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Experimental and Computational Thermochemical Study of the Three Monoiodophenol Isomers

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Ⓢ *Supporting Information*

ABSTRACT: The present work reports the values of the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed phase of the three isomers of monoiodophenol derived from the standard molar energies of combustion, in oxygen, to yield $CO_2(g)$, $I_2(cr)$, and $H_2O(l)$, at $T = 298.15$ K, measured by rotating-bomb combustion calorimetry, as well as the values of the standard molar enthalpies of sublimation, at $T = 298.15$ K, determined using high-temperature Calvet microcalorimetry. Combining the former two experimental quantities, the standard molar enthalpies of formation in the gaseous phase were derived, at $T = 298.15$ K: $\Delta_f H_m^\circ$(2-iodophenol, g) = $-(15.3 \pm 2.0)$ $kJ \cdot mol^{-1}$, $\Delta_f H_m^\circ$(3-iodophenol, g) = $-(7.2 \pm 2.1)$ $kJ \cdot mol^{-1}$, and $\Delta_f H_m{}^\circ$(4-iodophenol, g) = $-(14.3 \pm 2.3)$ $kJ \cdot mol^{-1}$. The experimental values of the gas-phase enthalpies of formation of each compound were compared with estimates using the empirical scheme developed by Cox and with the calculated values based on high-level density functional theory calculations using the B3LYP hybrid exchange-correlation energy functional at the 6-311G(d,p) basis set.

INTRODUCTION

The chemistry of phenols has attracted continuing interest in the last two centuries. Phenol and phenolic derivatives have achieved considerable importance as a starting material for numerous intermediates and final products, which have several indispensable applications in our daily life. Phenolic derivatives constitute, among others, an important class of antioxidants[1,2] that inhibit or reduce the rate of the oxidative degradation of organic materials including a large number of biological aerobic organisms and commercial products. This antioxidant property can be related to the ability of phenols to trap the peroxyl radicals via the hydrogen transfer reaction. Hence, calculations of the hydrogen−oxygen bond strengths and ionization energies of the phenolic hydroxyl groups on various phenols allow for predictions of their potential as antioxidants.[2−5]

In addition, phenol and phenolic derivatives are widely used in the manufacturing of phenolic and epoxy resins, plastics, plasticizers, polycarbonates, antioxidants, lube oil additives, nylon, caprolactam, aniline insecticides, explosives, surface active agents, dyes and synthetic detergents, polyurethanes, wood preservatives, herbicides, fungicides (for wood preparation), gasoline additives, inhibitors, pesticides, and as raw material for producing drugs like aspirin.[3,6−9] Phenolic compounds are also known to suppress lipid peroxidation in living organisms and are also used as additives in food technology.[3]

For over a decade, we have been focusing deep attention on the thermochemistry of phenolic compounds. This paper is a contribution to the thermochemical investigation of halophenols, carried out by the Molecular Energetics Research Group of the University of Porto, following the studies of mono and dichlorophenols,[10,11] mono- and difluorophenols,[12,13] and mono- and dibromophenols.[14,15] In this paper, we present the calorimetric determination of the standard molar enthalpies of combustion, sublimation, and formation in the condensed and gas-phases of the 2-, 3-, and 4-iodophenol isomers (Figure 1).

For understanding the function of complicated large biological molecules, it is important to know the properties of their local units. From this point of view, phenol and its derivatives have been extensively studied due to their properties as models of biological systems. The thermochemical database on phenolic compounds has grown considerably in the past decade. There are quite a few reports in the literature about the energetics and the thermochemistry of several phenol derivatives, namely, 4-nitrosophenol,[16] *tert*-butyl- and di-*tert*-butylphenols,[17,18] cyanophenols,[19] mono-, di-, and trimethoxyphenols,[20,21] phenoxyphenol,[22] methoxynitrophenols,[23] pentafluorophenol,[24] pentachlorophenol,[25] chloronitrophenol isomers,[26] and cyanophenol and cyanothiophenol isomers.[27]

For iodophenol isomers no experimental values on the standard molar enthalpies of formation, in the condensed and gas phase, or on the standard molar enthalpies of sublimation are reported in the literature. Several articles have been published on the molecular structure of the monohalogenated phenols.[28−33] The possible occurrence of intramolecular halogen−hydrogen bonding plays an essential role in quite a number of (bio)chemical transformations, resulting in a considerable impact, among others, on conformational properties, as well as on molecular packing in crystal structures. The structure of 2-iodophenol was originally determined by Prout et al.[31] Recently Merk[34] has investigated the influence of the iodine atom on the crystal packing of iodophenols and determined the crystal structures of

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the three monoiodophenols. In that work, Merk shows that the crystalline 2-iodophenol packs preferentially in the *anti* conformation, while the 3-iodophenol adopts a *syn* conformation with the O−H bond 59.4° out of the ring plane. The solid state structure of the three iodophenol is established by OH−OH interactions, and in the case of 2-iodophenol, zigzag OH−OH chains are observed, which are linked by I−I interactions.

Hence, to contribute to a better understanding of the relative reactivity and the relationship between the energetics and structural properties of this class of compounds, we have examined the thermochemical properties of 2-, 3-, and 4-iodophenol. The standard molar enthalpies of formation, in the condensed phase, of those three iodophenol isomers, at T = 298.15 K, were obtained from measurements of their standard ($p°$ = 0.1 MPa) molar energies of combustion, in oxygen, at T = 298.15 K, using a rotating-bomb combustion calorimeter. Direct measurements of the standard molar enthalpies of sublimation of the three compounds were performed using high temperature Calvet microcalorimetry. The standard ($p°$ = 0.1 MPa) molar enthalpies of formation of 2-, 3-, and 4-iodophenol, in the gaseous phase, at T = 298.15 K, were calculated combining the respective standard molar enthalpies of formation, in the crystalline phase, and the standard molar enthalpies of sublimation. The $\Delta_f H_m^\circ(g)$ parameter was also estimated for all of the isomers of monoiodophenol, using the Cox scheme[35] and also by means of computational thermochemical methods.

