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Experimental and Computational Thermochemical Study of the Three Monofluorophenol Isomers[†]

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The present work reports the values of the standard ($p^o = 0.1$ MPa) molar enthalpies of formation in the condensed phase of the three isomers of monofluorophenol derived from the standard molar energies of combustion, in oxygen, to yield CO_2(g) and $HF \cdot 10H_2O$(l), at $T = 298.15$ K, measured by rotating bomb combustion calorimetry, as well as the values of the standard molar enthalpies of sublimation or vaporization, 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: $\Delta_f H_m^o$(2-fluorophenol, g) $= -(294.5 \pm 1.6)$ kJ$\cdot$mol^{-1}, $\Delta_f H_m^o$(3-fluorophenol, g) $= -(292.8 \pm 1.7)$ kJ$\cdot$mol^{-1}, and $\Delta_f H_m^o$(4-fluorophenol, g) $= -(287.6 \pm 2.1)$ 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 6-311++G(d,p) basis set.

1. Introduction

This work is part of a wider investigation on the energetics of phenolic derivatives, a class of chemical compounds that have generated continuing interest in the last century since they include a large number of synthetic and naturally occurring antioxidants, which play a major role in the chemistry of living organisms and life-supporting substances.[1,2] Antioxidants are compounds that, in low concentration, can inhibit the oxidative degradation of organic materials including a large number of biological aerobic organisms and commercial products.[3]

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 of the thermochemistry of several phenol derivatives, namely, 4-nitrosophenol,[4] *tert*-butyl- and di-*tert*-butylphenols,[5,6] cyanophenols,[7] mono-, di-, and trimethoxyphenols,[8,9] and methoxynitrophenols.[10] For halogenated phenols, thermochemical parameters have been reported for pentafluorophenol,[11] pentachlorophenol,[12] chloronitrophenol isomers,[13] cyanophenol, and cyanothiophenol isomers,[14] as well as for the mono- and dichlorophenol isomers.[15,16] For fluorophenols, the only experimental values known in the literature are the standard molar enthalpies of formation, in the condensed phase, of 2-fluorophenol[17] and 4-fluorophenol.[17] However, the method used in that work to measure the standard molar enthalpies of formation of 2- and 4-fluorophenol, in the condensed phase, is not very reliable since they were determined by static bomb combustion calorimetry, a method that is well-known to be unsuitable for the combustion calorimetry of fluorine compounds.[18] These, in principle, erroneous experimental results for 2- and 4-fluorophenols lead us to perform the determination of all three isomers of the monofluorophenols (Figure 1).

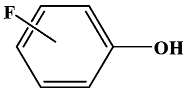

Figure 1. Structural formula of monofluorophenol isomers.

Beyond the significant biological effects of fluorophenolic compounds, they have also received special attention for the understanding of degradation and biodegradation processes.[19,20] Fluorophenol derivatives are extensively used as intermediates in the synthesis of agrochemicals and pharmaceutical drugs,[21−24] leading to their accumulation in the environment. So, it is of great importance to correlate their behavior in terms of energetics, structure, and reactivity.

Due to the applications of the phenolic derivatives as antioxidants, the thermochemical database on energetics of phenolic O−H bonds has grown significantly in the last years. The experimental values of the homolytic O−H bond dissociation enthalpies, BDEs, at $T = 298.15$ K, reported in the review of Borges dos Santos and Martinho Simões,[25] for 2-, 3-, and 4-fluorophenol relative to the value of O−H bond dissociation enthalpy of phenol, (371.3 ± 2.3) kJ$\cdot$mol^{-1},[25] are $-(8.8 \pm 8)$ kJ$\cdot$mol^{-1}, (6 ± 8) kJ$\cdot$mol^{-1}, and $-(4 \pm 4)$ kJ$\cdot$mol^{-1}, respectively. These values were based on the experimental BDEs reported by Suryan,[26] Lias,[27] Arnett,[28] Lind,[29] Wu,[30] and collaborators. The experimental and theoretical proton affinities of monofluorophenols were reported by Bogdanov et al.,[31] and the experimental ionization constants in aqueous solution at $T = 298.15$ K for these compounds were given by Crimmins and co-workers.[32] The crystal structures of the monofluorophenols at low temperature and high pressure have been reported by Oswald et al.[33,34]

Several articles have been published on the molecular structure of the three monofluorophenol isomers (see, e.g., ref 35 and references therein). For 3-fluorophenol, the analysis of the microwave rotational spectra[36] and of its

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Table 1. Typical Combustion Results at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for the Monofluorophenol Isomers[a]

experiment	2-fluorophenol	3-fluorophenol	4-fluorophenol
m(cpd)/g	0.53522	0.57750	0.71547
m'(fuse)/g	0.00279	0.00264	0.00355
m''(polyethylene)/g	0.17626	0.16394	---
m'''(Melinex)/g	---	---	0.04053
T_i/K	297.4231	297.2350	297.4136
T_f/K	298.3133	298.1488	298.2017
ΔT_{ad}/K	0.87718	0.89680	0.77221
$\varepsilon_i/J \cdot K^{-1}$	51.62	51.39	51.24
$\varepsilon_f/J \cdot K^{-1}$	53.30	53.33	52.73
$\varepsilon(\text{calor})_{\text{corr.}}/J \cdot K^{-1}$	25157.0	25152.8	25158.7
$\Delta m(H_2O)$/g	−0.1	−1.1	0.3
$-\Delta U(\text{IBP})^b$/J	22111.45	22601.79	19466.16
ΔU(fuse)/J	45.31	42.87	57.65
ΔU(polyethylene)/J	8157.74	7587.54	---
ΔU(Melinex)/J	---	---	928.22
$\Delta U(HNO_3)$/J	4.66	2.27	3.94
ΔU(ign)/J	1.30	1.29	1.26
ΔU_Σ/J	25.21	23.96	17.64
$-\Delta_c u^\circ/J \cdot g^{-1}$	25930.51	25879.05	25799.42

