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N-Heterocyclic Molecules as Potential Liquid Organic Hydrogen Carriers: Reaction Routes and Dehydrogenation Efficacy

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Abstract: This study is focused on the development of liquid organic hydrogen carriers (LOHC) based on N-heterocyclic compounds. These LOHC-substrates are attractive for their lower hydrogen extraction temperature compared to cycloalkanes, which is caused by the low enthalpy of the dehydrogenation reaction of the N-heterocyclic compounds. The low hydrogen extraction temperature, as well as the low volatility of the heterocycles, provide high purity hydrogen from the reaction. Under similar reaction conditions, the comparison of the efficacy of three promising heterocycles (1-methyl-octahydroindole (8HMI), tetradecahydrophenazine and decahydroquinoline) was carried out in the presence of palladium-containing catalysts. As a result, the advantages of using catalysts supported by alumina, and the high perspectivity of the 8MHI application as a LOHC-substrate, were shown.

The dehydrogenation of 8HMI in the presence of 1 wt.% Pd/Al2O3 allowed for reaching a 100% yield in hydrogen under the conditions of the standard catalytic test (1 h, 240 °C). In order to study the high reactivity of 8HMI, thermodynamic dehydrogenation reaction profiles were computationally evaluated, which showed that 8HMI was the most energetically preferred in the field of hydrogen storage from the studied heterocyclic compounds.

Keywords: LOHC; hydrogen storage; N-heterocycles; Pd catalysts; dehydrogenation; acceptorless dehydrogenation; reaction pathway; density functional theory

1. Introduction

Currently, the research and study of alternative energy sources is becoming increasingly important. From this viewpoint, hydrogen is considered an attractive energy carrier [1]. However, the properties of hydrogen, such as high explosiveness, low fluidization temperature, low density in the gaseous form, and its ability to diffuse into metals and embrittle structural materials, result in the need to develop efficient and safe systems for its storage and transportation [2]. Hydrogen can be stored in a covalently bound form in chemical compounds of various compositions, which, under certain conditions, can release hydrogen (the catalytic decomposition of ammonia, methanol, and formic acid; hydrogenation and the subsequent dehydrogenation of unsaturated hydrocarbons) [3]. Of interest is the use of liquid organic hydrogen carriers (LOHC), which are liquids or low-melting solids that can be easily hydrogenated and dehydrogenated in the presence of a catalyst [1]. The use of LOHC provides high weight and volume density of hydrogen storage, as well as potentially low risk and low capital investment, since existing infrastructure can be used for their transportation and storage [4].

A key step in the development of hydrogen storage technologies, based on the use of liquid hydrogen carriers, is the development of a process for dehydrogenation of a H2-saturated form of a substrate, from which hydrogen is extracted [5]. Generally, for the
opportunity to apply a compound and its perhydrogenated form as a hydrogen storage pair, it must satisfy the following list of criteria [5,6]:

- the hydrogen capacity must not be less than 5.5 wt.% and 1.5 kWh/kg [7];
- be economically accessible and non-toxic;
- the boiling point of the compound must ensure a good separation of hydrogen and the dehydrogenated form of a LOHC; thence, the LOHC system boiling temperature must be not less than 300 °C, and the melting point should also be quite low (less than −30 °C);
- the compound must be stable in the process conditions;
- the dehydrogenation enthalpy must be 40–70 kJ/mol to ensure the stability of a LOHC molecule.

Many papers reported that the substitution of a carbon atom by nitrogen in the ring can reduce the dehydrogenation enthalpy [8]. For nitrogen-containing cyclic molecules, as a rule, lower enthalpies of hydrogen release are characteristic, and, thus, the reaction takes place at lower temperatures (140–240 °C). Moreover, the heterocyclic molecules are less volatile and, thus, a higher purity of obtained hydrogen can be reached. This is an additional advantage, since the high purity of the releasing hydrogen (close to 100%) is suitable for its direct utilization in fuel cells, without the necessity of additional purification [9].

It was also shown that the dehydrogenation of non-heterocyclic LOHC-substrates such as methylcyclohexane (MCH), perhydrobenzyltoluene (18H-DBT), and decalin (DEC) over Pt- and Pd-containing catalysts took place as a result of high-temperature reactions (>300 °C) [10]. The high temperature needed to carry out these reactions can lead to a decrease in selectivity and decomposition of the substrates, as well as, in the case of volatile substrates, to pollution of the releasing hydrogen by the dehydrogenated form of the LOHC (e.g., toluene for MCH).

