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Revisiting dibenzothiophene thermochemical data: Experimental and computational studies

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ABSTRACT

Thermochemical data of dibenzothiophene were studied in the present work by experimental techniques and computational calculations. The standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation, at $T = 298.15$ K, in the gaseous phase, was determined from the enthalpy of combustion and sublimation, obtained by rotating bomb calorimetry in oxygen, and by Calvet microcalorimetry, respectively. This value was compared with estimated data from G3(MP2)//B3LYP computations and also with the other results available in the literature.

1. Introduction

Fossil fuels (coal, petroleum, and natural gas) contain sulphur compounds that are oxidized, in the combustion processes, to sulphur dioxide (SO_2), which leads to irreversible damages in the environment upon reaction with other atmospheric gases (*e.g.* smog and acid rain) [1]. This fact has been causing concern over the environmental impact of the use of those fuels as power sources and that is the reason why stringent air-quality regulations have been introduced, aiming at reducing the emission of sulphur compounds [2,3]. Consequently, refineries have been improving the deep desulphurization processes to remove efficiently sulphur from fuels, hence, converting this theme in an important area of research [4–7]. In the literature, there are several studies showing that some S-containing polyaromatic species, such as the methylated dibenzothiophenes, are resilience to deep desulphurization and present low reactivity, in particular, the 4-methyl and 4,6-dimethyl derivatives, which are only removed from the fuels by hydrodesulphurization (HDS) [4,6,8–11]. The knowledge of the thermochemical and thermophysical properties of these molecules is very important for the performance of the HDS mechanism and also for other processes like coal pyrolysis. Many other S-containing aromatic and polyaromatic compounds are also found in fuels, although their thermochemical and thermophysical data are not available. To circumvent this problem, the strategy generally employed is to focus the attention on key compounds and, then, use their values to estimate thermodynamic properties for other species in the absence of measured values.

Dibenzothiophene is considered as a S-containing polyaromatic "key" compound, and probably this is one of the reasons for the considerable number of thermochemical and thermophysical studies published in the literature for this compound since the 1970s [12–25]. Table 1 contains a compilation of data available in the literature for dibenzothiophene, namely values of the enthalpy of sublimation, $\Delta^{g}_{cr}H^\circ_m$, and values of the enthalpies of formation, in the crystalline, $\Delta_f H^\circ_m(cr)$, and gaseous, $\Delta_f H^\circ_m(g)$, phases, at $T = 298.15$ K. Despite the strong efforts done for the fulfillment of the gaps on the thermodynamic properties of dibenzothiophene, the analysis of the values shown in table 1 allows one to detect that some results are of questionable reliability, as can be discerned by the large disagreement among the results determined by different groups. Since our research group is directly interested in the thermochemistry of sulphur containing compounds, the assessment of the quality of the results reported in table 1, especially the gas-phase enthalpy of formation at $T = 298.15$ K, requires new experimental determinations that will be further compared with values calculated with state of the art computational approaches.

In this work, rotating bomb combustion calorimetry and Calvet microcalorimetry experiments were performed aimed at the

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TABLE 1
Values in kJ · mol^{-1} of the enthalpies of formation (crystalline and gaseous phases) and of sublimation, at T = 298.15 K available in the literature for dibenzothiophene.[a]

References[b]		$\Delta_f H^\circ_m$(cr)	$\Delta^g_{cr} H^\circ_m$	$\Delta_f H^\circ_m$(g)
Good [13]	E	120.3 ± 1.5		
Aubry *et al.* [14]	E		97.5	
Sabbah [15]	E		85.09 ± 0.35	205.99 ± 0.78
Sabbah and Antipine [16]	E	104.2 ± 4.5		189.3 ± 4.5
Stein and Barton [17]	R		85.77	206.3
Edwards and Prausnitz [18]	E		91.7	
Sivaraman and Kobayashi [19]	E		91.0	
Mraw and Keweshan [20]	E		93.8 ± 3.6	
Hansen and Eckert [21]	E		91.2	
Chirico *et al.* [22]	E		93.3	213.2 ± 0.7
Steele *et al.* [23]	E		93.9	213.8 ± 0.8
Pedley *et al.* [24]	R	120.0 ± 1.4	85.1 ± 0.5	205.1 ± 1.5
Gomes and Ribeiro da Silva [25]	C			218.5; 216.0; 224.0
Freitas *et al.*[c]	E	118.1 ± 4.5	93.2 ± 0.5	211.3 ± 4.5
Freitas *et al.*[c]	C			214.1; 213.6; 213.9
				211.8; 209.3; 210.7

[a] The standard deviation of the mean for some results were not available.
[b] (E)xperimental result; (R)eview; (C)alculated value.
[c] This work.

determination of the enthalpy of formation in the crystalline phase and the enthalpy of sublimation, respectively, of dibenzothiophene. Details of the experimental and computational procedures are given in Sections 2 and 3, respectively, while the thermodynamic values obtained in this work are compared and discussed with those reported in the literature in Section 4. Finally, the most important conclusions are presented in Section 5.

