



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

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ABSTRACT

The standard molar enthalpy of vaporisation of diphenyl oxide was derived from the vapour pressure temperature dependences measured by the transpiration method. Thermodynamic data on vaporisation processes available in the literature were collected. They were evaluated and combined with our own experimental results. Additional combustion experiment on the highly pure diphenyl oxide helped to resolve ambiguity in the enthalpy of formation for this compound. We have evaluated and recommended the set of vaporisation and formation enthalpies for the diphenyl oxide at 298.15 K (in $\text{kJ}\cdot\text{mol}^{-1}$): $\Delta_f^{\circ}H_m^{\circ} = (66.7 \pm 0.2)$, $\Delta_r^{\circ}H_m^{\circ}(\text{liq}) = -(15.8 \pm 1.4)$, and $\Delta_r^{\circ}H_m^{\circ}(\text{g}) = (50.9 \pm 1.4)$, as the reliable benchmark properties for further thermochemical calculations. Gas phase molar enthalpy of formation of diphenyl oxide calculated by the high-level quantum-chemical method G4 was in an excellent agreement with the recommended experimental data. The standard molar Gibbs function of formation and the standard molar entropy of formation of diphenyl oxide were estimated. The hydrogenation/dehydrogenation reaction enthalpy of diphenyl oxide was calculated and compared with the data for other potential liquid organic hydrogen carriers.

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1. Introduction

The concept of the 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 discussed to date [1]. Our recent experimental and computational studies on heteroaromatic compounds, such as carbazole, N-ethylcarbazole, as well as on the benzyl and dibenzyltoluenes have established the thermodynamic background for applications of this fully reversible hydrogen storage [2–5]. Our current activities have been focused on a search for new low-cost LOHC compounds for the effective hydrogen storage. Diphenyl oxide [CAS 101-84-8, see Fig. 1] could be considered as one of the possible LOHC candidates for the hydrogen storage mostly due to its commercial availability on the large scale. Diphenyl oxide 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. The accurate and reliable thermodynamic properties of diphenyl oxide are required for analysis of the effectiveness of the hydrogen storage. In this context, we have collected in the literature thermodynamic data for diphenyl oxide, but the evaluation of the available results has been thwarted with complications, because the melting temperature of this compound ($T_{\text{fus}} = 300.0 \text{ K}$) is slightly above the reference temperature. This fact is especially important for the combustion calorimetry, where the initial state must be defined clearly. For this reason, Furukawa et al. [6] have deliberately changed the conventional combustion procedure and measured combustion energies at 303.15 K in order to keep sample definitely in the liquid state. The published later combustion result by Cass et al. [7] was derived from only three experiments but on the solid sample. The consistency of two data sets is rather poor. Another example, the available enthalpies of vaporisation of diphenyl oxide spread from 60 kJ mol^{-1} [8] to 70 kJ mol^{-1} [9]. New additional thermochemical experiments with diphenyl oxide have been conducted to help with establishing of consistency in the available thermodynamic data. The aim of this study was to evaluate the thermochemical data available for

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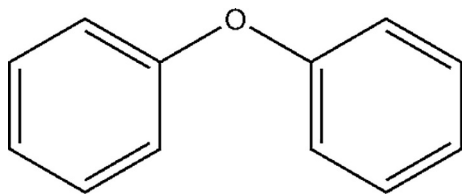


Fig. 1. The structure of diphenyl oxide.

diphenyl oxide with the complementary experimental and computational methods in order to recommend benchmark thermochemical properties for this compound.

2. Materials and methods

2.1. Materials

Two commercially available samples of diphenyl oxide (see Table S1) have been used in this work: the first sample from Sigma-Aldrich 67334 Selectophore™, with the purity, better than 0.999 mass fraction (as stated by the manufacturer) and the second sample from Aldrich 240834 ReagentPlus®, with the purity better than 0.99 mass fraction (according to the specification). Both samples were additionally purified by the fractional sublimation in a vacuum. No impurities (greater than 0.0002 mass fraction) could be detected in both 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. Water mass fraction in the samples was determined using a Mettler Toledo DL38 Karl Fischer titrator using the HYDRANAL™ as the reagent. A not significant mass fraction of water at the level of $(15\text{--}20) \times 10^{-6}$ was measured by Karl Fisher titration.

