



Comprehensive thermophysical and thermochemical studies of vanillyl alcohol



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ABSTRACT

In this work, energetic and structural studies concerning vanillyl alcohol, based both on experimental and computational studies, were developed. The massic energy of combustion and the vapour pressures at different temperatures were measured by static bomb combustion calorimetry and Knudsen mass-loss effusion techniques, respectively. The computational studies were performed using the G3(MP2)//B3LYP method. The combination of experimental and computational data enabled the determination of the enthalpies, entropies and Gibbs energies of sublimation and formation of this compound both in the crystal and gas phase. The intramolecular hydrogen bond energy present in vanillyl alcohol was evaluated, together with the O–H homolytic bond dissociation enthalpy. The new data are very useful for process design and development in the biorefinery.

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1. Introduction

Bio oil produced from fast pyrolysis oil is promising second generation biofuel. Unfortunately, the application range for bio oil is limited due to the high acidity and presence of oxygen in variety chemical functionalities. Typical compound classes in bio oil are organic acids, aldehydes, ketones, phenolics, and alcohols [1]. Vanillyl alcohol, with the systematic name of 4-(hydroxymethyl)-2-methoxyphenol (Fig. 1), is the compound found in bio oil as degradation of lignin [1] and also considered as key-intermediate compound on the synthesis of bio-based polymers. Thermophysical and thermochemical properties of vanillyl alcohol are very important for process design and process development of upgrading bio oil and also in valorization of lignin into high value applications. This research follows our previous energetic studies involving biomass derivatives, namely the levoglucosan [2] and the cellulose allomorphs [3]. None of thermophysical neither thermochemical properties of the title compound are found in the literature, thus in this work, the vapour pressures at different temperatures and the massic energy of combustion of vanillyl alcohol are measured. The static bomb combustion calorimetry was used on the measurement of the standard massic energy of combustion of vanillyl alcohol, which allowed to derive the corresponding standard ($p^\circ = 0.1 \text{ MPa}$) molar enthalpy of

formation, in the crystalline phase, at $T = 298.15 \text{ K}$. The vapour pressures were measured, at several temperatures, by Knudsen effusion technique, and by application of the Clausius–Clapeyron equation to the results obtained, the molar enthalpy and entropy of sublimation of vanillyl alcohol were derived. The values of the standard molar enthalpy of formation, in the crystalline phase, and the standard molar enthalpy of sublimation were combined to derive the standard molar enthalpy of formation, in the gaseous phase, at $T = 298.15 \text{ K}$. This value was also derived from G3(MP2)//B3LYP calculations considering a conformational equilibrium composition of the optimized molecular structures and the energetics of several hypothetical group substitution reactions. Experimental and computational results were compared and discussed. The energetics of the cleavage of the two O–H bonds and the intramolecular hydrogen bonding (O···H) present in vanillyl alcohol were investigated using theoretical methods. The frontier molecular orbitals and the electrostatic potential energy surfaces, and the estimation of the standard molar entropies and Gibbs energies of formation are also addressed.

2. Experimental study

2.1. Purification of vanillyl alcohol

The crystalline sample of vanillyl alcohol (CAS Registry No. 498-00-0) was purchased from Sigma Aldrich®, with a

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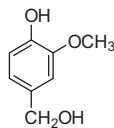


Fig. 1. Structural formula for vanillyl alcohol.

minimum assured mole fraction purity of 0.994 (GC). The sample was further purified to obtain the minimum purity required for the calorimeter studies, which is 0.999. The purification involved successive re-crystallisation using mixed solvents (water/ethanol) followed by vacuum sublimation to remove the remaining solvent residue. Other details about the purification and provenience of the studied compound are summarized in Table 1.

The purity was analysed with gas chromatography using a non-polar capillary column (Hewlett-Packard, HP-5) with a bonded and cross-linked stationary phase composed by 5%-phenyl and 95%-methylpolysiloxane (15 m of length \times 0.530 mm i.d. \times 1.5 μ m film thickness). The purity of vanillyl alcohol was also assessed from the average ratio of the mass of carbon dioxide recovered in the combustion experiments to those calculated from the mass of sample used in each experiment with the following result: 1.0003 ± 0.0001 (the standard uncertainty correspond to the estimated standard deviation of the mean for six experiments).