As a promising alternative, the application of perhydrogenated forms of nitrogen-containing heterocycles has been considered. In this area, the most studied are N-alkyl substituted carbazole, and in particular, N-ethylcarbazole [11]. For example, Yang et al. studied the dehydrogenation of perhydro-N-ethylcarbazole (12H-NEC) over alumina-supported noble metal catalysts (at 180 °C) [12]. In this report, an effect of the metals on the initial catalytic activity of the tested samples was shown, the values of which increased in the following order: Rh < Ru < Pt < Pd. Despite its high hydrogen capacity (5.8 wt.%), and relatively low dehydrogenation enthalpy (−50.5 kJ/mol H₂) [13], the high melting temperature of N-ethylcarbazole (70 °C) has led to interest in other compounds in the N-alkylcarbazole series, which maintain high capacities for hydrogen [14,15] and have significantly lower melting temperatures [16].

Beside carbazoles, other types of heterocyclic compounds attract attention as nitrogen-containing LOHCs. For example, 1-methylindole meets all criteria listed above (H₂ capacity of 5.76 wt.%, melting point of −20 °C [5,17]), which, make it one of the most interesting candidates as a LOHC, especially taking into account its high accessibility. Yang and coworkers carried out the study of indole derivatives as LOHCs, such as N-ethylindole [18], 2-methyl-indole [19], and 1-methyl-indole [17]. The dehydrogenation of the hydrogenated forms of these compounds was conducted in the presence of a 5 wt.% Pd/Al₂O₃ catalyst at 160–190 °C for 1-methylindole and N-ethylindole, as well as at 160–200 °C for 2-methylindole.

Also, almost all the criteria are met by quinoline and phenazine that are solid at room temperature, either as themselves or in their perhydrogenated forms. Their high hydrogen capacities (the theoretical capacity is 7.2 wt.%) and meeting of all other criteria make them promising substrates for hydrogen storage. In [20], it was shown that tetradecahydrophenazine (perhydrophenazine) could be successfully dehydrogenated in the presence of a Pd₂Ru@SiCN catalyst at 190 °C for several hydrogenation/dehydrogenation cycles. Furthermore, this compound could be synthesized from lignocellulose hydrolysis products.

In this work, the efficacy of a series of N-containing heterocycles was investigated within identical reaction conditions in the process of hydrogen release. For the investigation,
the following potential pairs of LOHC substrates were chosen: 1-methyl-indole/1-methyl-octahydroindole (MI/8HMI) and phenazine/tetradecahydrophenazine (P/14HP). Also, for the comparison, the pair quinoline/decahydroquinoline was selected for its similar phenazine hydrogen capacity, but different molecular structure (Q/10HQ) [21]. Various approaches to the impregnation of Pd onto alumina were studied, and the activity of the alumina- and carbon-supported Pd metal catalysts were compared in the dehydrogenation of N-heterocycles.

2. Results and Discussion

2.1. Dehydrogenation of Nitrogenic Heterocycles over Palladium-Containing Catalysts

At the first step, the catalytic testing technique was optimized, including the choice of a solvent for the dehydrogenation reaction of the nitrogen-containing heterocyclic compounds. When comparing the activity of the heterocycles in the catalytic dehydrogenation, a standard 1 h test was used. For identical reaction conditions for comparison, all dehydrogenation processes were carried out using a solvent at the same concentration of heterocycles (1 mmol in 3 mL of solvent). In preliminary tests using tetradecahydrophenazine (14HP), the optimal solvent was selected. The problem of selecting and using a solvent in the dehydrogenation is of fundamental importance for many nitrogenous heterocycles. While 1-methyl-octahydroindole (8HMI, m.p. −25 °C) or decahydroquinoline (as a melt; 10HQ, m.p. 35 °C) can be used alone, both forms of phenazine (H$_2$-rich and H$_2$-lean) are solids even at the dehydrogenation temperatures (m.p. 135 and 172 °C, respectively). According to the data obtained, tetraglyme (YH$_2$ = 78%; 240 °C, 14HP, 1 h) was the most effective in the tested series (mesitylene (YH$_2$ = 5%), decalin (YH$_2$ = 10%), hexadecane (YH$_2$ = 24%)). This was presumably due to the high polarity of the tetraglyme compared to the hydrocarbons, which increased the solubility of the heterocycles. Moreover, according to [21], it reduced the efficiency of adsorption of the dehydrogenated forms of heterocycles on the palladium surface. This process occurred during the complex formation of the Pd with nitrogen atoms in the composition of quinoline or phenazine, and led to blocking of the catalyst active sites by the reaction products.

