

Article

Comprehensive Thermodynamic Study of Alkyl-Cyclohexanes as Liquid Organic Hydrogen Carriers Motifs

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Abstract: Alkyl-cyclohexanes can be considered as suitable model compounds to understand the thermochemistry of aromatic compounds and their hydrogenated counterparts discussed as Liquid Organic Hydrogen Carrier systems. Thermochemical measurements on these hydrogen-rich compounds are thwarted by complications due to the 99.9 % purity limitation and sample size specific to these methods. However, the data on vaporisation and formation enthalpies are necessary to optimize the hydrogenation/dehydrogenation processes. In this work, various empirical and theoretical methods are described to reliably assess the gas phase enthalpies of formation and vaporization enthalpies of alkyl-substituted cyclohexanes. The empirical and quantum-chemical methods have been validated against reliable literature data and provide reasonable estimates with an accuracy comparable to that of the experimental data. The liquid phase enthalpies of formation of differently shaped alkyl-cyclohexanes were derived and used to estimate the energetics of their dehydrogenation reactions. The influence of alkyl substituents on the reaction enthalpy is discussed. The vapour pressures of typical hydrogen-rich compounds at technically relevant temperatures were calculated and compared to vapour pressures of biodiesel fuels measured in this work using the static method.

Keywords: cyclohexane derivatives; LOHC; enthalpy of vaporisation; enthalpy of formation; structure-property correlation; quantum-chemical calculations; vapour pressure



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1. Introduction

Hydrogen storage technologies based on dehydrogenation and reversible hydrogenation of liquid organic compounds (LOHC) are considered promising for a future sustainable energy system [1]. LOHC systems are usually composed of aromatic molecules that are reversibly hydrogenated over a catalyst and under pressures of 8–50 bar. The release of hydrogen also takes place catalytically at temperatures of 220 to 340 °C and under hydrogen partial pressures from sub-atmospheric to 10 bar [2,3]. The key benefit of hydrogen storage in LOHC systems is that the hydrogen is stored within the liquid carrier, which has physical properties (viscosity, density, vapour pressure, etc.) which enable easy handling. Therefore, the LOHC compounds can be stored, transported and distributed using technologies similar to the current fuel infrastructure. The carrier itself is recovered after hydrogen release and can be utilized in further storage cycles.

Homocyclic molecules (i.e., without any heteroatom in the ring) have the advantage of high stability in the multicycle reaction process [4]. Coking might occur to a certain extent during dehydrogenation, but if the catalytic reaction is performed properly, this decomposition becomes negligible. Alkylation of these molecules can have a positive effect on their properties, such as a decreased melting point. Yet, substitution on the ring can also have impact on the reaction thermodynamic properties. The aim of this work is the systematic evaluation of the thermochemical data for fully hydrogenated LOHCs based on alkylated homocyclic structures. Experimental methods, backed by quantum chemical calculations for validation, have been applied to obtain a consistent database for a reliable comparison of the different types of molecules from this substance class with regard to their reaction thermodynamics. A significant part of this work deals with the energetics of vaporisation processes and absolute vapour pressures. This is not only indispensable for the development of chemical engineering for hydrogenation/dehydrogenation processes, but also for the storage and distribution of the hydrogen-rich LOHC. Indeed, low volatility of LOHC compounds is desired in order to reduce evaporation during dehydrogenation and mitigate safety risks.

In previous work, LOHC-systems composed of pairs of hydrogen-lean (aromatic) molecules and hydrogen-rich (aliphatic) molecules have been studied [5–7]. The thermodynamics of fully hydrogenated products have turned out to be very difficult to predict because of the high flexibility and complex conformational behavior. The main idea of this work is to study the structure-property relationships in the flexible cyclic aliphatic molecules and to develop empirical and theoretical methods to predict their thermodynamic properties. These findings will also be useful for verifying the reliability of existing data. On the other hand, these methods allow the assessment of properties for molecules that are required for the optimization of the hydrogenation/dehydrogenation processes but have not yet been subject to experimental investigation of their thermodynamic properties.

2. Methodology

The standard molar reaction enthalpies, $\Delta_r H_m^0$, are one of the fundamentals of process optimization. The enthalpies of the dehydrogenation reactions are desired to be as low as possible to decrease the energy demand of hydrogen release [8]. The reaction takes place under pressure, and the reactants are liquids (except for hydrogen) under the reaction conditions. According to Hess's Law, the liquid-phase standard molar enthalpies, $\Delta_f H_m^0(\text{liq})$, of the reactants are required to calculate the dehydrogenation enthalpy for any hydrogen storage LOHC-system. As a matter of fact, the thermochemical properties of aromatic compounds as the hydrogen-lean counterpart to the LOHC systems have been intensively studied in the past [9]. In contrast, the partially and fully hydrogenated products—aliphatic cyclic molecules—have received far less attention. With increasing interest in these molecules as hydrogen-rich compounds of LOHC systems, the lack of thermodynamic data becomes problematic. Moreover, the available data are very inconsistent and questionable, which can lead to errors in process engineering. The following example shows the problematic current situation. Only recently an interesting LOHC system based on the eutectic mixture (diphenylmethane + biphenyl) leading to the liquid hydrogen carrier (dicyclohexylmethane + bicyclohexyl) was proposed [10]. We have extensively studied the thermochemistry of biphenyl and bicyclohexyl, and the data have proven to be reliable [11,12]. Therefore, there were no troubles in determining the enthalpy of dehydrogenation of bicyclohexyl [12]. However, one question remains to be answered reliably: What is the reaction enthalpy for dehydrogenation of dicyclohexyl-methane (see Figure 1)?

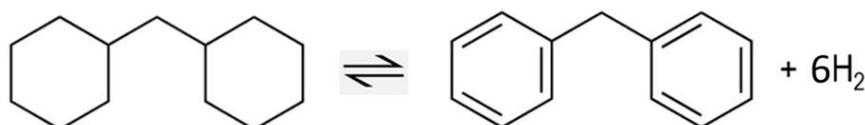


Figure 1. Reaction of dehydrogenation of dicyclohexyl-methane.

Consistent thermochemical data have also been reported in the literature for diphenylmethane [13–15]. However, for dicyclohexylmethane three completely different $\Delta_f H_m^o(\text{liq})$ -values are found in the most commonly used NIST-webbook [16]. The numerical results are given in Table 1.

Table 1. The reaction enthalpy of the dehydrogenation of dicyclohexyl-methane (see Figure 1), calculated from the data available in the literature at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$, in $\text{kJ}\cdot\text{mol}^{-1}$).

$\Delta_f H_m^o(\text{liq})$ Dicyclohexyl-Methane	$\Delta_f H_m^o(\text{liq})$ Diphenyl-Methane	$\Delta_r H_m^o(\text{liq})^a$	$\Delta_r H_m^o(\text{liq})/\text{H}_2^b$
−824.0 [17]	96.6 ± 0.8 [13–15]	920.6	153.4
−295.0 [18]	96.6 ± 0.8 [13–15]	391.6	65.3
−375.1 [19]	96.6 ± 0.8 [13–15]	471.7	78.6
-307.1 ± 2.0^c	96.6 ± 0.8 [13–15]	403.7	67.3

^a Calculated according to Hess's Law from the enthalpies of formation of the reactants given in this table.

^b The reaction enthalpy refers to 1 mole of hydrogen released by the dehydrogenation. ^c Calculated using the "centerpiece" approach (see text). Uncertainties are expressed as two times the standard deviation.

The results calculated in Table 1 from the data available in the literature for the enthalpy of dehydrogenation, $\Delta_r H_m^o(\text{liq})/\text{H}_2$, referred to 1 mole of hydrogen evolved, are not helpful in deciding whether adding diphenyl-methane to the biphenyl is a good idea or not. Indeed, for comparison, the energetic effect $\Delta_r H_m^o(\text{liq})/\text{H}_2 = 65.4 \text{ kJ}\cdot\text{mol}^{-1}$ was determined for bicyclohexyl [11,12]. So if the value $\Delta_r H_m^o(\text{liq})/\text{H}_2 = 153.4 \text{ kJ}\cdot\text{mol}^{-1}$ (see Table 1) is correct, the idea is questionable. However, if the value $\Delta_r H_m^o(\text{liq})/\text{H}_2 = 65.3 \text{ kJ}\cdot\text{mol}^{-1}$ (see Table 1) is correct, the total energy of dehydrogenation remains more or less the same for the mixture. The only question left to answer is which value is correct. Therefore, the main task of this study is to develop a straightforward algorithm that allows a reasonably accurate assessment of the liquid-phase standard molar enthalpies of formation of the hydrogen-rich compounds of given LOHC systems.

A textbook equation that relates the thermochemical properties relevant to this work is:

$$\Delta_f H_m^o(\text{g}) = \Delta_f H_m^o(\text{liq}) + \Delta_1^g H_m^o \quad (1)$$

where $\Delta_f H_m^o(\text{g})$ is the gas-phase standard molar enthalpy of formation and $\Delta_1^g H_m^o$ is the standard molar enthalpy of vaporisation. The $\Delta_f H_m^o(\text{liq})$ -values are usually derived from combustion experiments, from solution calorimetry or from chemical equilibrium studies [20]. The $\Delta_1^g H_m^o$ -values are usually directly measured calorimetrically or derived from the vapour pressure-temperature dependences [21]. There are at least two aggravating limitations related to the experimental thermochemical measurements. First, the purity of the samples is required to be better than 99.9%. Secondly, the measurements are material-intensive. As a rule, about 5–10 g of the high-purity sample is needed to measure both contributors to Equation (1). Unfortunately, both of these limitations make systematic thermochemical studies with typical hydrogen-rich LOHC compounds not straightforward, since the most interesting samples are not commercially available. Moreover, for custom synthesis, sample purities are very difficult to achieve, even at levels of 95–98%, since the naturally occurring cis- and trans-isomers of cyclic compounds are virtually impossible to separate. These apparent limitations force us to conclude that only structure-property correlations and theoretical methods could provide a remedy to obtain the reliable thermochemical data for the hydrogen-rich counterparts. In this work, the focus has been restricted to $\Delta_f H_m^o(\text{liq})$ as a goal thermochemical property that is relevant to the energetics of hydrogen storage. In the first step, Equation (1) has been re-written as follows:

$$\Delta_f H_m^o(\text{liq}, 298.15 \text{ K}) = \Delta_f H_m^o(\text{g}, 298.15 \text{ K}) - \Delta_1^g H_m^o(298.15 \text{ K}) \quad (2)$$

The symbols for enthalpies have been extended to include temperatures, since it is common in thermochemistry to refer all enthalpies given in Equations (1) and (2) to an

arbitrary but common reference temperature. In this work, $T = 298.15$ K was chosen as the reference temperature. Since all three enthalpies are related, in the second step a decision has to be made which enthalpies are better suited for structure-property correlations and theoretical methods. From a practical point of view, the gas phase enthalpies of formation are the best choice. The reason for this is that $\Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K})$ -values reflect the energy content of a single molecule flying freely in vacuum (or gas, but without interacting with other molecules). Therefore, the energetics of this single molecule is easy to understand and correlates with the peculiarities of its structure. In contrast, the $\Delta_f H_m^{\circ}(\text{liq}, 298.15 \text{ K})$ -values reflect not only the intrinsic energetics of the molecule but also the intensity of the intermolecular interactions in the liquid phase. Therefore, the interpretation of these combined intra- and inter-molecular interactions is still possible but is influenced by many factors, making it difficult to understand. The enthalpy of vaporisation accounts for the total amount of intermolecular interactions in the liquid phase. According to our experience [22], the $\Delta_f^{\text{S}} H_m^{\circ}(298.15 \text{ K})$ -values are subject to a group additivity rule and different correlations with the structural elements. Therefore, to draw the conclusion for the second step, it makes sense to develop appropriate tools to correlate and predict the $\Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K})$ and $\Delta_f^{\text{S}} H_m^{\circ}(298.15 \text{ K})$ and finally to calculate the $\Delta_f H_m^{\circ}(\text{liq}, 298.15 \text{ K})$ -values as their difference according to Equation (2). This guideline helps in following the logic of combining experimental methods for determining thermochemical properties with theoretical methods based on quantum-mechanics for validation as applied in this work.