EXPERIMENTAL SECTION

Materials and Purity Control. The compounds 2-iodophenol [CAS 533-58-4], 3-iodophenol [CAS 626-02-8], and 4-iodophenol [CAS 540-38-5] were purchased from Sigma-Aldrich Chemical Co., with an assessed minimum purity of 0.98 (mole fraction). The crystalline 2-, 3-, and 4-iodophenols were purified by repeated vacuum sublimations. The final purity of each iodophenol isomer was checked by gas chromatography, performed on an Agilent 4890D gas chromatograph equipped with a flame ionization detector and an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m × 0.530 mm i.d. × 1.5 μm film thickness), and with nitrogen as carrier gas. The temperature of the injector was set at 473 K, and the oven temperature was programmed as follows: 313 K (1 min), ramp at 5 K·min^{-1}, 473 K (5 min). No impurities greater than 10^{-3} in mole fraction could be detected in the samples of the monoiodophenol isomers used for the rotating bomb combustion calorimetry and Calvet microcalorimetry measurements. Details on the compounds and their purification are given in Table 1.

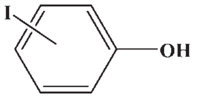


Figure 1. Structural formulas of monoiodophenol isomers.

A differential scanning calorimeter (Setaram 141) was used to detect possible phase transitions in the crystalline phase of the purified samples, from room temperature to their melting temperatures. The crystalline samples of the three isomers were sealed in aluminum crucibles. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction >0.99999). The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high purity reference materials:[36] naphthalene, benzoic acid, and indium. For each compound the scannings were performed under nitrogen atmosphere using a heating rate of $3.3\cdot10^{-1}$ K·s^{-1}. No crystalline transitions were detected between the temperature 298 K and the temperature of fusion of the studied compounds.

Rotating-Bomb Combustion Calorimetry Measurements. The combustion of the isomers of iodophenol was made as suggested by Carson et al.,[37] who applied the rotating-bomb calorimetry to the combustion of four iodomethanes using a technique in which the iodine produced in the combustion process is dissolved in aqueous potassium iodide. This procedure was also previously used in our laboratory in the combustion of 2- and 4-iodobenzoic acids[38,39] and monoiodoanilines[40] by rotating-bomb calorimetry.

The isoperibol rotating-bomb calorimeter used in these experiments was originally constructed at the University of Lund according to the design of Sunner.[41] Both the apparatus and the operating technique have been described elsewhere,[42−44] so only a brief description of the apparatus will be given here. The bomb, whose internal volume is 0.258 dm^3 and wall thickness of 1 cm, is a twin-valve platinum-lined bomb with all of the internal fittings machined from platinum. The bomb is suspended from the lid of the calorimeter can, to which a mass of nearly 5222.5 g of water is added. A Mettler PM 11-N balance, with a sensitivity of ± $(1\cdot10^{-1})$ g, was used to weigh the amount of distilled water added to the calorimeter from a weighed Perspex vessel, for each experiment of calibration or of combustion of the studied compounds; a correction to the energy equivalent was made for the difference between the mass of water used and the reference mass of 5222.5 g. Temperature measurements were automatically collected every 10 s, within the bounds of ± $(1\cdot10^{-4})$ K, using a Hewlett-Packard (HP-2804A) quartz crystal thermometer interfaced to a PC programmed to collected data and to compute the adiabatic temperature change, by means of a version of the LABTERMO program.[45] At least 100 temperature readings were taken for the main period and for both initial and final periods. For all combustion experiments, the ignition temperature was chosen so that the final temperature would be close to T = 298.15 K. The electrical energy for ignition was determined from the change in potential across a condenser (1400 μF) when discharged through a platinum wire (ϕ = 0.05 mm, Goodfellow, mass fraction 0.9999). The rotating mechanism allowed simultaneous axial and end-overend rotation of the bomb, causing the bomb solution (deionized water or aqueous

Table 1. Purification Details of the Three Iodophenol Isomers

chemical name	CAS	initial mole fraction purity	purification method	final mole fraction purity	analysis method
2-iodophenol	533-58-4	0.98	sublimation	0.9994	GC[a]
3-iodophenol	626-02-8	0.98	sublimation	0.9993	GC[a]
4-iodophenol	540-38-5	0.99	sublimation	0.9996	GC[a]

[a] Gas−liquid chromatography.

solution of KI) placed in the bomb to wash all internal surfaces of the bomb, yielding a homogeneous final solution. For each combustion experiment of the iodophenol isomers and for the measurement of the effective energy equivalent of the calorimeter, the rotation of the bomb was started when the temperature rise in the main period reached about 0.63 of its total value and was continued throughout the rest of the experiment. By adopting this procedure, the frictional work of the bomb rotation and stirring is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the thermostatted jacket, as shown by Good et al.[46] This isothermal jacket consists of a thermostatic bath containing a cavity of exactly the same shape as the calorimeter can, but 1 cm larger in overall dimensions, enclosed by a hollow lid. The jacket and lid were filled with water maintained at a temperature ca. 303.5 K to $\pm (1 \cdot 10^{-3})$ K using a temperature controller (Tronac PTC 41).

The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (NIST Standard Reference Material 39j), having a massic energy of combustion under bomb conditions of $-(26434 \pm 3)\ \mathrm{J \cdot g^{-1}}$.[47] Calibration experiments were carried out in oxygen, at the pressure of 3.04 MPa, with 1.00 cm^3 of water added to the bomb, according to the procedure suggested by Coops et al.,[48] without bomb rotation. One set of seven calibration experiments was performed leading to the value of the energy equivalent of the calorimeter: $\varepsilon(\text{calor}) = (25157.4 \pm 1.1)\ \mathrm{J \cdot K^{-1}}$; the uncertainty quoted is the standard deviation of the mean. The calorimeter was recalibrated by the combustion of benzoic acid in the presence of a 1.0 g of solid iodine enclosed in previously weighed polyester bags made of Melinex (0.025 mm of thickness) and a volume of 10.00 cm^3 of an aqueous solution of KI 0.8725 mol·dm^{-3}. The value of effective energy equivalent was found to be $\varepsilon(\text{calor})_{\text{ef.}} = (25179.1 \pm 1.2)\ \mathrm{J \cdot K^{-1}}$, where the quoted uncertainty refers to the standard deviation of the mean.