2.2. Determination of energy of combustion

The massic energy of combustion of vanillyl alcohol was measured using the static bomb combustion calorimetry method. The description of the apparatus used has been reported previously [4,5]. Details of the calibration and additional information about the experiments are given as Supplementary Material. For the combustion experiments, pellets of crystalline vanillyl alcohol were prepared. Due to the incomplete combustion of the compound in some experiments, it was necessary to use *n*-hexadecane (supplied by Aldrich Gold Label, molar fraction > 0.99) as a combustion auxiliary with a standard massic energy of combustion of $\Delta_c u^\circ = -(47136.7 \pm 2.3) \text{ J} \cdot \text{g}^{-1}$, measured in our laboratory; the standard uncertainty quoted corresponds to the estimated standard deviation of the mean for ten experiments.

The samples were ignited in oxygen at $T = (298.150 \pm 0.001) \text{ K}$ under a pressure of 3.04 MPa (the bomb was previously flushed to remove air) and with 1.00 cm³ of deionized water inside the bomb. The combustion products were analysed as follows: the carbon dioxide formed was collected in absorption tubes [6] and the nitric acid produced was quantified by acid-base titration. The quantity of compound burnt in each experiment was determined from the total mass of carbon dioxide produced, taking into account that formed from the combustion of the cotton thread fuse and of *n*-hexadecane.

2.3. Determination of vapour pressure

The study of the temperature dependency of the vapour pressures of vanillyl alcohol was performed using the mass-loss

Knudsen effusion technique. The description of the apparatus and the general procedure are reported in the literature [7] and the additional experimental details are given as Supplementary Material. The vapour pressure measurements of vanillyl alcohol were performed in the temperature range of (332–350) K, chosen to correspond to measured vapour pressure in the range 0.1 Pa to 1.0 Pa.

For each effusion experiment, considering a system evacuated to a pressure near to $1 \cdot 10^{-4} \text{ Pa}$, the mass of sublimated compound (loss of mass of the cells), m , during a convenient effusion time period, t , was determined by weighing the effusion cells to $\pm 0.01 \text{ mg}$, before and after the effusion experiments. At the temperature T of the experiment, the vapour pressure of each effusion cell, p , was calculated by the Eq. (1), where A_0 is the area of the effusion orifice, R is the gas constant ($R = 8.3144621 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) [8] M is the molar mass of the compound, and w_0 is the Clausing probability factor.

$$p = (m/A_0 w_0 t) \cdot (2\pi RT/M)^{1/2}. \quad (1)$$

3. Computational study

The computational approach used to determine the gas-phase enthalpy of formation of vanillyl alcohol was based on gas-phase hypothetical reactions [9–12], designed in such a way that the electronic environments of the atoms in the reactants and in the products were as similar as possible to reduce the errors inherent to the computational method employed in the calculations. These reactions were established on the availability of accurate experimental thermochemical data for the auxiliary species used.

Molecular calculations concerned with this work were performed with the Gaussian-03 software package [13] using the composite method G3(MP2)//B3LYP [14], a variation of Gaussian-3 (G3) theory [15].

The natural bonding orbital (NBO) analyses were performed using NBO 3.1 [16] program as implemented in the Gaussian-03 software package [13] at the B3LYP/6-31G(*d,p*) level.

The topological properties of the electron density at the selected bond critical point (intramolecular hydrogen bond) were evaluated using the theory of the atoms in molecules (AIM) [17] as implemented in the AIM11 program (version 13.11.04) [18].

4. Results and discussion

The mean value of the standard massic energy of combustion of vanillyl alcohol in the crystalline state, $\Delta_c u^\circ(\text{cr})$, at $T = 298.15 \text{ K}$, reported in Table 2, was obtained from a set of six combustion experiments (combustion results are reported in Table S1 of Supplementary Material). From this quantity the values of standard molar energy and enthalpy of combustion, respectively, $\Delta_c U_m^\circ(\text{cr}) = (-4030.6 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_c H_m^\circ(\text{cr}) = (-4033.1 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$, were derived. The standard molar enthalpy of formation of vanillyl alcohol, $\Delta_f H_m^\circ(\text{cr}) = (-544.1 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$, was determined from the above value of the $\Delta_c H_m^\circ(\text{cr})$ and from the values of the $\Delta_f H_m^\circ$ of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$, at $T = 298.15 \text{ K}$, respectively, $(-285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$ [19] and $(-393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$ [19], according with the

Table 1
Purification and provenance details of vanillyl alcohol.

CAS Registry No.	Provenance	Initial purity	Purification methods	Final mass fraction purity
498-00-0	Sigma Aldrich ^a	0.994 ^a	Recrystallisation Vacuum sublimation	0.9990 ^b 1.0003 \pm 0.0001 ^c

^a Values stated in the certificate of analysis of the supplier;

^b Results obtained from gas-liquid chromatography;

^c Results obtained from combustion calorimetry, based on mass fraction of carbon dioxide recovery (mean and standard deviation of the mean for six experiments).

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