2.1. Basics of the Group-Additivity Concept (“Centerpiece” Approach)

Group additivity (GA) methods are successfully used to predict both the gas-phase enthalpies of formation and vaporisation enthalpies [22]. The idea behind conventional GA methods is to split the experimental enthalpies of molecules into relatively small groups in order to obtain well-defined numerical contributions for them. The prediction then proceeds as construction of a framework of a desired model molecule from the appropriate number and type of these contributions. Comprehensive systems of group contributions (or increments) are developed, covering the main classes of organic compounds [22–24]. Admittedly, the applicability of GA in the case of cyclic molecules is limited. To overcome this limitation, various ring corrections are implemented in the GA parameterization; however, each correction term is specific only to a particular unsubstituted ring (e.g., for cyclobutane, cyclopentane, cyclohexane, etc.). However, any type of substitution significantly affects ring strain due to intense interactions of the substituent(s) with the ring. This general GA limitation cannot be overcome easily [25]; however, previous work with the hydrogen-rich LOHC compounds has shown that a variation of the GA method, referred to as the “centerpiece” approach [26,27], gives acceptable results for the gas phase enthalpies of formation and for vaporisation enthalpies of these technically important molecules. The idea of the “centerpiece” approach is to select a potentially large “centerpiece” molecule that has a reliable enthalpy and that can generally mimic the structure of the molecule of interest. Then the necessary groups or blocks are attached to the “centerpiece”, resulting in the construction of the desired molecule. A prerequisite for this method is that reliable experimental data are available for the selected “centerpiece” molecule.

For example, for dicyclohexyl-methane, either ethyl-cyclohexane or methyl-cyclohexane can be selected as the suitable “centerpieces”. The enthalpies of formation and enthalpies of vaporisations for both molecules are well-established [9]. The idea is illustrated in Figures 2–4.

First, by cutting off the CH_3 group from ethyl-cyclohexane and from methyl-cyclohexane, the two “fragments” needed to construct the dicyclohexyl-methane were derived (see Figure 2).

Second, both “fragments” are merged to give the desired molecule dicyclohexyl-methane (see Figure 3). Alternatively, the molecule dicyclohexyl-methane can be constructed from two “-(cyclohexane)” fragments and the methylene group (see Figure 4).

The numerical values for the species involved in these calculations are given in Table S1 (electronic supporting materials).

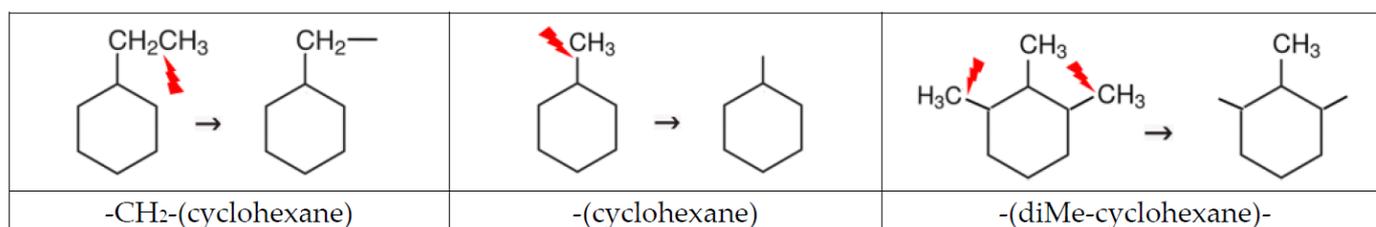


Figure 2. The development of the “centerpieces” for calculating the enthalpies of cyclic aliphatic hydrocarbons.

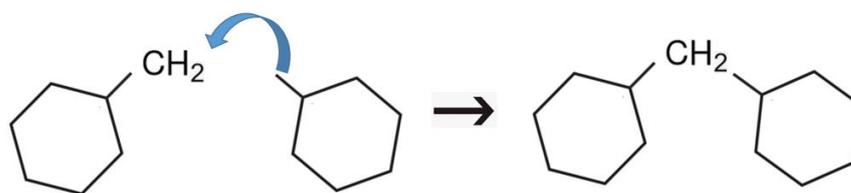


Figure 3. Calculating the enthalpy of formation or enthalpy of vaporisation of dicyclohexyl-methane using the “-CH₂-(cyclohexane)” and “-(cyclohexane)” as the “centerpieces”.

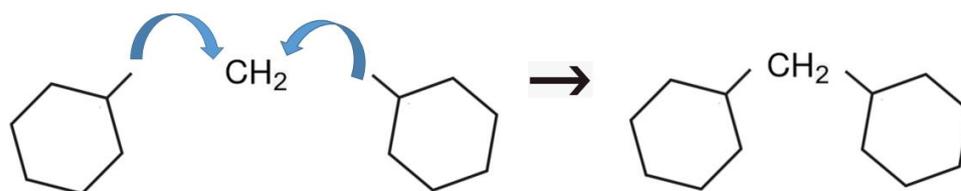


Figure 4. Calculating the enthalpy of formation or enthalpy of vaporisation of dicyclohexyl-methane using the “-(cyclohexane)” as the “centerpiece”.

The results obtained by both methods are essentially the same, e.g., the vaporisation enthalpy $\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K}) = 64.7 \pm 1.0\text{ kJ}\cdot\text{mol}^{-1}$ according to Figure 3 and $\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K}) = 64.5 \pm 1.0\text{ kJ}\cdot\text{mol}^{-1}$ according to Figure 4. Therefore, using the gas-phase enthalpy of formation of dicyclohexyl-methane, $\Delta_f H_m^{\circ}(\text{g}, 298.15\text{ K}) = -242.4 \pm 2.0\text{ kJ}\cdot\text{mol}^{-1}$ assessed as shown in Figure 3 with the corresponding $\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K}) = 64.7 \pm 1.0\text{ kJ}\cdot\text{mol}^{-1}$, the “empirical” liquid-phase enthalpy of formation was estimated to be $\Delta_f H_m^{\circ}(\text{liq}, 298.15\text{ K}) = -242.4 - 64.7 = -307.1 \pm 2.2\text{ kJ}\cdot\text{mol}^{-1}$, which was further re-calculated into $\Delta_r H_m^{\circ}(\text{liq})/\text{H}_2 = 67.3\text{ kJ}\cdot\text{mol}^{-1}$ (see Table 1) for comparison with other values available from the literature data. These “empirical” results are now helping to resolve contradictions that are evident from the available data. Furthermore, the estimate value of $\Delta_r H_m^{\circ}(\text{liq})/\text{H}_2 = 67.3\text{ kJ}\cdot\text{mol}^{-1}$ (see Table 1) could be considered more reliable than the value of $\Delta_r H_m^{\circ}(\text{liq})/\text{H}_2 = 65.3\text{ kJ}\cdot\text{mol}^{-1}$ calculated from Ref. [18] (see Table 1), because of the questionable purity of the sample studied by Wise et al. [18].

To further validate the “centerpiece” approach by a more challenging task, the enthalpies of formation and enthalpies of vaporisation of the perhydro-dibenzyltoluene, which is the hydrogen-rich component of the LOHC system based on dibenzyltoluene (Marlotherm SH[®]) [25], have been calculated. Obviously 1,2,3-trimethylcyclohexane is the perfect “centerpiece” to start the calculations. The “fragment” required to construct perhydro-dibenzyltoluene was derived by splitting off two CH₃ groups from 1,2,3-trimethylcyclohexane (see Figure 2). The desired molecule is built up by fusing this “centerpiece” with two “-CH₂-(cyclohexane)” fragments (see Figure 5).

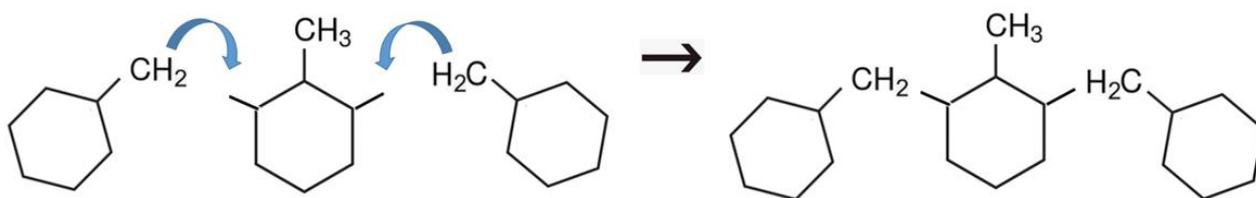


Figure 5. Calculating the enthalpy of formation or enthalpy of vaporisation of perhydro-dibenzyltoluene using “-diMe-(cyclohexane)-” as the “centerpiece”.

It was found that the vaporisation enthalpy $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K}) = 90.9 \pm 1.5\text{ kJ}\cdot\text{mol}^{-1}$ estimated in this way agrees with the experimental value $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K}) = 88.2 \pm 1.5\text{ kJ}\cdot\text{mol}^{-1}$ [25] within the experimental uncertainty. The “empirical” gas-phase enthalpy of formation of perhydro-dibenzyltoluene, $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}, 298.15\text{ K}) = -380.9 \pm 2.0\text{ kJ}\cdot\text{mol}^{-1}$, assessed as shown in Figure 5, also agrees with the experimental value $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}, 298.15\text{ K}) = -387.4 \pm 7.7\text{ kJ}\cdot\text{mol}^{-1}$, within the experimental uncertainty.

