



Experimental and computational study on the molecular energetics of the three monofluoroanisole isomers

Manuel A.V. Ribeiro da Silva *, Ana I.M.C. Lobo Ferreira

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the liquid phase of three isomers of fluoroanisole were derived from the standard molar energies of combustion, in oxygen, to yield $\text{CO}_2(\text{g})$ and $\text{HF} \cdot 10\text{H}_2\text{O}(\text{l})$, at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The standard molar enthalpies of vaporization of these compounds, also at $T = 298.15$ K, were determined using Calvet microcalorimetry.

	$-\Delta_c U_m^\circ(\text{l})/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_f H_m^\circ(\text{l})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_1^g H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$
2-Fluoroanisole	3629.7 ± 1.0	301.9 ± 1.5	52.2 ± 1.1
3-Fluoroanisole	3617.1 ± 1.1	314.5 ± 1.6	48.1 ± 1.1
4-Fluoroanisole	3622.4 ± 1.2	309.2 ± 1.6	48.7 ± 1.1

The standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, were derived from the former two experimental quantities. These values are also compared with estimates based on two different methodologies: one using the empirical scheme developed by Cox and the other one 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. The computed values and the estimated values using the Cox method compare well with the experimental results obtained in this work.

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1. Introduction

Recently, we have reported experimental thermochemical studies of the monochloroanisole (monochloromethoxybenzene) [1] and dichloroanisole (dichloromethoxybenzene) [2] isomers. In view of the sparse knowledge and the great importance of the thermochemical data of the halogenated anisoles, this work presents the study of the monofluoroanisole (monofluoromethoxybenzene) isomers, figure 1, with the purpose of extending the thermochemical database for halogenated aromatic compounds and for a better understanding of the effect of substitutions of the halogen atom in the aromatic ring of benzene derivatives [3–6].

For understanding the function of complicated large biological molecules, it is important to know the thermochemical properties of their local units. From this point of view, anisole (methoxybenzene) and its derivatives have been extensively studied due to their properties as models of biological systems. Fluoroanisoles are widely used in the synthesis of fluorine substituted medicals com-

pounds with pharmacological activity [7–10] and agro agents [11]. The 4-fluoroanisole isomer was applied in the synthesis of poly(paraphenylene) a polymer marked by thermal and chemical stability, with potential applications in areas such as optoelectronics, batteries, and sensors [12].

The intramolecular isomerism plays a significant role in biologically relevant molecular systems. As a result, the conformational properties of anisole and monofluoroanisole isomers have been subject of many experimental and theoretical investigations over the past years. Some researchers groups have investigated the conformational properties of anisole molecule, by electron diffraction [13], microwave spectroscopy [14,15], high resolution spectroscopy [16], fluorescence spectroscopy [17], and high-level *ab initio* calculations and DFT calculations [15–19], and have concluded that anisole exists only as a single conformer with planar heavy atom skeleton, being this sterically unfavourable structure stabilized by the electron delocalization between the oxygen lone pairs and the electron system of the ring. The molecular geometry of 2-fluoroanisole has been studied using gas-phase electron diffraction, low-temperature matrix isolated FT-IR spectroscopy and quantum chemical methods [20,21], and it was demonstrated that the

* Corresponding author. Tel.: +351 22 0402 521; fax: +351 22 0402 522.
E-mail address: risilva@fc.up.pt (M.A.V. Ribeiro da Silva).

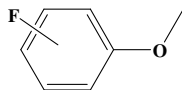


FIGURE 1. Structural formula of monofluoroanisole isomers.

preferred conformation is a planar conformer with *anti* orientation of the methyl group with respect to fluorine, $\varphi = 180^\circ$, while the minor conformer is non-planar with the CH_3 group rotated toward the fluorine atom by $\varphi \approx 60^\circ$. Lister *et al.* [22–24] have done some studies using microwave spectroscopy aiming the understanding of the molecular conformation of 3- and 4-fluoroanisole, but the molecular conformation of the 3- and 4-fluoroanisoles, was only better understood more recently, with the work developed by Oberhammer *et al.* [25,26], using gas-phase electron diffraction and quantum chemical methods. They have demonstrated that for fluoroanisoles with the fluorine atoms in the *meta* and *para* positions the planar conformer is the stable molecular structure like anisole itself, and that the 3-fluoroanisole exists as a mixture of two conformers, *syn* and *anti* form, in approximately equal abundance, the *anti* conformation being the most stable. So, with those studies, it was verified that the orientation of the methoxy group in anisoles, in the ring plane or perpendicular to it, depends mainly on a delicate balance between two opposing effects: the orbital interactions between the oxygen lone pairs and the benzene ring and the steric effects between the methyl group and the *ortho* atoms in the benzene ring.