The accuracy of the combustion calorimetry for organic iodine compounds was checked in a previously work,[40] by measuring the energy of combustion of the recommended test substance,[49] 2-iodobenzoic acid, in the presence of an aqueous solution of KI 0.8995 mol.dm^{-3}, yielding $\Delta_c u^\circ = -(12772.5 \pm 1.7)\ \mathrm{J \cdot g^{-1}}$ in excellent agreement with the recommended value $\Delta_c u^\circ = -(12771.3 \pm 2.4)\ \mathrm{J \cdot g^{-1}}$.[49]

The crystalline samples of 2-, 3-, and 4-iodophenol were pressed in pellet form and enclosed in sealed polyester bags made of Melinex [0.025 mm thickness, $\Delta_c u^\circ = -(22902 \pm 5)\ \mathrm{J \cdot g^{-1}}$, a value confirmed in our laboratory] using the technique described by Skinner and Snelson.[50] The mass of carbon dioxide produced from the Melinex combustion was calculated using the factor previously reported.[50] The combustion experiments were carried out with 3.04 MPa of oxygen and with 10.00 cm^3 of an aqueous solution of KI $\approx$ 0.9 mol·dm^{-3}, placed in the bomb. In the end of the combustion experiments, the amount of iodine present in the final solution was determined by titration with $Na_2S_2O_3(aq)$, to confirm if it was the expected one. A value of $\Delta_{\text{sol}}U_m(I_2) = (3.7 \pm 0.1)\ \mathrm{kJ \cdot mol^{-1}}$[37] was used for the molar energy of solution of $I_2(cr)$ in aqueous KI solution. All of the necessary weighing was made on a Mettler Toledo AE 240 balance, with a sensitivity of $\pm (1 \cdot 10^{-5})$ g, and corrections from apparent mass to true mass were introduced.

The HNO_3 formed from traces of atmospheric N_2 remaining inside the bomb was analyzed by the Devarda's alloy method,[51] and corrections for nitric acid formation were based on $-59.7\ \mathrm{kJ \cdot mol^{-1}}$ for the standard molar energy of formation in which 0.1 mol·dm^{-3} $HNO_3(aq)$ is formed from $O_2(g)$, $N_2(g)$, and $H_2O(l)$.[52] For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ = -16240\ \mathrm{J \cdot g^{-1}}$,[48] a value that has been confirmed in our laboratory. Corrections to the standard state, ΔU_Σ, were made by the procedure given by Smith,[53] for iodine-containing compounds, based on the method developed by Hubbard et al.[54] The values for the pressure coefficient of massic energy, $(\partial u/\partial p)_T$, for the title compounds were assumed to be $-0.2\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$ at $T = 298.15$ K, a typical value for most organic compounds.[55] The specific densities for 2-, 3-, and 4-iodophenol were taken as 1.947 g·cm^{-3},[56] 1.238 g·cm^{-3},[34] and 1.294 g·cm^{-3},[34] respectively. The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2009;[57] using those values, the molar mass for the 2-, 3-, and 4-iodophenol isomers is 220.0078 g·mol^{-1}.

Table 2. Typical Combustion Results at $T = 298.15$ K ($p^\circ = 0.1$ MPa), for the Monoiodophenol Isomers[a]

experiment	2-iodophenol	3-iodophenol	4-iodophenol
m(cpd)/g	1.03925	1.03842	1.21243
m'(fuse)/g	0.00353	0.00249	0.00304
m''(Melinex)/g	0.08386	0.07802	0.04053
T_i/K	297.5048	297.5042	297.5730
T_f/K	298.1574	298.1510	298.2733
ΔT_{ad}/K	0.63710	0.63050	0.68890
ε_i/ J·K^{-1}	51.28	51.21	51.20
ε_f/ J·K^{-1}	59.12	59.05	58.96
$[\varepsilon(\text{calor})_{\text{ef.}}]_{\text{corr}}$/ J·K^{-1}	25183.70	25170.70	25163.20
$\Delta m(H_2O)$/g	1.1	-2.0	-3.8
$-\Delta U(\text{IBP})^b$/J	16075.85	15900.98	17369.76
ΔU(fuse)/J	57.33	40.44	49.37
ΔU(Melinex)/J	1920.63	1786.75	928.22
$-\Delta U(I_2)$/J	8.74	8.73	10.20
$\Delta U(HNO_3)$/J	4.18	3.58	1.64
ΔU(ign)/J	1.29	1.31	1.31
ΔU_Σ/J	22.00	21.75	23.68
$-\Delta_c u^\circ$/ J·g^{-1}	13548.66	13537.09	13507.63

[a] m(cpd), m'(fuse), and m''(Melinex) are the mass of compound burnt, the mass of fuse (cotton), and the mass of Melinex respectively, used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i and ε_f are the energy equivalent of contents in the initial and final states, respectively; $[\varepsilon(\text{calor})_{\text{ef.}}]_{\text{corr}}$ is the corrected energy equivalent effective of the calorimeter for the amount of water used; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 5222.5 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the combustion energy of the fuse (cotton); ΔU(Melinex) is the energy of combustion of Melinex; $\Delta U(I_2)$ is the energy correction for the solution of $I_2(cr)$ in KI(aq); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; $\Delta_c u^\circ$ is the standard massic energy of combustion. [b] ΔU (IBP) includes ΔU (ign).