It should be mentioned that the conventional GA procedure really failed to correctly predict the energetics of perhydro-dibenzyltoluene properly: the values $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K}) = 94.7\text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}, 298.15\text{ K}) = -409.2\text{ kJ}\cdot\text{mol}^{-1}$, as estimated in previous work [25], differ significantly from the experiment. The secret of the success of the “centerpiece” approach lies in the fact that the main energetic contribution(s) is already stored in the “centerpiece”(s) and the attached groups are precisely parameterized [21–23]. The “centerpiece” as a “pen and paper” approach is used frequently to quickly assess the quality of the available literature data, but also to estimate the “expected” value of the ongoing thermochemical experiment, and in this way to avoid possible systematic errors. However, in the 21st century, everyday laboratory work is unthinkable without modern quantum chemical methods.

2.2. Quantum Chemistry: From Doubts to Enthusiasm

Since 2012 [28] we have applied high-level quantum chemical methods to calculate the gas-phase enthalpies of formation of the hydrogen-lean and hydrogen-rich counterparts of LOHC systems. From this experience, there are few problems with the composite methods (G3MP2 and G4) when applied to the “relatively” large LOHC molecules containing at least 20–30 “heavy” atoms. The first is the time commitment, which is gradually becoming bearable (the G3MP2 calculations with perhydro-dibenzyltoluene in 2015 [25] took two months with the facilities of the University of Rostock computing center). The second issue is an ambiguity related to the choice of compounds for the different reaction types used to convert the H_{298} enthalpies to the standard molar enthalpies of formation. The details of this issue can be found elsewhere [29]. However, the years of “mutual validation” of the experimental and quantum chemical (theoretical) enthalpies of formation performed in our laboratory allowed the conclusion that only if both results agree within the combined uncertainties can the final result can be considered reliable. If this is not the case, the experimental efforts (additional purification of the sample, variation of experimental conditions) as well as computational work (search for possibly more stable conformers, use of another method) are continued. Furthermore, the independent structure-property correlations (e.g., the “centerpiece” approach) are involved to obtain an unbiased value for the property under investigation. To give an example of such a successful continuity: for perhydro-dibenzyltoluene, the experimental enthalpy of formation $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}, 298.15\text{ K})_{\text{exp}} = -387.4 \pm 7.7\text{ kJ}\cdot\text{mol}^{-1}$ [25] was combined from the combustion experiments and the vapour pressure measurement, the empirical value $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}, 298.15\text{ K})_{\text{emp}} = -380.9 \pm 2.0\text{ kJ}\cdot\text{mol}^{-1}$ (see above) was calculated according to the “centerpiece” approach, and finally the theoretical G3MP2 result $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}, 298.15\text{ K})_{\text{theor}} = -379.7 \pm 4.1\text{ kJ}\cdot\text{mol}^{-1}$ was calculated earlier [25] and corrected in this work (as shown in Section 3.1). It is evident that all three values agree within their combined uncertainties, providing confidence in the thermochemical results for this compound. In this work, the G3MP2 method was applied

to calculate the gas phase enthalpies of formation of differently shaped alkyl-substituted cyclohexanes (see Section 3.1) for “mutual validation” of the experimental and theoretical results useful for calculations of the hydrogen-rich LOHC components.

2.3. Empirical Correlations: Vaporisation Enthalpies vs. Kovats Retention Indices

Kovats retention indices are widely used in analytical chemistry to identify molecules in the reaction mixture. According to Kovats [30], the index of an analyte x is its relative time position between the nearest n -alkanes eluting immediately before and after a target analyte. The Kovats retention index, J_x , is calculated with help of retention times of n -alkanes used as standards [30,31]:

$$J_x = \frac{\lg(t_x) - \lg(t_N)}{\lg(t_{N+1}) - \lg(t_N)} \times 100 + 100N \quad (3)$$

where x refers to the adjusted retention time t , N is the number of carbon atoms of the n -alkane eluting before, and $(N + 1)$ is the number of carbon atoms of the n -alkane eluting after the peak of interest.

The fundamental variable tracked in GC is the retention time, which is a strong function of the experimental conditions. However, the main idea of the Kovats index is to trap the analyte in the network of alkanes and to reduce this dependence on experimental conditions. The retention indices are usually given for non-polar and polar types of GC columns. It is well-known that the vaporisation enthalpies of structurally similar molecules show a linear dependence when correlated with retention indices:

$$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\text{K}) / (\text{kJ}\cdot\text{mol}^{-1}) = A + B \times J_x \quad (4)$$

This correlation can be used to estimate the vaporisation enthalpies of compounds for which the retention indices are available. Collections and compilations of Kovats indices are available and ready to use [31,32]. The correlation is good for both non-polar and polar columns [33]; however, the range of “similarly shaped” compounds is less specific and broader when the non-polar column is used. The experimental reproducibility of the retention index is usually very good (within a few units) when measured isothermally or with the temperature raising program. It is noticeable that the retention indices, measured on non-polar columns with different stationary phases, hardly differ. The fluctuations do not exceed 5–10 units when comparing the data at the same column temperature. This feature is particularly valuable for analyte identification. Temperature has a moderate effect on J_x , and even the J_x measured on the temperature program are not significantly different from isothermal results. For numerous individual compounds, it has been investigated how the fluctuations in the retention indices affect the vaporisation enthalpies derived from the linear relationships. It was found that fluctuations in J_x -values of 15–20 units caused the scatter in $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\text{K})$ -values to be well below $1.5\text{ kJ}\cdot\text{mol}^{-1}$, which is comparable to the experimental uncertainties of vaporisation enthalpies measured by conventional methods. Retention indices of alkyl-substituted cyclohexanes related to hydrogen storage were collected and used to correlate with vaporisation enthalpies in Section 3.2.

2.4. Empirical Correlations: Vaporisation Enthalpies vs. Normal Boiling Temperatures

The normal boiling temperatures, T_{b} , of chemicals are one of the mandatory physico-chemical properties most frequently reported in the literature, as these values are measured by distillation and are traditionally used to identify compounds. The normal boiling temperatures, T_{b} , are directly related to the vaporisation enthalpies $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(T_{\text{b}})$, but the robust correlations with the $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\text{K})$ -values are also known from the literature [34]. Such correlations are particularly successful for a series of structurally similar molecules and the linear dependence:

$$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\text{K}) / (\text{kJ}\cdot\text{mol}^{-1}) = A + B \times T_{\text{b}} \quad (5)$$

is usually established and used to estimate the vaporisation enthalpies of compounds for which the normal boiling temperatures are available in the literature [16,35].

Correlations of vaporisation enthalpies with the retention indices and with normal boiling temperatures are expected to provide the basis for evaluation of the $\Delta_f^g H_m^o(298.15\text{ K})$ -values related to hydrogen storage.

3. Results and Discussion

3.1. Quantum Chemistry: Theoretical Enthalpies of Formation

It is common practice to test any empirical or theoretical method against a set of reliable experimental data. There are fourteen gas-phase enthalpies of formation of alkyl-substituted cyclohexanes (see Table 2) in the most recognized compilation of thermochemical data by Pedley et al. [9].

Table 2. Comparison of experimental and G3MP2 calculated gas-phase enthalpies of formation for alkyl-cyclohexanes (at $T = 298.15\text{ K}$, $p^\circ = 0.1\text{ MPa}$, in $\text{kJ}\cdot\text{mol}^{-1}$).

Compound	$\Delta_f H_m^o(\text{g, AT})_{\text{G3MP2}}^a$	$\Delta_f H_m^o(\text{g})_{\text{exp}}^b$	$\Delta_f H_m^o(\text{g})_{\text{theor}}^c$	Δ^d
cyclohexane	−122.6	−123.4 ± 0.8	−122.1	−1.3
Me-cyclohexane	−154.7	−154.7 ± 1.0	−153.3	−1.4
trans-1,2-di-Me-cyclohexane	−182.8	−179.9 ± 1.9	−180.5	0.6
cis-1,2-di-Me-cyclohexane	−175.9	−172.1 ± 1.8	−173.8	1.7
trans-1,3-di-Me-cyclohexane	−179.3	−176.5 ± 1.7	−177.1	0.6
cis-1,3-di-Me-cyclohexane	−186.7	−184.6 ± 1.8	−184.3	−0.3
trans-1,4-di-Me-cyclohexane	−186.6	−184.5 ± 1.8	−184.2	−0.3
cis-1,4-di-Me-cyclohexane	−179.4	−176.6 ± 1.8	−177.2	0.6
Et-cyclohexane	−173.8	−171.7 ± 1.6	−171.8	0.1
n-Pr-cyclohexane	−195.3	−192.5 ± 1.0	−192.6	0.1
n-Bu-cyclohexane	−216.8	−213.3 ± 1.3	−213.5	0.2
n-Dec-cyclohexane	−344.9	−339.5 ± 2.5	−337.8	−1.7
n-Dodec-cyclohexane	−387.6	−378.7 ± 3.7	−379.2	0.5
trans-1,4-di-tBu-cyclohexane	−330.5	−323.2 ± 2.4	−323.8	0.6
1,3,5-tri-Me-cyclohexane	−218.8	(−212.1 ± 3.2)	−215.4	
n-Heptyl-cyclohexane	−280.9	(−289.2 ± 2.4)	−275.7	
trans-4-Me-iPr-cyclohexane	−229.7	(−230.7 ± 3.2)	−226.0	
1,2,3-trimethyl-cyclohexane	−208.7		−205.6	
dicyclohexyl-methane	−246.0		−241.8	
perhydro-dibenzyl-toluene	−388.1 [25]	−387.4 ± 7.7 [25]	−379.7	

^a Calculated by G3MP2 and atomization reaction. ^b From Pedley et al. [9]. Uncertainties in this table are expressed as two times the standard deviation. The values given in brackets appear to be in error. ^c Calculated according to Equation (6). ^d Difference between column 3 and column 4.

This dataset was utilized to validate the results of the composite method G3MP2 [36]. Stable conformers were found by using a computer code named CREST (conformer-rotamer ensemble sampling tool) [37] and optimised with the B3LYP/6-31g(d,p) method [38]. The energies E_0 and the enthalpies H_{298} of the most stable conformers were finally calculated by using the G3MP2 method implemented in the Gaussian Software [39].