In some reports on the dehydrogenation of saturated nitrogen-containing heterocycles, a high potential for systems based on gamma alumina was pointed out [21]. Thus, the next step of the study was to optimize the technique of synthesis of the Pd/γ-Al$_2$O$_3$ catalytic systems. A 1 wt.% Pd/C (BIC SB RAS) system was utilized as a reference (prototype) catalyst, and its synthesis technique was developed in detail in [22–24]. This system was additionally characterized, and, according to the data obtained, consisted of metallic palladium particles (3–6 nm, metal dispersion, CO chemisorption data (D$_{CO}$) was 41%), on the surface of the mesoporous carbon support (S$_{BET}$ was 325 m$^2$/g, V$_{pore}$ was 0.46 mL/g).

For the development of the synthesis technique for 1 wt.% Pd/γ-Al$_2$O$_3$ systems, methods of wet impregnation and adsorptive sedimentation were tested. Also, a comparison of the structure and catalytic properties of the systems obtained from various palladium precursors was carried out. According to XRD data, as a result of calcination of the initial pseudoboehmite, the $\gamma$-Al$_2$O$_3$ phase predominantly formed (Figure 1). Thermal treatments and impregnation of the metal precursor within the next steps of synthesis of the catalytic systems did not affect the support phase composition significantly.

In Figure 2, typical HRTEM (A1, A3, B1, B3) and HAADF (A2, B2) images for the samples synthesized using various palladium precursors (H$_2$[PdCl$_4$] (A1–A3) and H$_2$[Pd(NO$_3$)$_4$] (B1–B3)) are presented. For both samples, the high-contrast areas on the HAADF images were apparently related to palladium particles. The size of the found particles was in the diapason of 2–5 nm for both precursors. The similarity of the active component particle sizes for both samples was indirectly confirmed by CO chemisorption (Table 1). CO absorption for the PdA-WI-N and PdA-WI-Cl samples, reduced at 100 and 200 °C, and at room temperature, was within the D$_{CO}$ range of 23–27% and was weakly varied, which indicated a quite close dispersion of the palladium particles for these catalysts.
The necessity of the stage of high temperature pretreatment with Cl ions in the synthesis of catalysts was established. Previous preparation steps contain metal particles on the next preparation step.

The effectiveness of metal reduction from chloride precursors facilitates the catalytic characteristics of the prototypic Pd/C system, which was in agreement with the data from [26].

In the series of catalytic activity tests, it was shown (Table 1) that the adsorptive dehydrogenation of these catalysts was slightly lower than for the incipient wetness impregnation (AI) technique, which was equal to the effectiveness of metal reduction from chloride precursors. The size of the found component particle sizes for both samples was apparent (Figure 1, Table 1). CO absorption for the high-temperature calcination of PdA-WI-Cl and PdA-AI samples, reduced at 100 °C, was within the D series for PdA-WI-Cl; (A1–A3) series for PdA-WI-Cl; (B1–B3) series for PdA-WI-N. A1 it B1—HAADF images of the corresponding catalysts.

**Figure 1.** XRD diffractograms of initial Pural SB-1, Pural SB-1 calcinated at 550 °C and PdA-AI-500-N catalyst.

**Figure 2.** HRTEM images of 1 wt.% Pd/γ-Al₂O₃: (A1–A3) series for PdA-WI-Cl; (B1–B3) series for PdA-WI-N. A1 it B1—HAADF images of the corresponding catalysts.
In the series of catalytic activity tests, it was shown (Table 1) that the adsorptive impregnation (AI) of Pd onto the γ-Al₂O₃ surface allowed for obtaining more effective systems than the incipient wetness impregnation technique (WI). The activity of the catalysts in the dehydrogenation of 14HP was in agreement with the data on CO chemisorption studies of the dispersity of the metallic particles: with the increase in dispersity of the particles, i.e., the specific surface area of the Pd, the activity also increased. Also, the necessity of the stage of high-temperature calcination (500 °C) in an air environment was shown for the synthesis of the Pd/γ-Al₂O₃ with high values of \( Y_{\text{H}_2} \) and \( D_{\text{CO}} \). Carrying out this stage was necessary for the decomposition of the palladium precursors to oxygen-containing forms of PdO₃, which facilitated more effective reduction of the oxidized metal particles on the next preparation step. The activity of all the catalytic systems synthesized from chloride precursors was slightly lower than for the nitrate analogues. Earlier, it was thought that the use of H₂PdCl₄ gave rise to the pollution of the catalytic system surface with Cl⁻ ions, which decreased the effectiveness of metal reduction on the next preparation step [25]. At equal contents of the impregnated metal, this led to less effective catalyst systems. The optimized compositions of Pd/γ-Al₂O₃ systems were exceeded by the catalytic characteristics of the prototypic Pd/C system, which was in agreement with the data from [26].

