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Experimental and computational study on the molecular energetics of monobromoanisole isomers

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the liquid phase of three isomers of bromoanisole were derived from the standard molar energies of combustion, in oxygen, which yields CO_2(g) and $HBr \cdot 600H_2O(l)$, at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The determination of the standard molar enthalpies of vaporization of these compounds, at $T = 298.15$ K, was done by Calvet microcalorimetry using the high-temperature vacuum sublimation technique. Combining the former sets of experimental results, the standard molar enthalpies of formation, in the gas-phase, were derived. The gas-phase enthalpies of formation were also estimated by means of the empirical scheme developed by Cox and by density functional theory calculations performed at the B3LYP/6-31+G(d) level of theory.

	$-\Delta_c U_m^\circ(l)/(kJ \cdot mol^{-1})$	$-\Delta_f H_m^\circ(l)/(kJ \cdot mol^{-1})$	$\Delta_l^g H_m^\circ/(kJ \cdot mol^{-1})$
2-Bromoanisole	3629.0 ± 1.4	101.5 ± 1.7	61.8 ± 1.3
3-Bromoanisole	3624.0 ± 1.4	106.5 ± 1.7	58.0 ± 1.2
4-Bromoanisole	3623.8 ± 1.5	106.7 ± 1.8	58.3 ± 1.2

1. Introduction

The anisole (methoxybenzene) and its derivatives have received considerable attention mainly in pharmaceutical industries, as well as in new technologies and development of new materials. The bromoanisole (bromomethoxybenzene) isomers are used as starting material of many drugs with high therapeutic potential, such as analgesics [1,2], antidepressant [3], anti-cancer and drugs [4,5]. Recently, it was investigated the complexation of [60]fullerene [6,7] and [70]fullerene [8] with anisole, 3- and 4-bromoanisole, in order to provide novel materials with unusual conducting and magnetic properties. The 3-bromoanisole was used in the synthesis of 9,9′-spirobifluorene-1,1′-diol [9], a backbone molecule with a wide range of applications in molecular electronics, light-emitting materials and enantioselective molecular recognition. Although halogenated anisoles are not produced in large quantities, they have been extensively detected in the environment [10,11], as result of the *O*-methylation of the respective halogenated phenols.

Hence, 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 complicated large biological molecules. As part of our interest on the thermochemistry of halogenated benzene derivatives and in view of a better understanding of the energetic effect of the substitution of a bromine atom in the aromatic ring, we have studied, in previous works, the thermochemical properties of bromine substituted benzoic acids [12], naphthalenes [13], anilines [14], pyridines [15] and indolines [16]. In the present paper, we extend our study to the mono bromine substituted anisoles. This paper reports the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the liquid phase, at $T = 298.15$ K, of the title compounds, derived from the standard molar energies of combustion, in oxygen, measured by rotating-bomb combustion calorimetry, and also the respective standard molar enthalpies of vaporization, measured by high temperature Calvet microcalorimetry, at $T = 298.15$ K. These two sets of values allowed the derivation of the standard molar enthalpies of formation, in the gaseous state, of 2-, 3- and 4-bromoanisole, and were compared with the results estimated by the Cox scheme [17] and those obtained by density functional theory calculations.

2. Experimental details

2.1. Materials and purity control

The three liquid isomers of monobromoanisole namely, 2-bromoanisole [CAS 578-57-4], 3-bromoanisole [CAS 2398-37-0],

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4-bromoanisole [CAS 104-92-7], with the assessed minimum purity of, respectively, 0.97, 0.98 and 0.99 (mass fraction), were supplied by Sigma–Aldrich Chemical Co and purified by repeated fractional distillations under reduced pressure, having been stored under nitrogen atmosphere. The final purity of all monobromoanisole isomers 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 carrier gas. The 4-bromobenzoic acid [18] [CAS 586-76-5], BDH Organic Analytical Standard, recommended as test material for combustion calorimetry of bromine compounds [19], was obtained commercially from BDH Chemicals Ltd. and used as supplied.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005 [20] yielding the following molar masses: $187.0346\ \text{g} \cdot \text{mol}^{-1}$ for the monobromoanisoles and $201.0182\ \text{g} \cdot \text{mol}^{-1}$ for 4-bromobenzoic acid.

The benzoic acid NIST Standard Reference Material, sample 39j [21] and the *n*-undecane (Aldrich, mass fraction purity > 0.999) were used, respectively, to calibrate the rotating bomb calorimeter and the high-temperature Calvet microcalorimeter.

2.2. Combustion calorimetry measurements

The isoperibolic rotating-bomb combustion calorimeter that was formerly used at the National Physical Laboratory, Teddington, UK, was used to measure the massic energies of combustion of the 2-, 3- and 4-bromoanisole and 4-bromobenzoic acid. Both the apparatus and the operating technique have been described [22–25], so only a brief description of the apparatus will be given here. For the combustion of bromine containing compounds it is recommend the use of tantalum-lined bombs [26]. So, in this work, the combustion experiments were performed with a twin-valve bomb lined with tantalum and with all the internal fittings also made from tantalum, having an internal volume of $0.329\ \text{dm}^3$.

The calorimetric system was calibrated with benzoic acid (NBS Standard Reference Material 39j), having a massic energy of combustion under standard bomb conditions of $-(26434 \pm 3)\ \text{J} \cdot \text{g}^{-1}$ [21]. Ten calibration experiments were made in oxygen, at $p = 3.04$ MPa, with $1.00\ \text{cm}^3$ of deionised water added to the bomb, according to the procedure suggest by Coops *et al.* [27], leading to the value of the energy equivalent of the calorimeter: $\varepsilon(\text{calor}) = (20369.0 \pm 2.3)\ \text{J} \cdot \text{K}^{-1}$. The quoted uncertainty refers to the standard deviation of the mean. The calibration results, as well as the results of the combustion experiments of all the studied compounds (monobromoanisoles and of 4-bromobenzoic acid), were corrected to give the energy equivalents corresponding to the average mass of water added to the calorimeter: 3969.2 g. A Mettler PC 8000 balance, sensitivity $\pm 10^{-1}$ g, was used to weigh the amount of distilled water added to the calorimeter from a weighed Perspex vessel.