[a] m(cpd), m'(fuse), m''(polyethylene), and m'''(Melinex) are the mass of compound burnt, the mass of fuse (cotton), and the mass of polyethylene or 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; $\varepsilon(\text{calor})_{\text{corr.}}$ is the energy equivalent of the calorimeter; $\Delta m(H_2O)$ 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 energy combustion of the fuse (cotton); ΔU(polyethylene) is the energy of combustion of polyethylene; ΔU(Melinex) is the energy of combustion of Melinex; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; and $\Delta_c u^\circ$ is the standard massic energy of combustion. [b] ΔU(IBP) includes ΔU(ign).

Table 2. Individual Values of the Standard ($p^\circ = 0.1$ MPa) Massic Energies of Combustion, $\Delta_c u^\circ$, for the Monofluorophenols, at $T = 298.15$ K

2-fluorophenol	3-fluorophenol	4-fluorophenol
	$-\Delta_c u^\circ/J \cdot g^{-1}$	
25930.51	25865.85	25810.84
25930.94	25867.04	25799.42
25938.81	25879.05	25791.35
25932.26	25880.71	25790.05
25920.71	25882.59	25792.11
25927.18	25880.29	25806.49
	$-\langle \Delta_c u^\circ \rangle/(J \cdot g^{-1})^a$	
25930.1 ± 2.4	25875.9 ± 3.0	25798.4 ± 3.6

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

Table 3. Derived Standard ($p^\circ = 0.1$ MPa) Molar Values in the Condensed Phase, at $T = 298.15$ K[a]

compound	$(-\Delta_c U_m^o(\text{cr, l}))$ $(kJ \cdot mol^{-1})^a$	$(-\Delta_c H_m^o(\text{cr, l}))$ $(kJ \cdot mol^{-1})$	$(-\Delta_f H_m^o(\text{cr, l}))$ $(kJ \cdot mol^{-1})$
2-fluorophenol (l)	2906.8 ± 0.9	2908.0 ± 0.9	346.8 ± 1.4
3-fluorophenol (l)	2900.7 ± 1.0	2901.9 ± 1.0	352.9 ± 1.4
4-fluorophenol (cr)	2892.1 ± 1.1	2893.3 ± 1.1	361.5 ± 1.5

[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.

deuterated[37] species has established that this molecule is planar with the two substituents in *trans* conformation, which was also recently confirmed by Jaman.[38] Recently, Zierkiewicz and co-workers[39] performed an experimental study of the infrared spectra of 4-fluorophenol and its OD-deuterated derivative in inert solvents, complemented by the theoretical investigation of the molecular structures. Larsen[40] has done a microwave study of the *para*-halogenophenols, and together with Nicolaisen[41] have reported a few bands in the far-infrared spectra of 4-fluorophenol in the vapor phase. The frequencies and infrared intensities of the OH stretching vibrations in 4-fluorophenol have also been determined by Cabana et al.[42] Much more information is available on 2-fluorophenol. The experimental geometry of this isomer has been determined by Dutta et al.[43] on the basis of the microwave spectra of normal and deuterated species of 2-fluorophenol and by Hargittai et al.[44] by means of gas-phase electron diffraction. The vibrational properties of 2-fluorophenol have also been investigated.[45,46] The torsional frequencies and the enthalpies of intramolecular hydrogen bonds of *o*-halophenols have been analyzed by Carlson et al.[47] The conformational properties of 2-fluorophenol have also been investigated by means of quantum chemical methods,[35,48−50] and together with the experimental results it was found that for the 2-fluorophenol molecule the hydroxyl group is in plane with the benzenic ring, adopting *cis* configuration relative to the fluorine atom in the 2-position, yielding the formation of a halogen−hydrogen bond.[44−46] The occurrence of intramolecular hydrogen bonding plays an essential role in quite a number of (bio)chemical transformations, as a consequence of which there is a considerable impact, among others, on conformational properties, as well as on molecular packing in crystal structures.

In this paper, we report the standard ($p^o = 0.1$ MPa) molar enthalpies of formation of 2-, 3-, and 4-fluorophenol isomers, in the gaseous phase, obtained from measurements of the standard molar energies of combustion using a rotating bomb calorimeter and from the values of the standard molar enthalpies of sublimation or vaporization measured by Calvet microcalorimetry. In addition to the experimental work, density functional theory calculations at the B3LYP/6-311++G(d,p) level of theory for each compound were carried out to estimate the gaseous phase enthalpies of formation and to get a better understanding of the structure and energetics relation. The values of gas-phase enthalpies of formation of the studied monofluorine substituted phenols were also estimated using the empirical method suggested by Cox.[51]

2. Experimental Section

Materials and Purity Control. The compounds 2-fluorophenol [CAS 367-12-4], 3-fluorophenol [CAS 372-20-3], and 4-fluorophenol [CAS 371-41-5] were purchased from Sigma-Aldrich Chemical Co., with an assessed minimum purity of 0.98 (mass fraction). The liquids 2- and 3-fluorophenol were purified by successive fractional distillations under reduced pressure and stored under nitrogen atmosphere. The crystalline 4-fluorophenol was purified by repeated vacuum sublimations. The final purity of each fluorophenol isomer was checked by gas chromatography, performed on an Agilent 4890D Gas Chromatograph equipped with 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 the 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 $K \cdot min^{-1}$, 473 K (5 min). No impurities greater than 10^{-3} in mass fraction could be detected in the samples of the monofluorophenol isomers used for the rotating bomb combustion calorimetry and Calvet microcalorimetry measurements.