To the best of our knowledge both the enthalpies of combustion, in the liquid state, and the enthalpies of vaporization of the 2-, 3-, and 4-fluoroanisole isomers have never been reported. For 3-fluoroanisole and 3,4-difluoroanisole, have been recently published the gas-phase enthalpies of formation obtained by theoretical calculations, as well as the standard entropies, $S^\circ(T)$, heat capacities, $C_p^\circ(T)$ and enthalpies, $[H^\circ(T) - H^\circ(0)]$ [26]. The proton affinities (PA) of the three monofluoroanisole isomers are known having been determined with the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry [27]. Hence, this paper reports the standard ($p^\circ = 0.1$ MPa) molar energies of combustion of the three liquid isomers of monofluoroanisole, measured by rotating bomb combustion calorimetry, as well as their standard molar enthalpies of vaporization, at the $T = 298.15$ K, measured by Calvet microcalorimetry, and the derived values for the standard molar enthalpies of formation, in the gas phase, at $T = 298.15$ K. In addition to the experimental work, we have calculated the gas-phase enthalpies of formation for the three monofluoroanisoles by applying the empirical method suggested by Cox [28] and by computational thermochemistry using the density functional theory at the B3LYP/6-311++G(d,p) level of theory.

2. Experimental

2.1. Materials and purity control

The 2-fluoroanisole [CAS 321-28-8], 3-fluoroanisole [CAS 456-49-5], and 4-fluoroanisole [CAS 459-60-9] were purchased from Sigma–Aldrich Chemical Co., with an assessed minimum purity of 0.98 (mass fraction). The three compounds, which are liquid at room temperature were purified by successive fractional distillations under reduced pressure and stored under nitrogen atmosphere.

The final purity of each isomer (mass fraction purity greater than 0.9995) 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 \times 0.530 mm i.d. \times 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: 323 K (1 min),

ramp at 10 K \cdot min $^{-1}$, 423 K (5 min). Determination of purities for the three isomers showed that the mass fractions of impurities were $<10^{-3}$.

The specific densities [29] for 2-, 3-, and 4-fluoroanisole were taken as (1.124, 1.104, and 1.114) g \cdot cm $^{-3}$, 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 [30]; using those values, the molar mass for the 2-, 3-, and 4-fluoroanisole isomers is 126.1289 g \cdot mol $^{-1}$.

The benzoic acid used in the calibration of the rotating bomb calorimeter was the NIST Standard Reference Material, sample 39j [31], while *n*-undecane (Aldrich, mass fraction purity >0.999) was used to calibrate the high-temperature Calvet microcalorimeter. 4-Fluorobenzoic acid, used as a reference substance for rotating-bomb combustion calorimetry of organic fluorine compounds, was supplied by Sigma–Aldrich Chemical Co., with a mass fraction purity of 0.99 and further purified by zone melting.

2.2. Combustion calorimetry measurements

The combustion experiments were performed with an isoperibol rotating-bomb calorimeter, originally constructed at the University of Lund according to the design of Professor Stig Sunner [32]. Both the apparatus and the operating technique have been described [33–35] so only a brief description of the apparatus will be given here. The stainless steel combustion bomb, internal volume of 0.258 dm 3 and wall thickness of 1 cm, is a twin-valve bomb platinum-lined 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 $\pm(1 \cdot 10^{-1})$ 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 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.

Calorimeter temperatures were measured within the bounds of $\pm(1 \cdot 10^{-4})$ K, at time intervals of 10 s, using a Hewlett–Packard (HP-2804A) quartz crystal thermometer interfaced to a PC programmed to compute the adiabatic temperature change. At least 100 temperature readings were taken for the main period and for both the fore and after periods. Data acquisition and control of the calorimeter were performed using the program LABTERMO [36]. 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 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 fluoroanisole 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 [37]. 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 ca. 303.5 to 10 $^{-4}$ K using a temperature controller (Tronac PTC 41).

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