



Energetics and structural properties of neutral and deprotonated phenyl carbinols



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ABSTRACT

Theoretical and experimental studies on the energetics, structure and other physicochemical properties of neutral 1-phenylethanol (**1OH**), diphenylmethanol (**2OH**) and triphenylmethanol (**3OH**) and their corresponding deprotonated anions (oxyanions, formed by deprotonation of the OH group) are reported in this work. The standard enthalpies of formation in the gas phase at $T = 298.15$ K, $\Delta_f H_m^0(\text{g})$ have been determined. Quantum chemical calculations, at the DFT (particularly M05-2X method) and in some cases at the *ab initio* (G3) levels, have shed light on structural and electronic effects on the thermodynamic stability and intrinsic acidity of the studied compounds. These calculations confirmed the excellent consistency of the experimental results.

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1. Introduction

This work is part of a systematic investigation of the energetics and structural properties of large conjugated organic molecules [1] with biological, medicinal and industrial applications.

For the present study, we have chosen a set of phenyl carbinol compounds namely, racemic-1-phenylethanol (**1OH**, $\text{C}_8\text{H}_{10}\text{O}$), diphenylmethanol (**2OH**, $\text{C}_{13}\text{H}_{12}\text{O}$) and triphenylmethanol (**3OH**, $\text{C}_{19}\text{H}_{16}\text{O}$). These important molecules are in biochemistry and medicine, as well as in the cosmetic and food industries [2–4].

The lack of reliable thermochemical data in the literature for these molecules, has led us to carry out an experimental and theoretical investigation of structural effects on the intrinsic thermodynamic stability of neutral and deprotonated anions of phenyl carbinols (scheme 1) in the gas phase. Reliable data for these molecules have been obtained by differential scanning calorimetry (DSC), static bomb combustion calorimetry, Knudsen effusion technique, as well as by quantum chemical calculations at the density functional theory (DFT) level and composite *ab initio* G3 method.

This work was focused on two goals: (i) to check the consistency of the experimental results of $\Delta_f H_m^0(\text{g})$ for the compounds

studied, particularly by means isodesmic reactions, with the DFT calculations (M05-2X and B3LYP); (ii) to study the effect of α -alkyl and phenyl substituents on both, the thermodynamical stability and the acidity of the compounds studied.

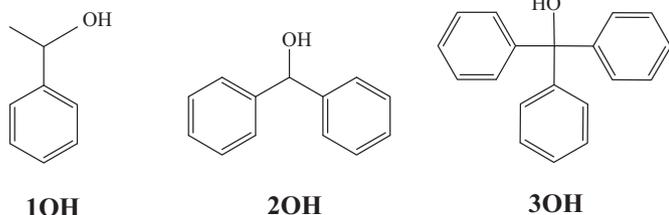
2. Experimental

2.1. Materials and purity control. DSC measurements

Racemic (*R,S*)-1-phenylethanol (**1OH**, $\text{C}_8\text{H}_{10}\text{O}$), diphenylmethanol (**2OH**, $\text{C}_{13}\text{H}_{12}\text{O}$) and triphenylmethanol (**3OH**, $\text{C}_{19}\text{H}_{16}\text{O}$) were purchased from Sigma–Aldrich. **2OH** and **3OH** samples were carefully dried under vacuum used without further purification, whereas the racemic liquid **1OH** was further purified by repeated distillation using a spinning-band column at reduced pressure. Table 1 summarizes relevant information on purification and provenance of samples. From the thermoanalysis study of the samples by DSC (Perkin Elmer Pyris 1) over the temperature ranges considered (see below), no phase transitions were observed. Molar heat capacities at constant pressure $C_{p,m}^0$ were also experimentally determined by DSC, following the methodology “scanning method” previously described in the literature [5]. Full details are given in the supporting information.

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SCHEME 1. Molecular structure of (R,S)-1-phenylethanol (1OH), diphenylmethanol (2OH) and triphenylmethanol (3OH).

2.2. Static bomb combustion calorimetry

The combustion experiments for **1OH** and **2OH** were carried out in an *isoperibol* static *macro*-bomb calorimeter, described in detail elsewhere [7]. The calorimetric temperatures were measured to within (± 0.0001) K by means of a 100 Ω platinum resistance thermometer, using a calibrated resistance bridge (Model F300, Automatic System Laboratories Ltd.) interfaced to a microcomputer programmed to calculate the adiabatic temperature change. The energy of reaction was always referred to the final temperature of 298.15 K. The energy equivalent of the calorimeter, $\varepsilon(\text{calor})$, was determined from the combustion of benzoic acid (NIST standard reference sample 39j) with a massic energy of combustion of ($-26,434 \pm 3$) J \cdot g $^{-1}$, under certificate conditions. From ten calibration experiments, carried out in oxygen at $p = 3.04$ MPa with 1 cm 3 of water added to the bomb, we have obtained the value $\varepsilon(\text{calor})$ of (14283.1 \pm 2.5) J \cdot K $^{-1}$, where the uncertainty quoted is the standard deviation of the mean.

The liquid samples of **1OH** were placed in sealed polyethylene bags. The empirical formula and massic energy of combustion of the polyethylene were C $_{0.968}$ H $_{2.000}$ and (-46339.3 ± 6.6) J \cdot g $^{-1}$, respectively, both determined in our laboratory. The uncertainty quoted corresponds to the standard deviation of the mean for ten experiments. The solid samples of **2OH** were pressed in pellet forms. The empirical formula and massic energy of combustion of the cotton-thread fuse, CH $_{1.740}$ O $_{0.871}$ and ($-17,410 \pm 37$) J \cdot g $^{-1}$ were determined in our laboratory. The uncertainty quoted corresponds to the standard deviation of the mean for ten experiments.

