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Enthalpies of formation of dihydroxybenzenes revisited: Combining experimental and high-level ab initio data

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Dedicated to the memory of the late Professor Manuel Ribeiro da Silva

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ABSTRACT

Accurate values of standard molar enthalpies of formation in condensed phases can be obtained by combining high-level quantum chemistry calculations of gas-phase enthalpies of formation with experimentally determined enthalpies of sublimation or vapourization. The procedure is illustrated for catechol, resorcinol, and hydroquinone. Using W1-F12, the gas-phase enthalpies of formation of these compounds at $T = 298.15$ K were computed as (−270.6, −269.4, and −261.0) kJ · mol^{-1}, respectively, with an uncertainty of ∼0.4 kJ · mol^{-1}. Using well characterised solid samples, the enthalpies of sublimation were determined with a Calvet microcalorimeter, leading to the following values at $T = 298.15$ K: (88.3 ± 0.3) kJ · mol^{-1}, (99.7 ± 0.4) kJ · mol^{-1}, and (102.0 ± 0.9) kJ · mol^{-1}, respectively. It is shown that these results are consistent with the crystalline structures of the compounds.

1. Introduction

The accuracy of experimentally derived gas-phase standard enthalpies of formation of organic compounds is often lower than *ca.* 4 kJ·mol^{-1} [1] – the so-called chemical accuracy limit. As outlined in figure 1, most of these data rely on combustion calorimetry experiments, yielding condensed-phase enthalpies of formation [2], and on several other methodologies (including calorimetry and vapour pressure *vs.* temperature plots) [2,3], which lead to enthalpies of sublimation or vaporisation.

The problems and rewards of combustion calorimetry have been thoroughly discussed [2]. Sample purity and (in)complete combustion are two of the most important factors that an experimentalist has to consider. For instance, a minor impurity with a high heat of combustion may cause sizeable errors. Moreover, the number of researchers who are proficient in combustion calorimetry is steadily decreasing, suggesting that we are now seeing the dusk of the practise of this technique.

It can be argued that the experimental determination of phase-change enthalpies, on the other hand, does not require the same level of expertise as combustion calorimetry. But if this statement were true, then, for example, most of the available enthalpy of sublimation data should be highly accurate. Unfortunately this is not observed for many organic compounds, as illustrated by our case study, involving catechol, resorcinol, and hydroquinone.

What can we do to take the thermochemical database to the chemical accuracy limit? Two decades ago, or even less, most experimentalists were sceptical about the reliability of thermochemical values obtained from quantum chemistry calculations. This suspicion, often justified by frequent disagreements between experimental and theoretical data, was first addressed by developing error-cancellation computational procedures, such as isodesmic and homodesmic reactions [4]. Although these procedures are still very useful, the application of higher-level quantum chemistry methods, together with much better computational resources, ensures that we can obtain chemically accurate values for the gas-phase enthalpies of formation of molecules with ten or even more heavy atoms [5]. In other words, stating that high-level quantum chemistry calculations are now as reliable as the best experimental procedures is no longer heresy [5–11]. Nevertheless, a limitation of theory still prevails: the previous statement only applies to molecules in the gas phase. The theoretical methodologies which address the energetics of intermolecular interactions are not yet able to predict chemically accurate enthalpy of sublimation data for organic molecules. Therefore, the experimental determinations of enthalpies of sublimation remain indispensable and our efforts should now be focused on improving the reliability and the accuracy of these data. This implies, in turn, that the solid sample under study must be properly characterised and that the occurrence of

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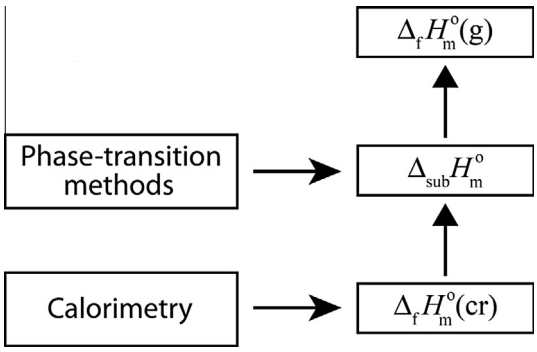

FIGURE 1. Most gas-phase standard enthalpies of formation of organic compounds were determined according to this outline, here applied to solid compounds.

thermal events, such as solid–solid phase or glass transitions, must be investigated [12]. There is enough evidence that some discrepancies between experimental enthalpies of sublimation can be attributed to the use of solid samples with different crystalline structures (i.e. different polymorphs) or crystallinity [13].

In summary, as illustrated in figure 2, molecular energetics lives a new paradigm: some of the most accurate gas-phase data are now obtained with quantum chemistry methods, which, together with experimentally determined phase-change enthalpies, may afford accurate enthalpies of formation of substances in liquid and solid phases.

The present work applies the above ideas to the redetermination of the standard molar enthalpies of formation of solid catechol, resorcinol, and hydroquinone. It involved the determination of the standard molar enthalpies of sublimation of the dihydroxybenzenes by Calvet drop microcalorimetry, using well characterised samples in terms of chemical and phase purity. The gas-phase enthalpies of formation were determined using high-level quantum chemistry methods.