### 2.2. Comparative Testing of the Heterocycles

For decahydroquinoline (10HQ), it was shown that the reaction temperature of 140 °C, described as acceptable for the dehydrogenation of 1,2,3,4-tetrahydroquinoline (4HQ-c) [27], was insufficient for the dehydrogenation of 10HQ. This difference in the behavior of the substrates was presumably explained by their thermodynamics. For example, 4HQ-c dehydrogenation is a thermodynamically favorable process that leads to the completion of the aromatic system. Also, at a reaction temperature of 140 °C, despite the thermodynamic advantage (the presence of two nitrogen atoms) of the dehydrogenation of the 14HP central ring, hydrogen evolution and the formation of octahydrophenazines were not observed. Under these reaction conditions, only 1-methyl-octahydroindole (8HMI, \( Y_{\text{H}_2} =15\% \)) turned out to be relatively active, for which the formation of 1-methyl-4,5,6,7-tetrahydroindole (4HMI) was detected by GC-MS analysis. At temperatures of 190–220 °C (1 h), the activity of the 10HQ and 14HP heterocycles during dehydrogenation was also quite low. An increase in the reaction time (from 1 h to 3 h) and catalyst loading (increasing the ratio of Pd to substrate from 1:200 to 1:20) had no significant effect on the 14HP dehydrogenation rate—the \( Y_{\text{H}_2} \) was 17% instead of 5%. The results obtained are consistent with the data from [20], in which a high conversion of the starting compounds at comparable ratios of Pd to substrate (1:100) was achieved only as a result of a long dehydrogenation process (more than 10 h). With an increase in temperature to 240 °C, a significant increase in the hydrogen yield was observed for all heterocycles. Thus, for 10HQ and 14HP, \( Y_{\text{H}_2} \) values

### Table 1. Characteristics of palladium-containing catalysts and activity in dehydrogenation of 14HP.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Synthesis Details</th>
<th>( D_{\text{CO}} ), %</th>
<th>( S_{\text{BET}} ), m²/g</th>
<th>( Y_{\text{H}_2} ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>[23]</td>
<td>39</td>
<td>325</td>
<td>78</td>
</tr>
<tr>
<td>A</td>
<td>AlO(OH), 550 °C</td>
<td>27</td>
<td>205</td>
<td>79</td>
</tr>
<tr>
<td>PdA-wi-N</td>
<td>Al₂O₃ wi by H₂[Pd(NO₃)₄], 500 °C</td>
<td>27</td>
<td>205</td>
<td>79</td>
</tr>
<tr>
<td>PdA-wi-Cl</td>
<td>Al₂O₃ wi by H₂[PdCl₄], 500 °C</td>
<td>27</td>
<td>205</td>
<td>79</td>
</tr>
<tr>
<td>PdA-ai120-N</td>
<td>Al₂O₃ ai by H₂[Pd(NO₃)₄], 120 °C</td>
<td>41</td>
<td>198</td>
<td>85</td>
</tr>
<tr>
<td>PdA-ai120-Cl</td>
<td>Al₂O₃ ai by H₂[PdCl₄], 120 °C</td>
<td>39</td>
<td>198</td>
<td>85</td>
</tr>
<tr>
<td>PdA-wi500-N</td>
<td>Al₂O₃ ai by H₂[Pd(NO₃)₄], 500 °C</td>
<td>59</td>
<td>43</td>
<td>94</td>
</tr>
<tr>
<td>PdA-wi500-Cl</td>
<td>Al₂O₃ ai by H₂[PdCl₄], 500 °C</td>
<td>59</td>
<td>46</td>
<td>89</td>
</tr>
</tbody>
</table>

1 Pd dispersion, according to CO chemisorption data measured for initial systems and after reduction at 100 °C (H₂, 1 h). 2 Yield of hydrogen. 14HP dehydrogenation (1 mmol) in 3 mL of tetraglyme at 240 °C, in presence of 50 mg of catalyst (Pd: substrate was nearly 1:200). 3 Sample of Pural SB-1 calcinated at 550 °C (3 h).
of 74% and 78%, respectively, were obtained. In the case of the 8HMI, a near-quantitative yield of 94% was detected (Figure 3).