Table 4. Standard ($p^o = 0.1$ MPa) Molar Enthalpies of Sublimation or Vaporization, $\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^{\text{o}}$, at $T = 298.15$ K

compound	no. of expts	T/K	$(\Delta_{\text{cr,l},298.15\text{K}}^{\text{g},T}H_{\text{m}}^{\text{o}})$ (kJ·mol^{-1})	$(\Delta_{298.15\text{K}}^{T}H_{\text{m}}^{\text{o}}(\text{g}))$ (kJ·mol^{-1})	$(\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\text{ K}))$ (kJ·mol^{-1})
2-fluorophenol (l)	5	314.8	54.3 ± 0.1	2.0	52.3 ± 0.8
3-fluorophenol (l)	5	314.8	62.1 ± 0.1	2.0	60.1 ± 0.9
4-fluorophenol (cr)	5	314.8	75.9 ± 0.2	2.0	73.9 ± 1.4

Table 5. Standard ($p^o = 0.1$ MPa) Molar Enthalpies of Formation, in Condensed and Gaseous Phases, and Standard Molar Enthalpies of Vaporization or Sublimation, at $T = 298.15$ K

compound	$(-\Delta_{\text{f}}H_{\text{m}}^{\text{o}}(\text{cr, l}))$ (kJ·mol^{-1})	$(\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\text{ K}))$ (kJ·mol^{-1})	$(-\Delta_{\text{f}}H_{\text{m}}^{\text{o}}(\text{g}))$ (kJ·mol^{-1})	$\delta_{-\text{F}}$[a] kJ·mol^{-1}
benzene			−82.6 ± 0.7[81]	
phenol			96.4 ± 0.9[81]	
anisole			67.9 ± 0.8[81]	
aniline			−87.1 ± 1.1[81]	
fluorobenzene			115.9 ± 1.4[81]	−198.5 ± 1.6
2-fluorophenol	346.8 ± 1.4	52.3 ± 0.8	294.5 ± 1.6	−198.1 ± 1.8
3-fluorophenol	352.9 ± 1.4	60.1 ± 0.9	292.8 ± 1.7	−196.4 ± 1.9
4-fluorophenol	361.5 ± 1.5	73.9 ± 1.4	287.6 ± 2.1	−191.2 ± 2.3
2-fluoroanisole			249.7 ± 1.9[88]	−181.8 ± 2.1
3-fluoroanisole			266.4 ± 1.9[88]	−198.5 ± 2.1
4-fluoroanisole			260.5 ± 1.9[88]	−192.6 ± 2.1
2-fluoroaniline			107.2 ± 1.4[60]	−194.3 ± 1.8
3-fluoroaniline			115.6 ± 1.3[60]	−202.7 ± 1.7
4-fluoroaniline			109.6 ± 1.6[60]	−196.7 ± 1.9

[a] Enthalpic increment for substitution of a fluorine atom into the aromatic ring of benzene, phenol, anisole, or aniline.

Rotating Bomb Combustion Calorimetry Measurements. The standard molar enthalpies of combustion were determined with an isoperibol rotating-bomb calorimeter, originally constructed at the University of Lund according to the design of Sunner.[52] The apparatus and the operating technique have been described elsewhere,[53−55] 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 is 1 cm, is a twin valve platinum lined bomb with all 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, sensitivity ± (1·10^{-1}) g, was used to weigh the amount of distilled water added to the calorimeter from a weighed Perspex vessel, and 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 ± (1·10^{-4}) K, using a Hewlett-Packard (HP-2804A) quartz crystal thermometer interfaced to a PC programmed to collect data and to compute the adiabatic temperature change, by means of a version of the LABTERMO program.[56] 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 ($\phi = 0.05$ mm, Goodfellow, mass fraction 0.9999). The rotating mechanism allowed simultaneous axial and end-overend rotation of the bomb, causing the deionized water placed in the bomb to wash all internal surfaces of the bomb, yielding a homogeneous final solution. For each combustion experiment of the fluorophenol isomers, 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.[57] 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 of ca. 303.5 K to ± (1·10^{-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 −(26 434 ± 3) J·g^{-1}.[58] 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.,[59] without bomb rotation. One set of seven calibration experiments was performed leading to the value of the energy equivalent of the calorimeter: ε(calor) = (25 157.4 ± 1.1) J·K^{-1}; the uncertainty quoted is the standard deviation of the mean.

The accuracies of the experimental procedure and of the calorimeter were checked in our laboratory by measuring the energy of combustion of 4-fluorobenzoic acid, recommended by Good et al.[57] as a test substance for combustion calorimetry of organic fluorine compounds, in which the atomic ratio of hydrogen to fluorine is equal to, or greater than, unity. Samples of 4-fluorobenzoic acid were burned in the pellet form under oxygen, at $p = 3.04$ MPa, in the presence of 10.00 cm^3 of water placed in the bomb. The standard massic energy of combustion obtained for 4-fluorobenzoic acid, as the mean of six independent experiments, was $\Delta_{\text{c}}u^\circ = -(21\,865.1 \pm 2.0)$ J·g^{-1},[60] in good agreement with the recommended value: $\Delta_{\text{c}}u^\circ = -(21\,860 \pm 4)$ J·g^{-1}.[61] The values of $\Delta_{\text{c}}u^\circ$ refer to the reaction with $\text{HF}\cdot 10\text{H}_2\text{O(l)}$ as the single fluorine-containing product in the final state.