2. Experimental

2.1. General

Diffuse reflectance infrared Fourier-transform (DRIFT) spectra were obtained in the (400 to 4000) cm^{-1} range, using a Nicolet 6700 spectrometer. The resolution was 2 cm^{-1} and the pellets were ~5% (w/w) of sample in KBr. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained in DMSO-d_6, (Aldrich 99.9% atom D, containing 0.03% v/v TMS) at ambient temperature, with a Bruker Ultrashield 400 MHz spectrometer. The GC–MS experiments were performed with an Agilent 6890 gas chromatograph equipped with an Agilent 7683 automatic liquid sampler coupled to an Agilent 5973 N quadrupole mass selective detector. A HP-5 column (5% diphenyl/95% dimethylpolysiloxane; 28.7 m × 0.25 μm I.D., 250 μm film thickness) was used. The sample was dissolved in acetonitrile (CHROMASOLV gradient grade, for HPLC, ⩾99.9%) and the injection volume was 1 μL. The carrier gas was helium maintained at a constant pressure of 119 kPa and with a flow rate of 1.3 mL · min^{-1}. A programmed temperature vaporisation injector with a septumless sampling head having a baffled liner (Gerstel) operating in the splitless mode was employed. The inlet temperature was set to 523 K and the oven temperature was programmed as follows: 353 K for 1 min, ramp at 5 K · min^{-1} to 373 K, and finally ramp to 573 K at 15 K · min^{-1}, for 18.33 min total running time. The transfer line, ion source, and quadrupole analyser were kept at (553, 503, and 423) K, respectively. A solvent delay of 4 min was selected. Electron ionisation mass spectra in the (35 to 550) m/z range were recorded in the full-scan mode, with 70 eV electron energy and an ionisation current of 34.6 μA. Data recording and instrument control were performed by using the MSD ChemStation software from Agilent (G1701CA; version C.00.00). The identity of the analysed compound was assigned by comparison of mass-spectrometric results with data in the Wiley reference spectral databank (G1035B, Rev D.02.00) and its purity was calculated from the normalised peak areas, without using correction factors to establish abundances.

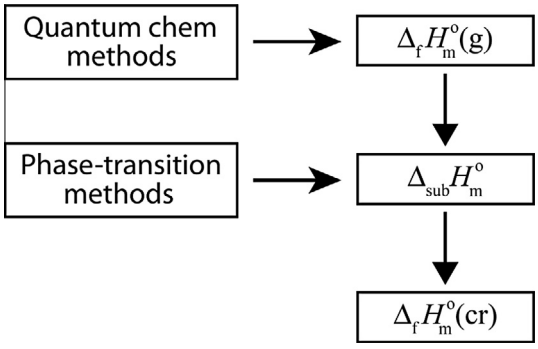

FIGURE 2. A new paradigm for determining accurate standard enthalpies of formation of substances in condensed states, here applied to solid compounds.

X-ray powder diffraction experiments were carried out with a Philips PW1730 diffractometer with automatic data acquisition (APD Philips v.35B), operating in the $\theta - 2\theta$ mode. The apparatus was equipped with a vertical goniometer (PW1820), a proportional xenon detector (PW1711), and a graphite monocromator (PW1752). A Cu Kα radiation source was used. The tube amperage was 30 mA and the tube voltage was 40 kV. The diffractograms were recorded at $T = (295 \pm 2)$ K in the range $5° \leqslant 2\theta \leqslant 35°$. The samples were mounted on an aluminium sample holder and the data were collected in the continuous mode with a step size of 0.015° (2θ), and an acquisition time of 1.5 s·$step^{-1}$. The indexation of the powder patterns was performed using the Celref program [14].

2.2. Materials and their purities

Catechol, resorcinol and hydroquinone samples were purified by sublimation. Catechol and resorcinol were purified at T = ~348 K and hydroquinone was purified at ~363 K at a pressure of *ca.* 10^{-2} Pa. ^{1}H NMR (400 MHz, DMSO-d_6/TMS) $\delta/10^{-6}$ = 8.82 (s, –O**H**, 2H), 6.74 (m, –C**H**, 2H), 6.601 (m, –C**H**, 2H), for catechol, $\delta/10^{-6}$ = 9.16 (s, –O**H**, 2H), 6.92 (t, –C**H**, 1H), 6.20 (d, –C**H**, 3H), for resorcinol and $\delta/10^{-6}$ = 8.64 (s, –O**H**, 2H), 6.58 (s, –C**H**, 4H), for hydroquinone. ^{13}C NMR (100 MHz, DMSO-d_6/TMS), $\delta/10^{-6}$ = 145.72 (–**C**OH), 119.75 (–CH**C**H–), 116.14 [–**C**HC(OH)-C(OH)**C**H–] for catechol, $\delta/10^{-6}$ = 158.89 (–**C**OH), 130.19 [–C(OH)CH**C**HCHC(OH)–], 106.67 [–C(OH)**C**H–], 102.92 [–C(OH)**C**HC(OH)–] for resorcinol and $\delta/10^{-6}$ = 150.18 [–CH**C**(OH)CH–], 116.12 [–C(OH)**C**H**C**HC(OH)–] for hydroquinone. The observed ^{1}H and ^{13}C NMR spectra are in good agreement with those reported in a reference database [15]. No impurities were detected by GC–MS.

The solid crystalline structures of the three isomers were characterised from X-ray diffractograms and were indexed. For catechol, the structure was indexed as monoclinic, space group $P2_1/c$, with a = 1.0106(40) nm, b = 0.5526(5) nm, c = 1.0962(43) nm, and β = 118.61(33)°, in agreement with that reported from single crystal X-ray diffraction at room temperature: $P2_1/c$, with a = 1.0082(1) nm, b = 0.5518(2) nm, c = 1.0943(1) nm, and β = 118.53(1)° [16,17]. For resorcinol, the structure was indexed as orthorhombic, space group $Pna2_1$, with a = 1.0514(7) nm, b = 0.9556(5) nm and c = 0.5665(4) nm, in agreement with that reported from single crystal X-ray diffraction, at room temperature: