



Calorimetric and computational thermochemical study of difluorophenol isomers

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ABSTRACT

The standard gas-phase enthalpies of formation of difluoro-substituted phenols have been determined experimentally, and have also been predicted by means of computational and empirical estimative methods.

Combustion calorimetric studies were used to determine the standard molar enthalpies of formation of the six difluorophenol isomers, whereas their standard molar enthalpies of sublimation or vaporization, at $T = 298.15$ K was measured by the Calvet drop calorimetric technique.

Difluorophenol isomer	$\Delta_f H_m^\circ(\text{cr, l})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr, l}}^\circ H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$
2,3-Difluorophenol (cr)	-529.4 ± 1.8	68.2 ± 1.5
2,4-Difluorophenol (l)	-529.1 ± 1.8	58.8 ± 0.9
2,5-Difluorophenol (cr)	-545.2 ± 1.8	68.0 ± 1.4
2,6-Difluorophenol (cr)	-548.5 ± 1.7	77.8 ± 2.0
3,4-Difluorophenol (cr)	-535.3 ± 1.8	72.9 ± 1.5
3,5-Difluorophenol (cr)	-555.8 ± 1.8	72.8 ± 1.5

From the values obtained for $\Delta_f H_m^\circ(\text{cr, l})$ and $\Delta_{\text{cr, l}}^\circ H_m^\circ(298.15 \text{ K})$, the standard molar enthalpies of formation in the gas-phase, at $T = 298.15$ K, were derived for the six isomers.

Moreover, the standard gas-phase enthalpies of formation of difluorophenols have been predicted based on two different methodologies: one using the empirical scheme developed by Cox and the other one based on density functional theory calculations performed at the B3LYP/6-311++G(d,p) level of theory coupled with suitable homodesmotic reactions and were compared to the experimental values.

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1. Introduction

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. Phenolic compounds are capable of suppressing radical mediated oxidative damage, by curtailing reactive species and so they are used as antioxidants for the conservation of foodstuff [1]. The halogenated phenol derivatives are used in antiseptic or disinfectant formulations, and are also used as intermediates for pesticides, pharmaceuticals and dyes [2]. Recently the fluorine phenolic derivatives have been used in the synthesis of polymers [3], in particular the 2,6-difluorophenol isomer, which has been used in the preparation of polymers for biosensor applications [4].

Some important research work has been undertaken concerning the conformational properties of phenol and substituted halogenated phenols, especially on the molecular structure of the *ortho*-halogenated phenol isomers [see, e.g., reference [5–8] and references therein]. The intramolecular isomerism plays a significant role in biologically relevant molecular systems, exerting a considerable impact on molecular properties. The dominant reasons for the altered functionalities are ascribed to steric effects and, in the case of electronegative substituents, intramolecular hydrogen bonding.

Structural information on the 2,6-difluorophenol compound is available from NMR [9] and gas-phase electron diffraction (ED) [10], vibrational spectroscopy [11] and quantum chemical calculations [11–13].

The microwave spectrum of 2,4-difluorophenol has been investigated by Chakrabarti and Jaman [14], and the analysis of the spectrum led to the identification of the *cis* conformer of the molecule.

Only for 3,5-difluorophenol has X-ray crystallography been performed [15], where it was shown that the crystal structure has an

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amphiphilic layer-like arrangement, with a hydrophilic contact involving the hydroxyl groups and hydrogen atoms, and a hydrophobic contact involving the fluorine atom.

To the best of our knowledge, both the enthalpies of combustion, in the condensed phase, and the enthalpies of sublimation or vaporization of the isomeric difluorophenols have never been reported. Hence, this paper reports the standard ($p^\circ = 0.1$ MPa) molar energies of combustion of the six isomers of difluorophenol, measured by rotating bomb combustion calorimetry, as well as their standard molar enthalpies of sublimation or vaporization, at $T = 298.15$ K, measured by Calvet microcalorimetry.

In addition to the experimental work, we have calculated the gas-phase enthalpies of formation for the six difluorophenol isomers by applying the empirical method suggested by Cox [16] and by computational thermochemistry using the density functional theory at the B3LYP/6-311++G(d,p) level of theory. These estimated values were compared with the derived experimental values of the standard molar enthalpies of formation, in the gas phase, at $T = 298.15$ K, of the six difluorophenols.

