromo-, and 3-iododerivatives, the energy of the anti-syn conformer is 0.2–0.4 kJ mol^{-1} lower than that of the syn-syn conformer, while for 3-fluorobenzoic acid, the anti-syn and syn-syn conformers are energetically equivalent within 0.01 kJ mol^{-1}. The anti-anti and syn-anti conformations for all 3-halobenzoic acids are in excess of 26 kJ mol^{-1} higher in energy and were not considered in further analysis. As was found for 4-halobenzoic acids, all computed conformations of 3-halobenzoic acids have planar geometries.

TABLE 3. Computed conformer energies and barriers (both are in kJ mol^{-1}) for COOH internal rotation (relative to the syn conformer) for benzoic acids and 4-halobenzoic acids

Computation method[a]	syn	anti	Barrier (syn → syn)
Benzoic acid			
B3LYP/def2-QZVPD	0	25.50[b]	26.97
DF-MP2/def2-QZVPP	0	–	25.60
DLPNO-CCSD(T)/def2-QZVPP// DF-MP2/def2-QZVPP	0	–	25.90
4-fluorobenzoic acid			
B3LYP/def2-QZVPD	0	27.56[b]	29.51
DF-MP2/def2-QZVPP	0	–	27.44
DLPNO-CCSD(T)/def2-QZVPP// DF-MP2/def2-QZVPP	0	–	27.89
4-chlorobenzoic acid			
B3LYP/def2-QZVPD	0	27.30[b]	28.33
DF-MP2/def2-QZVPP	0	–	26.90
DLPNO-CCSD(T)/def2-QZVPP// DF-MP2/def2-QZVPP	0	–	26.85
4-bromobenzoic acid			
B3LYP/def2-QZVPD	0	27.26[b]	28.00
DF-MP2/def2-QZVPP	0	–	26.81
DLPNO-CCSD(T)/def2-QZVPP// DF-MP2/def2-QZVPP	0	–	26.64
4-iodobenzoic acid			
B3LYP/def2-QZVPD	0	27.03[b]	27.72
DF-MP2/def2-QZVPP	0	–	26.66
DLPNO-CCSD(T)/def2-QZVPP// DF-MP2/def2-QZVPP	0	–	26.30

[a]The level of theory increases from top to bottom for each compound, with DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP being the highest.
[b]This conformer was neglected in further analysis.

TABLE 4. Computed conformer energies and barriers (both are in kJ mol^{-1}) for COOH internal rotation (relative to the anti-syn conformer) for 3-halobenzoic acids

Computational method	anti-syn	syn-syn	Barrier(anti-syn → syn-syn)	anti-anti	syn-anti
3-fluorobenzoic acid					
B3LYP/def2-QZVPD	0	0.03	26.43	26.84[a]	26.00[a]
DF-MP2/def2-QZVPP	0	−0.03	25.97	–	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	−0.01	25.64	–	–
Experiment; Daly et al. (2015)[76]		0.1			
3-chlorobenzoic acid					
B3LYP/def2-QZVPD	0	0.26	26.36	26.68[a]	26.70[a]
DF-MP2/def2-QZVPP	0	0.23	25.31	–	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	0.26	25.48	–	–
3-bromobenzoic acid					
B3LYP/def2-QZVPD	0	0.31	26.38	26.70[a]	26.86[a]
DF-MP2/def2-QZVPP	0	0.29	25.14	–	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	0.29	25.51	–	–
3-iodobenzoic acid					
B3LYP/def2-QZVPD	0	0.32	26.36	26.54[a]	26.81[a]
DF-MP2/def2-QZVPP	0	0.33	24.97	–	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	0.38	25.58	–	–

[a]This conformer was neglected in further analysis.

TABLE 5. Computed conformer energies and barriers (both are in kJ mol^{-1}) for COOH internal rotation (relative to the anti-syn conformer) for 2-halobenzoic acids

Computational method	anti-syn	syn-syn	Barrier (anti-syn → syn-syn)	anti-anti	syn-anti
2-fluorobenzoic acid					
B3LYP/def2-QZVPD	0	3.05	15.96	5.79	26.91[a]
DF-MP2/def2-QZVPP	0	2.47	13.27	5.14	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	2.72	13.92	5.06	–
experiment; Daly et al. (2015)[76]		2.8		7.7	
2-chlorobenzoic acid					
B3LYP/def2-QZVPD	0	−0.52	6.55	6.47	20.11[a]
DF-MP2/def2-QZVPP	0	−1.02	5.17	7.09	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	−0.63	5.47	7.34	–
2-bromobenzoic acid					
B3LYP/def2-QZVPD	0	−1.21	5.17	8.01	19.01[a]
DF-MP2/def2-QZVPP	0	−1.65	3.91	8.72	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	−1.28	4.08	8.83	–
2-iodobenzoic acid					
B3LYP/def2-QZVPD	0	−2.99	4.72	11.86	17.74[a]
DF-MP2/def2-QZVPP	0	−3.02	3.27	11.85	–
DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP	0	−2.75	3.63	12.21	–

[a]This conformer was neglected in further analysis.

For 2-halobenzoic acids, the ortho interactions play an important role, and the conformer mappings become more complicated. For 2-fluorobenzoic acids, the anti-syn conformer remains the most energetically favored, followed by the syn-syn conformer with a computed energy ~3 kJ mol^{-1} higher than the anti-syn configuration (Table 5). In addition, the strong F–H interaction in the anti-anti configuration (Fig. 2) lowers the energy of this conformer close to the two most favored conformers, with only ~5 kJ mol^{-1} separating this conformer from the most stable anti-syn conformation. The syn-anti conformer, without the benefit of F–H interactions, remains ~27 kJ mol^{-1} above the most energetically favored configuration. All conformations of 2-fluorobenzoic acid remain planar.

For 2-chloro-, 2-bromo-, and 2-iodo derivatives, the situation changes in two ways. First, the lowest energy is exhibited by the syn-syn conformation, which is (0.6 to 2.8) kJ mol^{-1} below that for the anti-syn conformation that favored previously (Table 5).
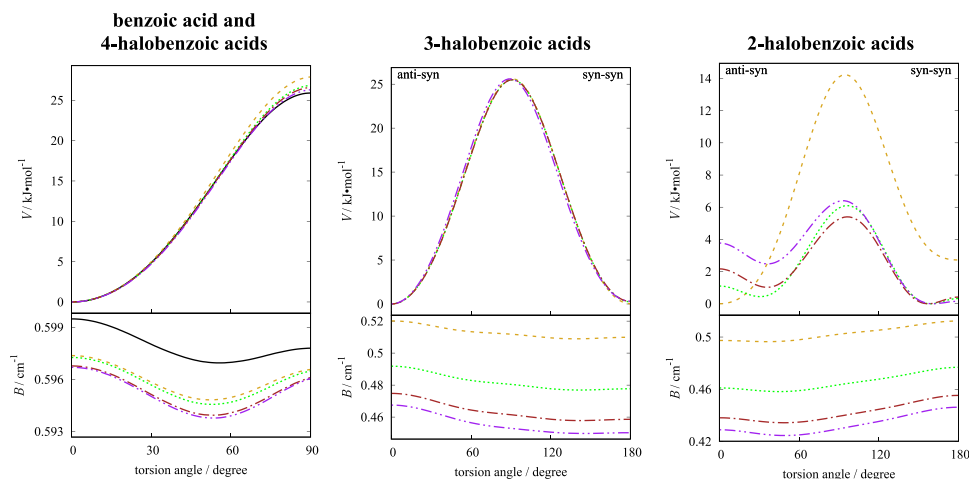
Fig. 3. Rotational potentials (top) and rotational constants (bottom) for benzoic acid and halobenzoic acids as a function of torsion angle. —, benzoic acid; – – –, fluorocompound; · · ·, chlorocompounds; – · –, bromocompounds; – · · –, iodocompounds. For 2- and 3-halobenzoic acids, the rotation proceeds from anti-syn to syn-syn conformation, and the portion from 180° to 360° is omitted due to mirror symmetry. For benzoic acid and 4-halobenzoic acids, the portion from 90° to 180° is also omitted due to mirror symmetry, while the portion from 180° to 360° due to periodicity.

Second, the anti-syn and syn-syn conformations are no longer planar, and the planar anti-syn and syn-syn configurations correspond to very small rotational barriers between the corresponding non-planar stationary points (Fig. 3). All 2-halobenzoic acids exhibit a drastic reduction in the main COOH torsion barrier in comparison to those for 4- and 3-halobenzoic acids, as seen in Fig. 3. The importance of the anti-anti conformation decreases with the halogen size. Its energy above the most stable conformer gradually increases from 5 kJ mol^{-1} for 2-fluorobenzoic acid to 12 kJ mol^{-1} for 2-iodobenzoic acid. The geometry of the anti-anti conformer is planar for 2-fluorobenzoic and 2-chlorobenzoic acids and nonplanar for 2-bromo- and 2-iododerivatives.

As seen in Tables 4 and 5, the computed conformational energies for 2- and 3-fluorobenzoic acids are in good agreement (with 2.6 kJ mol^{-1}) with recent results by Daly *et al.*[76] based on the analysis of microwave spectra. The present work represents the most complete conformational analysis of halobenzoic acids to-date, as previous efforts were typically confined to a single— and not always lowest energy—conformer.[77–79]

The above computational results allow the evaluation of thermodynamic properties for the ideal-gas state of halobenzoic acids as follows. The geometries and vibrational frequencies, except for the COOH torsion, were taken from B3LYP/def2-QZVPD calculations with the vibrational scaling factors established earlier. The COOH torsion was treated as a one-dimensional hindered quantum rotor using rotational constants and potentials also obtained at the B3LYP/def2-QZVPD level. Rotational potentials were further scaled to match the barriers predicted at the DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP level. This approach rigorously accounts for the most stable conformers: syn for 4-halobenzoic acids and anti-syn and syn-syn for 3- and 2-halobenzoic acids. For 2-fluorobenzoic and 2-chlorobenzoic acids, the importance of minor contributions of the anti-anti conformations was tested by computing the properties of the equilibrium mixture of conformations (anti-syn + syn-syn + anti-anti) in which the properties of the anti-anti conformation were

approximated with the conventional rigid-rotor harmonic-oscillator approximation without special treatment of the COOH torsion. The addition of anti-anti conformations resulted in the differences under 0.4% and 0.2% for the entropy and heat capacity, respectively. For 2-bromobenzoic and 2-iodobenzoic acids, the computed energies of anti-anti conformations were higher, 9 kJ mol^{-1} and 12 kJ mol^{-1} above the most stable conformation, with the added complexity of non-planar geometries (resulting in two equivalent anti-anti conformers connected via a barrier at planar configuration). Considering that the contributions of anti-anti conformations are very small in the tests for 2-fluorobenzoic and 2-chlorobenzoic acids, a more detailed and complex analysis for 2-bromobenzoic and 2-iodobenzoic acids was not justified, and the contributions of anti-anti conformations were neglected for these two cases. Heat capacities, standard entropies, and enthalpy increments for the ideal-gas state for all of the halobenzoic acids are given in the Appendix (Table 25). Based on the quality of the computations, validated through rigorous comparison with experimental ideal-gas entropies and heat capacities for benzoic acid, benzene, and halobenzenes, we estimate the relative expanded uncertainty (0.95 level of confidence) of the computed thermodynamic properties to be 0.2% for the temperature range considered (up to ∼500 K). At higher temperatures, the adopted approximations (i.e., not taking into account the higher-energy conformations and anharmonicity of associated torsions) will lead to larger errors, up to ∼2% at 1000 K.

4. Enthalpies of Formation for the Crystalline State of the Halobenzoic Acids from Experiment

4.1. Enthalpies of combustion and formation

Rotating bomb combustion calorimetry has been long established as the primary method for the determination of

enthalpies of combustion for the lighter (F, Cl, and Br) halogen-containing compounds.[80] This is due to the highly energetic dissolution of combustion product gases [HF(g), HCl(g), or HBr(g)] in water that is present in the reaction chamber. Complete dissolution of the gas to a known and reproducible final state is achieved by the rotation (or rocking[14]) of the bomb after ignition of the sample. Combustion of iodine-containing compounds have been treated with less complexity because I_2(cr), rather than an acid, is the primary halogen product, and the use of static bomb calorimetry yields results similar to measurements involving bomb rotation, as shown by Ribeiro da Silva *et al.*[81] In that study, both static and rotating bomb calorimetry was used, and results were within the combined uncertainties.

Enthalpies of combustion have been determined experimentally for all of the monohalogenated benzoic acids. The idealized combustion reactions associated with the standard molar enthalpies of combustion $\Delta_c H_m^o$ are as follows:

$$C_7H_5O_2F \text{ (cr)} + 7\ O_2(g) + (n-2)H_2O(l)$$
$$= 7\ CO_2(g)\ +\ HF \cdot nH_2O(aq), \tag{3}$$

$$C_7H_5O_2Cl(cr) + 7\ O_2(g) + (n-2)\ H_2O(l)$$
$$= 7\ CO_2(g) + HCl \cdot nH_2O(aq), \tag{4}$$

$$C_7H_5O_2Br(cr) + 7\ O_2(g) + (n-2)\ H_2O(l)$$
$$= 7\ CO_2(g) + HBr \cdot nH_2O(aq), \tag{5}$$

$$C_7H_5O_2Br(cr) + 7.25\ O_2(g)$$
$$= 7\ CO_2(g) + 2.5\ H_2O(l) + 0.5Br_2(l), \tag{6}$$

$$C_7H_5O_2I(cr) + 7.25\ O_2(g)$$
$$= 7\ CO_2(g) + 2.5\ H_2O(l) + 0.5\ I_2(cr). \tag{7}$$
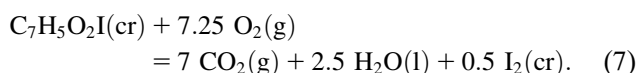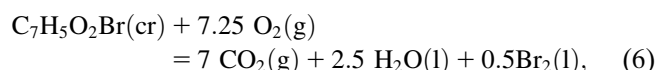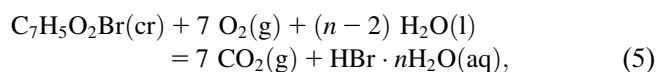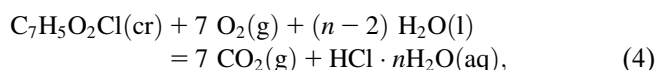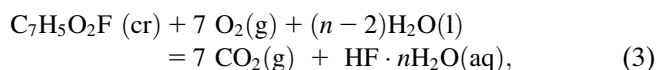
Combustion of halogen-containing compounds, generally, yields a mixture of halogenated products. For organofluorine compounds, products include HF(g) and CF_4(g), while for organochlorine and organobromine compounds, products include Cl_2(g) and HCl(g), and Br_2(l) and HBr(g), respectively. In practice, all chloro- and bromo-products are converted to HCl(aq) and HBr(aq) through the addition of water and

a reducing agent (As_2O_3), coupled with bomb rotation at the end of the combustion.

Although the combustion reaction for bromobenzoic acids is well represented by Eq. (5), results are traditionally reported as Eq. (6), with Br_2(l) as the halogen-containing product. As noted by Cox and Pilcher,[82] this leads to "hidden" calculations for the conversion of measured enthalpies for Eq. (5) to those of Eq. (6), as details of this computation are rarely, if ever, reported. For example, Ferrao and Pilcher[83] reported the size of the adjustment for single sample combustion, without giving the concentration of HBr or the source of the literature data used. Ribeiro da Silva *et al.*[84] reported that enthalpies of formation for the "appropriate" concentration of HBr were taken from the NBS (National Bureau of Standards) tables of chemical thermodynamic properties without providing the concentrations, and Sabbah and Aguilar[85] discussed the necessity of conversion of HBr(aq) to Br_2(l) but reported results only for the reaction involving Br_2(l) without information about the underlying calculations. Consequently, the conversions cannot be checked nor can they be updated if improved values of $\Delta_f H_m^o$ for HBr(aq) become available.

Enthalpies of combustion for fluorobenzoic acids [Eq. (3)] are typically adjusted to a value of $n = 50$, but values as a low as $n = 10$ have been reported.[86] For chlorobenzoic acids, n is typically 600, but some key results predate this convention, and values as low as $n = 74$ have been reported.[80] As noted above, n for the combustion of bromobenzoic acids is not reported.