![Figure 3](image_url)

Figure 3. Comparative activity of the studied heterocycles in the dehydrogenation process in presence of 1 wt.% Pd/C.

Figure 4 shows the kinetic curves of H₂ release depending on reaction time, obtained using a weight system. The curves were obtained by subtracting data recorded during the catalytic reaction (heating a mixture of catalyst, substrate, and tetraglyme) from data recorded at a similar temperature heating profile of the reactor without the catalytic reaction (substrate and tetraglyme only). In general, the data obtained indicated a significantly greater activity of the 8HMI compared to the 14HP and 10HQ. The high activity of the 8HMI in dehydrogenation was presumably caused by two factors. First, the presence of a five-membered ring facilitated the reduction of the dehydrogenation enthalpy and increased the process efficiency. Also, according to the data from [28], the presence of an alkyl substituent at the nitrogen atom reduced the efficiency of adsorption of the reaction product on Pd particles, thus, increasing the availability of active sites on the catalyst.

Table 2 shows the distribution of the reaction products from the dehydrogenation of 10HQ, 14HP, and 8HMI (240 °C, 1 wt.% Pd/C and PdA-WI-500-N catalyst, 1 h). In all cases, no side products formed as a result of the hydrogenolysis of CN bonds of the heterocycles. However, in the case of the phenazine and quinoline, the formation of trace amounts of 1-methyl- and 1-ethyl-1,2,3,4-tetrahydroquinoline, as well as similar compounds for 5,10-dihydrophenazine, was noted (Table 2). Their formation was associated with a slight (<0.1%) degradation of the process solvent tetraglyme, which led to the formation of methyl and ethyl fragments alkylating unprotected nitrogen atoms. Also, trace amounts of the products of the tetraglyme hydrogenolysis of triethylene and diethylene glycols were detected in the chromatograms. At the same time, it should be noted that the decomposition of tetraglyme occurred as a result of a catalytic reaction. According to the thermal stability analysis of 0.1 M solutions of 10HQ, 14HP, and 8HMI heterocycles in tetraglyme (260–270 °C; 3 h), the GC-MS chromatograms of the initial and final solutions were the same.
Figure 3. Comparative activity of the studied heterocycles in the dehydrogenation process in presence of 1 wt.% Pd/C.

Figure 4. Kinetic curves of hydrogen evolution (reaction conditions: 240 °C, 50 mg 1 wt.% Pd/C, 1 mmol of substrate in 3 mL of tetraglyme, ratio of palladium and substrate close to 1 to 200).

Table 2. Distribution of dehydrogenation products of nitrogenous heterocycles 10HQ, 14HP, and 8HMI.

<table>
<thead>
<tr>
<th>LOHC Pairs</th>
<th>GC-MS Detected Compounds</th>
<th>Yi 1, mol.%</th>
<th>Pd/C</th>
<th>Pd/Al₂O₃ 2</th>
<th>YH₂, %</th>
<th>Pd/C</th>
<th>Pd/Al₂O₃ 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q/10HQ</td>
<td>«10H»: (cis, trans)-decahydroquinoline (10HQ)</td>
<td>8</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«4H»: 1,2,3,4-tetrahydroquinoline (4HQ-c);</td>
<td>7.4</td>
<td>3.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5,6,7,8-tetrahydroquinoline (4HQ-n);</td>
<td>26.6</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1-methyl-4HQ-c, 1-ethyl-4HQ-c</td>
<td>trace</td>
<td>trace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«0H»: quinoline (Q)</td>
<td>57.9</td>
<td>81</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MI/8HMI</td>
<td>«8H»: (cis, trans)-1-methyl-octahydroindole (8HMI)</td>
<td>0.8</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«4H»: 1-methyl-4,5,6,7-tetrahydroindole (4HMI)</td>
<td>6</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«2H»: 1-methyl-indoline (2HMI)</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«0H»: 1-methyl-indole (MI)</td>
<td>91</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P/14HP</td>
<td>«14H»: tetradecahydrophenazine (14HP)</td>
<td>trace</td>
<td>trace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«8H»: 1,2,3,4,6,7,8,9-octahydrophenazine (8HP-n);</td>
<td>0.3</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(cis, trans)-1,2,3,4,4a,5,10,10a-octahydrophenazine (8HP-c)</td>
<td>21</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«4H»: 1,2,3,4-tetrahydrophenazine (4HP)</td>
<td>28.9</td>
<td>11.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«2H»: 5,10-dihydrophenazine (2HP);</td>
<td>1.8</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5-methyl-2HP, 5,10-dimethyl-2HP, 5-ethyl-2HP</td>
<td>trace</td>
<td>trace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>«0H»: phenazine (P)</td>
<td>48.4</td>
<td>82.7</td>
<td></td>
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</tr>
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</table>

