Benchmark properties of biphenyl as a liquid organic hydrogen carrier: Evaluation of thermochemical data with complementary experimental and computational methods

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ABSTRACT

Vapor pressures of highly pure biphenyl were measured by the transpiration method over a broad temperature range that included both the crystalline and the liquid phases. The standard molar enthalpies of sublimation/vaporization of biphenyl were derived from the vapor pressure temperature dependences. Thermodynamic data on sublimation/vaporization processes available in the literature were collected, evaluated, and combined with our experimental results. Additional combustion experiment on the highly pure biphenyl helped to resolve an ambiguity on the crystalline phase enthalpy of formation of biphenyl. We recommend the set of sublimation/vaporization and formation enthalpies for biphenyl at 298.15 K (in kJ·mol^{-1}): $\Delta_{cr}^{g}H_{m}^{o} = (81.8 \pm 0.2)$, $\Delta_{l}^{g}H_{m}^{o} = (65.8 \pm 0.2)$, $\Delta_{f}H_{m}^{o}(cr) = (97.9 \pm 1.1)$, and $\Delta_{f}H_{m}^{o}(g) = (179.7 \pm 1.1)$, as the reliable benchmark properties for further thermochemical calculations. Gas phase molar enthalpies of formation of biphenyl, calculated by high-level quantum-chemical method G3MP2, were found in excellent agreement with the recommended experimental data. The standard molar entropy of formation and the standard molar Gibbs function of formation of biphenyl were estimated. The hydrogenation/dehydrogenation reaction enthalpy was calculated and compared with the data for other liquid organic hydrogen carriers.

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1. Introduction

Hydrogen has been considered as a clean and efficient energy carrier for a variety of industrial utilizations, especially for mobile applications [1]. However, the large-scale utilization of hydrogen energy still remains a substantial challenge, because the efficient hydrogen storage technologies should be compatible with the current energy infrastructure, offer high storage density and operate at near ambient conditions. The concept of liquid organic hydrogen carriers (LOHCs), in which hydrogen is covalently bonded to an organic molecule of a liquid substance, was proposed in the 1980s and a variety of organic molecules has been proposed to date [2]. Our recent extensive experimental and computational work on heterocyclic aromatic compounds, such as carbazole, N-ethylcarbazole, as well as on benzyl and dibenzyltoluenes have established the thermodynamic background for this fully

reversible hydrogen storage [3–6]. Our current activities have been focused on a search of new low-cost LOHC compounds for effective hydrogen storage. However, it has turned out, that hydrogenation and dehydrogenation processes with the LOHC are both kinetically and thermodynamically difficult, which requires a highly active catalyst and an elevated temperature [2]. Biphenyl [CAS 92-52-4] could be considered as one of the possible LOHC candidates for hydrogen storage mostly due to its commercial availability on a large scale. Biphenyl as an ingredient of organic heat transfer fluids Therminol® VP-1, Dowtherm™ and Diphyl®, is used in concentrated solar power technology to transfer the heat from the solar collectors to the power cycle. Moreover, the biphenyl could serve as a model compound for studies of kinetic and thermodynamic limitations of the hydrogenation and dehydrogenation processes with LOHC. In this context, very accurate thermodynamic properties for biphenyl are required. However, according to the most recent compilation by Roux et al. [7], the spread of available thermodynamic data for biphenyl is too large. For example, reported literature values of sublimation enthalpies at the reference temperature 298.15 K segregate into two sets; one set appears to be

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centered about a mean of 76.0 kJ mol^{-1} and the other about a mean of 82.0 kJ mol^{-1}. Another example, enthalpies of formation in the crystalline state. The spread of available results from 92 kJ mol^{-1} to 125 kJ mol^{-1} is definitely too large, even taking into account that the outlying results were measured at the beginning of the last century. In addition to the compilation by Roux et al. [7], we have tried to collect as complete as possible all available literature data on vaporization/sublimation and formation enthalpies of biphenyl. New additional thermochemical experiments with biphenyl were intended to help with establishing consistency in the available data. The aim of this study was an evaluation of thermochemical data available for biphenyl augmented with more recent complementary experimental and computational methods in order to recommend benchmark thermochemical properties for this compound.