2.2. Transpiration method: Vapour pressure measurements

Vapour pressures of diphenyl oxide over the liquid sample (ReagentPlus®) were measured using the transpiration method [10–12]. About 0.5 g of the sample was mixed with small glass beads and placed in the thermostatted U-shaped saturator. A nitrogen stream with well-defined flow rate 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 *n*-dodecane as an external standard. The absolute vapour pressure p_{sat} at each temperature T_i was calculated from the amount of the product, collected within a definite period. Assuming validity of Dalton's law, applied to the nitrogen stream saturated with the substance, values of p_{sat} were calculated with Eq. (1):

$$p_{\text{sat}} = m_i \cdot R \cdot T_a / V \cdot M_i; \quad \text{where } V = V_{\text{N}_2} + V_i \quad (1)$$

where $R = 8.3144598 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the universal gas constant; 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_{N_2} 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_{N_2} was determined from the flow rate and the time measurements.

2.3. Combustion calorimetry: Liquid state enthalpy of formation determination

The standard molar energy of combustion of diphenyl oxide was measured with a self-made isoperibolic calorimeter with a sta-

tic bomb and a stirred water bath. Prior to the combustion experiments, the hermetically closed flask with a fresh sublimed sample was melted and kept at 313 K for about 10 min. The liquid sample was transferred (in the glove box) into the polyethylene bulb (Fa. NeoLab, Heidelberg, Germany) with a syringe. The neck of the bulb was compressed with special tweezers and was sealed by heating the neck in a close proximity to a glowing wire. We have observed, that prepared in such way sample remains liquid in the sealed bulb at room temperature of 295 K even overnight. Moreover, the sample remains liquid after pressurizing of the polyethylene bulb in the calorimetric bomb. This observation assured the liquid state of the diphenyl oxide before the ignition and allowed to keep the conventional combustion procedure with the ignition temperature below 298 K. Thus, the bulb with the liquid sample was placed in the crucible and it was burned in oxygen at a pressure of 3.04 MPa. The detailed procedure has been described previously [13,14]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). Correction for nitric acid formation was based on titration with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH (aq). For the reduction of the data to standard conditions, conventional procedures [15] were used. Auxiliary data required for the reduction are shown in Table S2.

3. Results and discussion

3.1. Vapour pressures of diphenyl oxide from the transpiration method

The temperature dependence of vapour pressure p_{sat} for the diphenyl oxide measured in this work by transpiration over the liquid sample was fitted with the following Eq. (2) [10]:

$$R \ln(p_{\text{sat}}/p^\circ) = a + \frac{b}{T} + \Delta_1^{\text{g}} C_{p,m}^{\text{g}} \ln\left(\frac{T}{T_0}\right), \quad (2)$$

where a and b are adjustable parameters and $\Delta_1^{\text{g}} C_{p,m}^{\text{g}}$ is the difference of the molar heat capacities of the gas and the liquid phases respectively. T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature (which has been chosen to be $T_0 = 298.15 \text{ K}$), $p^\circ = 1 \text{ Pa}$, and R is the molar gas constant.

3.2. Comparison of available vapour pressures

There are no vapour pressures data available for diphenyl oxide measured over the crystalline sample. However, altogether five vapour pressure data sets over the melted diphenyl oxide have been found in the literature since 1947 [8] (see the compilation in Table 2). Comparison of the available data sets is presented in Fig. 1. The vapour pressures measured by different methods are generally in a good agreement (see Fig. 1), except for the data by Stull [8] (which are originated from the Dow Chemical Co. files) and a few low-temperature data points measured with the static method by Thomas and Smith [16]. Vapour pressures measured in this work by the transpiration are consistent with the most of the available data sets (see Fig. 1). In fact, the conventional representation of the vapour pressure temperature dependences ($\ln p_{\text{sat}}$ against $1/T$) presented in Fig. 1 is not sufficient while working over the broad temperature range. More detailed insight into the quality of vapour pressures measured by different methods can be obtained from the “arc representation” developed by Oonk et al. [17–19]. The main idea of this approach is to collect all available data in a possibly broad temperature range and to approximate vapour pressures at the beginning and the end of the temperature range with the linear equation.

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