



Experimental and computational study of the molecular energetics of the monoiodoanisole isomers

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the condensed phase, of the three monoiodoanisoles, were derived from the respective enthalpies of combustion, measured by rotating-bomb combustion calorimetry. Their enthalpies of sublimation/vaporization, at $T = 298.15$ K, were obtained by Calvet microcalorimetry using the high-temperature vacuum sublimation technique. Moreover the standard molar enthalpy, entropy and Gibbs energy of sublimation, at $T = 298.15$ K, of 4-iodoanisole were derived from the Knudsen mass-loss effusion technique.

Combining the former sets of experimental results, the standard molar enthalpies of formation in the gas-phase, at $T = 298.15$ K, of 2-, 3- and 4-iodoanisole were derived, respectively, as: (15.1 ± 2.1) $\text{kJ} \cdot \text{mol}^{-1}$; (11.8 ± 2.2) $\text{kJ} \cdot \text{mol}^{-1}$, and (12.4 ± 1.6) $\text{kJ} \cdot \text{mol}^{-1}$.

The experimental values of the gas-phase enthalpies of formation of each iodoanisole were also estimated by means of the empirical scheme developed by Cox and by density functional theory calculations employing the B3LYP/6-311++G(d,p) approach. Estimated values are in excellent agreement with the reported experimental ones derived in the present paper.

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1. Introduction

Thermochemical data, more specifically enthalpies of formation in the gaseous state, are important to establish correlations between structure, energetic and reactivity, for a better understanding of the properties of the molecules, which are local units of large biological molecules. As part of our interest on the thermochemistry of halogenated benzene derivatives, such as anilines [1–13], phenols [14–20] or nitrobenzenes [2,10–13,21–27], and in view of a better understanding of the energetic effect of the substitution of a halogen atom in the aromatic ring of anisole, we have previously studied, the thermochemical properties of monofluoroanisoles [28], mono and dichloroanisoles [29,30] and monobromoanisoles [31]. In the present paper, we extend our study to the mono iodine substituted anisoles, whose structural formulae are depicted in figure 1.

The anisole (methoxybenzene) and its derivatives have received considerable attention mainly in pharmaceutical industries [32–34], as well as in new technologies and development of new materials [35]. Regarding to the compounds studied in this work, the 2- and 4-iodoanisoles are used in the synthesis of 4-hydroxycoumarins [36] which constitute an important class of benzopyrones, used as

anticoagulants for the treatment of disorders in which there is excessive or undesirable clotting, and also display other important pharmacological effects, including analgesic [37], anti-inflammatory [38], anti-viral [39], and anti-cancer [40] properties. These compounds also found applications in the area of new materials in the synthesis of optoelectronic and electronic devices such as solar cells, organic light-emitting diodes and organic thin-film transistors [41,42]. For the 3-iodoanisole there has been solved the low-resolution microwave spectra [43] and it has been published by Schaefer and Lee [44] the ^1H NMR study of the conformational distribution of this compound in solution.

Hence, in order 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-iodoanisole. The standard molar enthalpies of formation, in the condensed phase, of those three iodoanisole isomers, at $T = 298.15$ K, were obtained from measurements of their standard ($p^\circ = 0.1$ 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/vaporization of the three compounds were performed using high temperature Calvet microcalorimetry.

The Knudsen mass-loss effusion technique was used to measure the vapor pressures as a function of temperature of the crystalline

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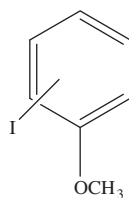


FIGURE 1. Structural formulae of the 2-, 3- and 4-iodoanisole.

4-iodoanisole. From the vapor pressure dependence of the temperature, and by application of the Clausius–Clapeyron equation, the standard molar enthalpy of sublimation, at the mean temperature of the experimental temperature range, was derived. Standard molar enthalpy, entropy, and Gibbs energy of sublimation, at the temperature of 298.15 K, were calculated using estimated values of the heat capacity differences between the gas and the crystal phases of the 4-iodoanisole.