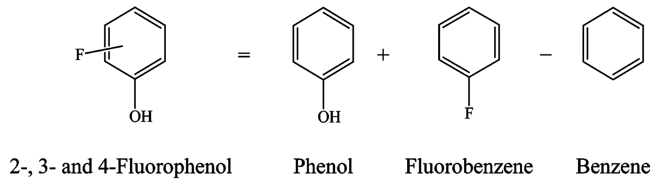


Figure 2. Empirical scheme for estimation of $\Delta_f H_m^o$(g) by the Cox scheme.

The combustion experiments of the three monofluorophenols were also carried out in oxygen, at $p = 3.04$ MPa in the presence of 10.00 cm^3 of water. The liquid 2- and 3-fluorophenol were burnt enclosed in polyethylene bags [$\Delta_c u° = -(46\,282.4 \pm 4.8)$ J·g^{-1},[62] a value measured in our laboratory by combustion of polyethylene samples]. The crystalline 4-fluorophenol was burnt in pellet form, enclosed in sealed polyester bags made of Melinex (0.025 mm thickness, $\Delta_c u° = -(22\,902 \pm 5)$ J·g^{-1}, a value confirmed in our laboratory) using the technique described by Skinner and Snelson.[63] The mass of carbon dioxide produced from the Melinex combustion was calculated using the factor previously reported.[63] The necessary weighing was carried out on a Mettler Toledo AE 240 balance, with a sensitivity of ± ($1 \cdot 10^{-5}$) 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 Devarda's alloy method,[64] and corrections for nitric acid formation were based on −59.7 kJ·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).[65] For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u° = -16240$ J·g^{-1},[59] a value that has been confirmed in our laboratory. Corrections to the standard state, ΔU_Σ, were made by the procedure given by Good and Scott,[18] for fluorine containing compounds, based on the method developed by Hubbard et al.,[66] including the values for the solubility of carbon dioxide in hydrofluoric acid solutions, as given by Cox et al.[67] The values for the pressure coefficient of massic energy, $(\partial u/\partial p)_T$, for the title compounds were assumed to be −0.2 J·g^{-1}·MPa^{-1} at $T = 298.15$ K, a typical value for most organic compounds.[68] The specific densities for 2-, 3-, and 4-fluorophenol were taken as 1.256 g·cm^{-3},[69] 1.238 g·cm^{-3},[69] and 1.294 g·cm^{-3},[70] respectively. The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005;[71] using those values, the molar mass for the 2-, 3-, and 4-fluorophenol isomers is 112.1022 g·mol^{-1}.

Calvet Microcalorimetry Measurements. The standard molar enthalpies of sublimation or vaporization of the title compounds were measured in a high temperature Calvet microcalorimeter (Setaram HT 1000), using for the vaporization of the liquid monofluorophenol a technique[72] similar to that described by Skinner and co-workers[73] for the sublimation of solid compounds. The measuring procedures, as well as the detailed description of the apparatus, have been recently reported.[74] 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), $\Delta_{cr}^{g} H_m^o(T = 298.15\text{K}) = (76.60 \pm 0.60)$ kJ·mol^{-1},[75] and of vaporization of *n*-decane (Aldrich, mass fraction purity > 0.99), $\Delta_l^g H_m^o(T = 298.15\text{K}) = (51.42 \pm 0.21)$ kJ·mol^{-1}.[76] The calibration procedure was the same as for the samples. From five independent experiments, the calibrations constants, k, of the calorimeter at experimental temperature were found to be $k(T = 314.9 \text{ K}) = (1.0062 \pm 0.0062)$ for the vaporization experiments of the 2- and 3-fluorophenol and $k(T = 314.9 \text{ K}) = (1.0056 \pm 0.0045)$ for the sublimation experiments of 4-fluorophenol; 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 or (6 to 9) mg of the liquid compounds were placed into small glass capillary tubes sealed at one end and weighed with a precision of ± 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 $T = 314.9$ K. 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 or vaporization of the compound was acquired. The thermal corrections for the glass capillary tubes were determined in separate experiments[74] and were evaluated and minimized in each experiment by dropping glass capillary tubes of near equal mass into both measuring cells. The observed standard molar enthalpies of sublimation or vaporization, $\Delta_{cr,l,298.15K}^{g,T} H_m^o$, have been corrected to $T = 298.15$ K using the corrective term $\Delta_{298.15K}^{T} H_m^o(g) = \int_{298.15K}^{T} C_{p,m}^o(g)\, dT$, where T is the temperature of the hot reaction vessel, $C_{p,m}^o$(g) is the molar heat capacity of the compounds in the gas phase, obtained by means of DFT calculations with the B3LYP functional and the 6-311++G(d,p) basis set, as

$$C_{p,m}^o(\text{2-FPhenol, g})/\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -1.902\cdot10^{-4}(T/\text{K})^2 + 0.4178(T/\text{K}) + 11.213$$

$$C_{p,m}^o(\text{3-FPhenol, g})/\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -1.892\cdot10^{-4}(T/\text{K})^2 + 0.4162(T/\text{K}) + 11.676$$

$$C_{p,m}^o(\text{4-FPhenol, g})/\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -2.290\cdot10^{-4}(T/\text{K})^2 + 0.4671(T/\text{K}) + 2.138$$