Calvet Microcalorimetry Measurements. The standard molar enthalpies of sublimation of the title compounds were measured in a high-temperature Calvet microcalorimeter (Setaram HT 1000), using the technique described by Skinner and co-workers[58] for the sublimation of solid compounds. The measuring procedures, as well as the detailed description of the

Table 3. Individual Values of the Standard (p° = 0.1 MPa) Massic Energies of Combustion, $\Delta_c u^\circ$, for the Monoiodophenols, at T = 298.15 K

2-iodophenol	3-iodophenol	4-iodophenol
	$-\Delta_c u^\circ / \mathrm{J \cdot g^{-1}}$	
13548.66	13542.67	13507.63
13558.72	13534.35	13512.21
13550.86	13537.09	13492.99
13553.69	13537.84	13506.40
13563.02	13532.93	13503.09
13558.45	13533.95	13493.74
	$-\langle \Delta_c u^\circ \rangle / (\mathrm{J \cdot g^{-1}})^a$	
13555.6 ± 2.2	13536.5 ± 1.5	13502.7 ± 3.2

[a] Mean value and standard deviation of the mean.

apparatus, have been recently reported.[59] The microcalorimeter was calibrated in situ for these measurements using the reported standard molar enthalpy of sublimation of naphthalene (Aldrich, mass fraction purity >0.99), $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(T = 298.15\ \mathrm{K}) = (76.60 \pm 0.60)\ \mathrm{kJ \cdot mol^{-1}}$.[60] The calibration procedure was the same as for the samples. From five independent experiments, the calibration constants, k, of the calorimeter at experimental temperature, were found to be $k(T = 323.4\ \mathrm{K}) = (0.9987 \pm 0.0024)$, $k(T = 339.8\ \mathrm{K}) = (1.0004 \pm 0.0038)$, and $k(T = 339.8\ \mathrm{K}) = (1.0038 \pm 0.0009)$, respectively, for the sublimation experiments of the 2-, 3-, and 4-iodophenol; the quoted uncertainty is the standard deviation of the mean. In a typical experiment, the samples with a mass of (4 to 6) mg of solid compounds were placed into small glass capillary tubes sealed at one end and weighed with a precision of $\pm(1 \cdot 10^{-6})$ g on a Mettler CH-8608 analytical balance. The sample and reference capillaries were simultaneously dropped at room temperature into the hot reaction cells, held at a working temperature. After dropping, an endothermic peak due to the heating of the sample from room temperature to the temperature of the calorimeter was first observed. When the signal returned to the baseline, the sample and reference cells were simultaneously evacuated, and the measuring curve corresponding to the sublimation of the compound was acquired. The thermal corrections for the glass capillary tubes were determined in separate experiments[59] and were evaluated and minimized in each experiment by dropping glass capillary tubes of near equal mass into both measuring cells.

RESULTS

Experimental Enthalpies of Formation. Detailed results for a typical combustion experiment of each compound are given in Table 2. The values of the energy associated to the isothermal bomb process, $\Delta U(\mathrm{IBP})$, were calculated from eq 1, according to ref 54

$$\begin{aligned}\Delta U(\mathrm{IBP}) = {} & -\{\varepsilon(\mathrm{calor})_{\mathrm{ef.}} + \Delta m(\mathrm{H_2O}) c_p(\mathrm{H_2O, l})\} T_{\mathrm{ad}} \\ & + (T_{\mathrm{i}} - 298.15\mathrm{K})\varepsilon_{\mathrm{i}} + \\ & + (298.15\mathrm{K} - T_{\mathrm{i}} - \Delta T_{\mathrm{ad}})\varepsilon_{\mathrm{f}} + \Delta U_{\mathrm{ign}} \qquad (1)\end{aligned}$$

where $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to $\varepsilon(\mathrm{calor})_{\mathrm{ef.}}$, $c_p(\mathrm{H_2O, l})$ is the heat capacity of liquid water, ε_{i} and ε_{f} are, respectively, the energy equivalent of the bomb contents in the initial and final state, ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange, work of stirring and the frictional work of bomb rotation, and ΔU_{ign} is the electrical energy of ignition. ΔU_{Σ} is the energy correction to the standard state (Washburn correction). The remaining quantities are as previously defined.[53−55] The detailed results for all of the combustion experiments of each compound, together with the mean value of the standard massic energies of combustion, $\Delta_c u^\circ$, are presented in the Supporting Information (Tables S1 to S3).

Table 4. Derived Standard (p° = 0.1 MPa) Molar Values in the Condensed Phase, at T = 298.15 K[a]

compound	$-\Delta_c U_{\mathrm{m}}^{\circ}(\mathrm{cr})^a$ $\mathrm{kJ \cdot mol^{-1}}$	$-\Delta_c H_{\mathrm{m}}^{\circ}(\mathrm{cr})$ $\mathrm{kJ \cdot mol^{-1}}$	$-\Delta_f H_{\mathrm{m}}^{\circ}(\mathrm{cr})$ $\mathrm{kJ \cdot mol^{-1}}$
2-iodophenol (cr)	2982.3 ± 1.2	2984.2 ± 1.2	91.4 ± 1.4
3-iodophenol (cr)	2978.1 ± 1.0	2980.0 ± 1.0	95.6 ± 1.3
4-iodophenol (cr)	2970.7 ± 1.6	2972.6 ± 1.6	103.0 ± 1.8

[a] The uncertainties are twice the overall standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of auxiliary materials.

The individual values of the standard massic energy of combustion, $\Delta_c u^\circ$, for all of the combustion experiments of each compound, together with the mean values, $\langle \Delta_c u^\circ \rangle$, and their standard deviations of the mean, are listed, for each compound, in Table 3. The values of $\Delta_c u^\circ$ refer to the idealized combustion reaction of monoiodophenols, yielding $\mathrm{I_2(cr)}$ as the only iodine-containing product in the final state, according to eq 2

$$\begin{aligned}\mathrm{C_6H_5OI(cr)} + 6.75\mathrm{O_2(g)} \rightarrow 6\mathrm{CO_2(g)} + 0.5\mathrm{I_2(cr)} \\ + 2.5\mathrm{H_2O(l)} \qquad (2)\end{aligned}$$