Calorimeter temperatures were measured within the bounds of $\pm 10^{-4}$ K, with time intervals of 10 s 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 [28]. At least 100 readings were taken for the main period and 125 for initial and final periods. For all combustions experiments, the ignition temperature was chosen so that the final temperature would be close to $T = 298.15$ K, and the rotation of the bomb was started when the temperature rise of the main period reached about 0.63 of its total value and was continued throughout the experiment. Employing this procedure, Good *et al.* [29] 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 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. The water bath temperature was maintained at $T = (299.050 \pm 0.001)$ K using a temperature controller (Tronac PTC 41).

To check the accuracy of the benzoic acid calibration and the experimental procedure, combustion experiments of 4-bromobenzoic acid, recommended as a test material for the combustion calorimetry of bromine compounds with an atomic ratio of hydrogen to bromine equal to or greater than unity [19], were performed. From six combustions done with 4-bromobenzoic acid in the pellet form, enclosed in polyester bags made from Melinex (0.025 mm thickness) using the technique described by Skinner and Snelson [30], at a pressure $p = 3.04$ MPa and in the presence of $20.00\ \text{cm}^3$ of aqueous solution of As_2O_3 ($\approx 0.09\ \text{mol} \cdot \text{dm}^{-3}$), $\Delta_c u^\circ = -(15260.9 \pm 2.2)\ \text{J} \cdot \text{g}^{-1}$, where the uncertainty quoted is the overall standard deviation of the mean. Our experimental value is in excellent agreement with the recommended value [19], $\Delta_c u^\circ = -(15261.0 \pm 4.2)\ \text{J} \cdot \text{g}^{-1}$, and with the previous value for the enthalpy of formation of 4-bromobenzoic acid obtained in this Laboratory using the same calorimetric system, $\Delta_f H_m^\circ(\text{cr}) = -(379.6 \pm 1.3)\ \text{kJ} \cdot \text{mol}^{-1}$ [12] (this work: $\Delta_f H_m^\circ(\text{cr}) = -(379.5 \pm 1.6)\ \text{kJ} \cdot \text{mol}^{-1}$). The values of $\Delta_c u^\circ$ refer to the reaction with $HBr{\cdot}600H_2O(l)$ as the single bromine-containing product in the final state. At the end of some experiments with 4-bromobenzoic acid a small residue of carbon was found due to incomplete combustion. If the carbon soot formed was found only on the walls of the platinum crucible, and not in the combustion solution or on the walls of the bomb, and if the amount of carbon soot formed was equal or lower than 1 mg, an energy correction was done based on the standard massic energy of combustion of carbon, $\Delta_c u^\circ = -33\ \text{kJ} \cdot \text{g}^{-1}$ [27].

The liquid samples of bromoanisole isomers were also burnt enclosed in polyester bags made from Melinex (0.025 mm thickness), at a pressure $p = 3.04$ MPa and in the presence of $15.00\ \text{cm}^3$ of an aqueous solution of As_2O_3 ($\approx 0.09\ \text{mol} \cdot \text{dm}^{-3}$), in order to reduce all the free bromine produced by the combustion to hydrobromic acid. The extent of the oxidation of $As_2O_3(aq)$ was determined by titration with a standardized iodine solution. For the calculation of the energetic term $\Delta U(As_2O_3)$, corresponding to the energy of oxidation of $As_2O_3(aq)$ to $As_2O_5(aq)$ in aqueous solution, the procedure described by Hu *et al.* [31], which uses the enthalpies of oxidation of $As_2O_3(aq)$ by Br_2 [32] and the thermal effects of mixing $As_2O_5(aq)$ with strong acids [33], was followed. Within the precision of the analytical method, no evidence was found for oxidation of $As_2O_3(aq)$ within about 5 h at room temperature in the presence of oxygen at $p = 3.04$ MPa.

The nitric acid formed was determined using the Devarda's alloy method [34], and corrections were based on $-59.7\ \text{kJ} \cdot \text{mol}^{-1}$ [35] for the standard molar energy of formation ($\Delta_f U_m^\circ$), in which $0.1\ \text{mol} \cdot \text{dm}^{-3}$ $HNO_3(aq)$ is formed from $O_2(g)$, $N_2(g)$ and $H_2O(l)$. The amount of $H_2PtBr_4(aq)$ formed was determined from the mass loss of the platinum crucible and its supporting ring, which leads to an energy correction based on $\Delta_f H_m^\circ(H_2PtBr_4, aq) = -(368.2 \pm 0.1)\ \text{kJ} \cdot \text{mol}^{-1}$ [35]. For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ = -16{,}240\ \text{J} \cdot \text{g}^{-1}$ [27] and for dry Melinex, $\Delta_c u^\circ = -(22{,}902 \pm 5)\ \text{J} \cdot \text{g}^{-1}$ [30]; these values have been confirmed in our Laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from it was calculated using the factor previously reported [30]. The electrical energy for ignition was measured from the change in potential difference on the discharge of a capacitor (1281 μF) across a platinum wire ($\phi = 0.05$ mm, Goodfellow, mass fraction 0.9999).

The values of $(\partial u/\partial p)_T$ at $T = 298.15$ K, were assumed to be $-0.2\ \text{J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ [36] and $-0.12\ \text{J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ [12], respectively,