3. Results

Experimental Enthalpies of Formation. Detailed results for a typical combustion experiment of each compound are given in Table 1. The values of the energy associated to the isothermal bomb process, ΔU(IBP), were calculated from eq 1, according to ref 66

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + \Delta m(\text{H}_2\text{O})c_p(\text{H}_2\text{O, l})\}\Delta T_{\text{ad}} + (T_i - 298.15 \text{ K})\varepsilon_i + (298.15 \text{ K} - T_i - \Delta T_{\text{ad}})\varepsilon_f + \Delta U_{\text{ign}} \quad (1)$$

where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to ε(calor); $c_p(H_2O, l)$ 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) derived as recommended in the literature for compounds containing fluorine.[18] The remaining quantities are as previously defined.[66,68] The detailed results for all the combustion experiments of each compound, together with the mean value of the standard massic energies of combustion, $\Delta_c u°$, are presented in the Supporting Information (Tables S1 to S3).

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

	$-\Delta_f H^o_m(g)/kJ \cdot mol^{-1}$			$\Delta^a/kJ \cdot mol^{-1}$	
compound	experimental	Cox scheme	calculated[b]	Cox scheme	calculated[b]
2-fluorophenol	294.5 ± 1.6	290.9 ± 1.8	290.8	−4.6 ± 2.4	−3.7
3-fluorophenol	292.8 ± 1.7	294.9 ± 1.8	294.2	2.1 ± 2.5	1.4
4-fluorophenol	287.6 ± 2.1	294.9 ± 1.8	288.9	7.3 ± 2.8	1.3

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

Table 7. Gas-Phase Relative Bond Dissociation Enthalpies, $\Delta DH°$(O−H), for Substituted Fluorophenols[a]

	$\Delta DH°$(O − H)	$DH°$(O−H)/kJ·mol^{-1}	
compound	kJ·mol^{-1}	this work	ref 25
phenol			371.3 ± 2.3
2-fluorophenol	4.0	375.3	362.5 ± 8.3
3-fluorophenol	6.3	377.6	377.3 ± 8.3
4-fluorophenol	−6.3	364.5	367.3 ± 4.6

[a] O−H bond dissociation enthalpy, $DH°$(O−H).

The individual values of the standard massic energy of combustion, $\Delta_c u°$, for all the combustion experiments of each compound, together with the mean values, $\langle \Delta_c u° \rangle$, and their standard deviations of the mean, are listed, for each compound, in Table 2. The values of $\Delta_c u°$ refer to the idealized combustion reaction of monofluorophenols, yielding $HF \cdot 10H_2O(l)$ as the only fluorine-containing product in the final state, according to eq 2

$$C_6H_5OF(l) + 6.5O_2(g) + 8H_2O(l) \rightarrow 6CO_2(g) + HF \cdot 10H_2O(l) \quad (2)$$

Table 3 lists the derived values of the standard molar energies and enthalpies of combustion, $\Delta_c U^o_m$(cr, l) and $\Delta_c H^o_m$(cr, l), as well as the standard molar enthalpies of formation, $\Delta_f H^o_m$(cr, l), for the three isomers in the condensed phase, at $T = 298.15$ K, which were derived from the values of $\Delta_c H^o_m$(cr, l) and from the standard molar enthalpies formation, at $T = 298.15$ K, of the following compounds: $\Delta_f H^o_m(CO_2, g) = -(393.51 \pm 0.13)$ kJ·mol^{-1};[77] $\Delta_f H^o_m(H_2O, l) = -(285.830 \pm 0.040)$ kJ·mol^{-1};[77] and $\Delta_f H^o_m(HF \cdot 10H_2O, l) = -(322.034 \pm 0.650)$ kJ·mol^{-1}.[78] 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 or polyethylene used as combustion auxiliaries.[79,80]

Results of the measurements of the enthalpies of vaporization or sublimation, $\Delta^{g,T}_{cr,l,298.15K} H^o_m$, for the title compounds, obtained by Calvet microcalorimetry, are given in Table 4, with the respective uncertainties, taken as the standard deviations of the mean of five individual results. The associated uncertainties for the standard molar enthalpies of vaporization or sublimation, $\Delta^{g}_{cr,l} H^o_m(T = 298.15K)$, at $T = 298.15$ K, are twice the overall standard deviation of the mean which include the uncertainties in calibration with *n*-decane and naphthalene.[79,80] In Table 5 are summarized the derived standard molar enthalpies of formation in the gaseous phase, $\Delta_f H^o_m(g)$, at $T = 298.15$ K, for the three monofluorophenols, as well as the values of the enthalpic increments of substitution of a fluorine atom in the phenol ring, δ_{-F}.

Enthalpies of Formation Estimated with the Cox Scheme. Considering the empirical scheme suggest by Cox,[51] for the estimation of the enthalpies of formation in the gaseous state, based on the transferability of enthalpic group contributions in benzene derivatives, it is possible to estimate the gas-phase standard molar enthalpies of formation for the different isomers of monofluorophenol. So, the values of $\Delta_f H^o_m(g)$ for each isomer can be estimated from the literature data given in Table 5 for benzene, phenol, and fluorobenzene,[81] and taking into account the scheme presented in Figure 2. For 2-fluorophenol, it is necessary, as suggested by Cox,[51] to consider a correction term of 4 kJ·mol^{-1} since the fluorine atom and the hydroxyl group are bonded in *ortho*-position of the aromatic ring.