Enthalpies of formation were calculated in the present work using standard molar enthalpies of formation of $\Delta_f H_m^o$ (l, H_2O, 298.15 K) $= -(285.83 \pm 0.04)$ kJ mol^{-1} and $\Delta_f H_m^o$ (g, CO_2, 298.15 K) $= -(393.51 \pm 0.13)$ kJ mol^{-1} recommended by CODATA, the Committee on Data for Science and Technology.[87] Enthalpies of formation for HCl(aq) were those reported in the NBS tables,[88] while those for HF(aq) were those evaluated at Argonne National Laboratory by Johnson *et al.*[89] Uncertainties for the enthalpies of formation of the acid solutions are dominated by those for HCl(g) ($U = 0.07$ kJ mol^{-1}) and HF(g) ($U = 0.31$ kJ mol^{-1}) with 0.95 level of confidence. These

TABLE 6. Experimental standard enthalpies of combustion $\Delta_c H_m^o$ (cr) and derived standard enthalpies of formation $\Delta_f H_m^o$ (cr) for crystalline fluorobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	n^a	$-\Delta_c H_m^o$(cr)/(kJ mol^{-1})	$\Delta_f H_m^o$ (cr)/(kJ mol^{-1})
2-fluorobenzoic acid				
Good *et al.*[92]	1956	50	3080.6 ± 1.5	−567.9 ± 2.0
Johnson and Prosen[94]	1975	50	3080.0 ± 1.0	−568.5 ± 1.6
3-fluorobenzoic acid				
Good *et al.*[92]	1956	50	3066.1 ± 0.8	−582.5 ± 1.5
4-fluorobenzoic acid				
Good *et al.*[92]	1956	50	3061.5 ± 1.2	−587.1 ± 1.7
Cox *et al.*[91]	1964	20	3063.2 ± 0.9	−585.2 ± 1.5
Johnson and Prosen[94,b]	1975	50	3063.0 ± 0.7	−585.6 ± 1.4
Johnson and Prosen[94,b]	1975	50	3063.8 ± 0.8	−584.7 ± 1.5
Schaffer *et al.*[95]	1997	50	3063.0 ± 0.6	−585.6 ± 1.4
Ribeiro da Silva *et al.*[86]	2007	10	3063.6 ± 0.5	−584.7 ± 1.3

[a]The number of waters associated with the combustion product HF · n H_2O (l). See Eq. (3).
[b]Measurements were made by Johnson and Prosen on two chemical samples.

TABLE 7. Experimental standard enthalpies of combustion $\Delta_c H_m^o$ (cr) and derived standard enthalpies of formation $\Delta_f H_m^o$ (cr) for crystalline chlorobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	n^a	$-\Delta_c H_m^o(\mathrm{cr})/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f H_m^o\ (\mathrm{cr})/(\mathrm{kJ\ mol^{-1}})$
2-chlorobenzoic acid				
Smith et al.[97]	1953	600	3093.6 ± 8[b]	−399.2 ± 8[b]
Johnson and Prosen[98]	1974	200	3087.9 ± 0.7	−404.6 ± 1.4
Sabbah and Rojas Aguilar[99]	1995	600	3087.8 ± 0.5	−405.0 ± 1.4
Holdiness[96]	1983	600	(3073.1 ± 20)[c]	(−419.7 ± 20)[c]
3-chlorobenzoic acid				
Smith et al.[97]	1953	600	3068.8 ± 8	−424.1 ± 8[b]
Johnson and Prosen[98]	1974	600	3068.1 ± 1.5	−424.8 ± 2.0
Sabbah and Rojas Aguilar[99]	1995	600	3069.7 ± 1.1	−423.2 ± 1.7
4-chlorobenzoic acid				
Smith et al.[97]	1953	600	3066.5 ± 8[b]	−426.3 ± 8[b]
Bjellrup and Smith[102]	1954	600	3065.5 ± 1.3	−427.3 ± 1.8
Hajiev and Agarunov[103]	1968	∞^d	3064.7 ± 1.6	−428.7 ± 2.0
Hu et al.[104]	1972	600	3063.0 ± 0.8	−429.9 ± 1.4
Hu et al.[104]	1972	600	3062.8 ± 1.0	−430.1 ± 1.6
Hu et al.[104]	1972	600	3062.9 ± 0.8	−429.9 ± 1.5
Kolesov et al.[105]	1972	600	3065.9 ± 1.2	−426.9 ± 1.7
Hajiev et al.[106]	1974	600	3062.7 ± 1.5	−430.1 ± 1.9
Johnson and Prosen[98]	1974	200	3064.4 ± 0.7	−428.1 ± 1.4
Lyubarskii et al.[107]	1975	600	3063.8 ± 1.0	−429.0 ± 1.6
Kamaguchi et al.[108]	1977	600	3062.6 ± 1.0	−430.2 ± 1.6
Erastov et al.[109]	1978	600	3063.9 ± 0.6	−428.9 ± 1.3
Platonov et al.[110]	1981	600	3066.6 ± 0.5	−426.3 ± 1.3
An et al.[111]	1982	600	3062.0 ± 1.1	−430.8 ± 1.6
Gromova et al.[112]	1989	600	3064.5 ± 0.8	−428.4 ± 1.4
Sabbah and Rojas Aguilar[99]	1995	600	3065.6 ± 1.0	−427.3 ± 1.6
Sabbah and Rojas Aguilar[113]	1995	600	3063.5 ± 3.0	−429.3 ± 3.2
Santos et al.[114]	1999	600	3063.0 ± 1.5	−429.9 ± 2.0
Ribeiro da Silva and Ferreira[101]	2008	600	3063.8 ± 0.8	−429.1 ± 1.4

[a]The number of waters associated with the combustion product HCl · n H$_2$O (l). See Eq. (4).
[b]This uncertainty was assigned by Cox and Pilcher[82] in 1970 as a part of their extensive review of the combustion literature.
[c]The expanded uncertainty for this value is, at least, 20 kJ mol^{-1}, as explained in the text. This value is included here in the interest of completeness only.
[d]The combustion reaction was reported with infinitely dilute HCl.

TABLE 8. Experimental standard enthalpies of combustion $\Delta_c H_m^o$ (cr) and derived standard enthalpies of formation $\Delta_f H_m^o$ (cr) for crystalline bromobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	$-\Delta_c H_m^o(\mathrm{cr})/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f H_m^o\ (\mathrm{cr})/(\mathrm{kJ\ mol^{-1}})$
2-bromobenzoic acid			
Ferrao and Pilcher[83]	1987	3100.8 ± 1.0	−368.3 ± 1.6
Sabbah and Rojas Aguilar[115]	1996	3126.3 ± 4.2[a]	−342.8 ± 4.4
Sabbah and Rojas Aguilar[115]	1996	3128.7 ± 10.6[b]	−340.4 ± 10.7
Holdiness[96]	1983	(3084.9 ± 20.0)[c]	(−384.3 ± 20.0)[c]
3-bromobenzoic acid			
Ferrao and Pilcher[83]	1987	3074.4 ± 0.8	−394.7 ± 1.6
Sabbah and Rojas Aguilar[115]	1996	3101.6 ± 1.5[a]	−367.5 ± 2.0
Sabbah and Rojas Aguilar[115]	1996	3104.5 ± 2.0[b]	−364.6 ± 2.4
4-bromobenzoic acid			
Bjellrup[93]	1959	3090.8 ± 2.1	−378.3 ± 2.5
Ferrao and Pilcher[83]	1987	3089.5 ± 0.9	−379.6 ± 1.6
Zhang et al.[116]	1990	3091.8 ± 2.6	−377.3 ± 2.9
Sabbah and Rojas Aguilar[115]	1996	3090.1 ± 2.6	−379.0 ± 2.9

[a]Determined with a "micro-bomb" calorimeter with ~0.0075 g of sample.
[b]Determined with a traditional bomb calorimeter with ~0.5 g of sample.
[c]The expanded uncertainty for this value is, at least, 20 kJ mol^{-1}, as explained in the text. This value is included here in the interest of completeness only.

TABLE 9. Experimental standard enthalpies of combustion $\Delta_c H_m^o$ (cr) and derived standard enthalpies of formation $\Delta_f H_m^o$ (cr) for crystalline iodobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	$-\Delta_c H_m^o$(cr)/(kJ mol^{-1})	$\Delta_f H_m^o$ (cr)/(kJ mol^{-1})
2-iodobenzoic acid			
Smith[117]	1956	3166.9 ± 4.2	−302.2 ± 4.4
Ribeiro da Silva et al.[118]	1995	3167.4 ± 1.1[a]	−301.8 ± 1.7
Ribeiro da Silva et al.[118]	1995	3167.7 ± 0.8[a]	−301.5 ± 1.6
Sabbah and Rojas Aguilar[115]	1996	3173.7 ± 3.4	−295.4 ± 3.7
Holdiness[96]	1983	(3228.8 ± 20)[b]	(-240.4 ± 20)
3-iodobenzoic acid			
Smith[117]	1956	3152.2 ± 4.2	−316.9 ± 4.4
Sabbah and Rojas Aguilar[115]	1996	3153.8 ± 4.4	−315.3 ± 4.6
4-iodobenzoic acid			
Smith[117]	1956	3153.1 ± 4.2	−316.1 ± 4.4
Sabbah and Rojas Aguilar[119]	1996	3153.6 ± 2.6	−315.5 ± 2.9
Ribeiro da Silva et al.[81]	1999	3151.4 ± 1.4[a]	−317.7 ± 1.9
Ribeiro da Silva et al.[81]	1999	3153.2 ± 1.4[a]	−315.9 ± 1.9

[a]The two values reported by Ribeiro da Silva et al.[81,118] were determined with a static (first value) and rotating bomb calorimeter (second value), respectively. The difference between these values is 1.8 kJ mol^{-1}.
[b]The expanded uncertainty for this value is, at least, 20 kJ mol^{-1}, as explained in the text. This value is included here in the interest of completeness only. The deviation of 60 kJ mol^{-1} in the enthalpy of formation implies a 2 percent deviation in the enthalpy of combustion.

uncertainties were applied for all acid concentrations. For bromobenzoic acids, all reported enthalpies of combustion were reported in terms of Eq. (6) [i.e., with Br$_2$(l) as a product], and we necessarily assumed that adjustments leading to the reported combustion enthalpies were done consistently and correctly.

In this work, uncertainties for combustion experiments were evaluated, where possible, on a consistent basis, according to the guidelines of Olofsson.[90] Uncertainties for the standard molar enthalpy of combustion and formation are expanded uncertainties (0.95 level of confidence) and include contributions from the calibration with benzoic acid and from the values of the auxiliary quantities used. Uncertainties assigned to $\Delta_f H_m^o$ (cr) include uncertainties of the enthalpies of formation of the reaction products: H$_2$O(l), CO$_2$(g), and aqueous acid solutions. Reported enthalpies of combustion $\Delta_c H_m^o$ and enthalpies of formation $\Delta_f H_m^o$ for halobenzoic acids are compiled in Tables 6–9. Results for each halide group are reviewed briefly in Secs. 4.1.1.–4.1.4. Except for bromobenzoic acids, results are generally consistent, and in most cases, results have been reported by multiple research groups with extensive experience. In particular, the para-substituted halobenzoic acids have been measured repeatedly, and their combustion energies have been recommended as reference compounds for the testing of rotating combustion bomb calorimeters (Refs. 80, 82, and 91–93).

4.1.1. Fluorobenzoic acids: $\Delta_c H_m^o$ (cr) and $\Delta_f H_m^o$ (cr)

Standard enthalpies of combustion and derived standard enthalpies of formation for fluorobenzoic acids are compiled in Table 6. Results for compounds for which multiple independent studies have been done are in good accord, with all values within the combined uncertainties. Combustion experiments on 2-, 3-, and 4-fluorobenzoic acids were first performed at the Bartlesville Thermodynamics Laboratory (Bartlesville, Oklahoma,

USA) by Good et al.[92] as a part of the development of general methods for combustion calorimetry of organic fluorine compounds. In that work, they proposed 4-fluorobenzoic acid as a reference substance for the intercomparison of bomb-calorimetric data for fluorine compounds. Subsequently, Cox et al.[91] at the National Chemistry Laboratory (Teddington, U.K.) reported confirming results for 4-fluorobenzoic acid and Johnson and Prosen[94] at the National Bureau of Standards (Washington, DC) reported confirming enthalpies of combustion for 2- and 4-fluorobenzoic acids. Further confirmation of the enthalpy of combustion for 4-fluorobenzoic is provided through later measurements by Schaffer et al.[95] (Freiburg, Germany) and Ribeiro da Silva et al.[86] (Porto, Portugal). 4-Fluorobenzoic acid was formally recommended as a reference material for the combustion of fluorine compounds by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) in 1999.[26]

4.1.2. Chlorobenzoic acids: $\Delta_c H_m^o$ (cr) and $\Delta_f H_m^o$ (cr)

Standard enthalpies of combustion and derived standard enthalpies of formation for chlorobenzoic acids are compiled in Table 7. With few exceptions, agreement amongst the independent determinations is within the combined uncertainties. An exception is the result reported for 2-chlorobenzoic acid by Holdiness,[96] who used a commercial calorimeter (Parr Instrument Company) with the static bomb (instead of commonly required rotating bomb) and determined an enthalpy of combustion that is ~0.5% more positive than those reported by other researchers[97–99] (as expected because of an incomplete reaction or dissolution of gases). The most recent version of the Parr bomb calorimeter[100] has an associated expanded uncertainty for a measured enthalpy of, at least, 0.6%, which corresponds to an expanded

uncertainty of ~20 kJ mol^{-1}, rather than 4 kJ mol^{-1}, as reported by Holdiness.[96] Furthermore, Holdiness[96] reported a standard deviation of 3% between his values and those in the literature, which is characterized as "excellent." It is clear that the uncertainties reported by Holdiness[96] are much too small and must be increased to, at least, 20 kJ mol^{-1}, making them of little value in the present review.

The value of $\Delta_f H_m^o$ (cr) reported by Smith *et al.*[97] for 2-chlorobenzoic acid is ~6 kJ mol^{-1} more positive than values reported by Johnson and Prosen[98] and Sabbah and Rojas Aguilar.[99] In their careful review of the combustion literature (published in 1970), Cox and Pilcher[82] estimated the uncertainties for the values given by Smith *et al.*[97] to be ~8 kJ mol^{-1} due to a lack of sufficient detail in the reported results, which were obtained with the "quartz wool" method, rather than with bomb rotation. Nonetheless, results reported by Smith *et al.*[97] for 3- and 4-chlorobenzoic acids are in agreement with later reliable results for these compounds (e.g., Johnson and Prosen[98] and Ribeiro da Silva and Ferreira[101]). The large number of combustion studies for 4-chlorobenzoic acid reflects its development and long acceptance as a reference material for the combustion of organic chlorine compounds.[97–99,101–114] The agreement amongst nearly twenty measurement results is excellent, as seen in Table 7.

4.1.3. Bromobenzoic acids: $\Delta_c H_m^o$ (cr) and $\Delta_f H_m^o$ (cr)

Standard enthalpies of combustion and derived standard enthalpies of formation for bromobenzoic acids are compiled in Table 8. The enthalpy of combustion for 4-bromobenzoic acid has been reported four times with excellent agreement amongst the studies.[83,93,115,116] In contrast, results for 2- and 3-bromobenzoic acids show large inconsistencies between the reported values. As discussed earlier, all results by Holdiness[96] have very large uncertainties and can be discounted. The disagreement between the results of Ferrao and Pilcher[83] and Sabbah and Rojas Aguilar[115] is surprising in that both laboratories have been the source of numerous data of demonstrated good quality. Sabbah and Rojas Aguilar[115] were sufficiently surprised by the discrepancies that they undertook additional measurements using a traditional rotating bomb calorimeter to confirm their initial results which were obtained using a rocking microcalorimeter that required less than 10 mg of sample. Because of the large magnitude of the discrepancies, we suspected an algebraic error of some type by the authors but could find no evidence for this in any of the reported results.

4.1.4. Iodobenzoic acids: $\Delta_c H_m^o$ (cr) and $\Delta_f H_m^o$ (cr)

Standard enthalpies of combustion and derived standard enthalpies of formation for iodobenzoic acids are compiled in Table 9. Here, except for the extraneous value reported by Holdiness,[96] all reported values are mutually consistent. The value of $\Delta_c H_m^o$ (cr) reported by Holdiness deviates by 2% from all other values, and this deviation converts to a 60 kJ mol^{-1} difference in the enthalpy of formation. A variety of calorimeters were used in the consistent results, including static bomb calorimetry,[81,117,118]

rotating-bomb calorimetry,[81,118] and rocking micro-calorimetry.[115,119] Values reported by Smith[117] in 1956 were recalculations of those reported in the thesis by Karlsson.[120]

5. Enthalpies of Sublimation for the Halobenzoic Acids from Experiment

5.1. Experimental sources of enthalpies of sublimation

All monohalobenzoic acids are solid compounds at ambient conditions with melting temperatures in the range T = 396–544 K. Enthalpies of sublimation $\Delta_{cr}^g H_m$ for these compounds at various temperatures have been determined calorimetrically with a Tian-Calvet microcalorimeter equipped with a Knudsen cell (C)[121–123] and with the "vacuum-sublimation drop-calorimetric (DC) method,"[83,124] as well as indirectly through the determination of the temperature dependence of sublimation pressures measured by the Knudsen effusion (K)[125,126] or transpiration (T) method.[79,127–130]

Enthalpies of sublimation with remarkably small relative uncertainties (less than 1%) were also reported by Holdiness[131] based on sublimation from a cell in a differential scanning calorimeter (DSC), using a method developed by Beech and Lintonbon.[132] Beech and Lintonbon estimated a relative uncertainty of 15% for their method, which is in accord with the very large deviations of results reported by Holdiness[131] from all others. Torsion-effusion (TE) measurements by Wolf and Weghofer[48] are included in the tables for completeness; however, these are systematically low.