1 Yield of intermediate dehydrogenation products measured by GC. 2 Sample of 1 wt.% Pd/γ-Al₂O₃ marked as PdA-WI-500-N.

2.3. Thermodynamic Regularities of Dehydrogenation Mechanism of the Studied N-Heterocycles

In order to further investigate the mechanism of dehydrogenation of the investigated substrates, potential-free energies of formation were calculated for the initial fully hydrogenated compounds and for the final fully dehydrogenated compounds, as well as for the most plausible intermediate states lying in between. Among the selected intermediates, those with separated double bonds were omitted, due to the fact that completion of aromatic fragments was much more energetically favorable, making it an obviously preferred reaction pathway. Additionally, when applicable, all geometry optimization and frequency calculations were performed for trans-conformations of the studied compounds.
and intermediates, due to their higher thermodynamic stabilities (Figure 5). The geometry coordinates of the optimized compounds are provided in Tables S1–S14 (Section SM.3 in the Supplementary Materials).

Figure 5. Thermodynamic profile of possible reaction pathways for: (a) 14HP, (b) 10HQ and (c) 8HMI. Values of potential-free energies (kJ/mol) shown below structural formulas for all compounds and intermediates were relative to initial, fully hydrogenated compounds for which respective enthalpies of formation was set to zero. Values (kJ/mol) shown above arrows corresponded to the difference in potential-free energies for each corresponding reaction.

As can be seen from the thermodynamic profiles presented in the Figure 5a–c, the energetically preferred reaction pathway for all investigated substrates was the initial dehydrogenation of the nitrogen-containing heterocyclic fragment. Moreover, heterocyclic fragments with higher nitrogen mass fractions (such as Figure 5a) demonstrated noticeably higher tendencies to dehydrogenate, which was, however, downplayed by further intermediate stages having high energy barriers.

As can be also concluded from the thermodynamic calculations, various nitrogen-containing heterocycles in the structures of the studied compounds affected the dehydrogenation barriers of the adjacent hydrocarbon aromatic fragments differently, with 1-methyl-octahydroindole having the lowest barrier of all, as follows: decahydroquinoline (64.5 kJ/mol) > tetradecahydrophenazine (55.8 kJ/mol) > 1-methyl-octahydroindole (35.8 kJ/mol). Additionally, 1-methyl-octahydroindole (Figure 5c) was shown to be the most active in the dehydrogenation reaction, which consisted of stages that exhibited relatively low energy barriers. Therefore, based on the two aforementioned factors, we concluded that 1-methyl-octahydroindole was the most preferred of the studied compounds in the field of hydrogen storage.

Both decahydroquinoline and 1-methyl-octahydroindole dehydrogenation thermodynamic profiles corresponded well with the experimental chromatography data, which clearly showed the prevalence of intermediates with dehydrogenated heterocycles (e.g., Figure S1). For instance, in the case of the 10HQ dehydrogenation, the preferred formation
of 4HQ was observed. Thus, we concluded that the dehydrogenation of aromatic rather than heteroaromatic fragments was a rate-limiting stage. A similar situation was also observed in the case of the 8HMI.