2. Experimental

2.1. Materials

Dibenzothiophene (diphenyl sulfide) [CAS 132-65-0] was obtained commercially from Aldrich Chemical Co. with mass fraction purity >0.99. The analysis by GLC and DSC showed that the compound was pure enough to be used without any further purification. The DSC thermogram did not show any transition phases before the melting point.

The value of density used for dibenzothiophene in the crystalline phase was 1.35 g · cm^{-3} [26].

The compounds used in the calibrations of the calorimetric systems were benzoic acid [CAS 65-85-0] Standard Reference Material (SRM), supplied by National Bureau Standard (NBS) and naphthalene [CAS 91-20-3] (scintillation grade, mass fraction purity >0.99) obtained from Aldrich Chemical Co.

2.2. Rotating bomb calorimetry

The combustion experiments were performed with an isoperibol calorimeter equipped with a twin valve rotating bomb (with an internal volume of 0.258 dm^3), formerly developed by Professor Stig Sunner at the University of Lund, Sweden, and installed in our department. The details of the apparatus have been described in the literature [27].

The energy equivalent of the calorimeter ε(calor) was determined using benzoic acid, NBS SRM 39j as having a massic energy of combustion, $\Delta_c u$, under standard bomb conditions of $-(26434 \pm 3)$ J · g^{-1}. Calibration experiments were carried out in oxygen at a pressure of 3.04 MPa (previously flushed) with 1.00 cm^3 of deionised water added to the bomb, without rotation of the bomb. From six experiments, the ε(calor) = (25164.0 ± 2.1) J · K^{-1} (the uncertainty quoted is the standard deviation of the mean) for an average mass of water added to the calorimeter of 5217.0 g.

For the combustion of the organo-sulphur compounds, the procedure followed was described by Waddington *et al.* [28]. The combustion experiments were carried out in pellet form, which were enclosed in polyester bags made from Melinex (0.025 mm thickness), since the compound evidenced volatility on weighing process. The Melinex bags were made using the technique described by Skinner *et al.* [29]. The samples were placed in a platinum crucible inside the bomb in contact with a cotton thread fuse attached to the platinum wire. All weighs were performed with a precision ±10^{-5} g, in a Mettler AE 240 balance. For each experiment, a volume of 10.00 cm^3 of water was added to the bomb, and the bomb was charged to a pressure of 3.04 MPa with oxygen without flushing, ensuring sufficient amounts of nitrogen oxides to oxidize the sulphur quantitatively to sulphur trioxide. The calorimeter temperature was measured to ±10^{-4} K at time intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz thermometer interfaced to an Olivetti M240E microcomputer programmed to compute the adiabatic temperature change. The temperature profile for each experiment was divided into three periods, *viz.* fore-, main- and after-periods, each one with, at least, one hundred points. Data acquisition and control of the calorimeter were performed using the LABTERMO program [30]. The energy of reaction was always referred to the final temperature of T_f = 298.15 K; taken this into consideration, the ignition of the sample in each experiment, was chosen so that the final temperature would be close to 298.15 K. The electrical energy for ignition ΔU(ign) was determined from the change in potential difference across a 1400 μF condenser when discharged through the platinum ignition wire. Rotation of the bomb was started when the temperature rise in the main period reached about 63% of its final value and continued until the end of the experiment, ensuring a homogeneous solution of H_2SO_4 (aq) in the bomb at the conclusion of the measurements. Good *et al.* [31] have shown that by adopting this procedure, the frictional work of bomb rotation is automatically included in the temperature corrections for the work of water stirring and heat exchanged with the surrounding isothermal jacket. This one consists of a thermostatic water 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 approximately 303.5 K to ±10^{-4} K using a temperature controller (Tronac PTC 41), so that the calorimeter was completely surrounded by a constant temperature. After the calorimetric measurements the combustion products were checked for unburned carbon and other products of incomplete combustion. In all cases, these undesired species were not detected. The nitric acid formed due to the presence of nitrogen residues in the oxygen, used in the fulfillment of the bomb, was determined by Devarda's alloy method [32]. Due to the relatively large amount of water used to ensure the homogeneous H_2SO_4 (aq) in the dibenzothiophene combustions, no carbon dioxide analyses were made.

The corrections for nitric acid formation were made on -59.7 kJ · mol^{-1} for the molar energy of formation of 0.1 mol · dm^{-3} HNO_3 (aq) from N_2 (g), O_2 (g), and H_2O (l) [33]. For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, the $-\Delta_c u^\circ = 16240$ J · g^{-1} [34], which is a value previously confirmed in our laboratory. In the case of Melinex, it was considered the massic energy of combustion of dry Melinex, $-\Delta_c u^\circ = -(22902 \pm 5)$ J · g^{-1} [29]; this value was also confirmed by combustion of Melinex samples in our laboratory. The value for the pressure coefficient of specific energy $(\partial u/\partial p)_T$ was assumed to be -0.2 J · g^{-1} · MPa^{-1}, at T = 298.15 K, a typical value for most organic compounds [35].