Table 4 lists the derived values of the standard molar energies and enthalpies of combustion, $\Delta_c U_{\mathrm{m}}^{\circ}(\mathrm{cr})$ and $\Delta_c H_{\mathrm{m}}^{\circ}(\mathrm{cr})$, as well as the standard molar enthalpies of formation, $\Delta_f H_{\mathrm{m}}^{\circ}(\mathrm{cr})$, for the three isomers in the condensed phase, at T = 298.15 K, which were derived from the values of $\Delta_c H_{\mathrm{m}}^{\circ}(\mathrm{cr})$ and from the standard molar enthalpies formation, at T = 298.15 K, of the following compounds: $\Delta_f H_{\mathrm{m}}^{\circ}(\mathrm{CO_2, g}) = -(393.51 \pm 0.13)\ \mathrm{kJ \cdot mol^{-1}}$;[61] and $\Delta_f H_{\mathrm{m}}^{\circ}(\mathrm{H_2O, l}) = -(285.830 \pm 0.040)\ \mathrm{kJ \cdot mol^{-1}}$.[61] The uncertainties assigned to the standard molar energies of combustion correspond, in each case, to twice the overall standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of Melinex used as combustion auxiliary.[62,63]

Results of the measurements of the enthalpies of sublimation, $\Delta_{\mathrm{cr,298.15K}}^{\mathrm{g},T} H_{\mathrm{m}}^{\circ}$ for the title compounds, obtained by Calvet microcalorimetry, are given in Table 5, with the respective uncertainties, taken as the standard deviations of the mean of five individual results.

The observed standard molar enthalpies of sublimation, $\Delta_{\mathrm{cr,298.15K}}^{\mathrm{g},T} H_{\mathrm{m}}^{\circ}$, at working temperature, have been corrected to T = 298.15 K according to the following eq 3

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = \Delta_{\mathrm{cr,\,298.15K}}^{\mathrm{g},\,T} H_{\mathrm{m}}^{\circ} - \Delta_{298\mathrm{K}}^{T} H_{\mathrm{m}}^{\circ}(\mathrm{g}) \qquad (3)$$

where the corrective term $\Delta_{298.15\mathrm{K}}^{T} H_{\mathrm{m}}^{\circ}(\mathrm{g}) = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}}^{\circ}(\mathrm{g})\, \mathrm{d}T$ represents the molar enthalpic correction for the heat capacity of the gaseous phase, derived from statistical thermodynamics using the vibrational frequencies from DFT calculations, the B3LYP/6-311G(d,p) approach[64] (scaled by 0.9672[65]), yielding the following

Table 5. Standard (p^o = 0.1 MPa) Molar Enthalpies of Sublimation, $\Delta_{cr}^{g}H_m^o$, at T = 298.15 K[a]

compound	no. of expts	T/K	$\Delta_{cr,298.15K}^{g,T}H_m^o$ kJ·mol^{-1}	$\Delta_{298.15K}^{T}H_m^o(g)$ kJ·mol^{-1}	$\Delta_{cr}^{g}H_m^o$(298.15 K) kJ·mol^{-1}
2-iodophenol (cr)	5	323.3	79.3 ± 0.2	3.2	76.1 ± 1.4
3-iodophenol (cr)	5	339.4	93.7 ± 0.1	5.3	88.4 ± 1.6
4-iodophenol (cr)	5	349.4	95.4 ± 0.2	6.7	88.7 ± 1.5

[a] The standard uncertainty of u is $u(T)$ = 0.01 K.

Table 6. Standard (p^o = 0.1 MPa) Molar Enthalpies of Formation, in Crystalline and Gaseous Phases, and Standard Molar Enthalpies of Sublimation, at T = 298.15 K

compound	$-\Delta_f H_m^o$(cr) kJ·mol^{-1}	$\Delta_{cr}{}^{g}H_m^o$(298.15 K) kJ·mol^{-1}	$\Delta_f H_m^o$(g) kJ·mol^{-1}	δ_{-I}[a] kJ·mol^{-1}
benzene			82.6 ± 0.7[66]	
phenol			−96.4 ± 0.9[66]	
aniline			87.1 ± 1.1[66]	
iodobenzene			164.9 ± 5.9[66]	82.3 ± 5.9
2-iodophenol	91.4 ± 1.4	76.1 ± 1.4	−15.3 ± 2.0	81.8 ± 2.2
3-iodophenol	95.6 ± 1.3	88.4 ± 1.6	−7.2 ± 2.1	89.2 ± 2.3
4-iodophenol	103.0 ± 1.8	88.7 ± 1.5	−14.3 ± 2.3	82.1 ± 2.7
2-iodoaniline			169.2 ± 1.8[40]	82.1 ± 2.1
3-iodoaniline			170.4 ± 1.9[40]	83.3 ± 2.2
4-iodoaniline			168.5 ± 2.0[40]	81.4 ± 2.3

[a] Enthalpic increment for the introduction of an iodine atom into the aromatic ring of benzene, phenol, or aniline.

corrections: $\Delta_{298.15K}^{T}H_m^o(g)$ = 3.2 kJ·mol^{-1}; $\Delta_{298.15K}^{T}H_m^o(g)$ = 5.3 kJ·mol^{-1} and $\Delta_{298.15K}^{T}H_m^o(g)$ = 6.7 kJ·mol^{-1}, respectively, for 2-, 3-, and 4-iodophenols

$$C_{p,m}^o(\text{2-iodophenol, g})/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 1.52\cdot 10^{-7}(T/\text{K})^3 - 3.42\cdot 10^{-4}(T/\text{K})^2 + 0.339(T/\text{K}) + 121.71 \quad (4)$$

$$C_{p,m}^o(\text{3-iodophenol, g})/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 1.53\cdot 10^{-7}(T/\text{K})^3 - 3.42\cdot 10^{-4}(T/\text{K})^2 + 0.342(T/\text{K}) + 122.06 \quad (5)$$

$$C_{p,m}^o(\text{4-iodophenol, g})/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 1.51\cdot 10^{-7}(T/\text{K})^3 - 3.39\cdot 10^{-4}(T/\text{K})^2 + 0.337(T/\text{K}) + 122.05 \quad (6)$$

The results of the measurements of the standard molar enthalpies of sublimations of the iodophenol isomers, by microcalorimetry, as well as the respective uncertainties, are given in Table 5. The uncertainties assigned to the standard molar enthalpies of sublimation, $\Delta_{cr}^{g}H_m^o(T = 298.15\text{K})$, are twice the overall standard deviation of the mean which include the uncertainties in calibration with naphthalene.[62,63]

In Table 6 the derived standard molar enthalpies of formation in the gaseous phase, $\Delta_f H_m^o$(g), at T = 298.15 K, for the three monoiodophenols, are summarized, as well as the values of the enthalpic increments of substitution of an iodine atom in the phenol ring, δ_{-I}.