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of 2-, 3- and 4-iodoanisole, in the gaseous phase, at $T = 298.15$ K, were calculated combining the respective standard molar enthalpies of formation, in the condensed phases, and the standard molar enthalpies of vaporization or sublimation. The $\Delta_f H_m^\circ(\text{g})$ parameter was also estimated for each isomer of monoiodoanisole, using the Cox scheme [45] and also by means of computational thermochemical methods. The gas-phase enthalpies of formation of the three isomers (figure 1) were calculated through B3LYP-6311++G(d,p) level and their molecular structures were established.

2. Experimental

2.1. Materials and purity control

The three isomers of monoiodoanisole namely, 2-iodoanisole, 3-iodoanisole and 4-iodoanisole, with the assessed minimum purity of, respectively, 0.98, 0.99 and 0.98 (mole fraction), were supplied by Sigma–Aldrich Chemical Co. The liquid 2- and 3-iodoanisole were purified by repeated fractional distillations under reduced pressure, having been stored under nitrogen atmosphere. The crystalline 4-iodoanisole was purified by successive vacuum sublimations, *c.f.* table 1. All the samples of iodoanisole isomers were stored protected from light.

The final purity of each sample of compound was checked by gas chromatography, using a column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m $\times$ 0.530 mm i.d. $\times$ 1.5 m 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 $^{-1}$, 473 K (10 min). No impurities greater than 10^{-3} in mole fraction could be detected in the samples of the isomers used for the calorimetric and vapor pressure measurements.

The specific densities were, $\rho = 1.799$ g $\cdot$ cm $^{-3}$ [46], $\rho = 1.965$ [46], $\rho = 1.984$ g $\cdot$ cm $^{-3}$ [47] for 2-, 3- and 4-iodoanisole, respectively.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2009 [48] yielding 234.0344 g $\cdot$ mol $^{-1}$ for the molar masses of the monoiodoanisoles.

2.2. Combustion calorimetry measurements

The combustion experiments of the iodoanisole isomers were performed with an isoperibol rotating-bomb calorimeter, originally constructed in the University of Lund according to the design of Sunner [49]. Both the apparatus and the operating technique have been described [2,50,51], 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, previously weighed in a Perspex vessel, 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, 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 $\pm (1 \cdot 10^{-4})$ 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 [52]. 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 μ F) when discharged through a platinum wire ($\phi = 0.05$ mm, Goodfellow, mass fraction 0.9999).

For each combustion experiment of the iodoanisole 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. The rotating mechanism allowed simultaneous axial and end-over end rotation of the bomb, causing the aqueous solution of potassium iodide placed in the bomb to wash all internal surfaces of the bomb, yielding a homogeneous final solution. Employing this procedure, Good *et al.* [53] have shown that 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. 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 K to $\pm (1 \cdot 10^{-3})$ K using a temperature controller (Tronac PTC 41).

The combustion of the iodoanisole isomers was made as suggested by Carson *et al.* [54] who applied the rotating-bomb combustion 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 [55,56], iodoanilines [6], 1-(4-iodophenyl)pyrrole [57] and iodophenols [20] by rotating-bomb combustion calorimetry. Following this procedure, the calorimeter was recalibrated by combustion of benzoic acid (NIST Standard Reference Material 39j) [58] in the presence of a mass of 1.0 g of

TABLE 1
Purification details of the three iodoanisole isomers.

Chemical name	CAS	Provenance	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
2-Iodoanisole (l)	529-28-2	Sigma–Aldrich Chemical Co	0.98	Distillation	0.9994	GC
3-Iodoanisole (l)	766-85-8	Sigma–Aldrich Chemical Co	0.99	Distillation	0.9998	GC
4-Iodoanisole (cr)	696-62-8	Sigma–Aldrich Chemical Co	0.98	Sublimation	0.9997	GC

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