The derivation of standard molar enthalpies of sublimation $\Delta_{cr}^g H_m^o$ at the reference temperature T_{ref} = 298.15 K from the experimentally determined values at higher temperatures (T^E) involves the measurement or estimation of enthalpy increments for the crystal and gas phases between the temperatures T^E and T_{ref}. The "vacuum-sublimation DC method" involves the measurement of the enthalpy increment between the crystal at T = 298.15 K and the gas at a higher temperature T^E. In this case, only the enthalpy increment between T^E and T^o for the gas is needed. The size of the adjustment is typically on the order of a few kilojoules per mole, which is only a few percent of the measured enthalpy of sublimation. Consequently, authors use various estimation methods for the crystal and gas states with little consideration for the uncertainties in these values; however, as T^E increases, the size of the adjustment is larger, and uncertainty in this value must be considered.

For the derivation of $\Delta_{cr}^g H_m^o$ (298.15 K) from $\Delta_{cr}^g H_m$ (T^E) in the present review, we used heat capacities for the gas phase computed with the methods described in Sec. 3 and validated with results for benzoic acid. Heat capacities for the solid state were estimated based on those for benzoic acid[33] incremented by 15 J K^{-1}·mol^{-1}, based on observed differences between heat capacities computed for the gas phase of halobenzoic acids and benzoic acids. The average increment, when summed over all of the halobenzoic acids for the temperature range (300 < T/K <500), is (15 ± 4) J K^{-1} mol^{-1}, where the uncertainty is twice the standard deviation of the increment. The magnitude of the increment was confirmed

based on comparisons of solid-state heat capacities for halogenated and non-halogenated aromatic pairs, such as fluorobenzene[71] and benzene,[133] 4-halotoluene[134] and toluene,[135] and 4-chlorobenzoic acid[136] and benzoic acid.[33]

In this review, we have reevaluated uncertainties for all experimental determinations of the enthalpy of sublimation $\Delta_{cr}^g H_m$ (T^E). As noted earlier, uncertainties for direct calorimetric determinations are difficult to assess beyond those provided by the authors. However, in further thermodynamic-consistency analyses, we will show that reported uncertainties are generally too small for these measurements. Uncertainties for enthalpies of sublimation for halobenzoic acids derived from Knudsen-effusion or transpiration studies were derived in this research with the method described in Sec. 3.2.1. for benzoic acid. The derived enthalpies of sublimation and uncertainties are given in Tables 10–13. In general, the property values are consistent with those in the original publications, although the uncertainties evaluated here are consistently larger.

TABLE 10. Experimental enthalpies of sublimation $\Delta_{cr}^g H_m$ (T_{mid}) and derived standard enthalpies of sublimation $\Delta_{cr}^g H_m^o$ at the reference temperature $T = 298.15$ K for fluorobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	Method[a]	Temperature range/(K)[b]	$\Delta_{cr}^g H_m$ (T_{mid})/ (kJ mol^{-1})[c]	$\Delta_{cr}^g H_m^o$ (298.15 K)/ (kJ mol^{-1})
2-fluorobenzoic acid					
Zherikova et al.[129]	2016	T	333.9–367.2	94.8 ± 2.4	96.0 ± 2.4
Monte and Hillesheim[126]	2000	K	309.1–323.2	93.6 ± 3.8	94.0 ± 3.8
3-fluorobenzoic acid					
Zherikova et al.[129]	2016	T	331.9–362.6	92.1 ± 2.0	93.2 ± 2.0
Monte and Hillesheim[126]	2000	K	303.2–317.2	93.3 ± 2.8	93.6 ± 2.8
4-fluorobenzoic acid					
Zherikova et al.[129]	2016	T	343.0–386.2	92.2 ± 1.6	93.7 ± 1.7
Cox et al.[127]	1969	T	358.9–381.7	91.0 ± 1.4	92.7 ± 1.6

[a]The methods are transpiration (T) and Knudsen effusion (K).
[b]The temperature range indicates the lowest and highest temperatures, T_l and T_h, respectively, of the study.
[c]$T_{mid} = (T_h + T_l)/2$.

TABLE 11. Experimental enthalpies of sublimation $\Delta_{cr}^g H_m$ (T_{mid}) and derived standard enthalpies of sublimation $\Delta_{cr}^g H_m^o$ at the reference temperature $T = 298.15$ K for chlorobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	Method[a]	Temperature range/(K)[b]	$\Delta_{cr}^g H_m$ (T_{mid})/(kJ mol^{-1})[c]	$\Delta_{cr}^g H_m^o$ (298.15 K)/(kJ mol^{-1})
2-chlorobenzoic acid					
Ribeiro da Silva et al.[125]	2005	K	320.2–339.2	105.1 ± 2.4	105.8 ± 2.4
Emel'yanenko et al.[79]	2005	T	338.1–402.6	100.0 ± 1.6	101.6 ± 1.6
Sabbah and Hirtz[123]	1991	C	323	100.0 ± 0.5[d]	100.5 ± 0.5[d]
Adedeji et al.[124]	1975	DC	413	72.4 (98.3)[e]	78.2 (101.1) ± 5[e]
Wolf and Weghofer[48]	1938	TE	333.2	79.5	80.3[f]
Holdiness[131]	1983	DSC	420–480	90.7	94.7 ± 15
3-chlorobenzoic acid					
Ribeiro da Silva et al.[125]	2005	K	320.1–340.1	101.2 ± 3.4	101.9 ± 3.4
Emel'yanenko et al.[79]	2005	T	348.5–404.1	98.8 ± 3.0	100.6 ± 3.0
Sabbah and Hirtz[123]	1991	C	323	100.6 ± 0.4[d]	101.0 ± 0.4[d]
Adedeji et al.[124]	1975	DC	414	99.6	102.5 ± 5.1[g]
Wolf and Weghofer[48]	1938	TE	328.2	80.8	81.4[f]
4-chlorobenzoic acid					
Reschke et al.[128]	2016	T	353.2–421.1	102.9 ± 1.4	105.0 ± 1.5
Ribeiro da Silva et al.[125]	2005	K	333.2–356.1	103.4 ± 3.4	104.4 ± 3.4
Emel'yanenko et al.[79]	2005	T	358.4–398.3	105.7 ± 3.2	107.6 ± 3.2
Sabbah and Hirtz[123]	1991	C	363	99.3 ± 0.4[d]	100.8 ± 0.5[d]
Adedeji et al.[124]	1975	DC	413	101.9	104.7 ± 5.2[g]
Wolf and Weghofer[48]	1938	TE	333.2	87.9	88.6[f]

[a]The methods are transpiration (T), Knudsen effusion (K), Tian-Calvet calorimetry (C), torsion-effusion (TE), vacuum-sublimation drop-calorimetry (DC), and differential scanning calorimetry (DSC).
[b]The temperature range indicates the highest and lowest temperatures, T_h and T_l, respectively, of the studies of sublimation pressure or the experimental temperature for the calorimetric or TE studies.
[c]$T_{mid} = (T_h + T_l)/2$.
[d]Uncertainties for results by Sabbah and Hirtz are those given by the authors. Based on the analysis of other results from the same laboratory later in this report, we estimate expanded uncertainties for these values to be near 10 kJ mol^{-1}.
[e]The value in parentheses is the reported value augmented by the enthalpy of fusion, as described in the text. The uncertainty is that estimated by the authors.
[f]All results reported by Wolf and Weghofer[48] are systematically low, as described in the text.
[g]The relative expanded uncertainty of 5% is that estimated by the authors. This value was accepted here.

TABLE 12. Experimental enthalpies of sublimation $\Delta_{cr}^{g} H_m$ (T_{mid}) and derived standard enthalpies of sublimation $\Delta_{cr}^{g} H_m^o$ at the reference temperature $T = 298.15$ K for bromobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	Method[a]	Temperature range/(K)[b]	$\Delta_{cr}^{g} H_m$ (T_{mid})/(kJ mol^{-1})[c]	$\Delta_{cr}^{g} H_m^o$ (298.15 K)/(kJ mol^{-1})
2-bromobenzoic acid					
Zherikova et al.[130]	2016	T	347.2–407.6	105.7 ± 1.8	107.5 ± 1.9
Ribeiro da Silva et al.[125]	2005	K	327.6–347.7	106.7 ± 3.6	107.5 ± 3.6
Ferrao and Pilcher[83]	1987	DC	423	NR[d]	110.9 ± 1.1 (3)[d]
Tan and Sabbah[121]	1994	C	333	94.6 ± 0.4[e]	95.3 ± 0.4[e]
Holdiness[131]	1983	DSC	425–480	60.3	64.3 ± 10[f]
3-bromobenzoic acid					
Zherikova et al.[130]	2016	T	355.2–417.2	102.8 ± 1.8	104.8 ± 1.9
Ribeiro da Silva et al.[125]	2005	K	327.7–347.6	104.2 ± 3.2	105.1 ± 3.2
Ferrao and Pilcher[83]	1987	DC	423	NR[d]	105.0 ± 1.1 (3)[d]
Tan and Sabbah[121]	1994	C	348	98.1 ± 0.1[e]	99.2 ± 0.3[e]
4-bromobenzoic acid					
Zherikova et al.[130]	2016	T	379.0–455.8	103.2 ± 2.2	106.1 ± 2.3
Ribeiro da Silva et al.[125]	2005	K	348.7-366.7	107.4 ± 3.8	108.7 ± 3.8
Ferrao and Pilcher[83]	1987	DC	435	NR[d]	107.6 ± 1.1 (3)[d]
Tan and Sabbah[121]	1994	C	363	100.7 ± 0.6[e]	102.2 ± 0.7[e]

[a]The methods are transpiration (T), Knudsen effusion (K), Tian-Calvet calorimetry (C), vacuum-sublimation drop-calorimetry (DC), and differential scanning calorimetry (DSC).
[b]The temperature range indicates the highest and lowest temperatures, T_h and T_l, respectively, of the studies of sublimation pressure or the experimental temperature for the calorimetric studies.
[c]$T_{mid} = (T_h + T_l)/2$.
[d]Experimental enthalpy increments for the gas at $T = 423$ K and the crystal at $T = 298.15$ K were not reported. The authors estimated the uncertainty to be 1.1 kJ mol^{-1}. The value in brackets is our estimate of the expanded uncertainty with 0.95 level of confidence.
[e]Uncertainties listed for the work of Tan and Sabbah[121] are those of the authors. These will later be shown to be too small.
[f]The uncertainty given for the results of Holdiness[131] are those estimated by the developers of the method.[132] The value of $\Delta_{cr}^{g} H_m^o$ is highly inconsistent with all other results.

TABLE 13. Experimental enthalpies of sublimation $\Delta_{cr}^{g} H_m$ (T_{mid}) and derived standard enthalpies of sublimation $\Delta_{cr}^{g} H_m^o$ at the reference temperature $T = 298.15$ K for iodobenzoic acids (all uncertainties are estimates of the expanded uncertainty with 0.95 level of confidence)

Authors	Year	Method[a]	Temperature range/(K)[b]	$\Delta_{cr}^{g} H_m$ (T_{mid})/(kJ mol^{-1})[c]	$\Delta_{cr}^{g} H_m^o$ (298.15 K)/(kJ mol^{-1})
2-iodobenzoic acid					
Zherikova et al.[129]	2016	T	362.4–411.5	109.2 ± 2.2	111.2 ± 2.3
Monte and Hillesheim[126]	2000	K	345.2–359.2	111.4 ± 4.6	112.6 ± 4.6
Tan and Sabbah[122]	1994	C	363	90.0 ± 0.2[d]	91.4 ± 0.4[d]
Holdiness[131]	1983	DSC	440–480	76.7	80.8 ± 12[e]
3-iodobenzoic acid					
Zherikova et al.[129]	2016	T	366.6–422.0	106.7 ± 1.6	109.0 ± 1.7
Monte and Hillesheim[126]	2000	K	347.2–363.2	109.6 ± 3.2	110.9 ± 3.2
Tan and Sabbah[122]	1994	C	363	94.2 ± 0.2[d]	95.7 ± 0.4[d]
4-iodobenzoic acid					
Zherikova et al.[129]	2016	T	388.9–433.5	108.3 ± 1.4	111.0 ± 1.6
Monte and Hillesheim[126]	2000	K	363.2–379.1	111.0 ± 2.8	112.7 ± 2.8
Tan and Sabbah[122]	1994	C	363	97.7 ± 0.3[e]	99.1 ± 0.5[e]

[a]The methods are transpiration (T), Knudsen effusion (K), Tian-Calvet calorimetry (C), and differential scanning calorimetry (DSC).
[b]The temperature range indicates the highest and lowest temperatures, T_h and T_l, respectively, of the studies of sublimation pressure or the experimental temperature for the calorimetric studies.
[c]$T_{mid} = (T_h + T_l)/2$.
[d]Uncertainties listed for the work of Tan and Sabbah[122] are those of the authors.
[e]The uncertainty given for the results of Holdiness[131] are those estimated by the developers of the method.[132] The value of $\Delta_{cr}^{g} H_m^o$ is highly inconsistent with all other results.

5.1.1. Fluorobenzoic acids: $\Delta_{cr}^{g} H_m^o$

Enthalpies of sublimation at the temperatures of the experiments and derived standard enthalpies of sublimation for the temperature $T_{ref} = 298.15$ K are compiled in Table 10 for fluorobenzoic acids. Results from transpiration (T) and Knudsen effusion (K) methods are seen to be in excellent agreement.

5.1.2. Chlorobenzoic acids: $\Delta_{cr}^{g} H_m^o$

Enthalpies of sublimation and derived values for temperature $T_{ref} = 298.15$ K are compiled in Table 11 for chlorobenzoic acids. Results from transpiration studies[79,128] and Knudsen effusion methods[125] are seen to be in excellent agreement. The calorimetric measurements by Sabbah and Hirtz[123] are reported

with low uncertainties and agreement with results from transpiration and Knudsen effusion studies is fair, as seen in the table. Agreement, here, may be serendipitous, however, as later measurements from the same laboratory on bromobenzoic acids[121] and iodobenzoic acids[122] are quite low in comparison with other results.

The value reported by Adedeji *et al.*[124] for 2-chlorobenzoic acid was determined at 413 K, which is very near to the normal melting temperature for this compound. The value reported (72.4 kJ mol^{-1}) is apparently the enthalpy of vaporization, rather than the enthalpy of sublimation. Augmenting this value with the enthalpy of fusion (evaluated later in this report) yields 104.1 kJ mol^{-1}, in excellent agreement with the values determined by Knudsen effusion[125] and transpiration.[79]

Wolf and Weghofer[48] reported enthalpies of sublimation based on TE measurements for a large number of compounds, but, unfortunately, the reported values are systematically low. In addition to the results seen here (Table 11) for chlorobenzoic acids, this conclusion is based on comparisons with critically evaluated values for naphthalene[137] and biphenyl,[138] where values reported by Wolf and Weghofer[48] are low by 6 kJ mol^{-1} and 13 kJ mol^{-1}, respectively. The value reported by Holdiness[131] has a very large uncertainty and is included here for completeness only.

5.1.3. Bromobenzoic acids: $\Delta_{cr}^{g}H_{m}^{o}$

Enthalpies of sublimation and derived values for the temperature T_{ref} = 298.15 K are compiled in Table 12 for bromobenzoic acids. Results from transpiration studies[130] and Knudsen effusion methods[125] are in excellent agreement, as are the vacuum DC results by Ferrao and Pilcher,[83] though the uncertainties stated by the authors for the DC results are probably too small. Uncertainties given in Table 12 for values derived from the Knudsen effusion and transpiration studies are those estimated in the present work, as described earlier. For the DC measurements, we estimate the expanded uncertainty to be ~3 kJ mol^{-1}, based on the uncertainty in the measured enthalpy increment

(~2 kJ mol^{-1}), plus uncertainty associated with the adjustment of results to T = 298.15 K (~1 kJ mol^{-1}). Results reported by Tan and Sabbah[121] are 6–12 kJ mol^{-1} lower than those derived from the temperature dependence of the sublimation pressures (method = K and T) or vacuum DC. The origin of this discrepancy is not known. Values reported by Tan and Sabbah[122] for iodobenzoic acids show yet larger deviations from multiple consistent data sources. The single value determined with a DSC by Holdiness[131] is anomalously low and is included for completeness only.