Enthalpies of Formation Estimated with the Cox Scheme. The enthalpies of formation in the gaseous state may also be estimated by empirical methodologies such as the one suggested by Cox,[35] whose empirical scheme is based on the transferability of enthalpic group contributions in benzene derivatives, assuming that each group in the benzene ring produces a characteristic enthalpic increment in the enthalpy of formation in the gaseous phase. Using the methodology introduced by Cox and taking into account the scheme presented in Figure 2, the values of the gas-phase standard molar enthalpies of formation for the iodophenol isomers can be estimated from the literature data given in Table 6 for benzene, phenol, and iodophenol.[66] For 2-iodophenol it is necessary, as suggested by Cox,[35] to consider a correction term of 4 kJ·mol^{-1} since the iodine atom and the hydroxyl group are bonded in the *ortho*-position of the aromatic ring.

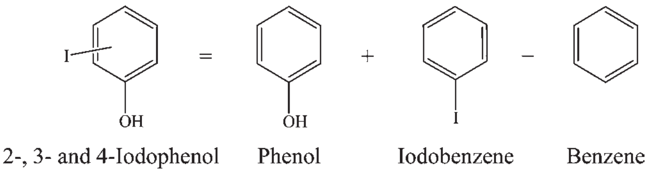


Figure 2. Empirical scheme for estimation of $\Delta_f H_m^o$(g) by the Cox scheme.

Thus, according to the Cox scheme,[35] the estimated value for the standard molar enthalpies of formation, in the gaseous state, of *ortho*-iodophenol is −(10.1 ± 6.0) kJ·mol^{-1}, whereas the estimated value for both the *meta* and *para* isomers is −(14.1 ± 6.0) kJ·mol^{-1} (cf. Table 7). These estimated values differ from the experimental ones by −(5.2 ± 6.3) kJ·mol^{-1}, (6.9 ± 6.4) kJ·mol^{-1}, and −(0.2 ± 6.4) kJ·mol^{-1} in the cases, respectively, of the *ortho*, *meta*, and *para* iodophenol isomers, deviations that are well within the limit of acceptance of ± 10 kJ·mol^{-1} indicated by Cox for his scheme.[35] Although this empirical method of $\Delta_f H_m^o$(g) estimation predicts the 2-iodophenol as the least stable isomer,

Table 7. **Experimental and Estimated (Cox Scheme and B3LYP/6-311G(d,p) Calculations) Gas-Phase Enthalpies of Formation of the Three Monoiodophenol Isomers**

	$-\Delta_f H_m{}^{\circ}(g)/kJ \cdot mol^{-1}$			$\Delta^a/kJ \cdot mol^{-1}$	
compound	experimental	Cox scheme	calculated[b]	Cox scheme	calculated[b]
2-iodophenol	15.3 ± 2.0	10.1 ± 6.0	20.0	−5.2 ± 6.3	4.7
3-iodophenol	7.2 ± 2.1	14.1 ± 6.0	13.9	6.9 ± 6.4	6.7
4-iodophenol	14.3 ± 2.3	14.1 ± 6.0	12.9	−0.2 ± 6.4	−1.4

[a] Difference between the experimental and the estimated values. [b] B3LYP/6-311G(d,p).

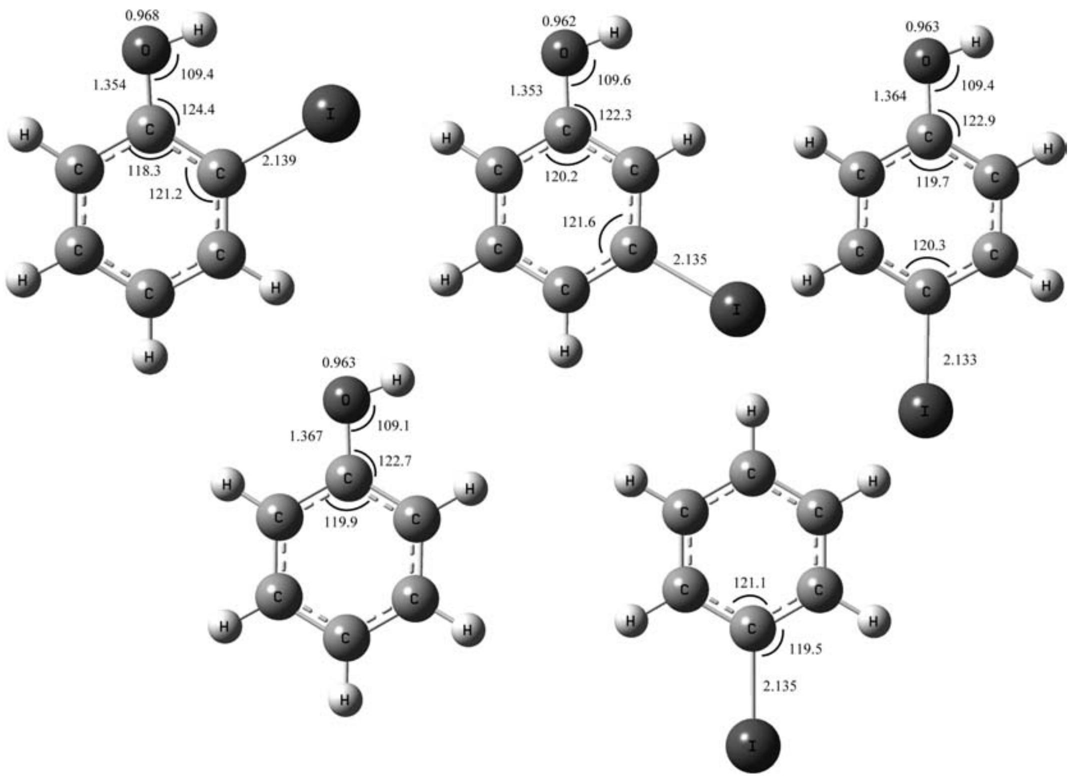
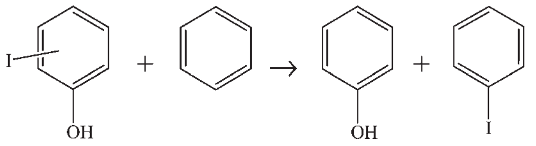


