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Experimental thermochemical study of 5-bromoindole and 5-bromoindoline

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) massic energies of combustion in oxygen of 5-bromoindole and 5-bromoindoline were determined at $T = 298.15$ K by rotating-bomb calorimetry. These values were used to derive the standard molar enthalpies of combustion and the standard molar enthalpies of formation, in the condensed phase, for these compounds. Further, the standard molar enthalpies of sublimation, at $T = 298.15$ K were determined by Calvet microcalorimetry. The combustion calorimetry results together with those from the Calvet microcalorimetry, were used to derive the standard molar enthalpies of formation, at $T = 298.15$ K, in the gaseous phase.

Compound	$-\Delta_c H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{cr}^{g} H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$
5-Bromoindole (cr)	4079.9 ± 2.3	92.3 ± 2.3
5-Bromoindoline (cr)	4321.1 ± 2.5	88.0 ± 1.9

1. Introduction

Bromoindoles are compounds with high potential for applications in various domains, especially in the electrochemical industry as electrocatalysts, anode materials in batteries, anticorrosion coating, and fast response potentiometric sensors [1,2]. These compounds have also attracted great attention in pharmacology, mainly because of their ability to develop antifungal and antibacterial agents, but also as candidates for anti-oxidant, direct oxidation/reduction of biomolecules, and other biological activities [1–4]. Due to their presence in water and soil as persistent organic pollutants, these organobromine compounds have also been the focus of considerable research work to determine their toxicity effects on the environment [4].

In this work, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the solid state, at $T = 298.15$ K, of 5-bromoindole and 5-bromoindoline, represented in figure 1, were determined from the values of the standard molar energies of combustion. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were measured by Calvet microcalorimetry. From these two sets of results, the standard molar enthalpies of formation in the gaseous state, at the temperature 298.15 K, were derived.

The derived standard molar enthalpies of formation of these two bromo derivatives are discussed in terms of enthalpic increments and interpreted in terms of molecular structure.

2. Experimental

2.1. Compounds and purity control

5-Bromoindole [CAS 10075-50-0] and 5-bromoindoline [CAS 22190-33-6] were obtained commercially from Aldrich Chemical Co., with an initial mass fraction purity of 0.993 and 0.997, respectively. In order to assure a minimum mass fraction purity of 0.999, they were further purified by repeated sublimations under reduced pressure. No impurities were detected by g.l.c.

The relative atomic masses recommended by the IUPAC Commission in 2005 [5] were used in the calculations of all the molar quantities.

2.2. Combustion calorimetry

The standard massic energies of combustion of these two bromo derivatives were measured by rotating-bomb calorimetry, whose apparatus and operating technique were previously described in the literature [6–8].

The twin-valve bomb used, originally constructed at the University of Lund according to the design of Sunner [9], is made of stainless steel, has an internal volume of 0.258 dm^3 and it is internally lined with platinum with all the internal fittings made in platinum. Both compounds were burned in a pellet form. Due to its high volatility, it was necessary in the experiments with 5-bromoindole to enclose the pellets of this compound in sealed polyester bags made of melinex (0.025 mm of thickness) with massic energy of

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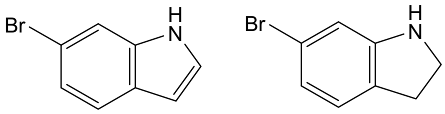

1 **2**

FIGURE 1. Structural formula of 5-bromoindole (**1**) and 5-bromoindoline (**2**).

combustion $\Delta_c u^\circ = -(22902 \pm 5)\ \mathrm{J \cdot g^{-1}}$ [10], a value confirmed in our laboratory. Since the combustion experiments of 5-bromoindoline yielded a small amount of carbon soot, in some of those experiments, dried *n*-hexadecane (Aldrich Gold Label, mass fraction > 0.999), stored under nitrogen, with massic energy of combustion $\Delta_c u^\circ = -(47150.4 \pm 1.3)\ \mathrm{J \cdot g^{-1}}$, a value determined in our laboratory, was used for auxiliary combustion.

In all the experiments, the bomb was purged twice with oxygen to remove air, before being charged with 3.04 MPa of oxygen. Aqueous solutions ($20.00\ \mathrm{cm^3}$) of As_2O_3 with concentrations of $(0.09050$ and $0.09119)\ \mathrm{mol \cdot dm^{-3}}$ in the experiments with 5-bromoindole and of $0.09168\ \mathrm{mol \cdot dm^{-3}}$ in the combustion of 5-bromoindoline were placed in the bomb to reduce all the bromine produced in the combustion to hydrobromic acid.

Water was added to the calorimeter from a weighed perspex vessel. As the mass of water was slightly different in each experiment, corrections were made to the energy equivalent of the calorimeter for the deviation from the average mass of 5222.5 g. The calorimeter temperatures were measured to $\pm(1 \cdot 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett–Packard HP 2804A) interfaced to a PC. The ignition of the samples was made when at least 100 readings at time intervals of 10 s were taken, after the start of the experiment, by the discharge of a 1400 μF capacitor through the platinum ignition wire, and using a cotton thread fuse, with an empirical formula $CH_{1.686}O_{0.843}$ and with $\Delta_c u^\circ(\text{cotton}) = -16250\ \mathrm{J \cdot g^{-1}}$ [11], a value also previously confirmed in our laboratory. The temperature of the ignition was chosen so that the final temperature would be as close as possible to $T = 298.15$ K. 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. With 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 [12]. After ignition, 100 readings were taken for the main and for the after periods. In all the experiments, data acquisition was performed by means of the LABTHERMO program [13].