5.1.4. Iodobenzoic acids: $\Delta_{cr}^{g}H_{m}^{o}$

Enthalpies of sublimation and derived values for the temperature T_{ref} = 298.15 K are compiled in Table 13 for iodobenzoic acids. Again, results from transpiration studies[129] and Knudsen effusion methods[126] are in excellent agreement. Enthalpies of sublimation derived from the direct calorimetric methods of Tan and Sabbah[122] are lower by 10–15 kJ mol^{-1}, while that determined by Holdiness for 2-iodobenzoic acid is nearly 30 kJ mol^{-1} lower.

6. Enthalpies of Formation for the Ideal-Gas State Derived from Experiment for the Halobenzoic Acids

Standard enthalpies of formation for the ideal-gas state $\Delta_f H_m^o$ (g) of the halobenzoic acids can be evaluated with Eq. (1), as the sum of standard molar enthalpies of formation for the crystal $\Delta_f H_m^o$ (cr) (Tables 6–9) and standard molar enthalpies of sublimation $\Delta_{cr}^g H_m^o$ (298.15 K) (Tables 10–13). Results of evaluation of the standard enthalpies of formation for the ideal-gas state, based entirely on experimental thermochemical and thermophysical properties of the halobenzoic acids, are summarized in Table 14. Values represent a weighted average of results for $\Delta_f H_m^o$ (cr) and $\Delta_{cr}^g H_m^o$ (298.15 K) from Tables 6–13 that are consistent within the

TABLE 14. Standard enthalpies of formation for the ideal-gas state $\Delta_f H_m^o$ (g) derived with averaged experimental standard enthalpies of formation for the crystal $\Delta_f H_m^o$ (cr) and experimental standard enthalpies of sublimation at the reference temperature T = 298.15 K[a]

Compound	$\Delta_f H_m^o$ (cr)	Sources[b]	$\Delta_{cr}^g H_m^o$ (298.15 K)	Sources[b]	$\Delta_f H_m^o$ (g)
2-fluorobenzoic acid	−568.3 ± 1.2	92,94	95.4 ± 2.0	126,129	−472.9 ± 2.3
3-fluorobenzoic acid	−582.5 ± 1.5	92	93.3 ± 1.6	126,129	−489.2 ± 2.2
4-fluorobenzoic acid	−585.4 ± 0.6	86,91,92,94,95	93.1 ± 1.1	127,129	−492.3 ± 1.3
2-chlorobenzoic acid	−404.8 ± 1.0	98,99	102.8 ± 1.3	79,124,125	−302.0 ± 1.7
3-chlorobenzoic acid	−423.9 ± 1.2	97–99	101.4 ± 2.1	79,124,125	−322.5 ± 2.4
4-chlorobenzoic acid	−428.8 ± 0.4	97–99,101–114	104.9 ± 1.3	79,124,125,128	−323.9 ± 1.5
2-bromobenzoic acid	−368.3 ± 1.6	83	108.3 ± 1.4	83,125,130	−260.0 ± 2.1[c]
2-bromobenzoic acid	−342.5 ± 4.2	115	108.3 ± 1.4	83,125,130	−234.2 ± 4.4[c]
3-bromobenzoic acid	−394.7 ± 1.6	83	104.9 ± 1.4	83,125,130	−289.8 ± 2.1[c]
3-bromobenzoic acid	−366.5 ± 2.0	115	104.9 ± 1.4	83,125,130	−261.6 ± 2.4[c]
4-bromobenzoic acid	−378.9 ± 1.1	83,93,115,116	107.1 ± 1.7	83,125,130	−271.8 ± 2.0
2-iodobenzoic acid	−301.6 ± 1.1	118,117	111.5 ± 2.0	126,129	−190.1 ± 2.3
3-iodobenzoic acid	−316.2 ± 3.2	115,117	109.4 ± 1.5	126,129	−206.8 ± 3.5
4-iodobenzoic acid	−316.6 ± 1.2	81,117,119	111.4 ± 1.4	126,129	−205.2 ± 1.8

[a]All uncertainties in the table represent the expanded uncertainty with 0.95 level of confidence. Units are kJ mol^{-1} for all enthalpies.
[b]Reference numbers of experimental data used in the calculation of the weighted average. See Tables 6–13 for property values from each source and uncertainties.
[c]Results of the combustion studies by Ferrao and Pilcher[83] and Sabbah and Rojas Aguilar[115] are inconsistent, and $\Delta_f H_m^o$ (g) is calculated with results from both studies.

evaluated uncertainties. Data sources used in the weighted average for each property are indicated.

For fluoro-, chloro-, and iodobenzoic acids, all results for $\Delta_f H_m^o$ (cr) are consistent, with the obvious exception of the results reported by Holdiness,[96] who used relatively crude experimental methods. For 2-chlorobenzoic acid, the results of Smith *et al.*[97] are only slightly low relative to those of Johnson and Prosen[94] and Sabbah and Rojas Aguilar.[99] Nonetheless, we have removed the results of Smith *et al.*[97] from the average for this compound. In the case of $\Delta_f H_m^o$ (cr) for bromobenzoic acids, good consistency is seen for 4-bromobenzoic acid, while values reported by Ferrao and Pilcher[83] and Sabbah and Rojas Aguilar[115] for 2- and 3-bromobenzoic acids are very inconsistent, and $\Delta_f H_m^o$ (g) is calculated with results from both studies. For iodobenzoic acids, results from the various research groups are consistent, except for the enthalpy of formation for the crystal $\Delta_f H_m^o$ (cr) reported by Sabbah and Rojas Aguilar[115] for 2-iodobenzoic acid (Table 9), which is slightly higher than those by Smith[117] and Ribeiro da Silva *et al.*[118] and was not included in the weighted average.

For enthalpies of sublimation $\Delta_{cr}^g H_m^o$ (298.15 K), good consistency is seen between results from Knudsen effusion and transpiration studies for all compounds (Tables 10–13). In addition, the vacuum DC of Ferrao and Pilcher[83] for bromobenzoic acids (Table 12) and Adedeji *et al.*[124] for chlorobenzoic acids (Table 11) is seen to be consistent with the Knudsen effusion and transpiration results. Results reported from the laboratory of Sabbah[123] for chlorobenzoic acids are only slightly lower than the results from Knudsen effusion and transpiration; however, these values were not included in the average, as results from the same laboratory[121,122] for bromobenzoic acids and iodobenzoic acids are low by 6–20 kJ mol^{-1}.

7. Comparison of Computational and Experimental Results

7.1. Selection of the homodesmic reactions for the halobenzoic acids

Comparison of computational and experimental results for the enthalpies of formation involves the comparison of results for homodesmic or isodesmic reactions. Ideally, a reaction is chosen for which enthalpies of formation are known with high confidence for all participants other than the compound of interest. In this research, the following homodesmic reaction was chosen:

(8)
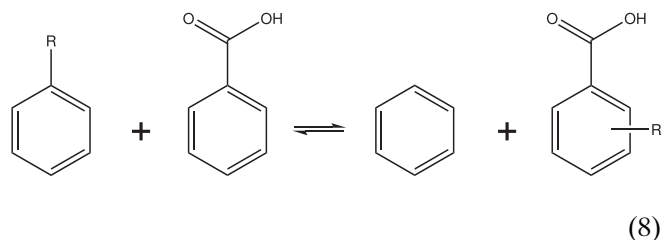
The structure at the far right represents the three isomers of the halobenzoic acids. The derivation of the properties of benzoic acid was discussed earlier. A discussion of the sources of the required properties for benzene and the halobenzenes follows.

7.2. Experimental enthalpies of formation from experiment for participants in the homodesmic reactions

Properties leading to the enthalpy of formation of benzene and the halobenzenes in the ideal-gas state are listed in Table 15. Reliable enthalpies of combustion have been reported for benzene,[139,140] 1-fluorobenzene,[92] and 1-chlorobenzene.[97,141,142] The enthalpy of formation of bromobenzene recommended by Cox and Pilcher[82] is based on an enthalpy of reaction involving diphenylmercury, as reported by Hartley *et al.*[143] and Chernick *et al.*[144] For iodobenzene, an analogous reaction was investigated by Hartley *et al.*[143] and Chernick *et al.*,[144] and this was used by Cox and Pilcher,[82] in combination with an enthalpy of combustion reported by Smith,[117] to derive a recommended enthalpy of formation for the liquid.

Enthalpies of vaporization for benzene and the halobenzenes are, generally, well established. Direct measurements of the enthalpy of vaporization for benzene have been reported by Osborne and Ginnings,[145] Svoboda *et al.*,[146] and Todd *et al.*[147], and these are mutually consistent as well as are consistent with the high quality equation of state for benzene.[148] The enthalpy of vaporization for fluorobenzene was measured calorimetrically by Scott *et al.*,[71] and these are consistent with vapor pressures reported in the same article and with those determined with transpiration by Verevkin *et al.*[149] For chlorobenzene and bromobenzene, the enthalpy of

TABLE 15. Standard enthalpies of formation for the ideal gas $\Delta_f H_m^o$ (g) derived with experimental standard enthalpies of formation for the liquid phase $\Delta_f H_m^o$ (l) and experimental standard enthalpies of vaporization for benzenes and halobenzenes at the reference temperature T = 298.15 K[a]

Compound	$\Delta_f H_m^o$ (l)	Source[b]	$\Delta_l^g H_m^o$ (298.15 K)	Source[b]	$\Delta_f H_m^o$ (g)[c]	$\Delta_f H_m^o$ (g)[d]
1	2	3	4	5	6	7
Benzene	49.0 ± 1.1	139,140	33.8 ± 0.2	145,146,147	82.8 ± 1.1	83.20 ± 0.26
Fluorobenzene	−151.1 ± 1.7	92	34.6 ± 0.2	71,149	−116.5 ± 1.7	−115.3 ± 1.1
Chlorobenzene	10.5 ± 0.9	97,141,142	41.0 ± 0.2	73,149	51.5 ± 1.2	52.23 ± 0.61
Bromobenzene	60.7 ± 4.2	143,144[e]	44.2 ± 0.3	73,74	104.9 ± 4.2	104.9 ± 1.3
Iodobenzene	115.9 ± 2.9	117,143,144[e]	48.5 ± 1.4	74	164.4 ± 3.2	161.9 ± 1.1

[a]All uncertainties in the table represent the expanded uncertainty with 0.95 level of confidence. Units are kJ mol^{-1} for all enthalpies.
[b]Reference numbers of experimental data that support the property values and uncertainties.
[c]Enthalpy of formation for the ideal gas $\Delta_f H_m^o$ (g) calculated as the sum of columns 2 and 4.
[d]Enthalpy of formation for the ideal gas $\Delta_f H_m^o$ (g) reported in the Active Thermochemical Tables.[150–152]
[e]Enthalpies of reaction reported in Refs. 143 and 144 are summarized by Cox and Pilcher.[82]

vaporization at $T = 298.15$ K was measured calorimetrically by Wadsö.[73] Vapor pressures measured by Verevkin *et al.*[149] (chlorobenzene) and Verevkin *et al.*[74] (bromobenzene) are consistent with the direct measurements. Enthalpies of vaporization for iodobenzene are based on the vapor pressures determined with transpiration by Verevkin *et al.*[74]

Enthalpies of formation for the ideal-gas state for benzenes and halobenzenes (Table 15, column 6) were calculated as the sum of the enthalpy of formation for the liquid $\Delta_f H_m^o$ (l) (column 2) and enthalpy of vaporization $\Delta_l^g H_m^o$ at $T = 298.15$ K (column 4). These values are in agreement with those evaluated within the *Active Thermochemical Tables* maintained by Ruscic and coworkers,[150–152] as seen in Table 15 (columns 6 and 7).

The *Active Thermochemical Tables* are based on thermodynamic consistency enforcement for a network of reaction properties derived from the experiment and computation for 1058 chemical species, including radicals and ions, as well as some common chemical compounds. The number of chemical compounds with more than a few atoms is small (i.e., ~75 compounds have more than 5 atoms), and, of these, ~10 have six or more carbon atoms. Nonetheless, this group includes benzene and the four monohalobenzenes, and the enthalpies of formation for the gas phase evaluated in the *Active Thermochemical Tables* (version 1.118) were used in all further

calculations here. For $\Delta_f H_m^o$ (g) of benzenes and halobenzenes, the use of the value derived here (Table 15, column 6) or that from the *Active Thermochemical Tables*[150] (column 7) would not alter the conclusions of this research. The values of $\Delta_f H_m^o$ (g) for bromobenzene and iodobenzene (Table 15, column 6) derived in this research have relatively large uncertainties, which are reduced considerably in the more extensive analysis of the thermochemical network by Ruscic and co-workers.[150]

7.3. Enthalpies for the homodesmic reactions by computation

Enthalpies for the homodesmic reaction $\Delta_r H_m^o$ (g) [Eq. (8)] from computation are evaluated as the sum of three terms involving differences between products and reactants for the ZPVE, $\Delta ZPVE$, thermal correction ΔH_T (i.e., the enthalpy change from temperature $T = 0$ to $T = 298.15$ K of the gas computed with the models described in Sec. 3.3.), and electronic energy ΔE. Details of these contributions for each halobenzoic acid are summarized in Table 16. Contributions from the first two terms ($\Delta ZPVE$ and ΔH_T) are small for all cases (Table 16, columns 3 and 4), and the computed enthalpy of reaction is dominated by the difference in electronic energies ΔE. Energy differences computed at five different levels of

TABLE 16. Enthalpy of the homodesmic reaction (8) (halobenzene + benzoic acid = benzene + halobenzoic acid) at temperature $T = 298.15$ K and its individual contributions (units of energy are kJ mol^{-1})

Halogen	Conformer[b]	$\Delta ZPVE$[c]	ΔH_T[d]	ΔE[a]					$\Delta_r H_m^o$ (g) conformer[e]	$\Delta_r H_m^o$ (g) total[e]
				B3LYP/def2-QZVPD	DF-MP2/ def2-QZVPP	G4	DLPNO-CCSD(T)/ def2-QZVPP// B3LYP/def2-QZVPD	DLPNO-CCSD(T)/ def2-QZVPP// DF-MP2/ def2-QZVPP		
1	2	3	4	5	6	7	8	9	10	11
4-halobenzoic acids										
F	syn	−0.21	0.17	−0.40	0.29	0.25	0.33	0.14	0.10	0.10
Cl	syn	−0.37	0.25	1.08	1.00	1.28	1.34	1.44	1.31	1.31
Br	syn	−0.47	0.31	1.56	1.13	1.68	1.61	1.73	1.58	1.58
I	syn	−0.52	0.34	1.70	1.16	–	1.83	1.94	1.77	1.77
3-halobenzoic acids										
F	anti-syn	−0.37	0.19	3.55	2.41	3.46	3.17	3.22	3.05	3.05
Cl	anti-syn	−0.42	0.35	3.83	3.08	3.10	3.25	3.36	3.29	3.29
Br	anti-syn	−0.48	0.43	3.88	3.20	3.16	3.20	3.29	3.24	3.24
I	anti-syn	−0.47	0.45	3.64	3.09	–	2.97	3.01	2.99	2.99
2-halobenzoic acids										
F	anti-syn	−0.21	0.77	17.46	17.92	17.17	17.58	17.56	18.12	18.33[f]
	anti-anti[g]	0.16	−0.10	23.25	23.06	–	–	22.62	22.69	
Cl	syn-syn	−0.73	0.14	27.86	22.53	24.30	24.70	24.77	24.17	24.31[f]
	anti-anti[g]	−0.85	0.06	34.85	30.64	–	–	32.74	31.97	
Br	syn-syn	−0.86	0.46	29.34	22.90	24.61	25.55	25.64	25.24	25.24[h]
	anti-anti			38.57	33.28	–	–	35.76		
I	syn-syn	−0.90	0.80	28.54	21.76	–	24.74	24.76	24.66	24.66[h]
	anti-anti	–	–	43.39	36.65	–	–	39.72		

[a]ΔE is the computed difference in electronic energy for the sum of the products minus the sum of the reactants for the homodesmic reaction.

[b]For the lowest-energy conformers, anti-syn or syn-syn, the contributions of syn-syn or anti-syn conformers, respectively, are included by the application of the one-dimensional quantum hindered rotor treatment.

[c]$\Delta ZPVE$ is the computed difference in ZPVE between the products and reactants of the homodesmic reaction.