Figure 3. Optimized most stable configurations for the monoiodophenol. Selected distances are in angstroms and angles in degrees.

the experimental results point it out as one of the most stable isomers. This fact is not surprising since the Cox scheme completely neglects any possible stabilization energetic effect between these two *ortho* substituents.

Computed Enthalpies of Formation. The theoretical calculations were performed with the Gaussian 03 software package,[67] using density functional theory (DFT) with the hybrid exchange correlation functional (B3LYP)[68−70] together with the 6-311G(d,p) extended basis set,[71] used for the smaller elements: carbon, hydrogen, and oxygen; for the iodine atom, due to its size, scalar relativistic effects were included by using relativistic effective core potentials (ECP's), from the EMSL basis set,[72,73] for the geometry optimizations and frequency calculations of the iodophenol isomers considered in this work, phenol, iodobenzene, and benzene. Zero-point vibrational energies and fundamental vibrational frequencies were scaled by a factor of 0.9887 and 0.9672, respectively.[65] The energies of all monoiodophenols, and those of phenol, benzene, and iodobenzene, calculated at the B3LYP/6-311G(d,p) and corrected for T = 298.15 K, were used to compute the enthalpy of the homodesmic reaction described by the following equation:



(7)

Combining those enthalpies of reaction with the experimental $\Delta_f H_m^{\circ}(g)$ of benzene, iodobenzene, and phenol given in Table 6, it was possible to estimate the $\Delta_f H_m^{\circ}(g)$ of the three monoiodophenol isomers, which are summarized in Table 7. The results clearly show that the computational estimates are in excellent agreement with the experimental results for 4-iodophenol, with high deviations observed for the 2- and 3-iodophenol, respectively, of (4.7 and 6.7) kJ·mol^{-1}. At the B3LYP/6-311G(d,p) level, the most stable isomer is the 2-iodophenol, followed by the 3-iodophenol, which is 6.1 kJ·mol^{-1} less stable

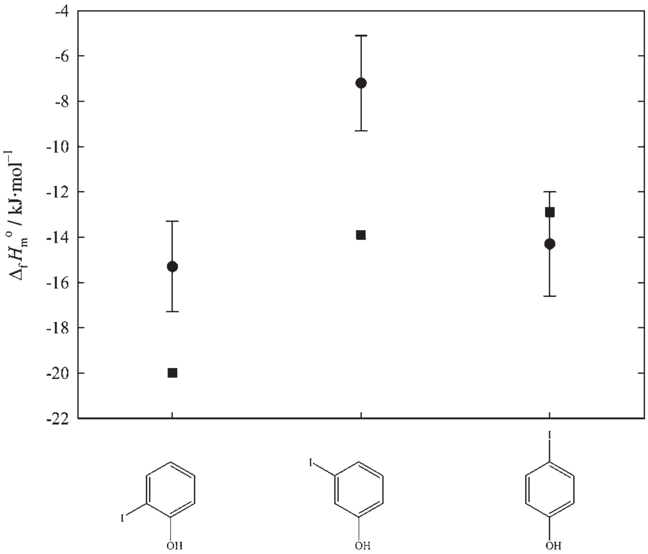


Figure 4. Comparison between ●, experimental, and ■, computed values of the gas-phase standard molar enthalpy of formation in the monoiodophenols.

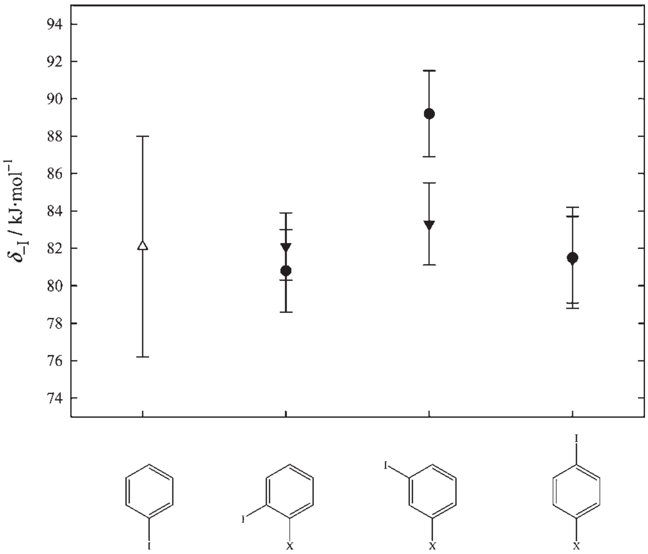


Figure 5. Enthalpic increment for the introduction of an iodine atom in benzene (△) and in the different positions of the aromatic ring of its derivatives: X = ●, —OH; and ▼, —NH$_2$.

and, finally, the 4-iodophenol, which lies 7.1 kJ·mol^{-1} above the most stable one.