Thus, according to the Cox scheme,[51] the estimated value for the standard molar enthalpies of formation, in the gaseous state, of *ortho*-fluorophenol is −(290.0 ± 1.8) kJ·mol^{-1}, whereas the estimated value for both the *meta* and *para* isomers is −(294.9 ± 1.8) kJ·mol^{-1} (cf. Table 6). These estimated values differ from the experimental ones by −(4.6 ± 2.4) kJ·mol^{-1} in the case of the *ortho* isomer, by (2.1 ± 2.3) kJ·mol^{-1} and (7.4 ± 2.8) kJ·mol^{-1} in the cases, respectively, of the *meta* and *para* isomers, deviations that are very well within the limit of acceptance of ± 10 kJ·mol^{-1} indicated by Cox for his scheme.[51] Although this empirical method of $\Delta_f H^o_m(g)$ estimation predicts the 2-fluorophenol as the least stable isomer, the experimental results point it out as the most stable one. This fact is not surprising since the Cox scheme completely neglects the stabilization effect caused by the existence of intramolecular hydrogen bonds. The formation of a weak intramolecular halogen−hydrogen bond, F···H−O, has been previously reported for 2-fluorophenol based on the results from microwave and gas phase electron diffraction experiments,[43,44] as well as from theoretical calculations.[35,48−50] In the case of 3-fluorophenol, the Δ value is lower than the associated uncertainty, yielding a very good estimate of $\Delta_f H^o_m(g)$, but for the *para* isomer, the Cox scheme predicts a higher stabilization effect for the introduction of a fluorine atom in the *para* position of the phenolic ring than was experimentally observed.

Computed Enthalpies of Formation. The theoretical calculations were performed with the Gaussian 03 software package,[82] using density functional theory (DFT) with the hybrid exchange correlation functional (B3LYP)[83−85] together with the split-valence polarized 6-311++G(d,p)[86] extended basis set, for the geometry optimizations and frequency calculations of the fluorophenol isomers considered in this work, phenol, phenoxy radical, and fluorine-substituted phenoxy radicals. Zero-point vibrational energies and fundamental vibrational frequencies were scaled by a factor of 0.9887 and 0.9688, respectively.[87] The above-mentioned exchange-correlation functional was chosen since a previous work devoted to the thermochemistry of fluoroanisoles[88] yielded an estimation of accurate gas-phase enthalpies of formation for this class of compounds. Also, it has been demonstrated that this theoretical level yields to a practically perfect agreement between the theoretical and experimental infrared spectra of phenol.[35]

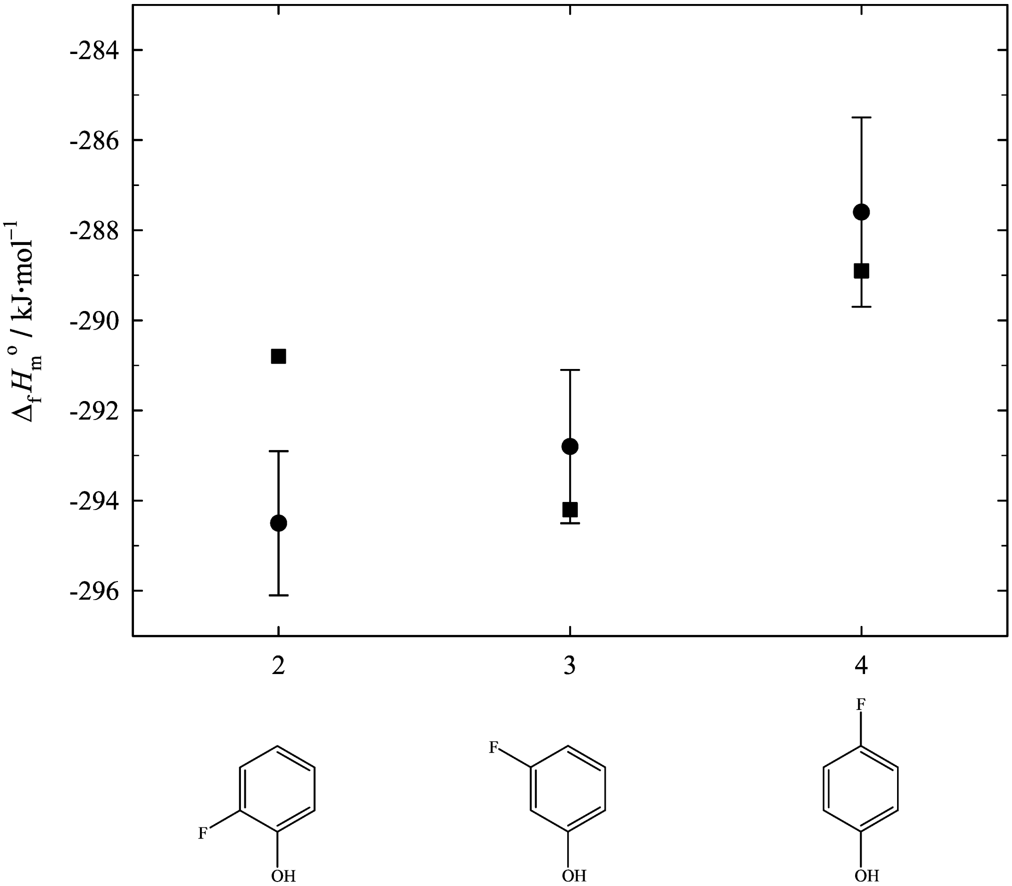
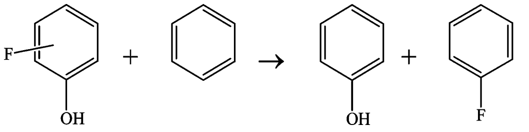


Figure 3. Comparison between experimental (●) and computed (■) values of the gas-phase standard molar enthalpy of formation in the monofluorophenols.