The enthalpies H_{298} from the output files were converted into the *theoretical* gas-phase enthalpies of formation of alkyl-cyclohexanes using an atomisation (AT) reaction [29]. As can be seen from Table 2, the enthalpies of formation calculated by AT are slightly but systematically more negative. Such a feature of AT reactions is known [40], but this disadvantage can be easily removed by correcting the calculated results. The latter correction was derived from the correlation between experimental enthalpies of formation (see Table 2) and the $\Delta_f H_m^o(\text{g, AT})_{\text{G3MP2}}$ -values directly calculated via atomisation reaction:

$$\Delta_f H_m^o(\text{g})_{\text{theor}}/\text{kJ}\cdot\text{mol}^{-1} = 0.970 \times \Delta_f H_m^o(\text{g, AT})_{\text{G3MP2}} - 3.2 \text{ with } R^2 = 0.9998 \quad (6)$$

The *theoretical* $\Delta_f H_m^0(g)_{\text{theor}}$ values of alkyl-cyclohexanes “corrected” in this way agree well with the experimental values (see Table 2, column 5). For most species involved in calculations in Table 2, the deviations between the experimental values and estimates are well below $1 \text{ kJ}\cdot\text{mol}^{-1}$, so it is reasonable to assess the real uncertainties of the G3MP2 calculated values to be $\pm 2 \text{ kJ}\cdot\text{mol}^{-1}$.

It is now interesting to compare the gas-phase enthalpy of formation of dicyclohexylmethane, $\Delta_f H_m^0(g, 298.15 \text{ K}) = -242.4 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ determined as in Figure 3 with the corresponding result from quantum chemical calculations for this molecule: $\Delta_f H_m^0(g, 298.15 \text{ K}) = -241.8 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ (see Table 3). The perfect agreement confirms the applicability of the two methods for molecules relevant to hydrogen storage.

Table 3. Comparison experimental and G3MP2-calculated gas-phase enthalpies of formation alkylbenzenes (at $T = 298.15 \text{ K}$, $p^\circ = 0.1 \text{ MPa}$, in $\text{kJ}\cdot\text{mol}^{-1}$).

Compound	$\Delta_f H_m^0(g, \text{AT})_{\text{G3MP2}}$ ^a	$\Delta_f H_m^0(g)_{\text{exp}}$ ^b	$\Delta_f H_m^0(g)_{\text{theor}}$ ^c	Δ ^d
toluene	42.7	50.4 ± 0.6	51.1	−0.7
ethylbenzene	23.2	29.9 ± 1.1	31.6	−1.7
n-propylbenzene	0.5	7.9 ± 0.8	8.9	−1.0
iso-propylbenzene	−3.9	4.0 ± 1.0	4.5	−0.5
n-butylbenzene	−20.9	-13.1 ± 1.1	−12.5	−0.6
iso-butylbenzene	−30.7	-21.5 ± 1.3	−22.3	0.8
tert-butylbenzene	−31.9	-23.7 ± 0.6 [41]	−23.5	−0.2
sec-butylbenzene	−28.4	-17.4 ± 1.2	−20.0	2.6
α -methylstyrene	109.2	119.0 ± 0.9 [42]	117.6	1.4

^a Calculated by G3MP2 and atomization reaction. ^b From Pedley et al. [9]. Uncertainties in this table are expressed as two times the standard deviation. ^c Calculated according to Equation (7). ^d Difference between column 3 and column 4.

In our experience, using the atomization reaction to derive the gas phase enthalpies of formation of H_{298} is an optimal way to get unbiased results, since using other types of different reactions is strongly influenced by the choice of molecules to set up the required reactions. Proper use of AT reactions, however, requires a representative set of similarly shaped molecules. For example, in Table 3 a series of alkylbenzenes with reliable experimental data have been compiled and their gas-phase enthalpies of formation by G3MP2 (see Table 3, column 2) are calculated.

For this set, too, the results calculated by G3MP2 are more negative than in the experiment, but to a much greater extent. Nevertheless, the correction of the calculated data by the simple linear equation:

$$\Delta_f H_m^0(g)_{\text{theor}}/\text{kJ}\cdot\text{mol}^{-1} = 1.0003 \times \Delta_f H_m^0(g, \text{AT})_{\text{G3MP2}} + 8.4 \text{ with } R^2 = 0.9992 \quad (7)$$

gives a good agreement between theory and experiment. Therefore, we recommend the application of Equations (6) and (7) in combination with the AT reaction for a reliable G3MP2 calculation of gas-phase enthalpies of the hydrogen-rich and hydrogen-lean counterparts of the LOHC systems.

The “centerpiece” approach can also be applied to estimate the enthalpies of formation of the di- and tri-alkyl-substituted cyclohexanes, but there are two obvious limitations of this method with respect to these molecules. First, the calculations of cyclohexanes that are alkyl-substituted in 1,2-positions on the ring make no sense since steric repulsions from substituents placed in close proximity cannot be modeled by GA methods. Second, according to the textbook, the trans-isomers of cyclic molecules are usually more stable than cis-isomers, but the differences between trans- and cis-isomers also cannot be accounted for by most GA methods, including the “centerpiece” approach. However, for the technical calculations a dominance of the trans-isomers in the reaction mixtures of hydrogenation/dehydrogenation processes can be assumed. With this assumption, the

“centerpiece” approach was applied to calculate the gas-phase enthalpies of formation of trans-alkyl-substituted cyclohexanes collected in Table 4.

Table 4. Calculation of the gas-phase enthalpies of formation, $\Delta_f H_m^0(g)$, of the alkyl-cyclohexanes using the “centerpiece approach” (at $T = 298.15$ K, $p^\circ = 0.1$ MPa, in $\text{kJ}\cdot\text{mol}^{-1}$)^a.

Trans-Alkyl-Cyclohexane	$\Delta_f H_m^0(g)_{CP}$ ^b	$\Delta_f H_m^0(g)$ ^c	Δ ^d
1,4-diMe-cyclohexane	-186.0 ± 2.0	-184.5 ± 1.8 [9]	1.5
1,3,5-tri-Me-cyclohexane	-217.3 ± 2.0	-215.4 ± 2.0	1.9
3-Me-1-Et-cyclohexane	-203.0 ± 2.0	-203.2 ± 1.7 [9]	-0.2
1,3-di-iso-propyl-cyclohexane	-264.6 ± 2.0	-268.8 ± 2.0	-4.2
1,4-di-iso-propyl-cyclohexane	-264.6 ± 2.0	-267.8 ± 2.0	-3.2
1,3,5-tri-iso-propyl-cyclohexane	-335.2 ± 2.0	-338.5 ± 2.0	-3.3
1,3-di-tert-butyl-cyclohexane	-321.8 ± 2.0	-324.4 ± 2.0	-2.6
1,4-di-tert-butyl-cyclohexane	-321.8 ± 2.0	-323.8 ± 2.0	-2.0

^a The uncertainties are given as the twice standard deviation. ^b Calculated as the sum of the $\Delta_f H_m^0(g)$, cyclohexane) = -123.4 ± 0.8 $\text{kJ}\cdot\text{mol}^{-1}$ [9] and contributions $\Delta_f H_m^0(H \rightarrow R)$ from Table S2. ^c Calculated by G3MP2 and atomization reaction, and corrected according to Equation (6). ^d Difference between columns 3 and 2 in this table.

As can be seen from Table 4, the “centerpiece” approach provides reasonable $\Delta_f H_m^0(g)$ -estimates of alkyl-cyclohexanes simply by using “pen and paper”.

The limitations of the “centerpiece” approach towards alkyl-cyclohexanes described above are also valid for calculations of their vaporisation enthalpies. However, reasonable $\Delta_1^g H_m^0$ -estimates were obtained even for tri-alkyl-substituted cyclohexanes, as shown in Table 5.

Table 5. Calculation of the enthalpies of vaporisation, $\Delta_1^g H_m^0$, of the alkyl-cyclohexanes using the “centerpiece” approach (at $T = 298.15$ K, in $\text{kJ}\cdot\text{mol}^{-1}$)^a.

Trans-Alkyl-Cyclohexane	$\Delta_1^g H_m^0(CP)$ ^b	$\Delta_1^g H_m^0(\text{exp})$	Δ ^c
trans-1,4-di-Me-cyclohexane	37.7 ± 1.5	38.0 ± 0.2	-0.3
trans-4-Me-Et-cyclohexane	42.9 ± 1.5	44.3 ± 1.1	-1.4
1,4-di-Et-cyclohexane	48.1 ± 1.5	50.7 ± 1.1	-2.6
1,3,5-tri-Me-cyclohexane	41.5 ± 1.5	43.5 ± 1.5	-2.0
trans-4-Me-iPr-cyclohexane	46.3 ± 1.5	46.8 ± 1.5	-0.5
1,4-di-iPr-cyclohexane	54.9 ± 1.5	54.9 ± 1.5	0.0
1,3,5-tri-iPr-cyclohexane	65.8 ± 1.5	64.3 ± 1.5	1.5
trans-4-Me-tBu-cyclohexane	49.3 ± 1.5	51.3 ± 1.5	-2.0
trans-1,4-di-tBu-cyclohexane	60.9 ± 1.5	61.3 ± 1.5	-0.4
1,3,5-tri-tBu-cyclohexane	74.8 ± 1.5	71.9 ± 1.5	2.9

^a The uncertainties are given as the twice standard deviation. ^b Calculated as the sum of the $\Delta_1^g H_m^0 = 33.1 \pm 0.2$ $\text{kJ}\cdot\text{mol}^{-1}$ [43] for cyclohexane and contributions $\Delta_1^g H_m^0(H \rightarrow R)$ from Table S2. ^c Difference between columns 3 and 2 in this table.

3.2. Empirical Correlations to Assess Vaporisation Enthalpies of Alkyl-Cyclohexanes

Significantly more data on experimental vaporisation enthalpies of alkyl-cyclohexanes (see Tables 6, S3 and S4) are available compared to data on formation enthalpies (see Table 3). The fourteen enthalpies of vaporisation were taken from the comprehensive book by Majer and Svoboda [43]; the seven enthalpies of vaporisation were compiled from the original literature [44,45]; for four alkyl-cyclohexanes enthalpies of vaporisation were derived from experimental vapour pressures found in the literature (see Table S4). Kovats retention indices were taken from the original literature [46–48] (see Table S3), and normal boiling points were taken from online databases [16,49,50] (see Table S4). Results for correlations of experimental enthalpies of vaporisation versus Kovats retention indices and versus normal boiling temperature are shown in Table 6.

Table 6. Correlation of vaporisation enthalpies, $\Delta_1^{\text{g}}H_m^{\text{o}}$ (298.15 K), of alkyl-cyclohexanes with their Kovats indices (J_x) and normal boiling temperatures (T_b).