2. Materials and methods

2.1. Materials

The sample of biphenyl was of commercial origin from Sigma-Aldrich (B34656) with the purity of 99.5% as stated by the manufacturer. The sample was additionally purified by fractional sublimation in a vacuum. No impurities (greater than 0.0003 mass fraction) could be detected in the samples used for the thermochemical measurements. The degree of purity was determined using a GC equipped with a FID. A capillary column HP-5 was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm.

2.2. Transpiration method: Vapor pressure measurements

Vapor pressures of biphenyl over the solid and over the melted sample were measured using the transpiration method [8–10]. About 0.5 g of a sample was mixed with small glass beads and placed in a thermostatted U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature (±0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using the dodecane as an external standard. The absolute vapor pressure p_{sat} at each temperature T_i was calculated from the amount of the product, collected within a definite period. Assuming validity of the Dalton's law, applied to the nitrogen stream, which was saturated with the substance, values of p_{sat} were calculated with Eq. (1):

$$P_{sat} = m_i \cdot R \cdot T_a / V \cdot M_i;$$
$$V = V_N 2 + V_i; \quad (V_N 2 \gg V_i) \tag{1}$$

where R = 8.3144598 J·K^{-1}·mol^{-1}; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for the flow rate measurements. The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement.

2.3. Combustion calorimetry: Crystal state enthalpy of formation determination

The standard molar energy of combustion of the biphenyl was measured with a self-made isoperibolic calorimeter with a static bomb and a stirred water bath [11]. The sample of 0.5–0.6 g was pressed into a pellet then was placed in the crucible and was burned in oxygen at a pressure of 3.04 MPa. Three from a total of six experiments were performed with the addition of few drops of mineral oil on the pellet in order to ensure completeness of

combustion. It has turned out that results with and without added oil were indistinguishable. The detailed procedure has been described previously [11,12]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither was detected. The energy equivalent of the calorimeter ε_{calor} = 14817.6 J·K^{-1}; $u(\varepsilon_{calor})$ = 0.9 J·K^{-1} was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). Correction for nitric acid formation was based on titration with 0.1 mol·dm^{-3} NaOH (aq). For the reduction of the data to standard conditions, conventional procedures [13] were used. Auxiliary data required for the reduction are collected in Table S1.

3. Results and discussion

3.1. Vapor pressures of biphenyl from the transpiration method

The temperature dependence of vapor pressures p_{sat} for the biphenyl measured in this work by transpiration over the solid sample was fit with the following equation [8]:

$$R \ln p_{sat} = a + \frac{b}{T} + \Delta_{cr}^g C_{p,m}^o \ln\left(\frac{T}{T_0}\right) \tag{2}$$

where a and b are adjustable parameters and $\Delta_{cr}^g C_{p,m}^o$ is the difference of the molar heat capacities of the gaseous and the condensed phase respectively. T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature (which has been chosen to be T = 298.15 K) and R is the molar gas constant.

3.2. Comparison of available vapor pressures over the crystalline biphenyl

Much research has been done on the sublimation and vaporization of biphenyl since 1904 [14]. A careful search for the vapor pressures of biphenyl measured over the solid samples has revealed fifteen datasets (see compilation in Table 2) measured mostly by the mass-loss effusion technique, the transpiration (or gas-saturation) method, as well as by the static method. Unfortunately, not all original papers contain the primary experimental data on p_{sat} and T, required for comparison among the available data. Fig. 1 shows temperature dependences of all available primary vapor pressures over crystalline biphenyl. As can be seen from this comparison, only a few data sets apparently deviate from the general trend. The results by Bright [15] from the effusion technique are significantly and systematically lower. However, the vapor pressure data measured by Bright [15] for dibenzyl and diphenylmethane were also systematically lower in comparison with data from other methods. The results by Seki et al. [16] are in agreement with the general trend at low temperatures, but with the rising temperatures of the experiment, the measured by effusion technique vapor pressures show the decreasing trend. Results from a modification of the gas-saturation method reported by Sharma and Palmer [17] are also systematically lower at temperatures between (326.2 and 334.2) K (when the sample was in the solid state), but at temperature between (344.2 and 354) K (when the sample was melted), the measured vapor pressures are in agreement with other available data. Thus, the disagreement observed for 326.2 K and 334.2 K is rather due to insufficient saturation of the carrier gas. Vapor pressures measured in this work by the transpiration are consistent with the most of the available data sets (see Fig. 1).

3.3. Comparison of available vapor pressures over the liquid biphenyl

Altogether sixteen vapor pressure data sets over melted biphenyl have been found in the literature since 1904 (see compilation