2. Experimental

2.1. Materials and purity control

Commercial samples of 2,3-difluorophenol [CAS 6418-38-8], 2,4-difluorophenol [CAS 367-27-1], 2,5-difluorophenol [CAS 2713-31-7], 2,6-difluorophenol [CAS 28177-48-2], 3,4-difluorophenol [CAS 2713-33-9], and 3,5-difluorophenol [CAS 2713-34-0] were obtained from Sigma–Aldrich Chemical Co., with mass fraction purities of 0.98, 0.99, 0.95, 0.98, 0.99 and 0.99, respectively. The crystalline 2,3-, 2,5-, 2,6-, 3,4- and 3,5-difluorophenol were purified by repeated vacuum sublimations, and the liquid 2,4-difluorophenol was purified by successive fractional distillations under reduced pressure and stored under nitrogen atmosphere.

The compounds 2,5-, 2,6-, and 3,4-difluorophenol were found to be slightly hygroscopic, absorbing a small amount of water when handled during the experiments. So, for each sample of these compounds used in the calorimetric measurements, the amount of water was determined by Karl Fischer titrations. The absence of other impurities than water, greater than 10^{-3} in mass fraction, 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 mm \times 0.530 mm i.d. \times 1.5 μ m film thickness), and with nitrogen as carrier gas.

The specific density of the liquid 2,4-difluorophenol was taken as 1.362 g \cdot cm $^{-3}$ [17]. For the crystalline 3,5-difluorophenol, it was used the value of 1.566 g \cdot cm $^{-3}$ [15], a value that was assumed for all the others crystalline difluorophenol isomers.

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005 [18].

2.2. 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 Professor Stig Sunner [19]. The apparatus and the technique have been previously described [20–22]. 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 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 PM11-N balance, sensitivity $\pm(1 \cdot 10^{-1})$ 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 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 of the calorimeter were automatically collected every 10 s, within the bounds of $\pm(1 \cdot 10^{-4})$ K, using a Hewlett–Packard (HP-2804A) quartz crystal thermometer interfaced to a PC programmed for data acquisition and to compute the adiabatic temperature change, by means of a version of the LABTERMO program [23]. At least 100 temperature readings were taken for the main period and for both the fore and after 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 μ F) when discharged through a platinum wire ($\phi = 0.05$ mm, Goodfellow, mass fraction 0.9999).

The rotating mechanism of the combustion bomb allows its simultaneous axial and end-over-end rotation, causing the deionised water placed in the bomb to wash all internal surfaces of the bomb, yielding a homogeneous final solution. For each combustion experiment of the difluorophenol isomers, the rotation of the bomb was started when the temperature rise of the main period reached about 0.63 of its total value and then continued throughout the experiment. It has been shown that by adopting this procedure, the frictional work due to the rotation of the bomb is automatically accounted in the temperature corrections for the work of water stirring and for the heat exchanged with the surrounding isothermal jacket [24]. This one 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 $\pm(1 \cdot 10^{-4})$ K, using a temperature controller (Tronac PTC 41).

Benzoic acid (NIST Standard Reference Material 39j) was used for calibration of the calorimeter. Its mass-related energy of combustion is $-(26434 \pm 3)$ J \cdot g $^{-1}$ [25], under bomb conditions. Calibration experiments were carried out in oxygen, at a pressure of 3.04 MPa, with 1.00 cm 3 of deionised water added to the bomb, according to the procedure in the conventional way suggested by Coops *et al.* [26], without bomb rotation. The obtained value of energy equivalent of the calorimeter was $\varepsilon(\text{calor}) = (25157.4 \pm 1.1)$ J \cdot K $^{-1}$, (0.0044%), as the mean of seven calibration experiments, where 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, recommend by Good *et al.* [24] 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 $\Delta_c u^\circ = -(21865.1 \pm 2.0)$ J \cdot g $^{-1}$ [27] in good agreement with the recommended value: $\Delta_c u^\circ = -(21860 \pm 4)$ J \cdot g $^{-1}$ [28]. The values of $\Delta_c u^\circ$ refer to the reaction with HF \cdot 10H $_2$ O(l) as the single fluorine-containing product in the final state.

The combustion experiments of the six difluorophenols were also carried out in oxygen, at $p = 3.04$ MPa in the presence of 10.00 cm 3 of water. The liquid 2,4-difluorophenol and the solids 2,3-, 2,5-, 3,4- and 3,5-difluorophenol were burnt enclosed in polyethylene bags, for which $\Delta_c u^\circ = -(46282.4 \pm 4.8)$ J \cdot g $^{-1}$ [29], a value measured in our laboratory by combustion of polyethylene

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