	$\Delta_1^{\text{g}}H_m^{\text{o}}$ (exp)	$\Delta_1^{\text{g}}H_m^{\text{o}}$ (J_x) ^a	$\Delta_1^{\text{g}}H_m^{\text{o}}$ (T_b) ^b	$\Delta_1^{\text{g}}H_m^{\text{o}}$ (Average) ^c
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
cyclohexane	33.1 ± 0.2 [43]	32.6	-	
Me-cyclohexane	35.4 ± 0.2 [43]	34.9	34.5	
trans-1,2-di-Me-cyclohexane	38.4 ± 0.2 [43]	38.7	38.8	
cis-1,2-di-Me-cyclohexane	39.7 ± 0.2 [43]	40.3	40.1	
trans-1,3-di-Me-cyclohexane	39.2 ± 0.2 [43]	39.0	39.0	
cis-1,3-di-Me-cyclohexane		37.8	38.2	38.0 ± 1.1
trans-1,4-di-Me-cyclohexane	38.0 ± 0.2 [43]	37.7	38.1	
cis-1,4-di-Me-cyclohexane	39.1 ± 0.2 [43]	38.9	39.0	
trans-2-Me-Et-cyclohexane		44.2	44.3	44.3 ± 1.1
cis-2-Me-Et-cyclohexane		44.6	44.9	44.8 ± 1.1
trans-3-Me-Et-cyclohexane		44.0	43.7	43.9 ± 1.1
cis-3-Me-Et-cyclohexane	44.7 ± 0.9 [Table S5]	43.2	43.5	
trans-4-Me-Et-cyclohexane		43.4	43.8	43.6 ± 1.1
cis-4-Me-Et-cyclohexane		44.2	44.5	44.4 ± 1.1
Et-cyclohexane	40.6 ± 0.2 [43]	39.9	40.4	
1,2-di-Et-cyclohexane		49.5	49.1	49.3 ± 1.1
1,3-di-Et-cyclohexane		48.4	48.3	48.4 ± 1.1
1,4-di-Et-cyclohexane		50.5	50.8	50.7 ± 1.1
i-Bu-cyclohexane	47.6 ± 0.2 [43]	47.8	48.0	
n-Pr-cyclohexane	45.1 ± 0.2 [43]	44.9	45.2	
1,3,5-tri-Me-cyclohexane	43.5 ± 1.5 [Table S5]	41.3	42.1	
1,2,4,5-tetra-Me-cyclohexane		49.3	48.4	48.9 ± 1.1
penta-Me-cyclohexane		51.1	-	51.1 ± 1.5
hexa-Me-cyclohexane		56.9	-	56.9 ± 1.5
n-Bu-cyclohexane	49.4 ± 0.2 [43]	50.6	49.9	
n-Pe-cyclohexane	53.9 ± 0.2 [43]	54.2	54.3	
n-Hex-cyclohexane	59.0 ± 0.5 [44]	59.0	58.3	
n-Hep-cyclohexane	63.7 ± 0.5 [44]	64.4	62.3	
n-Oct-cyclohexane	69.8 ± 1.0 [45]	69.4	-	
n-Dec-cyclohexane	78.8 ± 0.8 [44]	78.5	-	
n-Dodec-cyclohexane	88.9 ± 0.8 [44]	87.5	-	
n-tetra-Dec-cyclohexane	99.4 ± 1.0 [45]	99.9	-	
iso-Pr-cyclohexane	44.0 ± 0.2 [43]	44.4	44.9	
trans-2-Me-iPr-cyclohexane			48.0	48.0 ± 1.5
cis-2-Me-iPr-cyclohexane			48.0	48.0 ± 1.5
trans-3-Me-iPr-cyclohexane		48.0	47.4	47.7 ± 1.1
cis-3-Me-iPr-cyclohexane		49.4	47.6	48.5 ± 1.1
trans-4-Me-iPr-cyclohexane	46.8 ± 1.5 [Table S5]	48.4	47.9	
cis-4-Me-iPr-cyclohexane			48.3	48.3 ± 1.5
1,2,3-tri-methyl-cyclohexane		42.3	43.1	42.7 ± 1.1
1,2-di-iPr-cyclohexane			54.9	54.9 ± 1.5
1,3-di-iPr-cyclohexane			54.9	54.9 ± 1.5
1,4-di-iPr-cyclohexane			54.9	54.9 ± 1.5
1,3,5-tri-iPr-cyclohexane			64.3	64.3 ± 1.5
1,2,4,5-tetra-iPr-cyclohexane			72.8	72.8 ± 1.5
t-Bu-cyclohexane	47.0 ± 0.2 [43]	47.8	48.1	
2-Me-tBu-cyclohexane			50.5	50.5 ± 1.5
3-Me-tBu-cyclohexane			50.5	50.5 ± 1.5
trans-4-Me-tBu-cyclohexane		51.5	51.0	51.3 ± 1.1
cis-4-Me-tBu-cyclohexane		52.1	51.4	51.8 ± 1.1
1,2-di-tBu-cyclohexane			60.4	60.4 ± 1.5
1,3-di-tBu-cyclohexane	63.3 ± 2.6 [Table S6]	64.6	62.2	
trans-1,4-di-tBu-cyclohexane			61.3	61.3 ± 1.5

Table 6. Cont.

	$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(\text{exp})$	$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(J_x)^{\text{a}}$	$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(T_b)^{\text{b}}$	$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(\text{Average})^{\text{c}}$
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
cis-1,4-di-tBu-cyclohexane			61.8	61.8 ± 1.5
1,3,5-tri-tBu-cyclohexane			71.9	71.9 ± 1.5
dicyclohexyl-methane	64.5 ± 3.5 [Table S6]		63.8	63.9 ± 1.4^c

^a From Table S3, calculated using Equation (8). Uncertainties are estimated to account for $\pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$. ^b From Table S4, calculated using Equation (9). Uncertainties are estimated to account for $\pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$. ^c Weighted average calculated from data given in columns 3 and 4. Uncertainties in this table are expressed as two times the standard deviation. Values in bold are recommended for thermochemical calculations (e.g., Table S7).

The vaporisation enthalpies $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K})$ and Kovats indices, J_x , on non-polar columns correlate according to the following equation:

$$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) / (\text{kJ}\cdot\text{mol}^{-1}) = -0.9 + 0.0485 \times J_x \text{ with } (R^2 = 0.998) \quad (8)$$

The vaporisation enthalpies $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K})$ and normal boiling temperatures, T_b , correlate according to the following equation:

$$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) / (\text{kJ}\cdot\text{mol}^{-1}) = -37.6 + 0.1927 \times T_b \text{ with } (R^2 = 0.989) \quad (9)$$

The “empirical” vaporisation enthalpies derived from Equation (8) (see Table S3, column 5) and from Equation (9) (see Table S4, column 5) agree well with the experimental values taken for correlations. Such good agreement can be considered as evidence of good consistency of the experimental data included in correlations. The results given in Tables S3 and S4 indicate that differences between experimental vaporisation enthalpies and “empirical” values calculated according to Equations (8) and (9) are mostly below $1.0 \text{ kJ}\cdot\text{mol}^{-1}$. Therefore, the uncertainties of the enthalpies of vaporisation, which are estimated from the empirical correlation of $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K})$ with the Kovats indices and with the normal boiling points, are evaluated with an uncertainty of $\pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$. In addition, for the alkyl-cyclohexanes with known J_x and T_b , their vaporisation enthalpies were calculated using Equations (8) and (9) and significantly expand the database of molecules relevant to hydrogen storage.

Both of the empirical correlations proposed above require experimental input; therefore, predicting the enthalpy of vaporisation in the absence of these input data is not possible. In this case, empirical correlations based on the number of carbon atoms in the molecule might be helpful. For example, the simplest estimation procedure, linearity of $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K})$ with the number of carbons, has been shown to provide a high degree of accuracy for the homologous series of n-alkanes [51]. However, compared to their linear isomers, the branched hydrocarbons all have lower vaporisation enthalpies [52]. To account for this peculiarity, a simple two-parameter equation was previously suggested [52,53]:

$$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = 4.69 \times (\nu C - nC4) + 1.3nC4 + 3.0 \quad (10)$$

where νC denotes the total number of carbon atoms and $nC4$ the number of those that are quaternary. A good approximation to the experimental $\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K})$ can only be obtained from this two-parameter equation for the methyl- and ethyl-substituted cyclohexanes considered in this work (see Table S6). However, the iso-propyl and tert-butyl-substituted cyclohexanes are systematically overestimated by up to $9 \text{ kJ}\cdot\text{mol}^{-1}$ (see Table S7). To improve the quality of the prediction, it was decided to increase the number of parameters to account for the different types of carbon branching and the four-parameter equation:

$$\Delta_1^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = 5.65 \times nC1 + 5.23 \times nC2 + 3.08 \times nC3 + 0.02 \times nC4 \quad (11)$$

fit significantly better versus the numbers n of primary C1, secondary C2, tertiary C3, and quaternary C4, carbon atoms (see Table S7). Even the prediction for the 1,3,5-tri-iso-propyl and 1,3,5-tri-tert-butyl-substituted cyclohexanes could be considered fair considering the simplicity of Equation (11). A quick review of Table S7 shows the average discrepancy for new Equation (11) of $1.1 \text{ kJ}\cdot\text{mol}^{-1}$ and calculated for old according to Equation (10) of $1.6 \text{ kJ}\cdot\text{mol}^{-1}$. This quantity is small enough for both equations that it could be assumed that both methods can be useful in predicting $\Delta_f H_m^\circ(298.15 \text{ K})$ for the “not-highly branched” alkyl-cyclohexanes in cases where experimental data do not exist.

3.3. Liquid-Phase Enthalpies of Formation and Thermodynamic Analysis of the Dehydrogenation/Hydrogenation of the Alkyl-Cyclohexane-Based LOHC Systems

Having established the consistency of the data sets for enthalpies of formation and vaporisation enthalpies for alkyl-cyclohexanes, it is now interesting to follow the influence of structure on the dehydrogenation enthalpy. The compilation of the data required for this analysis is given in Table 7.

Table 7. Calculation of the liquid phase enthalpies of formation, $\Delta_f H_m^\circ(\text{liq})$, of the hydrogen-rich (HR) and hydrogen-lean (HL) counterparts of the LOHC systems based on alkyl-cyclohexanes (at $T = 298.15 \text{ K}$, $p^\circ = 0.1 \text{ MPa}$, in $\text{kJ}\cdot\text{mol}^{-1}$)^a.