The energies of all monofluorophenols, and those of phenol, benzene, and fluorobenzene, calculated at the B3LYP/6-311++G(d,p) and corrected for $T = 298.15$ K, were used to compute the enthalpy of the homodesmic reaction described by the following equation



(3)

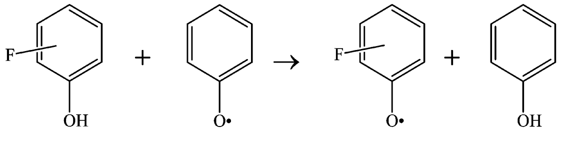
Combining those enthalpies of reaction with the experimental $\Delta_f H_m^o(g)$ of benzene, fluorobenzene, and phenol given in Table 5, it was possible to estimate the $\Delta_f H_m^o(g)$ of the three monofluorophenol isomers, which are summarized in Table 6. The results show clearly that the computational estimates are in good agreement with the experimental results, involving absolute deviations no larger than 3.7 kJ·mol^{-1}.

The most stable conformations obtained for all the three monofluorophenols, taking into account the geometry optimization performed at the B3LYP/6-311++G(d,p), are those where the hydroxyl group is coplanar with the aromatic benzene ring, likewise phenol,[89] the conjugation of the oxygen's lone pair with the π-electron of the benzene ring occurring. For 3-fluorophenol, the most stable configuration was found to be that where the hydroxyl group is in *trans* position with respect to the fluorine atom.

In the case of *ortho*-fluorophenol, the hydroxyl group adopts a *cis* conformation relative to the fluorine atom, favoring the formation of an intramolecular halogen−hydrogen bond, thus making this configuration more stable than the *trans*. This finding has been previously reported by several authors,[44−46] with Mulder et al.[50] and Tishchenko et al.[35] suggesting that the calculated enthalpy of the intramolecular hydrogen bond in *ortho*-fluorophenol was, respectively, −12.5 kJ·mol^{-1} and −11.7 kJ·mol^{-1}. In our computational calculations, the value of −11.7 kJ·mol^{-1} was also archived for the enthalpy of the intramolecular F···H−O bond in the 2-fluorophenol isomer, using the procedure suggested by Mulder et al.,[50] by calculating the difference between the DFT enthalpies, at $T = 298$ K, for the *cis* and the *trans* configurations in the 2-fluorophenol.

On the basis of the recently proposed *ortho*−*para* method[90] for the analysis of the energetics of intramolecular H-bonds, in which the 4-fluorophenol is used as a reference system for 2-fluorophenol, the enthalpy of the intramolecular F···H−O bond in 2-fluorophenol was calculated as −(6.9 ± 2.6) kJ·mol^{-1}, which is in close agreement with the value suggested by Carlson et al.[47] of −6.82 kJ·mol^{-1}.

Considering the enthalpy of reaction of eq 4, which expresses the change in bond dissociation enthalpy for the fluoro-substituted phenols (FPhOH) relative to phenol itself the



(4)

theoretical bond dissociation enthalpies of substituted fluorophenols, $DH°$(FPhO−H) can be obtained from the following equation.

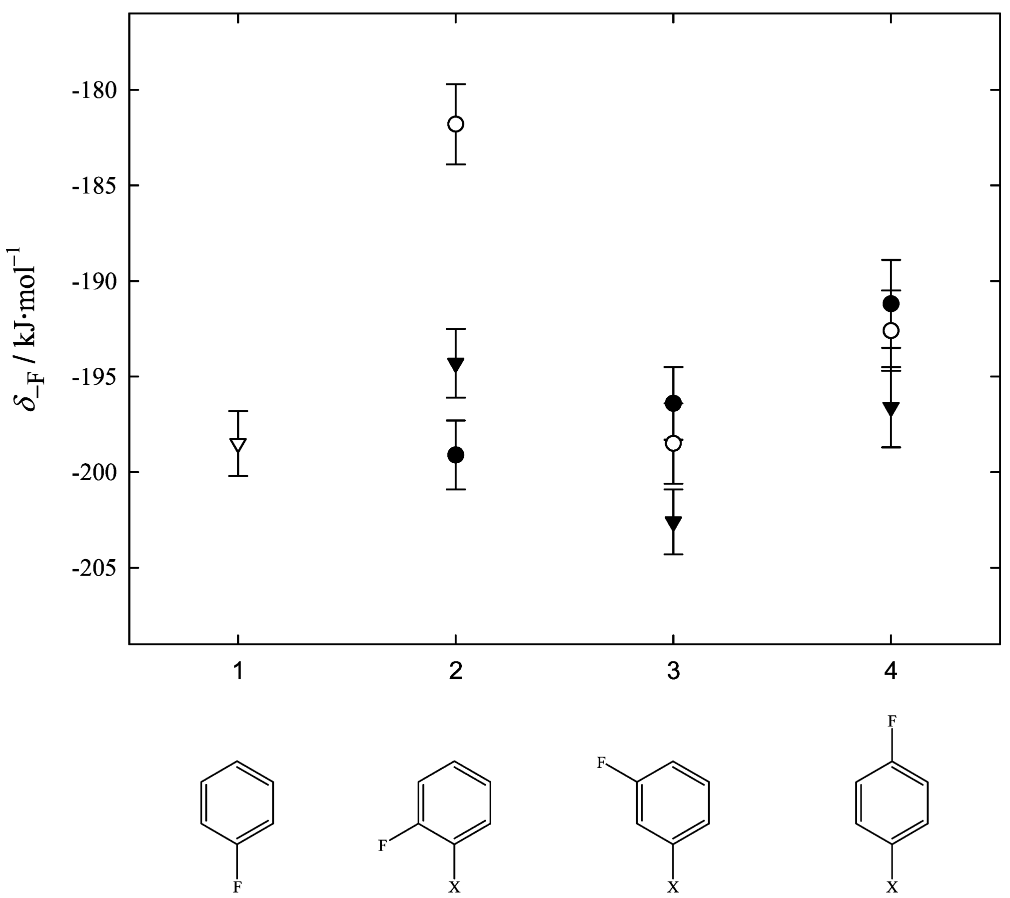


Figure 4. Enthalpic increment for substitution of a fluorine atom in benzene (▽) and in the different positions of the aromatic ring of its derivatives: X = −OH(●); −OCH$_3$(○), and −NH$_2$(▼).