[d]ΔH_T is the computed difference in the enthalpy change between the temperatures $T = 0$ and $T = 298.15$ K for the products and reactants of the homodesmic reaction.

[e]Based on DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP energy.

[f]Based on equilibrium mixture of anti-syn, syn-syn, and anti-anti conformers.

[g]The conformer is a minor contributor to the computed properties and was evaluated without the hindered rotor treatment.

[h]Contribution of anti-anti conformer was neglected.

theory are shown (columns 5 through 9). The accuracy of this term is determined by the level of theory used and—likely, to a larger extent—by "balancing energetic effects and canceling electronic structure errors."[153] This is most apparent in the results for 4- and 3-halobenzoic acids where energy differences computed at the B3LYP, DF-MP2, G4, and DLPNO-CCSD(T) levels agree within ~1 kJ mol^{-1}. The difference is even smaller (~0.2 kJ mol^{-1}) when only the high-level methods [G4 and DLPNO-CCSD(T)] are considered. For 2-halobenzoic acids, the balancing is less effective due to ortho interactions that are not present in the reactants, yet the agreement amongst the high-level methods for ΔE remains within 1 kJ mol^{-1}. This level of consistency is in accord with the extensive benchmark studies of Wheeler *et al.*[153] For comparison with the experiment, the results at the highest level of theory, DLPNO-CCSD(T)/def2-QZVPP//DF-MP2/def2-QZVPP, were used, and we estimate the expanded uncertainty of computed enthalpies of reaction to be 2 kJ mol^{-1} (0.95 level of confidence).

7.4. Enthalpies for the homodesmic reactions by experiment

Enthalpies of reaction for the homodesmic reaction [Eq. (8)] derived based on the experiment $\Delta_r H_m^o(g, \text{expt})$ and computation $\Delta_r H_m^o(g, \text{comp})$ are given in columns 6 and 7 of Table 17. All values of $\Delta_f H_m^o(g, \text{expt})$ used for the reaction participants in the calculation of $\Delta_r H_m^o(g, \text{expt})$ are given in the table. The agreement between the experimental and computed enthalpies of reaction for all fluoro- and chlorobenzoic acids is excellent, with deviations between $\Delta_r H_m^o(g, \text{expt})$ and $\Delta_r H_m^o(g, \text{comp})$ never exceeding the uncertainty in $\Delta_r H_m^o(g, \text{expt})$. This result contrasts sharply with that for 2- and 3-bromobenzoic acids, where deviations range from 9–18 kJ mol^{-1}. The experimental results of Ferrao and Pilcher[83] and Sabbah and Rojas Aguilar[115]

are both mutually inconsistent and inconsistent with the computations. We are unable to explain such diverse results, but the good agreement between experiment and computation seen for other compounds, plus the consistent results observed for computations for halogens at the 2-, 3-, and 4-positions, gives high confidence in the computed values. We estimate the expanded uncertainty in the computed values of $\Delta_r H_m^o(g)$ to be 2 kJ mol^{-1} (0.95 level of confidence). In contrast with the results for 2- and 3-bromobenzoic acids, agreement between the experimental and computed values of $\Delta_r H_m^o(g)$ for 4-bromobenzoic acid is within the experimental uncertainty.

For 2-iodobenzoic acid, the enthalpies of reaction for the gas phase based on the experiment and computation are in excellent agreement, while differences near 10 kJ mol^{-1} are seen for 3- and 4-iodobenzoic acids. The inconsistency for 3- and 4-iodobenzoic acids is surprising, given the general agreement of the combustion results reported by Smith,[117] Sabbah and Rojas Aguilar,[119] and Ribeiro da Silva *et al.*[81] Initial checks of group-additivity increments for iodine on the aromatic ring of benzoic acid relative to that on benzene were concluded to be successful by Ribeiro da Silva *et al.*[81] Unfortunately, this conclusion was based, in part, on the enthalpies of sublimation reported by Tan and Sabbah,[122] which are now seen to be 14–20 kJ mol^{-1} lower than mutually consistent values determined with Knudsen effusion[126] and transpiration,[129] and reported subsequently.

As seen in Tables 12 and 13, all enthalpies of sublimation reported by Tan and Sabbah,[121,122] are consistently low relative to those from other sources. If all other sources are ignored, the use of the enthalpies of sublimation reported by Tan and Sabbah[121,122] to calculate $\Delta_f H_m^o$ (g) for bromo- and iodobenzoic acids does not yield an interpretable trend in the resultant enthalpies of reaction $\Delta_r H_m^o(g, \text{expt})$ calculated as in Table 17. We conclude that the results of Tan and

TABLE 17. Comparison of enthalpies of reaction for the homodesmic reaction (8) (halobenzene + benzoic acid = benzene + halobenzoic acid) in the ideal-gas state at temperature T = 298.15 K and pressure p^o = 100 kPa derived from experiment $\Delta_r H_m^o(g, \text{expt})$ and computed $\Delta_r H_m^o(g, \text{comp})$[a]

	$\Delta_f H_m^o$ (g, expt)[b]/(kJ mol^{-1})				$\Delta_r H_m^o$ (g)/(kJ mol^{-1})	
Isomer[c]	Halobenzene	Benzoic acid	Benzene	Halobenzoic acid	$\Delta_r H_m^o(g, \text{expt})$	$\Delta_r H_m^o(g, \text{comp})$[d]
1	2	3	4	5	6	7
2-F	−115.3 ± 1.1	−294.5 ± 0.9	83.2 ± 0.3	−472.9 ± 2.3	20.1 ± 3	18.4
3-F	−115.3 ± 1.1	−294.5 ± 0.9	83.2 ± 0.3	−489.2 ± 2.2	3.8 ± 3	3.0
4-F	−115.3 ± 1.1	−294.5 ± 0.9	83.2 ± 0.3	−492.3 ± 1.3	0.7 ± 2	0.1
2-Cl	52.2 ± 0.6	−294.5 ± 0.9	83.2 ± 0.3	−302.0 ± 1.7	23.5 ± 2	24.3
3-Cl	52.2 ± 0.6	−294.5 ± 0.9	83.2 ± 0.3	−322.5 ± 2.4	3.0 ± 3	3.3
4-Cl	52.2 ± 0.6	−294.5 ± 0.9	83.2 ± 0.3	−323.9 ± 1.5	1.6 ± 2	1.3
2-Br	104.9 ± 1.3	−294.5 ± 0.9	83.2 ± 0.3	−260.0 ± 2.1[c]	(12.8 ± 3)[e]	25.2
2-Br	104.9 ± 1.3	−294.5 ± 0.9	83.2 ± 0.3	−234.2 ± 4.4[d]	(38.6 ± 5)[f]	25.2
3-Br	104.9 ± 1.3	−294.5 ± 0.9	83.2 ± 0.3	−289.8 ± 2.1[c]	(−17.0 ± 3)[e]	3.2
3-Br	104.9 ± 1.3	−294.5 ± 0.9	83.2 ± 0.3	−261.6 ± 2.4[d]	(11.2 ± 3)[f]	3.2
4-Br	104.9 ± 1.3	−294.5 ± 0.9	83.2 ± 0.3	−271.8 ± 2.0	1.0 ± 3	1.6
2-I	161.9 ± 1.1	−294.5 ± 0.9	83.2 ± 0.3	−190.1 ± 2.3	25.7 ± 3	24.7
3-I	161.9 ± 1.1	−294.5 ± 0.9	83.2 ± 0.3	−206.8 ± 3.5	(9.0 ± 4)	3.0
4-I	161.9 ± 1.1	-294.5 ± 0.9	83.2 ± 0.3	-205.2 ± 1.8	(10.6 ± 2)	1.8

[a]Values of $\Delta_r H_m^o(g, \text{expt})$ shown in brackets in column 6 are inconsistent with the computed values $\Delta_r H_m^o(g, \text{comp})$.
[b]Enthalpy of formation for the ideal-gas state used in the calculation of $\Delta_r H_m^o(g, \text{expt})$.
[c]The abbreviations represent the isomer of halobenzoic acid in the homodesmic reaction, e.g., 2-F indicates the reaction with 2-fluorobenzoic acid.
[d]The estimated expanded uncertainty (0.95 level of confidence) for the computed values $\Delta_r H_m^o(g, \text{comp})$ is 2 kJ mol^{-1}, as discussed in the text.
[e]This value was derived with the enthalpy of combustion reported by Ferrao and Pilcher.[83]
[f]This value was derived with the weighted average of the enthalpies of combustion reported by Sabbah and Rojas Aguilar.[115]

Sabbah[121,122] are systematically in error, or equivalently, their uncertainties are underestimated by 14–20 kJ mol^{-1}.

8. Validation of Computations through Comparison with Results for Halonaphthalenes

In comparison to that for halobenzoic acids, the literature of experimental results for thermophysical and thermochemical properties of 1- and 2-halonaphthalenes is relatively sparse. Nonetheless, adequate experimental information does exist to aid in the validation of the computational results, particularly for the aromatic bromocompounds, which show the most extensive inconsistency amongst halobenzoic acids.

For fluoronaphthalenes, the enthalpy of combustion of 1-fluoronaphthalene has been determined experimentally;[154] however, a commercial combustion calorimeter was used without the possibility of rotation, so these results must be considered unreliable. (In fact, the combustion reaction was not defined,[154] so the derivation of an enthalpy of formation is impossible from this work.) In addition to the absence of reliable enthalpies of formation, the few available vapor-pressure values[155,156] for fluoronaphthalenes are inadequate for the evaluation of the enthalpy of vaporization with any certainty.

Enthalpies of combustion for 1- and 2-chloronaphthalene were reported by Smith *et al.*[97] in 1953, based on measurements using "quartz wool" to increase the surface area of the product acid solution, rather than bomb rotation, as used in later measurements.[94] The quartz wool method was shown earlier to be somewhat successful for the combustion of the three chlorobenzoic acids. Nonetheless, Cox and Pilcher[82] estimated the uncertainties for the enthalpies of combustion for chloronaphthalenes to be quite large (8.4 kJ mol^{-1}), due to inadequate reporting of uncertainty information. We have used the uncertainty estimates of Cox and Pilcher[82] in further calculations. Verevkin[157] reported results of transpiration vapor/sublimation

pressures for 1- and 2-chloronaphthalene, allowing evaluation of the enthalpies of vaporization for these compounds.

Thermodynamic properties for halonaphthalenes are most well established for 1- and 2-bromonaphthalene, where Ribeiro da Silva *et al.*[84] have determined enthalpies of combustion, and Verevkin[157] has reported transpiration studies. This is fortuitous within the context of the present review, as results are most inconsistent for bromobenzoic acids, and the demonstration of consistency for bromonaphthalenes can support the conclusion that the inconsistency for bromobenzoic acids lies with the experimental combustion enthalpies.

For iodonaphthalenes, Smith[117] reported the enthalpy of combustion for both 1- and 2-iodonaphthalene. Uncertainties for these values were estimated by Cox and Pilcher[82] to be near 6 kJ mol^{-1} (i.e., 1.5 kcal mol^{-1}), due to a lack of reported uncertainty information. Verevkin[157] reported vapor pressures for 1-iodonaphthalene determined by transpiration, from which the enthalpy of vaporization can be derived. For 2-iodonaphthalene, Verevkin[157] derived the enthalpy of sublimation at $T = 298.15$ K by combining the enthalpy of vaporization, determined with correlation gas chromatography, with the enthalpy of fusion reported by Khanna *et al.*[158] The normal melting temperature for 2-iodonaphthalene is near $T = 330$ K, so adjustment to the reference temperature adds little uncertainty to the derived enthalpy of sublimation.

Properties leading to the enthalpy of formation of naphthalene in the ideal-gas state are given in Table 18. The enthalpy of combustion of naphthalene has been measured many times, and the enthalpy of formation for the crystal given in Table 18 is the weighted average of results of high-precision combustion calorimetry reported by Speros and Rossini[159] and Coleman and Pilcher,[160] as compiled by Cox and Pilcher.[82] The independent values are in excellent agreement. Similarly, there have been many determinations of the enthalpy of sublimation of naphthalene. The value used here, (72.7 ± 0.4) kJ mol^{-1}, is that evaluated by Chirico

TABLE 18. Standard enthalpies of formation for the ideal-gas state $\Delta_f H_m^o$ (g) derived with experimental standard enthalpies of formation for the condensed phase $\Delta_f H_m^o$ (cr or l) and experimental standard enthalpies of sublimation (or vaporization) for naphthalene and halonaphthalenes at the reference temperature $T = 298.15$ K[a]

Compound	Phase[b]	$\Delta_f H_m^o$ (cr or l)	Source[c]	$\Delta_{(cr\ or\ l)}^g H_m^o$ (298.15 K)	Source[c]	$\Delta_f H_m^o$ (g)
Naphthalene	cr	77.9 ± 2.2[d]	159,160	72.7 ± 0.4	137	150.6 ± 2.2
1-fluoronaphthalene	l	–	154[e]	–	–	–
2-fluoronaphthalene	cr	–	–	–	–	–
1-chloronaphthalene	l	54.5 ± 8.6 (5)[f]	97	61.4 ± 4.6	157	115.9 ± 10 (5)
2-chloronaphthalene	cr	55.3 ± 8.6 (4)[f]	97	76.3 ± 0.6	157	131.6 ± 9 (4)
1-bromonaphthalene	l	111.6 ± 2.9	84	62.2 ± 1.0	157	173.8 ± 3.1
2-bromonaphthalene	cr	94.4 ± 2.6	84	81.6 ± 1.6	157	176.0 ± 3.1
1-iodonaphthalene	l	161.4 ± 6.3 (2)[f]	117	67.8 ± 0.4	157	229.2 ± 7 (4)
2-iodonaphthalene	cr	144.3 ± 6.3 (2)[f]	117	85.8 ± 3	157,158[g]	230.1 ± 7 (4)

[a]All uncertainties in the table represent the expanded uncertainty with 0.95 level of confidence, and all enthalpies are expressed in units of kJ mol^{-1}.
[b]The equilibrium phase of the compound at temperature $T = 298.15$ K.
[c]Reference numbers of experimental data used in the calculation of the property value.
[d]The expanded uncertainty (0.95 level of confidence) for the standard enthalpy of combustion of naphthalene is 0.8 kJ mol^{-1}.
[e]An enthalpy of combustion was reported by Balcan *et al.*,[154] using a commercial calorimeter, without the rotation or analysis of products. The reported uncertainty for the enthalpy of combustion is ~100 kJ mol^{-1}, so these results were not considered further.
[f]Enthalpies of combustion reported by Smith *et al.*[97] and Smith[117] were adjusted by Cox and Pilcher[82] in their review. Cox and Pilcher also increased the uncertainties, due to inadequate reporting of the supporting information. Uncertainties estimated by Cox and Pilcher are given first and the original uncertainties given by Smith *et al.*[97] and Smith[117] are given in brackets for the values of $\Delta_f H_m^o$ (cr or l) and $\Delta_f H_m^o$ (g).
[g]The enthalpy of sublimation is the sum of the enthalpy of vaporization, determined with correlation gas chromatography,[157] and the enthalpy of fusion, determined with differential scanning calorimetry.[158]

et al.[137] through thermodynamic consistency enforcement for ideal-gas and condensed-phase properties. A more recent evaluation by Ruzicka *et al.*,[161] done without the consideration of consistency enforcement with ideal-gas properties, recommended a statistically indistinguishable value of 72.4 kJ mol^{-1}, with no indicated uncertainty.

Standard enthalpies of formation of halonaphthalenes for the ideal-gas state $\Delta_f H_m^o$ (g) derived with experimental standard enthalpies of formation for the condensed phase $\Delta_f H_m^o$ (cr or l) and experimental standard enthalpies of sublimation (or vaporization) for naphthalene and halonaphthalenes at the reference temperature $T = 298.15$ K are listed in Table 18. No calculation can be made for fluoronaphthalenes. The large difference ($\sim$16 kJ mol^{-1}) between the values of $\Delta_f H_m^o$ (g) for 1- and 2-chloronaphthalene is unexpected, and it is tempting to ascribe this difference to possible combustion of a supercooled liquid sample of 2-chloronaphthalene, as the enthalpy of fusion is $\sim$14 kJ mol^{-1}.[158,162] A report of the heat capacity of 2-chloronaphthalene by van Miltenburg and Verdonk[162] for the temperature range 5–370 K did not indicate any supercooling of the sample, which melted near $T = 331.2$ K, so we conclude that there is no support for this explanation in the literature.