Corrections of apparent mass to mass, nitric acid formation; conversion of the energy of the actual bomb process to that of the isothermal process and correction to standard states were made according to Hubbard *et al.* [8]. For these corrections were used specific density values of **1OH** and **2OH** as, respectively 1.02 (taken from XRD base Data) and (1.21 \pm 0.02) g \cdot cm $^{-3}$, measured in our laboratory – at room temperature – by submerging a compact tablet of the substance in a calibrated 10 cm 3 pycnometer filled with water. The uncertainty quoted is the standard deviation of the mean for five measurements. ($\partial V/\partial T$) $_p$ values for **1OH** and **2OH** were assumed to be respectively, in dm 3 \cdot g $^{-1}$ \cdot K $^{-1}$, 3.85 \cdot 10 $^{-7}$ (taken from reference [9]) and 2.99 \cdot 10 $^{-7}$ (determined by us). The molar masses used for the elements were those recommended by IUPAC commission [10]. Complementary details are given in S2 of supporting information.

TABLE 1
Provenance and mole fraction purity of **1OH**, **2OH** and **3OH** phenyl carbinols.

Chemical name	Provenance	CAS number	Mole fraction purity ^a	Purification method	Analysis method
Racemic (R,S)-1-phenylethanol (1OH)	Sigma-Aldrich	98-85-1	0.990 (≥ 0.98)	Distillation (spinning band column)	GC ^c , DSC ^d
Diphenylmethanol (2OH)	Sigma-Aldrich	91-01-0	0.999 (0.99)	None ^b	GC ^c , DSC ^d
Triphenylmethanol (3OH)	Sigma-Aldrich	76-84-6	0.999 (0.97)	None ^b	GC ^c , DSC ^d

^a Between brackets purity based on information provided by the supplier Sigma-Aldrich.

^b The samples were dried under vacuum at $T = 303$ K for **2OH** and $T = 333$ K for **3OH**.

^c Gas-chromatography (Agilent/Varian 450) using a HP-5 column.

^d Checked by differential scanning calorimetry (Perkin Elmer Pyris 1, DSC), using the fractional fusion technique [6].

2.3. Vapor pressure measurements

The vapor pressures of **2OH** and **3OH** as a function of temperature were measured by a mass loss Knudsen-effusion method, using the improved and tested technique and procedure previously described elsewhere (benzoic acid and naphthalene as reference materials) [11,12]. The Knudsen cell was placed in a stainless steel sublimation chamber, which was connected to a high-vacuum system ($1 \cdot 10^{-4}$ Pa) and immersed in a bath thermostatically controlled to ± 0.005 K. The vapor pressure, p , for each temperature, T , was calculated by means of the Knudsen-equation. Full details of this method is given in supporting information.

2.4. Computational methods

The quantum chemical calculations were carried out using the Gaussian 09 package. The geometries of the compounds under investigation were optimized using the Density Functional M05-2X method [13] with 6-31G(d), 6-311++G(d,p) and 6-311++G(3df,2p) basis sets, without symmetry restrictions. For comparative purposes, we have also used the B3LYP hybrid functional [14] and in some cases, the G3 composite method [15]. In all cases, the harmonic vibrational frequencies were computed at the same theory levels without scaling, in order to verify that all the stationary points correspond to minima in the potential energy surfaces. The levels of theory employed in the present work are expected to provide consistent and reliable results for the considered reactions, based on previous evidences [16–18]. Full details of the computational methods are given in supporting information.

3. Results and discussion

3.1. Thermophysical properties

The onset temperature of melting point and enthalpy of fusion of the compounds determined by DSC, (T_{fus}/K ; $\Delta_{\text{fus}}H_{\text{m}}^0/\text{kJ} \cdot \text{mol}^{-1}$), were (291.7 \pm 0.7; 16 \pm 2), (339.4 \pm 0.7, 23.7 \pm 0.1) and (435.2 \pm 0.4; 27.3 \pm 0.4) for **1OH**, **2OH** and **3OH**, respectively. The associated uncertainties are expressed as expanded uncertainties of the mean (0.95 level of confidence) for three experiments. All these values are in good agreement with those reported in the literature (see supporting information).

The least square fitting of the experimental data of molar heat capacities in the condensed state $C_{p,m}^0$ (in J \cdot K $^{-1}$ \cdot mol $^{-1}$) yielded the following equations:

$$\begin{aligned} \text{For } \mathbf{1OH}, \text{ in the range of } T = (297.15 \text{ to } 373.15) \text{ K,} \\ C_{p,m}^0(l, T)/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -1.56171 \cdot 10^{-3}(T/\text{K})^2 \\ + 1.69546(T/\text{K}) - 1.03997 \cdot 10^2 \quad (r^2 = 0.999). \end{aligned} \quad (1)$$

$$\begin{aligned} \text{For } \mathbf{2OH}, \text{ in the range of } T = (259.15 \text{ to } 332.15) \text{ K,} \\ C_{p,m}^0(\text{cr}, T)/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 2.24355 \cdot 10^{-3}(T/\text{K})^2 \\ - 4.82666 \cdot 10^{-1}(T/\text{K}) + 1.77502 \cdot 10^2 \quad (r^2 = 0.999). \end{aligned} \quad (2)$$

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