Compound	$\Delta_f H_m^\circ(\text{liq})_{\text{HR}}^b$	$\Delta_f H_m^\circ(\text{liq})_{\text{HL}}^c$	$\Delta_r H_m^\circ(\text{liq})^d$	$\Delta_r H_m^\circ/\text{H}_2^e$
cyclohexane	-156.4 ± 0.8	49.0 ± 0.6	-205.4 ± 1.0	68.5
Me-cyclohexane	-190.1 ± 1.0	12.4 ± 0.6	-202.5 ± 1.2	67.5
trans-1,2-di-Me-cyclohexane	-218.2 ± 1.9	-24.4 ± 1.1	-193.8 ± 2.2	64.6
cis-1,2-di-Me-cyclohexane	-211.8 ± 1.8	-24.4 ± 1.1	-187.4 ± 2.1	62.5
trans-1,3-di-Me-cyclohexane	-215.7 ± 1.7	-25.4 ± 0.8	-190.3 ± 1.9	63.4
cis-1,3-di-Me-cyclohexane	-222.9 ± 1.8	-25.4 ± 0.8	-197.5 ± 2.0	65.8
trans-1,4-di-Me-cyclohexane	-222.4 ± 1.8	-24.4 ± 1.0	-198.0 ± 2.1	66.0
cis-1,4-di-Me-cyclohexane	-215.6 ± 1.8	-24.4 ± 1.0	-191.2 ± 2.1	63.7
trans-2-Me-Et-cyclohexane	-240.2 ± 0.9	-46.4 ± 1.0	-193.8 ± 1.3	64.6
cis-2-Me-Et-cyclohexane	-236.2 ± 1.0	-46.4 ± 1.0	-189.8 ± 1.4	63.3
trans-3-Me-Et-cyclohexane	-247.1 ± 1.2	-48.7 ± 1.1	-198.4 ± 1.6	66.1
cis-3-Me-Et-cyclohexane	-246.4 ± 0.9	-49.8 ± 1.3	-196.6 ± 1.6	65.5
trans-4-Me-Et-cyclohexane	-238.9 ± 1.1	-49.8 ± 1.3	-189.1 ± 1.7	63.0
Et-cyclohexane	-211.9 ± 1.6	-12.3 ± 0.9	-199.6 ± 1.8	66.5
n-Pr-cyclohexane	-237.4 ± 1.0	-38.3 ± 0.8	-199.2 ± 1.3	66.4
1,3,5-tri-Me-cyclohexane	-258.9 ± 2.3^f	-63.4 ± 1.3	-195.5 ± 2.6	65.2
n-Bu-cyclohexane	-263.1 ± 1.3	-63.2 ± 1.1	-199.9 ± 1.7	66.6
n-Heptyl-cyclohexane	-339.4 ± 2.3^f	-140.9 ± 1.5^g	-198.5 ± 2.7	66.2
n-Decyl-cyclohexane	-418.2 ± 2.4	-218.3 ± 2.3	-199.9 ± 3.3	66.6
n-Dodecyl-cyclohexane	-467.6 ± 3.6	-269.7 ± 1.5^g	-197.9 ± 3.9	66.0
trans-1,4-di-tBu-cyclohexane	-384.5 ± 2.8	$-190.2 \pm 2.0 [54]$	-194.3 ± 3.5	64.8

^a The uncertainties are given as the twice standard deviation. ^b Enthalpies of formation of fully hydrogenated species (HR = “hydrogen-rich”) from Pedley et al. [9]. ^c Enthalpies of formation of fully dehydrogenated species (HL = “hydrogen-lean”) from Pedley et al. [9]. ^d Calculated according to Hess’s Law for the hydrogenation reaction (see text). ^e Calculated per mole of the hydrogen. ^f Calculated from data given in Tables 2 and 6. ^g Calculated using equation: $\Delta_f H_m^\circ(\text{liq}, 298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = -25.76 \times N_C + 39.4$ with ($R^2 = 0.9999$) developed in Table S8.

Cyclohexane dehydrogenation is the least complicated example (see Figure 6).

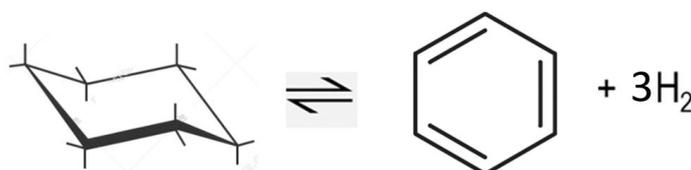


Figure 6. Reaction of dehydrogenation of cyclohexane.

Heat of reaction per mole of hydrogen is given in the last column of Table 7. As can be seen from this table, the $\Delta_r H_m^o/H_2$ -values for the alkyl-substituted cyclohexanes are very close, considering the experimental uncertainties of the reaction enthalpies. The results for dimethyl and methyl-ethyl-substituted cyclohexanes are slightly lower, indicating a preference of these molecules for hydrogen release. The highly branched di-tert-butyl-cyclohexane also has a comparatively low reaction enthalpy. The lengthening of the alkyl chain does not affect the reaction enthalpy. In summary, this work can show systematically for the first time that the structure of the alkyl substituents and their position on the cyclohexane ring has very little effect on the $\Delta_r H_m^o/H_2$ -values, but the reduction in reaction enthalpies from 205 to 187 $\text{kJ}\cdot\text{mol}^{-1}$ due to alkylation (see Table 7) can be important for technological aspects.

3.4. Absolute Vapour Pressures of Alkyl-Cyclohexane Based LOHC Systems

Enthalpy values of the substances are important for modeling of reaction equilibria of hydrogen uptake and release as well as energy demand of these reactions. However, a complete set of thermodynamic properties also includes the relevant phase change data such as vapour pressures. For instance, these data are highly relevant, as the reaction happens in a two-phase system and they determine how the individual compounds are distributed between liquid and vapour phase. Furthermore, they are highly relevant for the purification of hydrogen after release.

The experimental vapour pressures available in literature were approximated by the following equation [55]:

$$R \times \ln(p_i/p_{ref}) = a + \frac{b}{T} + \Delta_1^g C_{p,m}^o \times \ln\left(\frac{T}{T_0}\right) \quad (12)$$

where $R = 8.31446 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the molar gas constant, the reference pressure, $p_{ref} = 1 \text{ Pa}$, and a and b are adjustable parameters; the arbitrary temperature T_0 applied in Equation (12) was chosen to be $T_0 = 298.15 \text{ K}$ and $\Delta_1^g C_{p,m}^o$ (see Table S9) is the difference of the molar heat capacities of the gas and the liquid phases, respectively. Using the coefficients of Equation (12), the experimental absolute vapour pressures at 293 K, 323 K and 373 K were calculated for some alicyclic compounds that may be considered as hydrogen-rich LOHC components (see Table 8).

The selected temperatures are technically relevant for hydrogen storage. The results shown in Table 8 indicate that methyl- and ethyl-substituted cyclohexanes have relatively high vapour pressures at ambient temperatures, which affects the safe handling of these potentially interesting molecules for H_2 storage. However, the di-tert-butyl-substituted cyclohexane has an even lower vapour pressure than typical fossil-derived diesel fuel. Moreover, dicyclohexyl-methane and perhydro-dibenzyltoluene have vapour pressures that are suitable for safe storage. Perhydro-dibenzyltoluene has a very low vapour pressure at all three temperatures, and these parameters are comparable to those for different types of biodiesel measured in this work by using static methods for comparison (see Table S10).

Table 8. Absolute vapour pressures p of hydrogen-rich counterparts of the LOHC system at selected temperatures.

Compound	p/Pa at 293 K	p/Pa at 323 K	p/Pa at 373 K
cyclohexane [56]	10,224	36,159	170,862
3-Me-ethyl-cyclohexane [Table S5]	956	4874	35,685
4-Me-iso-Pr-cyclohexane [Table S5]	582	3112	24,136
1,4-di-tBu-cyclohexane [Table S6]	8.3	89	1578
dicyclohexyl-methane [Table S6]	4.4	48.9	960
perhydro-dibenzyltoluene [24]	0.0024	0.08	3.8
soy methyl ester (SME) a	0.007	0.17	9.5

Table 8. Cont.

Compound	p/Pa at 293 K	p/Pa at 323 K	p/Pa at 373 K
raps methyl ester (RME) a	0.001	0.04	4.8
biodiesel reference sample JRC a	0.05	0.76	20.6
fossil-derived diesel [57]	53	-	-

^a Reference samples from Joint Research Center of Institute for Reference Materials and Measurements (<https://www.confidence.eu/>, accessed 6 December 2022) measured (see Table S10) using the static method for the EU Project “Metrology of biofuels” ENG-09 REG01 project.

4. Conclusions

To overcome difficulties with experimental measurements, various empirical and theoretical methods have been proposed and tested to determine the gas-phase enthalpies of formation and vaporization enthalpies of alkyl-substituted cyclohexanes that represent possible hydrogen-rich organic molecules in LOHC systems for hydrogen storage. Both vaporisation and formation enthalpies are reliably predicted using the “centerpiece” approach. The vaporisation enthalpies correlate linearly with the retention Kovats indices, normal boiling points, and the number of carbon atoms in molecules. All three empirical methods are useful for expanding the database of available thermochemical data. The gas-phase formation enthalpies from the quantum chemical G3MP2 method agree very well with the reliable experimental data. This composite method is applicable even for relatively large molecules containing 20–25 heavy atoms. The liquid-phase enthalpies of formation of the hydrogen-rich counterparts of the LOHC systems were evaluated and used to calculate the dehydrogenation reaction enthalpies. The structure of the alkyl substituent was found to have virtually no effect on the heat of reaction, except for branched species. At technically relevant temperatures, di-tert-butyl-cyclohexane, dicyclohexyl-methane, and perhydro-dibenzyl-toluene have sufficiently low vapour pressures that are comparable to diesel fuel, while the vapour pressure of perhydro-dibenzyltoluene resembles that of typical biodiesel fuels.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/hydrogen4010004/s1>, Table S1: Group-additivity values for calculation of enthalpies of vaporisation, $\Delta_1^{\text{S}}H_m^{\text{O}}$, and enthalpies of formation, $\Delta_f H_m^{\text{O}}(\text{g})$, at 298.15 K (in kJ mol^{-1}); Table S2: Specific “transfer” contributions, $\Delta_f H_m^{\text{O}}(\text{g})(\text{H}\rightarrow\text{R})$ derived from gas-phase enthalpies of formation of alkyl-substituted cyclohexanes, as well as $\Delta_1^{\text{S}}H_m^{\text{O}}(\text{H}\rightarrow\text{R})$ derived from vaporization enthalpies of alkyl-substituted cyclohexanes, (at 298.15 K in $\text{kJ}\cdot\text{mol}^{-1}$); Table S3: Correlation of vaporisation enthalpies, $\Delta_1^{\text{S}}H_m^{\text{O}}(298.15\text{ K})$, of alkyl-cyclohexanes with their Kovats indices (J_x); Table S4: Correlation of vaporisation enthalpies, $\Delta_1^{\text{S}}H_m^{\text{O}}(298.15\text{ K})$, of alkyl-cyclohexanes with their normal boiling temperatures (T_b); Table S5: Compilation of enthalpies of vaporisation $\Delta_1^{\text{S}}H_m^{\text{O}}$ for alkyl-cyclohexanes derived in this work from the data available in the literature; Table S6: Vapor pressures, p_i , at different temperatures compiled from the literature, standard molar vaporisation enthalpies, $\Delta_1^{\text{S}}H_m^{\text{O}}$, and standard molar vaporisation entropies, $\Delta_1^{\text{S}}S_m^{\text{O}}$; Table S7: Correlation of vaporisation enthalpies, $\Delta_1^{\text{S}}H_m^{\text{O}}(298.15\text{ K})$, of alkyl-cyclohexanes with the number of carbon atoms; Table S8: Correlation of the liquid-phase enthalpies of formation of alkyl-benzenes with the chain length (at $T = 298.15\text{ K}$ in $\text{kJ}\cdot\text{mol}^{-1}$); Table S9: Compilation of data on molar heat capacities $C_{p,m}^{\text{O}}(\text{liq})$ and heat capacity differences $\Delta_1^{\text{S}}C_{p,m}^{\text{O}}$ at $T = 298.15\text{ K}$ (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$); Static method; Table S10: The results of the absolute vapor pressure determination for biodiesel samples, measured using the static method. The auxiliary experimental and computational details necessary to understand the main points of the paper are given in Refs. [58–76].