Experimental and computed thermodynamic properties for halonaphthalenes are assessed through the following homodesmic reaction:

(9)
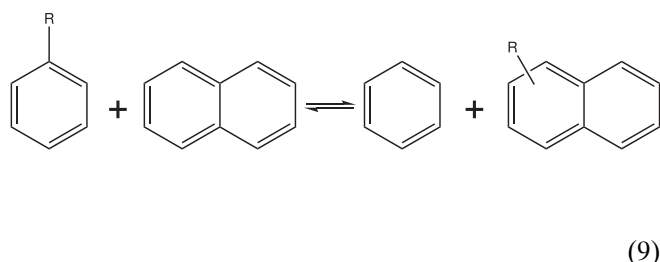
Gas-phase enthalpies of reaction $\Delta_r H_m^o$ (g) for this reaction based on experiment $\Delta_r H_m^o$(g, expt) and computation $\Delta_r H_m^o$(g, comp) are given in Table 19. The computations for naphthalenes were identical to those for halobenzoic acids, without the added complexity of internal rotation of the COOH group. The content of the table is analogous to that of Table 17 with naphthalene substituted for benzoic acid. No comparison can be made for the reactions involving fluoronaphthalenes. Agreement between $\Delta_r H_m^o$(g, expt) and $\Delta_r H_m^o$(g, comp) is within the uncertainty for the experiment-based values for all of the remaining halonaphthalenes, with the exception of 2-chloronaphthalene, which was discussed above. Results for 1-chloronaphthalene and 1- and 2-iodonaphthalene are based on enthalpies of combustion recalculated by Cox and Pilcher,[82] using values published by Smith *et al.*,[97,117] which are corrected values from the thesis of Karlsson.[120] Uncertainty estimates by Cox and Pilcher[82] are approximately twice as large as those reported by Smith *et al.*[97,117] Uncertainties for enthalpies of reaction evaluated with both uncertainty estimates are included in Table 19, where it is seen that, even with the smaller uncertainties reported by Smith *et al.*,[97,117] agreement with the computed enthalpy of reaction remains within the experimental uncertainty.

Experimental results for 1- and 2-bromonaphthalene given in Table 19 are based on enthalpies of combustion reported by Ribeiro da Silva *et al.*[84] in 1993 and transpiration studies by Verevkin[157] in 2003. The good agreement between the experimental and computed values of $\Delta_r H_m^o$(g) add confidence for the computational results obtained for bromobenzoic acids, where large inconsistencies are seen for the experimental values.

9. Validation of Results through Trend Analysis for Estimated Enthalpies of Vaporization

The correlation of thermophysical properties with a molecular structure is most successful for gas-phase properties, though some success has been achieved for the liquid phase,

TABLE 19. Comparison of enthalpies of reaction for the homodesmic reaction (9) (halobenzene + naphthalene = benzene + halonaphthalene) in the ideal-gas state at temperature $T = 298.15$ K and pressure $p° = 100$ kPa derived from experiment $\Delta_r H_m^o$(g, expt) and computed $\Delta_r H_m^o$(g, comp)

| | | $\Delta_f H_m^o$ (g, expt)[a]/(kJ mol^{-1}) | | | | $\Delta_r H_m^o$ (g)/(kJ mol^{-1}) | |
Halogen	Halobenzene	Naphthalene	Benzene	Isomer[b]	Halonaphthalene	$\Delta_r H_m^o$(g, expt)	$\Delta_r H_m^o$(g, comp)
1	2	3	4	5	6	7	8
F	-115.3 ± 1.1	150.6 ± 2.2	83.2 ± 0.3	1	–[c]	–[c]	1.8
F	-115.3 ± 1.1	150.6 ± 2.2	83.2 ± 0.3	2	–[d]	–[d]	0.8
Cl	52.2 ± 0.6	150.6 ± 2.2	83.2 ± 0.3	1	$115.9 \pm 10\ (5)$[e]	$-3.7 \pm 10\ (5)$	1.3
Cl	52.2 ± 0.6	150.6 ± 2.2	83.2 ± 0.3	2	$131.6 \pm 9\ (4)$[e]	$12.0 \pm 9\ (4)$	0.1
Br	104.9 ± 1.3	150.6 ± 2.2	83.2 ± 0.3	1	173.8 ± 3	1.5 ± 4	1.5
Br	104.9 ± 1.3	150.6 ± 2.2	83.2 ± 0.3	2	176.0 ± 3	3.7 ± 4	-0.1
I	161.9 ± 1.1	150.6 ± 2.2	83.2 ± 0.3	1	$229.2 \pm 7\ (4)$[e]	$-0.1 \pm 7\ (5)$	1.9
I	161.9 ± 1.1	150.6 ± 2.2	83.2 ± 0.3	2	$230.1 \pm 7\ (4)$[e]	$0.8 \pm 7\ (5)$	-0.4

[a]Enthalpy of formation for the ideal-gas state used in the calculation of $\Delta_r H_m^o$ (g, expt).
[b]The values 1 and 2 indicate the particular isomer of halonaphthalene.
[c]The enthalpy of combustion has been reported,[154] but the uncertainty is large and the combustion reaction was not reported. No evaluation of the enthalpy of formation is possible.
[d]The enthalpy of combustion for this compound has not been reported, so the reaction enthalpy cannot be calculated from experiment.
[e]Enthalpies of combustion reported by Smith *et al.*[97] and Smith[117] were adjusted by Cox and Pilcher[82] in their review. Cox and Pilcher[82] also increased the uncertainties, due to inadequate reporting of the supporting information. Uncertainties estimated by Cox and Pilcher[82] are given first and the original uncertainties given by Smith *et al.*[97] and Smith[117] are given in brackets for the values of $\Delta_f H_m^o$ (cr or l) and $\Delta_f H_m^o$ (g).

e.g., the predictive method of Chickos *et al.*[163] for liquid heat capacity and correlations of the enthalpy of vaporization by Verevkin and co-workers.[12] The correlation of properties involving solids is typically of limited application and has large uncertainties because the property values

are strongly dependent on the nature of the crystal packing and intermolecular associations in the solid state. For example, the group-additivity method of Domalski and Hearing[164] for heat capacities at $T = 298.15$ K is valid for hydrocarbons only, while the more widely applicable

TABLE 20. Normal melting temperatures T_m, enthalpies of fusion $\Delta_{cr}^l H_m^o (T_m)$, enthalpies of fusion adjusted to the reference temperature $\Delta_{cr}^l H_m^o (T_{ref})$, enthalpies of sublimation adjusted to the reference temperature $\Delta_{cr}^g H_m^o (T_{ref})$, derived enthalpies of vaporization at the reference temperature $\Delta_l^g H_m^o (T_{ref})$, and the difference in the enthalpy of vaporization at the reference temperature between that for the particular halobenzoic acid and that for benzoic acid $\Delta_l^g H_{inc}^o (T_{ref})$, where $T_{ref} = 298.15$ K (uncertainties represent 0.95 level of confidence)

Compound	Source	T_m (K)	$\Delta_{cr}^l H_m^o (T_m)$/(kJ mol^{-1})	$\Delta_{cr}^l H_m^o (T_{ref})$/(kJ mol^{-1})	$\Delta_{cr}^g H_m^o (T_{ref})$/(kJ mol^{-1})[a]	$\Delta_l^g H_m^o (T_{ref})$/(kJ mol^{-1})[b]	$\Delta_l^g H_{inc}^o (T_{ref})$/(kJ mol^{-1})
1	2	3	4	5	6	7	8
Benzoic acid	Furukawa *et al.*[33]	395.49	18.00 ± 0.05	12.4 ± 1.1	90.3 ± 0.3	77.9 ± 1.1	
2-fluorobenzoic acid	Umnahanant *et al.*[165]	397.4	20.1 ± 1.0	14.3 ± 1.5			
	Zherikova *et al.*[129]	396.7	20.3 ± 1.0	14.5 ± 1.5			
	Average	397.1	20.2 ± 1.0	14.4 ± 1.5	95.4 ± 2.0	81.0 ± 2.5	3.1 ± 2.7
3-fluorobenzoic acid	Zherikova *et al.*[129]	395.9	18.5 ± 0.9	12.7 ± 1.5			
	Average	395.9	18.5 ± 0.9	12.7 ± 1.5	93.3 ± 1.6	80.6 ± 2.2	2.7 ± 2.5
4-fluorobenzoic acid	Kang and Samulski[166]	451.0	20.9 ± 1.0	11.9 ± 2.1			
	Zherikova *et al.*[129]	456.1	21.6 ± 1.1	12.3 ± 2.2			
	Average	453.6	21.3 ± 1.0	12.1 ± 2.2	93.1 ± 1.1	81.0 ± 2.5	3.1 ± 2.7
2-chlorobenzoic acid	Andrews *et al.*[136]	413.4	25.7 ± 1.3	18.9 ± 1.9			
	Holdiness[131]	–[d]	25.5 ± 1.3	18.7 ± 1.9			
	Sabbah and Hirtz[123]	414.1	26.3 ± 1.3	19.5 ± 1.9			
	Ribeiro da Silva *et al.*[125]	414.0	25.3 ± 1.3	18.5 ± 1.9			
	Singh *et al.*[167]	414.1	27.5 ± 1.4	20.7 ± 1.9			
	Average	413.9	26.1 ± 1.4	19.2 ± 1.9	102.8 ± 1.3	83.6 ± 2.3	5.7 ± 2.6
3-chlorobenzoic acid	Andrews *et al.*[136]	427.4	23.8 ± 1.2	16.2 ± 1.9			
	Sabbah and Hirtz[123]	427.8	22.0 ± 1.1	14.4 ± 1.9			
	Ribeiro da Silva *et al.*[125]	427.9	23.7 ± 1.2	16.1 ± 1.9			
	Average	427.7	23.9 ± 1.2	16.5 ± 1.9	101.4 ± 2.1	84.9 ± 2.8	7.0 ± 3.1
4-chlorobenzoic acid	Andrews *et al.*[136]	512.9	32.3 ± 1.6	19.7 ± 3.0			
	Sabbah and Hirtz[123]	513.5	34.3 ± 1.7	21.6 ± 3.1			
	Tan *et al.*[168]	512.3	(13.5)[e]				
	Ribeiro da Silva *et al.*[125]	512.5	30.9 ± 1.4	18.3 ± 3.0			
	Average	512.8	32.5 ± 1.7	19.8 ± 3.1	104.9 ± 1.3	85.1 ± 3.4	7.2 ± 3.5
2-bromobenzoic acid	Holdiness[131]	–[d]	23.0 ± 1.2	15.7 ± 1.9			
	Tan and Sabbah[121]	422.4	24.5 ± 1.2	17.2 ± 1.9			
	Ribeiro da Silva *et al.*[125]	421.6	24.8 ± 1.2	17.5 ± 1.9			
	Average	422.0	24.1 ± 1.2	16.8 ± 1.9	108.3 ± 1.4	91.5 ± 2.4	13.6 ± 2.6
3-bromobenzoic acid	Tan and Sabbah[121]	429.7	21.3 ± 1.8	13.6 ± 2.4			
	Ribeiro da Silva *et al.*[125]	430.1	24.9 ± 1.8	17.1 ± 2.4			
	Average	429.9	23.1 ± 1.8	15.3 ± 2.4	104.9 ± 1.4	89.6 ± 2.8	11.7 ± 3.0
4-bromobenzoic acid	Tan and Sabbah[121]	527.6	28.7 ± 1.4	15.2 ± 3.1			
	Ribeiro da Silva *et al.*[125]	526.3	30.9 ± 1.5	17.5 ± 3.1			
	Zherikova *et al.*[130]	526.9	30.9 ± 1.5	17.4 ± 3.1			
	Average	526.9	30.2 ± 1.5	16.7 ± 3.1	107.1 ± 1.7	90.4 ± 3.5	12.5 ± 3.7
2-iodobenzoic acid	Holdiness[131]	–[d]	26.2 ± 1.3	18.2 ± 2.1			
	Tan and Sabbah[122]	435.1	(21.4)[e]				
	Zherikova *et al.*[129]	434.5	27.6 ± 1.4	19.6 ± 2.1			
	Average	434.8	26.9 ± 1.4	18.9 ± 2.1	111.5 ± 2.0	92.6 ± 2.9	14.7 ± 3.1
3-iodobenzoic acid	Tan and Sabbah[122]	460.4	28.7 ± 1.4	19.1 ± 2.4			
	Zherikova *et al.*[129]	458.9	27.7 ± 1.4	18.2 ± 2.3			
	Average	459.7	28.2 ± 1.4	18.7 ± 2.4	109.4 ± 1.5	90.7 ± 2.8	12.8 ± 3.1
4-iodobenzoic acid	Tan and Sabbah[122]	543.7	35.2 ± 1.8	20.7 ± 3.4			
	Sabbah and El Watik[169]	544.7	33.9 ± 1.7	19.4 ± 3.4			
	Zherikova *et al.*[129]	543.9	33.7 ± 1.7	19.2 ± 3.3			
	Average	544.1	34.3 ± 1.8	19.8 ± 3.4	111.4 ± 1.4	91.6 ± 3.7	13.7 ± 3.8

[a]Values of $\Delta_{cr}^g H_m^o (T_{ref})$ are repeated from Table 1 for benzoic acid and Table 14 for halobenzoic acids.
[b]Values of $\Delta_l^g H_m^o (T_{ref})$ (column 7) were derived as the difference between values in columns 6 and 5.
[c]Values of $\Delta_l^g H_{inc}^o (T_{ref})$ (column 8) were calculated as the difference between $\Delta_l^g H_m^o (T_{ref})$ (column 7) for the particular halobenzoic acid and that for benzoic acid (row 1 of column 7).
[d]Holdiness[131] did not report a normal melting temperature with his results.
[e]Highly inconsistent value not included in the average.

method of Chickos *et al.*[163] has a reported uncertainty of ~50 J K^{-1} mol^{-1} (twice the standard error), which for benzoic acid is 35% of the heat capacity of the crystal at T = 298.15 K.[33] For these reasons, we have chosen not to attempt the correlation of enthalpies of sublimation for halobenzoic acids, but instead we derive enthalpies of vaporization with the purpose of demonstrating trends for compound families.

The enthalpies of vaporization $\Delta_l^g H_m^o$ for halobenzoic acids were derived by combining the evaluated enthalpies of sublimation $\Delta_{cr}^g H_m^o$ (Table 14) and enthalpies of fusion $\Delta_{cr}^l H_m^o$ at a reference temperature T_{ref} with the thermodynamic relationship

$$\Delta_l^g H_m^o(T_{ref}) = \Delta_{cr}^g H_m^o(T_{ref}) - \Delta_{cr}^l H_m^o(T_{ref}), \quad (10)$$

where the reference temperature T_{ref} is 298.15 K. Enthalpies of fusion $\Delta_{cr}^l H_m^o$ (T_m) measured at the normal melting temperature T_m were adjusted to $\Delta_{cr}^l H_m^o$ (T_{ref}) with the assumption that the difference between the heat capacity of the crystal and liquid was the same as that for benzoic acid (58.9 J K^{-1} mol^{-1})[33] and was independent of temperature. The relative expanded uncertainty U_r (~0.95 level of confidence) for these enthalpy increments H_{adj} was estimated conservatively to be $U_r(H_{adj}) = 0.2$.

Normal melting temperatures T_m and enthalpies of fusion $\Delta_{cr}^l H_m^o$ (T_m) have been reported for fluoro-,[129,165,166] chloro-,[123,125,131,136,167,168] bromo-,[121,125,130,131] and iodobenzoic acids.[122,129,131,169] Most of these results were obtained with a DSC. Authors of such studies often report uncertainties of an undefined nature that are as small as a few hundredths of a Kelvin for T_m and less than 0.5% for $\Delta_{cr}^l H_m^o$. Based on our experience, such uncertainties are much too small, and, here, we have assigned an expanded uncertainty of $U(T_m) = 0.5$ K and relative expanded uncertainty $U_r(\Delta_{cr}^l H_m^o)$ equal to 5% for values obtained with a DSC (0.95 level of confidence). A scan of the reported values given in Table 20 shows that these uncertainties roughly represent the variation in results obtained by different research groups. Experimental values listed for benzoic acid are those of Furukawa *et al.*,[33] whose values were determined with high-precision adiabatic calorimetry and were later confirmed by Andon and Connett.[170]

Literature values for the normal melting temperature T_m and corresponding enthalpy of fusion $\Delta_{cr}^l H_m^o$ (T_m), the enthalpy of fusion adjusted to T = 298.15 K, the enthalpy of sublimation at T = 298.15 K (repeated from Table 14) $\Delta_{cr}^g H_m^o$ (298.15 K), and the derived enthalpy of vaporization at T = 298.15 K for benzoic acid and halobenzoic acids are given in Table 20. Values shown in brackets are inconsistent with other studies and were not used in the calculation of the average. Column 8 of Table 20 represents the increments in the enthalpy of vaporization observed on replacement of one hydrogen in the aromatic ring of benzoic acid with a halogen. An analogous evaluation can be made for halonaphthalenes, as described in the following paragraphs.