$$\Delta DH^{\circ}(\text{O}-\text{H}) = DH^{\circ}(\text{FPhO}-\text{H}) - DH^{\circ}(\text{PhO}-\text{H}) \quad (5)$$

The results that are summarized in Table 7 clearly show that the computational estimates are in good agreement with the values of bond dissociation enthalpies reported in the review of Borges dos Santos and Martinho Simões[25] for the 3- and 4-fluorophenols, but a large deviation is found in the case of 2-fluorophenol. Our calculated value is based on the most stable configuration of 2-fluorophenol which shows a stabilizing intramolecular F−H hydrogen bond, a fact that was not considered in the work cited by the paper Borges dos Santos and Martinho Simões.[25]

Discussion

Rotating-bomb calorimetry and Calvet microcalorimetry experiments have been performed to obtain the enthalpies of combustion in the condensed phase and the enthalpies of phase transition to the gaseous state of the three monofluorophenols. The derived gas-phase enthalpies of formation have been compared with DFT estimated values and those obtained by application of the Cox scheme. It is found that the Cox scheme yields good estimates for the three isomers, in particular for the 3-fluorophenol isomer, but this scheme fails completely in the differentiation between the 3- and 4-fluorophenol isomers since Cox did not provide any correction to differentiate substitutions at aromatic ring positions 3 or 4 due to the possibility of different resonance/inductive effects depending on the substituent, which could increase or decrease the overall compound stability. This method also predicts the 2-fluorophenol to be the least stable compound. The wrong prediction of 2-fluorophenol as the least stable isomer results from the fact that the Cox scheme completely neglected the stabilizing interaction between the fluorine atom in the *ortho* position and the hydroxyl group due to the formation of a weak internal halogen−hydrogen bond, which represents a higher energetic stabilization of the isomer substituted in that position.

The use of DFT calculations together with a homodesmic reaction scheme employing phenol, benzene, and fluorobenzene yields excellent estimates of the gaseous standard molar enthalpies of formation for the fluorophenol isomers. Both theoretical and experimental results point out the 4-fluorophenol isomer as the least stable one. A closer inspection of the results presented in Table 6 and in Figure 3 shows that the experimental enthalpies of formation in the gas phase give *ortho* and *meta* isomers with similar enthalpic stabilities, within the associated uncertainties, in agreement with the DFT computed values. However, the computational results predict a lower stabilization effect for the introduction of a fluorine atom in the *ortho* position of the phenolic ring than the experimentally observed results, showing a reversed order of stability, with the 3-fluorophenol isomer as the most stable of all the monofluorophenols.

In Table 5 are also presented the literature values for the enthalpies of formation in the gas phase for benzene, fluorobenzene, phenol, anisole, aniline, monofluoroanisoles,[88] and monofluoroanilines[60] and the respective enthalpic increment for introducing a fluorine atom in the different position of the aromatic ring, δ_{-F}, of benzene, phenol, anisole, and aniline. From the results presented in Table 5 and from Figure 4, it is possible to observe a similar order of enthalpic increment for the substitution of a fluorine atom in *ortho*, *meta*, and *para* positions of the aromatic ring of phenol, anisole, and aniline: *meta* < *para* < *ortho*, with the exception of the 2-fluorophenol isomer, which has an enthalpic stability similar to the 3-fluorophenol isomer, due to an additional effect of stabilization caused by the existence of an intramolecular hydrogen bond between the fluorine atom and the hydrogen of the hydroxyl group, not present in the 2-fluoroanisole[88] or 2-fluoroaniline.[60]

The fluorine atom exerts a σ electron-withdrawing inductive effect and a π electron-donating mesomeric effect on the aromatic ring. From Figure 4, it is possible to see that the introduction of a fluorine atom in *para* position of the benzene ring of the phenol, anisole, or aniline, which are all π electron donor groups, will provoke a higher energetic destabilization relative to the substitution in the *meta* position. This is possibly due to the direct mesomeric conjugation between the two substituents which does not occur when the fluorine atom is in the 3 position, where the conjugation effects between the oxygen or nitrogen electron lone pair(s) and the π electrons of the ring are favored.

The energetic effect of substitution of the fluorine in the *ortho* position of the aromatic ring of phenol, anisole, and aniline is governed by the balance between conjugation, steric effects, and the possible existence of an attractive H−F interaction.

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This paper is dedicated to Professor William A. Wakeham not only for his highly valuable contributions to the field of Chemistry and Chemical Engineering, during his scientific life, but also as a tribute for the excellent work he has done for the development of International Science, through relevant international collaborations he managed to establish with so many researchers from other countries.

Supporting Information Available:

Details of all the combustion calorimetry experiments for the three fluorophenols studied, as well as the fully optimized structures and the calculated energies of all compounds, are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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