Figure 3 presents the optimized geometries of the different isomers of iodophenol, phenol, and iodobenzene calculated at the B3LYP/6-311G(d,p), with selected geometrical parameters for those molecules. The most stable conformations obtained for all of the three monoiodophenols, taking into account the geometry optimization performed at the B3LYP/6-311G(d,p), are those where the hydroxyl group is coplanar with the aromatic benzene ring, likewise phenol,[74] occurring the conjugation of the oxygen's lone pairs with the π-electron of the benzene ring. It has been known that the electronic properties of substituents have effects on the phenolic hydroxyl group which are measurable in terms of variation in the endocyclic angle at the phenolic group, which associated with an electron-withdrawing substituent is a few degrees larger than 120°, and for an electron-releasing substituent, a few degrees less than 120°.[75] For 2- and 4-iodophenol the endocyclic angle at the phenolic group is respectively 118.3° and 119.7°, a lower value than the observed for the phenol, 119.9°. For the 3-iodophenol, the calculated value is 120.2°, which points out a lower π-delocalization with the aromatic ring. The 2- and 3-iodophenol isomers can exist in the *syn* and *anti* conformations, so we have performed computational calculations for the two possible conformations. In the case of the 3-iodophenol, the most stable conformation was found to be that where the hydroxyl group is in *syn* position with respect to iodine atom, being the calculated value of the gas-phase enthalpy of formation of the *syn* conformer 0.4 kJ·mol^{-1} lower than the *anti* conformer. But for the 2-iodophenol isomer large differences were observed. For the *syn* and *anti* 2-iodophenol the calculated values of the gas phase enthalpy of formation were of −20.0 kJ·mol^{-1} and −9.2 kJ·mol^{-1}, respectively, showing that for this isomer the most stable conformation is the one in which the hydroxyl group adopts a *syn* conformation relative to the iodine atom, which represents a higher energetic stabilization of the isomer substituted in that position. In previously works Carlson et al.[30] and Baker and Kaedin[32] suggested the formation of an intramolecular halogen—hydrogen bond of the 2-iodophenol, although the experimental value of the enthalpy of formation in the gas phase for the 2-iodophenol obtained in this work, differs from the computational values by 4.7 kJ·mol^{-1} for the *syn* conformer and by −6.1 kJ·mol^{-1} for the *anti* conformation, suggesting that the 2-iodophenol isomer possible exists in the gas phase as a mixture of the two forms.

■ DISCUSSION

Rotating-bomb calorimetry and Calvet microcalorimetry experiments have been performed to obtain the enthalpies of combustion in the crystalline phase and the enthalpies of sublimation of the three monoiodophenols.

The derived gas-phase enthalpies of formation have been compared with DFT estimated values and with those obtained by application of the Cox scheme. It is found that the Cox scheme yields good estimates for the three isomers, in particularly for the 4-iodophenol isomer. This method also predicts the 2-iodophenol to be the least stable compound, due to the fact that the Cox scheme completely neglected the stabilizing interaction between the iodine atom in the *ortho* position and the hydroxyl group.

The use of DFT calculations together with a homodesmic reaction scheme employing phenol, benzene, and iodobenzene yields good estimates of the gaseous standard molar enthalpies of formation for the iodophenol isomers, giving the 4-iodophenol isomer as the least stable isomer. A closer inspection of the results presented in Table 6 and in the diagram of Figure 4 shows that the experimental values of enthalpies of formation in the gas-phase point out the *ortho* and *para* isomers with similar enthalpic stabilities, within the associated uncertainties. However, the computational results predict a higher stabilization effect for the introduction of an iodine atom in the *ortho* position of the phenolic ring than experimentally observed.

In Table 6 are also presented the literature values for the enthalpies of formation in the gas-phase for benzene, iodobenzene, phenol, aniline, and monoiodoanilines,[40] and the respective enthalpic increment for introducing a iodine atom in the different position of the aromatic ring, δ_{-I}, of benzene, phenol, and aniline. From the results presented in Table 6 and from Figure 5, it is possible to observe that the enthalpic increment for the introduction of a iodine atom in the aromatic ring of benzene, phenol, and aniline is very similar within the associated uncertainties, with the exception of 3-iodophenol, which has a higher value of enthalpic increment. A close analysis of the results suggests a similar sequence of enthalpic increment for the substitution of a iodine atom in the positions of the aromatic ring of phenol and aniline: *ortho* ≈ *para* < *meta*.

The iodine atom exerts a weak σ electron-withdrawing inductive effect and a weak π electron-donating mesomeric effect on the aromatic ring. From Figure 5 it is possible to see that the introduction of a iodine atom in *para* position of the aromatic ring of the phenol or aniline, both of which are π electron donor groups, will develop a similar enthalpic effect in both, suggesting that the introduction of an iodine atom on that position will provoke an energetic destabilization in the aromatic ring, similar to the one observed in iodobenzene and independent of the functional substituent ($-$OH or $-NH_2$). The introduction of the iodine atom at the *meta* position of phenol or aniline also creates an enthalpic effect of destabilization, which is higher than the observed for the *para*-iodophenol or *para*-aniline. The energetic effect of substitution of the iodine in the *ortho* position of the aromatic ring of phenol and aniline is governed by the balance between conjugation, steric effects, and the possible existence of an attractive interaction between the iodine atom and the hydroxyl group, making these isomers the most stable ones. If we look to the contact distance between the hydrogen and iodine atom of the *syn* 2-iodophenol conformer, 2.63 Å, it is possible to see that it is shorter than the sum of the van der Waals radii[76] of contacting of the hydrogen and iodine atoms, 1.10 Å and 1.98 Å, respectively. The calculated Muliken atomic charge obtained for the most stable conformations of 2-iodophenol gives for both iodine and hydrogen atoms positive values, respectively, 0.031 *e* and 0.242 *e*, being the oxygen the only atom with a negative value of Mulliken atomic charge of −0.337 *e*, which suggests that the intramolecular electrostatic interaction for the 2-iodophenol could possible be between the iodine and the oxygen atom of the hydroxyl group. The van der Waals radii for the oxygen atom is 1.52 Å,[76] and the distance between the iodine atom and the oxygen atom in the hydroxyl group of 2-iodophenol is 3.29 Å.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of all combustion calorimetry experiments for the three iodophenols studied, as well as the calculated energies of all compounds used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

This paper is dedicated to Professor Kenneth N. Marsh for his long career of dedicated work in the field of chemical thermodynamics.

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