The enthalpy of fusion and heat capacities for the condensed phases of naphthalene have been measured with high-precision adiabatic calorimetry by McCullough *et al.*[171] and Chirico *et al.*,[172] and adjustment of the enthalpy of fusion to T = 298.15 K is achieved readily with heat capacities for the crystal and liquid reported there. The enthalpy of sublimation for naphthalene at T = 298.15 K was evaluated by Chirico *et al.*[137] through enforcement of thermodynamic consistency for the ideal-gas and condensed states. All of the 1-halonaphthalenes are liquids at T = 298.15 K and vapor pressures in this region for 1-fluoro, 1-chloro, and 1-bromonaphthalene have been measured with the transpiration method by Verevkin.[157] Enthalpies of vaporization were derived here, as described earlier for enthalpies of sublimation for halobenzoic acids.

All of the 2-halonaphthalenes are solids at T = 298.15 K, and conversion of measured enthalpies of sublimation to enthalpies of vaporization is complicated by the presence of a complex phase behavior between the melting temperatures (T_m ~ 330 K) and T = 298.15 K in 2-chloronaphthalene[162] and 2-bromonaphthalene.[173] 2-Chloronaphthalene was studied with adiabatic calorimetry by van Miltenburg and Verdonk, and these results were used to adjust the enthalpy of sublimation, derived with results of the transpiration study by Verevkin,[157] to yield the enthalpy of vaporization at T = 298.15 K. Phase changes in 2-bromonaphthalene between the melting temperature ($T_m \approx 330$ K) and T = 298.15 K were studied by Chanh *et al.*[173] with a DSC, and they report an enthalpy of fusion (14.4 kJ mol^{-1}) and excess enthalpy of ~3.5 kJ mol^{-1} for the temperature range 290–320 K. We combined these values to estimate the crystal-to-liquid enthalpy change at T = 298.15 K [(18 ± 2) kJ mol^{-1}]. The enthalpy of sublimation of 2-bromonaphthalene was determined with vacuum DC by Ribeiro da Silva *et al.*[84] and transpiration measurements by Verevkin,[157] and these are seen to be in good agreement (Table 21, column 6).

Details of the evaluation of the enthalpy of vaporization at T = 298.15 K for naphthalene and halonaphthalenes are given in Table 21. Column 8 of Table 21 lists the increments in the enthalpy of vaporization observed on replacement of a hydrogen in naphthalene with a halogen. There is insufficient experimental data available to complete a similar analysis for 1- and 2-fluoronaphthalene and 2-iodonaphthalene, although Monte *et al.*[174] referred to unpublished results from a master's thesis at their university that may eventually become available.

The trend in the derived enthalpies of vaporization at T = 298.15 K with halogen substitution of an aromatic ring for halobenzoic acids (Table 20, column 7), halobenzenes (Table 15, column 4), and halonaphthalenes (Table 21, column 7) is shown graphically in Fig. 4. Each of the four families of halogen compounds (F, Cl, Br, and I) is grouped on the horizontal axis. The vertical axis represents the difference between the enthalpy of vaporization at T = 298.15 K for the halogenated compound relative to that for the unsubstituted parent compound (benzoic acid, benzene, or naphthalene). The plotted differences for halobenzoic acids and halonaphthalenes are listed in column 8 of Tables 20 and 21, respectively.

TABLE 21. Normal melting temperatures T_m, enthalpies of fusion $\Delta_{cr}^l H_m^o (T_m)$, enthalpies of fusion adjusted to the reference temperature $\Delta_{cr}^l H_m^o (T_{ref})$, enthalpies of sublimation adjusted to the reference temperature $\Delta_{cr}^g H_m^o (T_{ref})$, derived enthalpies of vaporization at the reference temperature $\Delta_l^g H_m^o (T_{ref})$, and the difference in the enthalpy of vaporization at the reference temperature between that for the particular halonaphthalene and that for naphthalene $\Delta_l^g H_{inc}^o (T_{ref})$, where $T_{ref} = 298.15$ K (uncertainties represent 0.95 level of confidence)

Compound	Source	T_m/(K)	$\Delta_{cr}^l H_m^o (T_m)$/ (kJ mol^{-1})	$\Delta_{cr}^l H_m^o (T_{ref})$/ (kJ mol^{-1})	$\Delta_{cr}^g H_m^o (T_{ref})$/ (kJ mol^{-1})	$\Delta_l^g H_m^o (T_{ref})$/ (kJ mol^{-1})[a]	$\Delta_l^g H_{inc}^o (T_{ref})$/ (kJ mol^{-1})[b]
1	2	3	4	5	6	7	8
Naphthalene	McCullough et al.[171]	353.39	18.98 ± 0.02				
	Chirico et al.[172]	353.37	18.99 ± 0.02				
	Chirico et al.[137]				72.7 ± 0.4[c]		
	Evaluated	353.38	18.99 ± 0.02	18.04 ± 0.04	72.7 ± 0.4	54.7 ± 0.4	
1-chloronaphthalene	Verevkin[157]	–[d]	–	–	–	61.4 ± 4.6	
	Evaluated					61.4 ± 4.6	6.7 ± 4.6
2-chloronaphthalene	Khanna et al.[158]	332.0	14.7 ± 0.7				
	Miltenburg and Verdonk[162]	331.2	14.0 ± 0.1	14.2 ± 0.1			
	Verevkin[157]				76.3 ± 0.6		
	Evaluated	331.2	14.0 ± 0.1	14.2 ± 0.1	76.3 ± 0.6	62.1 ± 0.6	7.4 ± 0.7
1-bromonaphthalene	Verevkin[157]	–[d]	–	–	–	62.2 ± 1.0	
	Evaluated					62.2 ± 1.0	7.5 ± 1.1
2-bromonaphthalene	Chanh et al.[173]	329	(14.4 + 3.5) ± 0.9[e]	18 ± 2			
	Khanna et al.[158]	332	12[f]				
	Ribeiro da Silva et al.[84]				81.2 ± 2.0		
	Verevkin[157]				81.6 ± 1.6		
	Evaluated	330	17.9 ± 0.9	18 ± 2	81.4 ± 1.2	63.4 ± 2.3	8.7 ± 2.4
1-iodonaphthalene	Verevkin[157]	–[d]	–	–	–	67.8 ± 0.3	
	Evaluated					67.8 ± 0.3	13.1 ± 0.5

[a]Values of $\Delta_l^g H_m^o (T_{ref})$ (column 7) were derived as the difference between values in columns 6 and 5.

[b]Values of $\Delta_l^g H_{inc}^o (T_{ref})$ (column 8) were calculated as the difference between $\Delta_l^g H_m^o (T_{ref})$ (column 7) for the particular halonaphthalene and that for naphthalene (row 1 of column 7).

[c]The value of $\Delta_{cr}^g H_m^o (T_{ref})$ for naphthalene is based on a thermodynamic consistency analysis.[137]

[d]The compound is a liquid at T = 298.15 K, so only the measured enthalpy of vaporization is provided.

[e]Chanh et al.[173] reported an enthalpy of fusion, plus some additional excess enthalpy (3.5 kJ mol^{-1}) in the temperature range (298.15 K < (T/K) < T_m).

[f]Khanna et al.[158] reported an enthalpy of fusion with no mention of additional excess enthalpy at lower temperatures. This result was not considered further in the evaluation.
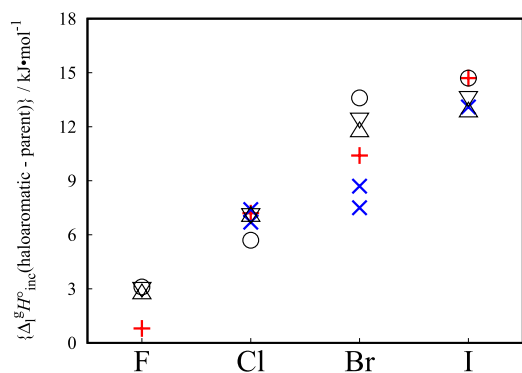
FIG. 4. Enthalpy increments for change in the enthalpy of vaporization on replacement of one hydrogen in the parent aromatic compound (benzene, benzoic acid, or naphthalene) with one halogen. Results for specific halogens are distributed evenly on the unitless horizontal axis. +, halobenzenes; ×, halonaphthalenes; ○, 2-halobenzoic acids; △, 3-halobenzoic acids; ▽, 4-halobenzoic acids.

uncertainty ($\sim$2 kJ mol^{-1}) for the increments listed in column 8 of Tables 20 and 21.

One of the possible group-additivity methods for the prediction of enthalpies of vaporization for haloaromatics was published recently by Monte et al.[174] The monotonic nature of the trend shown in Fig. 4 implies that any numerical attribute that varies smoothly with the halogen size could be used to develop an empirical correlation. Monte et al.[174] used excess atomic volume and electron affinity, where the excess is relative to the hydrogen that is replaced. Application to a wide variety of species is limited by the need for reliable results for parent (unsubstituted) compounds that are used to "anchor" the correlations. It can be inferred from Fig. 4 that the limit of uncertainty for any such correlation is near 3 kJ mol^{-1} (i.e., the vertical data scatter for a given halogen) and this is what is seen in the tables provided by Monte et al.,[174] provided an experiment-based enthalpy of vaporization for the parent compound is available.

10. Evaluated Enthalpies of Formation for the Halobenzoic Acids for the Crystal, Liquid, and Gas Phases

Standard enthalpies of formation $\Delta_f H_m^o$ for the crystal, liquid, and gas phases of halobenzoic acids evaluated in this

Figure 4 shows a clear trend in the enthalpy of vaporization with an increased size of the halogen atom, where the largest scatter ($\pm$3 kJ mol^{-1}) is seen for the bromo compounds. It is also apparent from the plot that the position of the halogen on the ring of benzoic acid (i.e., 2-, 3-, or 4-) does not affect the enthalpy of vaporization, as all values for a given halogen lie within a range of 2 kJ mol^{-1}, which is within the experimental

TABLE 22. Standard enthalpies of formation for the crystal $\Delta_f H^o_m$ (cr), ideal-gas $\Delta_f H^o_m$ (g), and liquid $\Delta_f H^o_m$ (l) evaluated in this research for halobenzoic acids at the reference temperature $T = 298.15$ K and pressure $p = 100$ kPa[a]

Compound	$\Delta_f H^o_m$ (cr)	Source	$\Delta_f H^o_m$ (g)	Source	$\Delta_f H^o_m$ (l)	Source
	1		2		3	
2-fluorobenzoic acid	−568.3 ± 1.2	b	−472.9 ± 2.3	c	−553.9 ± 1.9	d
3-fluorobenzoic acid	−582.5 ± 1.5	b	−489.2 ± 2.2	c	−569.8 ± 2.1	d
4-fluorobenzoic acid	−585.4 ± 0.6	b	−492.3 ± 1.3	c	−573.3 ± 2.3	d
2-chlorobenzoic acid	−404.8 ± 1.0	b	−302.0 ± 1.7	c	−385.6 ± 2.1	d
3-chlorobenzoic acid	−423.9 ± 1.2	b	−322.5 ± 2.4	c	−407.4 ± 2.2	d
4-chlorobenzoic acid	−428.8 ± 0.4	b	−323.9 ± 1.5	c	−409.0 ± 3.1	d
2-bromobenzoic acid	**−355.9 ± 2.9**	e	**−247.6 ± 2.6**	f	**−339.1 ± 3.5**	d
3-bromobenzoic acid	**−374.5 ± 2.9**	e	**−269.6 ± 2.6**	f	**−359.2 ± 3.8**	d
4-bromobenzoic acid	−378.9 ± 1.1	b	−271.8 ± 2.0	c	−362.2 ± 3.3	d
2-iodobenzoic acid	−301.6 ± 1.1	b	−190.1 ± 2.3	c	−282.7 ± 2.4	d
3-iodobenzoic acid	**−322.2 ± 2.9**	e	**−212.8 ± 2.5**	f	**−303.5 ± 3.8**	d
4-iodobenzoic acid	**−325.4 ± 2.8**	e	**−214.0 ± 2.5**	f	**−305.6 ± 4.4**	d

[a]All uncertainties in the table represent the expanded uncertainty with 0.95 level of confidence. Values shown in bold represent compounds for which inconsistencies are observed between experimental and computed enthalpies of reaction described in Table 17.

[b] $\Delta_f H^o_m$ (cr) derived as the weighted average of experimental enthalpies of combustion reported in sources listed in Table 14.

[c] $\Delta_f H^o_m$ (g) derived as the sum of column 1 and the enthalpy of sublimation $\Delta_{cr}^g H^o_m$ at the temperature $T = 298.15$ K listed in Table 14 and based on the experimental data sources given there.

[d] $\Delta_f H^o_m$ (l) derived as the sum of column 1 and the enthalpy of fusion $\Delta_{cr}^l H^o_m$ at the temperature $T = 298.15$ K listed in Table 20 (column 5) and based on the experimental data sources given there.

[e] $\Delta_f H^o_m$ (cr) derived as column 2 minus the enthalpy of sublimation $\Delta_{cr}^g H^o_m$ at the temperature $T = 298.15$ K listed in Table 14 and based on the experimental data sources given there.

[f] $\Delta_f H^o_m$ (g) calculated with the computed enthalpy of reaction of the homodesmic reaction (Table 17, column 7) and the evaluated values of $\Delta_f H^o_m$ (g) for the reaction components: halobenzene, benzoic acid, and benzene (Table 17, columns 2, 3, and 4).

research are listed in Table 22. Values shown in normal type (2-, 3-, 4-fluorobenzoic acids, 2-, 3-, 4-chlorobenzoic acids, 4-bromobenzoic acid, and 2-iodobenzoic acid) were derived entirely with the experimental thermodynamic properties, critically evaluated as described in the text, and validated with results of computational chemistry through the homodesmic reaction given in Eq. (8).

Values shown in bold (2- and 3-bromobenzoic acids and 3- and 4-iodobenzoic acids) represent compounds for which inconsistencies are observed (Table 17) between $\Delta_r H^o_m$(g, expt) and $\Delta_r H^o_m$(g, comp) for the homodesmic reaction [Eq. (8)]. For these compounds, $\Delta_f H^o_m$ (g) was evaluated with the computed enthalpy of reaction of the homodesmic reaction (Table 17, column 7) and the critically evaluated values of $\Delta_f H^o_m$ (g) for the reaction components: halobenzene, benzoic acid, and benzene (Table 17, columns 2, 3, and 4),

$$\Delta_f H^o_m(\text{halobenzoic acid, g}) = \Delta_r H^o_m(\text{g, comp})$$
$$- \Delta_f H^o_m(\text{benzene, g, expt}) + \Delta_f H^o_m(\text{halobenzene, g, expt})$$
$$+ \Delta_f H^o_m(\text{benzoic acid, g, expt}). \qquad (11)$$

The enthalpy of formation of the crystal $\Delta_f H^o_m$ (cr) was calculated from this value by subtraction of the evaluated enthalpy of sublimation at $T = 298.15$ K (Table 14). As described earlier, values of $\Delta_f H^o_m$ (g) used for halobenzenes in these calculations were those evaluated in the Active Thermochemical Tables.[150–152] If the $\Delta_f H^o_m$ (g) values for halobenzenes evaluated by Cox and Pilcher were used (see Table 15), the uncertainties for $\Delta_f H^o_m$ (g) of the 2- and 3-

bromobenzoic acid and 3- and 4-iodobenzoic acids would be only ~2 kJ mol^{-1} larger.

$$\Delta_f H^o_m(\text{halobenzoic acid, cr}) = \Delta_f H^o_m(\text{halobenzoic acid, g})$$
$$- \Delta_{cr}^g H^o_m(298.15 \text{ K}) \qquad (12)$$

The enthalpy of formation of the liquid $\Delta_f H^o_m$ (l) was, in turn, calculated from this value by the addition of the evaluated enthalpy of fusion at $T = 298.15$ K (Table 20, column 5).

In Table 22, the recommended values for the enthalpy of formation for the ideal-gas state of halobenzoic acids show smoothly and consistently varying increments across each halogen series. The enthalpy increment between the 2- and 3-isomer is approximately 5 kJ mol^{-1} less for the fluoro series than for the other halobenzoic acids. The origin of this difference is now understood based on the computations and conformational analysis described in this article.