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References

1. Abdin, Z.; Tang, C.; Liu, Y.; Catchpole, K. Large-scale stationary hydrogen storage via liquid organic hydrogen carriers. *iScience* **2021**, *24*, 102966. [CrossRef]
2. Müller, K.; Aslam, R.; Fikrt, A.; Krieger, C.; Arlt, W. Water Removal from LOHC Systems. *Hydrogen* **2020**, *1*, 1–10. [CrossRef]
3. Verevkin, S.P.; Emel’yanenko, V.N.; Siewert, R.; Pimerzin, A.A. Energetics of LOHC: Structure-Property Relationships from Network of Thermochemical Experiments and in Silico Methods. *Hydrogen* **2021**, *2*, 101–121. [CrossRef]
4. Cao, T.; Lee, W.; Huang, R.; Gorte, R.J.; Vohs, J.M. Liquid-Organic hydrogen carriers as endothermic fuels. *Fuel* **2022**, *313*, 123063. [CrossRef]
5. Konnova, M.E.; Li, S.; Bösmann, A.; Müller, K.; Wasserscheid, P.; Andreeva, I.V.; Turovtzev, V.V.; Zaitsau, D.H.; Pimerzin, A.A.; Verevkin, S.P. Thermochemical Properties and Dehydrogenation Thermodynamics of Indole Derivates. *Ind. Eng. Chem. Res.* **2020**, *59*, 20539–20550. [CrossRef]
6. Kondratev, S.O.; Zaitsau, D.H.; Vostrikov, S.V.; Li, S.; Bösmann, A.; Wasserscheid, P.; Müller, K.; Verevkin, S.P. Thermochemical properties of 6,7-benzindole and its perhydrogenated derivative: A model component for liquid organic hydrogen carriers. *Fuel* **2022**, *324*, 124410. [CrossRef]
7. Safronov, S.P.; Vostrikov, S.V.; Samarov, A.A.; Wasserscheid, P.; Müller, K.; Verevkin, S.P. Comprehensive thermodynamic study of substituted indoles/perhydro indoles as potential liquid organic hydrogen carrier system. *Fuel* **2023**, *331*, 125764. [CrossRef]
8. Müller, K.; Skeledzic, T.; Wasserscheid, P. Strategies for Low-Temperature Liquid Organic Hydrogen Carrier Dehydrogenation. *Energy Fuels* **2021**, *35*, 10929–10936. [CrossRef]
9. Pedley, J.B.; Naylor, R.D.; Kirby, S.P. *Thermochemical Data of Organic Compounds*; Hapman and Hall: New York, NY, USA, 1986; pp. 1–792.
10. Jang, M.; Jo, Y.S.; Lee, W.J.; Shin, B.S.; Sohn, H.; Jeong, H.; Jang, S.C.; Kwak, S.K.; Kang, J.W.; Yoon, C.W. A High-Capacity, Reversible Liquid Organic Hydrogen Carrier: H₂-Release Properties and an Application to a Fuel Cell. *ACS Sustain. Chem. Eng.* **2019**, *7*, 1185–1194. [CrossRef]
11. Zaitsau, D.H.; Emel’yanenko, V.N.; Pimerzin, A.A.; Verevkin, S.P. Benchmark properties of biphenyl as a liquid organic hydrogen carrier: Evaluation of thermochemical data with complementary experimental and computational methods. *J. Chem. Thermodyn.* **2018**, *122*, 1–12. [CrossRef]
12. Konnova, M.E.; Vostrikov, S.V.; Pimerzin, A.A.; Verevkin, S.P. Thermodynamic analysis of hydrogen storage: Biphenyl as affordable liquid organic hydrogen carrier (LOHC). *J. Chem. Thermodyn.* **2021**, *159*, 106455. [CrossRef]
13. Steele, W.; Chirico, R.D.; Smith, N.K. The standard enthalpies of formation of 2-methylbiphenyl and diphenylmethane. *J. Chem. Thermodyn.* **1995**, *27*, 671–678. [CrossRef]
14. Chirico, R.D.; Steele, W.V. Thermodynamic Properties of Diphenylmethane. *J. Chem. Eng. Data* **2005**, *50*, 1052–1059. [CrossRef]
15. Verevkin, S.P.; Vostrikov, S.V.; Leinweber, A.; Bösmann, A.; Wasserscheid, P.; Müller, K. Thermochemical properties of benzyl toluenes and their hydrogenated counter-parts as potential LOHC. *Fuel* **2023**, *335*, 126618. [CrossRef]
16. NIST Chemistry WebBook. Available online: <https://webbook.nist.gov/Chemistry/> (accessed on 5 December 2022).
17. Serijan, K.T.; Wise, P.H. Dicyclic Hydrocarbons. III. Diphenyl- and Dicyclohexylalkanes through C₁₅. *J. Am. Chem. Soc.* **1951**, *73*, 4766–4769. [CrossRef]
18. Wise, C.H.; Serijan, K.T.; Goodman, I.A. NACA Technical Report 1003. *NACA Tech. Rep.* **1951**, *1003*, 1–10.
19. Gollis, M.H.; Belenyessy, L.I.; Gudzinowicz, B.J.; Koch, S.D.; Smith, J.O.; Wineman, R.J. Evaluation of Pure Hydrocarbons as Jet Fuels. *J. Chem. Eng. Data* **1962**, *7*, 311–316. [CrossRef]
20. Verevkin, S.P. Gibbs Energy and Helmholtz Energy. In *Gibbs Energy and Helmholtz Energy: Liquids, Solutions and Vapours*; Wilhelm, E., Letcher, T.M., Eds.; Royal Society of Chemistry: Cambridge, UK, 2021; ISBN 978-1-83916-201-5.