At the end of the experiment, the extent of the oxidation of As_2O_3(aq) was determined by titration with a standardized iodine solution, and the nitric acid formed was analysed by Devarda's alloy method [14]. The energy of oxidation of aqueous As_2O_3 to As_2O_5, $\Delta U(As_2O_3)$, was calculated as described by Hu *et al.* [15], using the enthalpies of oxidation of As_2O_3(aq) by Br_2 [16] and the thermal effects of mixing As_2O_5(aq) with strong acids [17].

The corrections for nitric acid formation were based on $-59.7\ \mathrm{kJ \cdot mol^{-1}}$, for the molar energy of formation of $0.1\ \mathrm{mol \cdot dm^{-3}}$ HNO_3(aq) from N_2(g), O_2(g), and H_2O(l) [18].

The amount of H_2PtBr_4(aq) formed was determined from the mass loss of the platinum crucible and its supporting ring, and the corresponding energy correction was based on $\Delta_f H_m^\circ(H_2PtBr_4, aq) = -(368.2 \pm 0.1)\ \mathrm{kJ \cdot mol^{-1}}$[18].

In the combustion experiments with carbon residue soot formation, if all the residue stayed inside the crucible and none was in the combustion solution, the carbon was quantified by weighing the crucible before and after calcinations, and the necessary energetic corrections for its formation were based on $\Delta_c u^\circ = -33\ \mathrm{kJ \cdot g^{-1}}$ [19]. If the carbon residue was present on other parts of the bomb or in the solution, the experiment was discontinued. All the necessary weighing was made in a Mettler Toledo 240 balance, sensitivity $\pm(1 \cdot 10^{-5})$ g, and corrections from apparent mass to true mass were made. For each compound an estimated pressure coefficient of massic energy, $(\partial u/\partial p)_T$, at $T = 298.15$ K, was assumed to be $-0.2\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$, a typical value for most organic compounds [20]. For both compounds, $\Delta U_{\sum}$, the standard state corrections and the heat capacities of the bomb contents, ε_i and ε_f, were calculated by the procedure given by Bjellerup [21].

The energy equivalent of the calorimeter was determined by combustion of Thermochemical Standard benzoic acid, sample NBS 39j, with $\Delta_c u = -(26434 \pm 3)\ \mathrm{J \cdot g^{-1}}$ [22], without rotation of the bomb and following the same procedure described in the literature [11]. The energy equivalent of the calorimeter, for a reference mass of water of 5222.5 g, was found to be $\varepsilon_{cal} = (25164.0 \pm 2.1)\ \mathrm{J \cdot K^{-1}}$, as the average of six combustion experiments with benzoic acid, where the uncertainty quoted is the standard deviation of the mean.

TABLE 1
Combustion experiment data, at $T = 298.15$ K, of 5-bromoindole

	1	2	3	4	5	6
m(cpd)/g	0.94908	0.93446	0.97264	0.89428	0.90068	0.71480
m'(fuse)/g	0.00320	0.00330	0.00350	0.00294	0.00347	0.00360
m''(melinex)/g	0.04562	0.05004	0.04683	0.04275	0.03806	0.03973
T_i/K	297.2923	297.3006	297.2705	297.3412	297.3408	297.4987
T_f/K	298.1521	298.1524	298.1551	298.1524	298.1554	298.1560
ΔT_{ad}/K	0.84408	0.83540	0.86666	0.79440	0.79705	0.64162
$\varepsilon_i/(\mathrm{J \cdot K^{-1}})$	93.68	93.69	93.71	93.65	93.70	93.55
$\varepsilon_f/(\mathrm{J \cdot K^{-1}})$	92.43	92.40	92.33	92.41	92.45	92.33
$\varepsilon(\text{calor})_{corr}/(\mathrm{J \cdot K^{-1}})$	25173.2	25168.6	25172.8	25168.6	25156.9	25169.9
$\Delta m(H_2O)$/g	2.2	1.1	2.1	1.1	−1.7	1.4
$-\Delta U(\text{IBP})^a$/J	21326.02	21102.84	21896.20	20067.12	20124.72	16208.34
ΔU(fuse)/J	51.97	53.59	56.84	47.75	56.35	58.46
ΔU(melinex)/J	1044.73	1145.94	1072.60	979.16	871.56	909.94
$\Delta U(HNO_3)$/J	36.54	30.21	31.46	28.89	37.01	31.64
$\Delta U(As_2O_3)$/J	406.85	394.31	444.59	356.84	387.33	302.83
ΔU(ign)/J	1.27	1.29	1.29	1.23	1.28	1.21
$\Delta U(H_2PtBr_4)$/J	0.00	0.12	0.04	0.03	0.01	0.00
ΔU(carb)/J	0	0	0	0	0	0
$\Delta U_{\sum}$/J	47.45	47.14	48.64	44.84	44.74	36.30
$-\Delta_c u^\circ/(\mathrm{J \cdot g^{-1}})$	20797.49	20794.39	20811.43	20809.60	20792.87	20801.87
			$-\langle \Delta_c u^\circ \rangle = (20801.3 \pm 3.2)\ \mathrm{J \cdot g^{-1}}$			

[a] ΔU(IBP) includes ΔU(ign).