11. Conclusions

Thermodynamic properties for the twelve mono-halobenzoic acids were critically evaluated. Properties included enthalpies of combustion for the crystal phase, enthalpies of formation for the crystal, liquid, and gas phases, enthalpies of sublimation at the reference temperature $T = 298.15$ K, enthalpies of vaporization at the reference temperature $T = 298.15$ K, normal melting temperatures, and enthalpies of fusion. As part of this work, thermodynamic properties were also critically evaluated for 1- and 2-chloro-, bromo-, and iodohalonaphthalenes. Thermodynamic

properties for homodesmic reactions for the ideal-gas phase involving all of the halobenzoic acids and halonaphthalenes were computed with the recently proposed DLPNO-CCSD(T) approach[23] optimized with critically evaluated experiment-based gas-phase properties for benzoic acid. COOH torsions were addressed as hindered one-dimensional quantum rotors.

Comparison of enthalpies of reaction based on the experiment and computation for the homodesmic reactions revealed multiple inconsistencies in the experimental data, including large inconsistencies in reported enthalpies of combustion for 2- and 3-bromobenzoic acids and smaller, but significant, inconsistencies for 3- and 4-iodobenzoic acids. The reported enthalpy of combustion of 2-chloronaphthalene was also shown to be anomalous.

4-Iodobenzoic acid has been recommended as a reference material for the combustion of iodine containing compounds,[26] but the results of the present work indicate that more works in the field of organoiodine compounds are needed. Most reported enthalpies of combustion for iodine-containing compounds are from a single source,[117] based on results originally reported in a thesis by Karlsson[120] in 1941. In the present work, we find these values to be in agreement (Table 9) with more modern experimental results for iodobenzoic acids as well as with the computations of this research for 1- and 2-iodonaphthalene (Table 19). Results from this source, however, are not universally consistent, as shown by Verevkin et al.,[175] who demonstrated that the enthalpies of combustion for 1,3- and 1,4-diiodobenzene reported by Smith[117] are inconsistent by more than 20 kJ mol^{-1}, which far exceeds the expected experimental uncertainty of a few kilojoules per mole. We concur with the recommendation of Ribeiro da Silva et al.[118] that additional research into the thermodynamics of iodine-containing compounds is needed.

In this work, computational chemistry is shown to be a valuable aid in the critical assessment of thermodynamic properties for organic compounds by providing an independent and validated path for the evaluation of gas-phase properties. Enthalpies of reaction computed for the homodesmic reactions selected in this research were, generally, in excellent agreement (i.e., within the experimental uncertainty) with results based entirely on the experiment. This agreement and the observed smooth trends in reaction enthalpies with alternative halogen substitution allowed confident identification of inconsistent experimental results. In future work, this type of analysis will be extended to other compound types, with the goal of developing an algorithm that can be applied across numerous compounds to highlight inconsistencies in evaluated thermodynamic properties with limited user (human) intervention, as per the goals set for the NIST ThermoData Engine.[1–8]

Acknowledgments

12. Appendix

TABLE 23. Heat capacities, standard entropies, and enthalpy increments of benzoic acid in the ideal-gas state computed with the methods described in the text ($p° = 100$ kPa)

T (K)	$C_{p,m}^o$/(J K^{-1} mol^{-1})	S_m^o/(J K^{-1} mol^{-1})	$[H_m^o(T) - H_m^o(0)]$/ (kJ mol^{-1})
150.0	69.03	292.5	7.331
200.0	86.94	314.8	11.22
250.0	106.6	336.3	16.05
298.2	126.0	356.7	21.66
300.0	126.8	357.5	21.89
350.0	146.2	378.5	28.72
400.0	164.2	399.2	36.49
450.0	180.6	419.5	45.11
500.0	195.2	439.3	54.52
600.0	219.7	477.2	75.31
700.0	239.2	512.5	98.29
800.0	254.7	545.5	123.0
900.0	267.5	576.3	149.1
1000.0	278.1	605.0	176.4

TABLE 24. Comparison of experimental and computed molecular rotational constants (GHz)

		Model	
		B3LYP/	DF-MP2/
Conformer	Experimental[a]	def2-QZVPD	def2-QZVPP
Benzoic acid			
syn	3.882	3.903	3.894
	1.210	1.229	1.236
	0.923	0.935	0.938
2-fluorobenzoic acid			
anti-syn	2.294	2.301	2.299
	1.213	1.216	1.220
	0.794	0.794	0.796
syn-syn	2.272	2.277	2.278
	1.213	1.216	1.222
	0.792	0.793	0.796
anti-anti	2.285	2.293	2.292
	1.211	1.214	1.220
	0.792	0.794	0.796
3-fluorobenzoic acid			
anti-syn	2.636	2.650	2.652
	0.937	0.938	0.943
	0.691	0.693	0.696
syn-syn	2.685	2.699	2.696
	0.927	0.927	0.933
	0.689	0.690	0.693
4-fluorobenzoic acid			
syn	3.857	3.888	3.882
	0.775	0.775	0.779
	0.645	0.646	0.649

[a]For benzoic acid, values are computed from the geometry derived from gas-phase electron diffraction measurements reported by Aarset et al.[75] Values for fluorobenzoic acids were reported by Daly et al.,[76] based on microwave spectra.

TABLE 25. Heat capacities, standard entropies, and enthalpy increments for halobenzoic acids in the ideal-gas state computed with the methods described in the text ($p° = 100$ kPa)[a]

T (K)	$C_{p,\mathrm{m}}^{\mathrm{o}}$/(J K^{-1} mol^{-1})	$S_{\mathrm{m}}^{\mathrm{o}}$/(J K^{-1} mol^{-1})	$[H_{\mathrm{m}}^{\mathrm{o}}(T) - H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})]$/(kJ mol^{-1})	$x_{\mathrm{conformer}}$[b]
2-fluorobenzoic acid				
150.0	80.16	310.14	-16.23	0.993
200.0	99.68	336.15	-11.74	0.982
250.0	120.01	360.85	-6.25	0.969
298.15	139.36	383.87	0.00	0.956
300.0	140.09	384.74	0.26	0.956
350.0	159.07	407.95	7.74	0.943
400.0	176.45	430.48	16.14	0.932
450.0	192.05	452.29	25.35	0.922
500.0	205.90	473.33	35.31	0.913
600.0	228.99	513.12	57.10	0.898
700.0	247.17	549.92	80.94	0.886
800.0	261.74	583.97	106.41	0.876
900.0	273.64	615.56	133.20	0.867
1000.0	283.51	644.95	161.07	0.860
3-fluorobenzoic acid				
150.0	77.47	309.51	-15.98	
200.0	97.71	334.54	-11.60	
250.0	118.67	358.59	-6.20	
298.15	138.53	381.20	0.00	
300.0	139.28	382.06	0.26	
350.0	158.74	405.01	7.71	
400.0	176.58	427.39	16.10	
450.0	192.61	449.13	25.34	
500.0	206.84	470.18	35.33	
600.0	230.53	510.07	57.25	
700.0	249.07	547.06	81.27	
800.0	263.80	581.32	106.94	
900.0	275.72	613.10	133.94	
1000.0	285.52	642.67	162.01	
4-fluorobenzoic acid				
150.0	77.21	303.95	-15.94	
200.0	97.45	328.90	-11.58	
250.0	118.44	352.89	-6.18	
298.15	138.30	375.46	0.00	
300.0	139.04	376.32	0.26	
350.0	158.48	399.23	7.70	
400.0	176.29	421.58	16.08	
450.0	192.31	443.28	25.30	
500.0	206.54	464.30	35.28	
600.0	230.27	504.14	57.17	
700.0	248.88	541.09	81.16	
800.0	263.69	575.33	106.82	
900.0	275.69	607.10	133.81	
1000.0	285.54	636.67	161.88	
2-chlorobenzoic acid				
150.0	80.79	325.05	-16.37	0.999
200.0	100.73	351.13	-11.84	0.996
250.0	121.06	375.99	-6.29	0.990
298.15	140.22	399.18	0.00	0.983
300.0	140.94	400.06	0.26	0.982
350.0	159.67	423.45	7.78	0.973
400.0	176.83	446.13	16.20	0.962
450.0	192.26	468.08	25.44	0.951
500.0	205.98	489.25	35.41	0.939
600.0	228.92	529.25	57.21	0.917
700.0	247.05	566.23	81.06	0.897
800.0	261.61	600.43	106.54	0.878
900.0	273.54	632.15	133.34	0.860
1000.0	283.44	661.66	161.24	0.844
3-chlorobenzoic acid				
150.0	82.11	318.28	-16.61	
200.0	102.17	344.63	-12.00	
250.0	122.75	369.63	-6.38	
298.15	142.22	392.93	0.00	

TABLE 25. Heat capacities, standard entropies, and enthalpy increments for halobenzoic acids in the ideal-gas state computed with the methods described in the text ($p^\circ = 100$ kPa)[a]—Continued

T (K)	$C_{p,m}^{o}$/(J K^{-1} mol^{-1})	S_m^o/(J K^{-1} mol^{-1})	$[H_m^o(T) - H_m^o(298.15\text{ K})]$/(kJ mol^{-1})	$x_{conformer}$[b]
300.0	142.95	393.81	0.26	
350.0	162.05	417.30	7.89	
400.0	179.55	440.10	16.44	
450.0	195.28	462.17	25.82	
500.0	209.25	483.49	35.94	
600.0	232.47	523.78	58.07	
700.0	250.65	561.03	82.27	
800.0	265.10	595.48	108.08	
900.0	276.80	627.41	135.20	
1000.0	286.42	657.08	163.37	
4-chlorobenzoic acid				
150.0	81.73	312.90	−16.57	
200.0	101.87	339.15	−11.98	
250.0	122.52	364.10	−6.37	
298.15	142.04	387.36	0.00	
300.0	142.77	388.24	0.26	
350.0	161.87	411.70	7.89	
400.0	179.37	434.47	16.42	
450.0	195.10	456.53	25.79	
500.0	209.07	477.82	35.90	
600.0	232.32	518.08	58.02	
700.0	250.54	555.32	82.20	
800.0	265.04	589.75	108.01	
900.0	276.78	621.67	135.12	
1000.0	286.44	651.35	163.29	
2-bromobenzoic acid				
150.0	85.27	334.92	−16.80	
200.0	103.96	361.99	−12.07	
250.0	123.39	387.27	−6.39	
298.15	141.96	410.60	0.00	
300.0	142.66	411.48	0.26	
350.0	160.97	434.86	7.86	
400.0	177.82	457.47	16.34	
450.0	193.02	479.31	25.61	
500.0	206.56	500.36	35.61	
600.0	229.21	540.10	57.44	
700.0	247.11	576.83	81.29	
800.0	261.51	610.80	106.75	
900.0	273.28	642.31	133.51	
1000.0	283.06	671.62	161.34	
3-bromobenzoic acid				
150.0	85.16	328.53	−16.96	
200.0	104.74	355.69	−12.21	
250.0	124.87	381.23	−6.48	
298.15	143.99	404.86	0.00	
300.0	144.71	405.76	0.27	
350.0	163.51	429.49	7.98	
400.0	180.79	452.47	16.59	
450.0	196.34	474.68	26.03	
500.0	210.16	496.10	36.20	
600.0	233.17	536.53	58.41	
700.0	251.20	573.89	82.67	
800.0	265.54	608.40	108.53	
900.0	277.16	640.37	135.68	
1000.0	286.72	670.08	163.89	
4-bromobenzoic acid				
150.0	84.73	323.24	−16.92	
200.0	104.43	350.30	−12.19	
250.0	124.65	375.77	−6.47	
298.15	143.82	399.37	0.00	
300.0	144.54	400.26	0.27	
350.0	163.36	423.98	7.97	
400.0	180.64	446.94	16.58	
450.0	196.19	469.13	26.00	
500.0	210.01	490.53	36.17	

TABLE 25. Heat capacities, standard entropies, and enthalpy increments for halobenzoic acids in the ideal-gas state computed with the methods described in the text ($p° = 100$ kPa)[a]—Continued

T (K)	$C_{p,m}^{o}$/(J K^{-1} mol^{-1})	S_{m}^{o}/(J K^{-1} mol^{-1})	$[H_{m}^{o}(T) - H_{m}^{o}(298.15$ K)]/(kJ mol^{-1})	$x_{conformer}$[b]
600.0	233.04	530.94	58.37	
700.0	251.10	568.28	82.61	
800.0	265.49	602.78	108.47	
900.0	277.14	634.74	135.62	
1000.0	286.73	664.46	163.82	
2-iodobenzoic acid				
150.0	89.98	339.24	−17.37	
200.0	108.27	367.62	−12.42	
250.0	126.88	393.78	−6.54	
298.15	144.76	417.66	0.00	
300.0	145.43	418.56	0.27	
350.0	163.19	442.32	7.99	
400.0	179.63	465.20	16.57	
450.0	194.51	487.23	25.93	
500.0	207.81	508.43	35.99	
600.0	230.13	548.37	57.93	
700.0	247.82	585.23	81.86	
800.0	262.07	619.28	107.38	
900.0	273.74	650.84	134.19	
1000.0	283.44	680.20	162.06	
3-iodobenzoic acid				
150.0	86.97	336.29	−17.15	
200.0	106.16	363.91	−12.33	
250.0	125.99	389.73	−6.52	
298.15	144.91	413.54	0.00	
300.0	145.62	414.44	0.27	
350.0	164.26	438.31	8.02	
400.0	181.42	461.38	16.67	
450.0	196.88	483.66	26.14	
500.0	210.63	505.13	36.33	
600.0	233.54	545.64	58.59	
700.0	251.49	583.04	82.87	
800.0	265.79	617.59	108.76	
900.0	277.37	649.59	135.94	
1000.0	286.90	679.32	164.17	
4-iodobenzoic acid				
150.0	86.56	331.06	−17.11	
200.0	105.88	358.58	−12.31	
250.0	125.81	384.35	-6.52	
298.15	144.78	408.14	0.00	
300.0	145.49	409.03	0.27	
350.0	164.16	432.88	8.02	
400.0	181.32	455.94	16.66	
450.0	196.78	478.20	26.12	
500.0	210.53	499.66	36.31	
600.0	233.45	540.16	58.55	
700.0	251.42	577.55	82.83	
800.0	265.74	612.09	108.72	
900.0	277.34	644.09	135.89	
1000.0	286.90	673.82	164.12	

[a]Expanded uncertainties U (0.95 level of confidence) for all properties Φ are estimated to be $U(\Phi) = 0.002 \cdot \Phi$ up to ~500 K and increasing up to $0.02 \cdot \Phi$ at 1000 K.
[b]$x_{conformer}$ is the computed mole fraction of the most stable conformer for 2-fluorobenzoic and 2-chlorobenzoic acids. For all other compounds $x_{conformer} = 1$ at all temperatures.
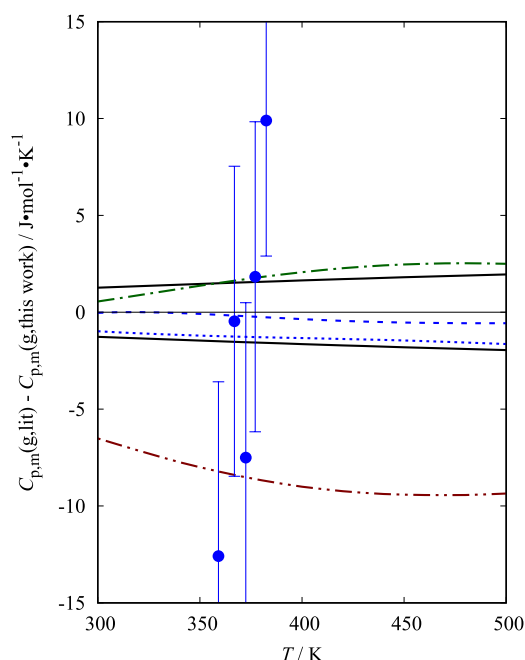
FIG. 5. Deviations relative to computed heat capacities of this research for the ideal-gas state of benzoic acid. (B3LYP/def2-QZVPD with the selected dual scaling factors and hindered rotor treatment described in the text.) Blue dashed line (- - -)— computed by Santos *et al.*[60] with an "isodesmic reaction schema"; black lines (——)—estimated uncertainties $(0.01 \cdot C_{p,m}^o)$ for values recommended by Santos *et al.*;[60] dotted blue line (· · ·)—computed statistically by Santos *et al.*[60] with experimental vibrational frequencies, when available, supplemented with frequencies predicted with (B3LYP/6-311++G(d,p)) theory; green dashed-dotted line (· —· —·)—NIST Web Thermo Tables (WTT), NIST Standard Reference Subscription Database 3—Professional Edition, Version 2-2012-1-Pro (Accessed September 2, 2016); blue filled circle (•)—experimental values reported by Santos *et al.*[60] with uncertainties recalculated in this research, as described in the text; brown dashed-double-dotted line (· —·· —·)—Burcat and Ruscic.[69,70] Deviations for values listed by Stull *et al.*[67] are large and exceed the range shown in the plot. Values listed by Stull *et al.*[67] were also reproduced by Frenkel *et al.*[68]

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