21. Verevkin, S.P.; Zaitsau, D.H.; Schick, C.; Heym, F. Development of Direct and Indirect Methods for the Determination of Vaporization Enthalpies of Extremely Low-Volatile Compounds. In *Handbook of Thermal Analysis and Calorimetry*; Elsevier: Amsterdam, The Netherlands, 2018; Volume 6, pp. 1–46.
22. Verevkin, S.P.; Emel'yanenko, V.N.; Diky, V.; Muzny, C.D.; Chirico, R.D.; Frenkel, M. New Group-Contribution Approach to Thermochemical Properties of Organic Compounds: Hydrocarbons and Oxygen-Containing Compounds. *J. Phys. Chem. Ref. Data* **2013**, *42*, 033102. [CrossRef]
23. Benson, S.W. *Thermochemical Kinetics*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, USA, 1976; pp. 1–320.
24. Ducros, M.; Gruson, J.F.; Sannier, H. Estimation des enthalpies de vaporisation des composés organiques liquides. Partie 1. Applications aux alcanes, cycloalcanes, alcènes, hydrocarbures benzeniques, alcools, alcanes thiols, chloro et bromoalcanes, nitriles, esters, acides et aldehydes. *Thermochim. Acta* **1980**, *36*, 39–65. [CrossRef]
25. Müller, K.; Stark, K.; Emelyanenko, V.N.; Varfolomeev, M.A.; Zaitsau, D.H.; Shoifet, E.; Schick, C.; Verevkin, S.P.; Arlt, W. Liquid Organic Hydrogen Carriers: Thermophysical and Thermochemical Studies of Benzyl- and Dibenzyl-Toluene Derivatives. *Ind. Eng. Chem. Res.* **2015**, *54*, 7967–7976. [CrossRef]
26. Verevkin, S.P.; Turovtsev, V.V.; Andreeva, I.V.; Orlov, Y.D.; Pimerzin, A.A. Webbing a network of reliable thermochemistry around lignin building blocks: Tri-methoxy-benzenes. *RSC Adv.* **2021**, *11*, 10727–10737. [CrossRef] [PubMed]
27. Verevkin, S.P.; Andreeva, I.V.; Zherikova, K.V.; Pimerzin, A.A. Prediction of thermodynamic properties: Centerpiece approach—How do we avoid confusion and get reliable results? *J. Therm. Anal. Calorim.* **2022**, *147*, 8525–8534. [CrossRef]
28. Verevkin, S.P.; Emel'yanenko, V.N.; Heintz, A.; Stark, K.; Arlt, W. Liquid Organic Hydrogen Carriers: An Upcoming Alternative to Conventional Technologies. *Thermochemical Studies. Ind. Eng. Chem. Res.* **2012**, *51*, 12150–12153. [CrossRef]
29. Wheeler, S.E.; Houk, K.N.; Schleyer, P.v.R.; Allen, W.D. A Hierarchy of Homodesmotic Reactions for Thermochemistry. *J. Am. Chem. Soc.* **2009**, *131*, 2547–2560. [CrossRef]
30. Kováts, E. Gas-chromatographische Charakterisierung organischer Verbindungen. Teil 1: Retentionsindices aliphatischer Halogenide, Alkohole, Aldehyde und Ketone. *Helv. Chim. Acta* **1958**, *41*, 1915–1932. [CrossRef]
31. Pacáková, V.; Felti, L. Chromatographic Retention Indices: An Aid to Identification of Organic Compounds. In *Ellis Horwood Series in Analytical Chemistry*; Ellis Horwood Ltd.: Chichester, UK, 1992.
32. The Pherobase: Database of Pheromones and Semiochemicals. Available online: <https://www.pherobase.com/Database/Kovats/> (accessed on 5 December 2022).
33. Verevkin, S.P. Vapour pressures and enthalpies of vaporization of a series of the linear *n*-alkyl-benzenes. *J. Chem. Thermodyn.* **2006**, *38*, 1111–1123. [CrossRef]
34. Benson, S.W. New Methods for Estimating the Heats of Formation, Heat Capacities, and Entropies of Liquids and Gases. *J. Phys. Chem. A* **1999**, *103*, 11481–11485. [CrossRef]
35. SciFinder—Chemical Abstracts Service. Available online: <http://scifinder.cas.org/> (accessed on 5 December 2022).
36. Curtiss, L.A.; Redfern, P.C.; Raghavachari, K.; Rassolov, V.; Pople, J.A. Gaussian-3 theory using reduced Moller-plesset order. *J. Chem. Phys.* **1999**, *110*, 4703–4709. [CrossRef]
37. Pracht, P.; Bohle, F.; Grimme, S. Automated exploration of the low-energy chemical space with fast quantum chemical methods. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169–7192. [CrossRef]
38. Petersson, G.A.; Bennett, A.; Tensfeldt, T.G.; Al-Laham, M.A.; Shirley, W.A.; Mantzaris, J. A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements. *J. Chem. Phys.* **1988**, *89*, 2193–2218. [CrossRef]
39. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. *Gaussian 16, Revision C.01*; Gaussian Inc.: Wallingford, CT, USA, 2016.
40. Verevkin, S.P.; Emel'yanenko, V.N.; Pimerzin, A.A.; Vishnevskaya, E.E. Thermodynamic Analysis of Strain in the Five-Membered Oxygen and Nitrogen Heterocyclic Compounds. *J. Phys. Chem. A* **2011**, *115*, 1992–2004. [CrossRef] [PubMed]
41. Verevkin, S.P.; Kozlova, S.A.; Emel'yanenko, V.N.; Goodrich, P.; Hardacre, C. Thermochemistry of Ionic Liquid-Catalyzed Reactions. Experimental and Theoretical Study of Chemical Equilibria of Isomerization and Transalkylation of Tert-Butylbenzenes. *J. Phys. Chem. A* **2008**, *112*, 11273–11282. [CrossRef]
42. Verevkin, S.P. Thermochemical investigation on α -methyl-styrene and parent phenyl substituted alkenes. *Thermochim. Acta* **1999**, *326*, 17–25. [CrossRef]
43. Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, UK, 1985.
44. Fuchs, R.; Peacock, L.A. Heats of vaporization of monoalkylcyclohexanes by the gas chromatography—Calorimetry method. *Can. J. Chem.* **1978**, *56*, 2493–2498. [CrossRef]
45. Reid, R.C.; Wilhort, R.C. *Handbook on Vapor Pressure and Heats of Vaporization of Hydrocarbons and Related Compounds*; Wilhort, R.C., R.C., Zwolinski, B.J., Eds.; Texas A&M Research Foundation: College Station, TX, USA, 1972; Volume 18, p. 1278. [CrossRef]
46. Antheaume, J.; Guiochon, G. Application de La Chromatographie En Phase Gazeuse à l'étude de La Composition Des Fractions Moyennes d'un Brut Pétrolier. *Bull. Soc. Chim. Fr.* **1965**, *2*, 298–307.
47. Rang, S.; Orav, A.; Kunigas, K.; Eisen, O. Capillary gas chromatography of monosubstituted cyclopentenes and cyclohexenes. *Chromatographia* **1977**, *10*, 115–122. [CrossRef]
48. Beens, J.; Tijssen, R.; Blomberg, J. Prediction of comprehensive two-dimensional gas chromatographic separations: A theoretical and practical exercise. *J. Chromatogr. A* **1998**, *822*, 233–251. [CrossRef]

49. PubChem. Available online: <https://pubchem.ncbi.nlm.nih.gov/> (accessed on 5 December 2022).
50. Guidechem Chemical Network. Available online: <https://www.guidechem.com> (accessed on 5 December 2022).
51. Månsson, M.; Sellers, P.; Stridh, G.; Sunner, S. Enthalpies of vaporization of some 1-substituted *n*-alkanes. *J. Chem. Thermodyn.* **1977**, *9*, 91–97. [[CrossRef](#)]
52. Chickos, J.S.; Hesse, D.G.; Hosseini, S.; Liebman, J.F.; David Mendenhall, G.; Verevkin, S.P.; Rakus, K.; Beckhaus, H.-D.; Rüchardt, C. Enthalpies of vaporization of some highly branched hydrocarbons. *J. Chem. Thermodyn.* **1995**, *27*, 693–705. [[CrossRef](#)]
53. Chickos, J.S.; Hyman, A.S.; Ladon, L.H.; Liebman, J.F. Measurement and estimation of the heats of vaporization of hydrocarbons. *J. Org. Chem.* **1981**, *46*, 4294–4296. [[CrossRef](#)]
54. Verevkin, S.P. Thermochemical properties of branched alkylsubstituted benzenes. *J. Chem. Thermodyn.* **1998**, *30*, 1029–1040. [[CrossRef](#)]
55. Kulikov, D.; Verevkin, S.P.; Heintz, A. Determination of Vapor Pressures and Vaporization Enthalpies of the Aliphatic Branched C₅ and C₆ Alcohols. *J. Chem. Eng. Data* **2001**, *46*, 1593–1600. [[CrossRef](#)]
56. Willingham, C.B.; Taylor, W.J.; Pignocco, J.M.; Rossini, F.D. Vapor pressures and boiling points of some paraffin, alkylcyclopentane, alkylcyclohexane, and alkylbenzene hydrocarbons. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 219. [[CrossRef](#)]
57. QS Study. Available online: <https://qsstudy.com/vapour-pressure-of-diesel-fuel/> (accessed on 5 December 2022).
58. Stephenson, R.M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Springer: Dordrecht, The Netherlands, 1987; ISBN 978-94-010-7923-5.
59. Osborn, A.G.; Douslin, D.R. Vapor-Pressure Relations for 15 Hydrocarbons. *J. Chem. Eng. Data* **1974**, *19*, 114–117. [[CrossRef](#)]
60. Lainez, A.; Rodrigo, M.M.; Wilhelm, E.; Grolier, J.P.E. Excess Volumes and Excess Heat Capacities of Some Mixtures with Trans,Trans,Cis-1,5,9-Cyclododecatriene at 298.15 K. *J. Chem. Eng. Data* **1989**, *34*, 332–335. [[CrossRef](#)]
61. Zaitsau, D.H.; Verevkin, S.P. Vapor Pressure of Pure Methyl Oleate—the Main Component of Biodiesel. *Russ. J. Gen. Chem.* **2021**, *91*, 2061–2068. [[CrossRef](#)]
62. Chickos, J.S.; Hosseini, S.; Hesse, D.G.; Liebman, J.F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271–278. [[CrossRef](#)]
63. Acree, W.; Chickos, J.S. Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds. Sublimation, Vaporization and Fusion Enthalpies From 1880 to 2015. Part 1. C 1–C 10. *J. Phys. Chem. Ref. Data* **2016**, *45*, 033101. [[CrossRef](#)]
64. Zaitsau, D.H.; Verevkin, S.P.; Sazonova, A.Y. Vapor Pressures and Vaporization Enthalpies of 5-Nonanone, Linalool and 6-Methyl-5-Hepten-2-One. Data Evaluation. *Fluid Phase Equilib.* **2015**, *386*, 140–148. [[CrossRef](#)]
65. Sabbah, R.; Xu-Wu, A.; Chickos, J.S.; Leitão, M.L.P.; Roux, M.V.; Torres, L.A. Reference Materials for Calorimetry and Differential Thermal Analysis. *Thermochim. Acta* **1999**, *331*, 93–204. [[CrossRef](#)]
66. Ambrose, D.; Lawrenson, I.J.; Angus, S.; Paule, R.C. *Recommended Reference Materials for Realization of Physicochemical Properties*; Herington, E.F.G., Ed.; Elsevier: Amsterdam, The Netherlands, 1977; ISBN 978-0-08-022340-7.
67. Marsh, K.N. *Recommended Reference Materials for the Realization of Physicochemical Properties*; Blackwell Scientific Publications: Oxford, UK; Boston, MA, USA, 1987; ISBN 063201718X 9780632017188.
68. Clarke, E.C.W.; Glew, D.N. Evaluation of Thermodynamic Functions from Equilibrium Constants. *Trans. Faraday Soc.* **1966**, *62*, 539. [[CrossRef](#)]
69. Ribeiro da Silva, M.A.V.; Monte, M.J.S.; Santos, L.M.N.B.F. The Design, Construction, and Testing of a New Knudsen Effusion Apparatus. *J. Chem. Thermodyn.* **2006**, *38*, 778–787. [[CrossRef](#)]
70. Malaspina, L.; Gigli, R.; Bardi, G. Microcalorimetric Determination of the Enthalpy of Sublimation of Benzoic Acid and Anthracene. *J. Chem. Phys.* **1973**, *59*, 387–394. [[CrossRef](#)]
71. Davies, M.; Jones, J.I. The Sublimation Pressures and Heats of Sublimation of Some Carboxylic Acids. *Trans. Faraday Soc.* **1954**, *50*, 1042–1047. [[CrossRef](#)]
72. Ribeiro Da Silva, M.A.V.; Cabral, J.I.T.A.; Gomes, P.; Gomes, J.R.B. Combined Experimental and Computational Study of the Thermochemistry of Methylpiperidines. *J. Org. Chem.* **2006**, *71*, 3677–3685. [[CrossRef](#)] [[PubMed](#)]
73. Site, A.D. The Vapor Pressure of Environmentally Significant Organic Chemicals: A Review of Methods and Data at Ambient Temperature. *J. Phys. Chem. Ref. Data* **1997**, *26*, 157–193. [[CrossRef](#)]
74. Shiu, W.-Y.; Ma, K.-C. Temperature Dependence of Physico-Chemical Properties of Selected Chemicals of Environmental Interest. I. Mononuclear and Polynuclear Aromatic Hydrocarbons. *J. Phys. Chem. Ref. Data* **2000**, *29*, 41–130. [[CrossRef](#)]
75. Růžicka, K.; Fulem, M.; Růžicka, V. Recommended Vapor Pressure of Solid Naphthalene. *J. Chem. Eng. Data* **2005**, *50*, 1956–1970. [[CrossRef](#)]
76. Kulikov, D.; Verevkin, S.P.; Heintz, A. Enthalpies of Vaporization of a Series of Aliphatic Alcohols. *Fluid Phase Equilib.* **2001**, *192*, 187–207. [[CrossRef](#)]

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