However, there was also a discrepancy between the thermodynamic calculations and the experimental data in the case of the tetradehydrophenazine, since chromatographical analysis showed a near absence of the 8HP-n intermediate, which corresponded to dehydrogenation of the central heteroaromatic fragment (Figures S2 and S3). This discrepancy could be attributed to kinetic effects originating from the fact that the prevalent trans–trans conformation of tetradehydrophenazine can hinder synchronous C-H bonds’ dissociation on the surface of the Pd-catalyst, due to hydrogen atoms facing opposite sides of the heterocycle, as can be seen in the Figure 6. Nevertheless, initial dehydrogenation of the adjacent cycle alleviates steric hindrance and allows for quick dehydrogenation of the central pyrazine fragment, which was observed according to chromatographical analysis. It also should be noted that, according to chromatographical analysis of the reaction pathway, once the 8HP-n intermediate was formed, its further conversion was hindered, which did correlate with thermodynamic calculations.

Figure 6. Molecular structure of (a) tetradehydrophenazine and its dehydrogenated intermediate (b) 8HP-c according to DFT calculations (B3LYP[GD3BJ]/6-31+G*). Red lines and circles denote hydrogen atoms facing the opposite sides of the molecular plane and thus creating sterically hindered for dehydrogenation reaction. Green lines and circles denote hydrogen atoms facing similar sides of the molecular plane and thus being stericly accessible to dehydrogenation.

3. Materials and Methods

3.1. Catalyst Preparation

To study the dehydrogenation of the series of heterocycles, a 1 wt.% Pd/C catalyst sample was used as a prototype, and was synthesized according to the technique developed at the Boreskov Institute of Catalysis by A.V. Romanenko and P.A. Simonov [22–24].

For the development of palladium-containing dehydrogenation catalytic systems, those based on alumina (γ-Al₂O₃) and commercially available pseudoboehmite (AlO(OH) Pural SB-1, Sasol, Sandton, South Africa) were used as precursors of the γ-Al₂O₃ support. The support precursors were precalcined at 550 °C (for 3 h) to obtain gamma alumina (γ-Al₂O₃) [26].

For the synthesis of the 1 wt.% Pd/γ-Al₂O₃ catalysts, wetness impregnation (the WI method) and adsorption impregnation (the AI method) techniques were utilized using H₂[Pd(NO₃)₃] and H₂[PdCl₄] (Reachim, Moscow, Russia) as active component precursors.

In the case of the WI method, the previously prepared and dried support was impregnated with the palladium salt solution of the required concentration to obtain 1 wt.% Pd⁴⁺/Al₂O₃-WI systems, and then calcined at a temperature of 500 °C. Next, the resulting samples were impregnated with a 3 mL 0.5 M aqueous solution of sodium borohydride (NaBH₄, Fluka Chemie, Buchs, Switzerland), washed with distilled water, and then with acetone, followed by drying in air flow to obtain PdA-WI-N and PdA-WI-Cl catalytic systems, depending on the type of metal precursor.

In the case of the adsorptive impregnation, 2 g of γ-Al₂O₃ were dispersed in 20 mL of an EDTA (56 mg) solution in distilled water using a magnetic stirrer (at 600 rpm), then
in 1 mL of an aqueous solution of the Pd precursor (H₂[Pd(NO₃)₄] or H₂[PdCl₄]) of the required concentration, which was then stirred for one hour (at 600 rpm). The resulting samples of 1 wt.% Pd²⁺/Al₂O₃-Al were filtered off, dried at 120 °C, and calcined at 500 °C. Next, the resulting systems were reduced in a solution of 20 mL of NaBH₄ solution (0.5 M) in distilled water using a magnetic stirrer (for 1 h, at 60 °C, at 600 rpm) to obtain the catalysts PdA-Al-500-N and PdA-Al-500-Cl, depending on the metal precursor type. A part of the 1 wt.% Pd²⁺/Al₂O₃-Al systems was reduced via a similar procedure, without isolating the calcination stage, to obtain PdA-Al-120-N and PdA-Al-120-Cl catalysts after filtration, which were then washed with acetone, followed by drying in air flow.

### 3.2. Catalyst Characterization

A number of techniques were used to characterize the initial support and the synthesized catalytic systems. X-ray diffraction analysis of the samples was carried out using an ARL X’tra (Thermo Fisher Scientific, Waltham, Massachusetts, USA) diffractometer using CuKα radiation (λ = 1.5418 Å). The survey was carried out in the angle range of 10–80° with a step of 2θ = 0.02° and a speed of 1°/min using a Mythen2R 1D linear detector (Decstris, Baden, Switzerland). The dispersity of the metal particles and the microstructure of the catalysts were studied using transmission electron microscopy. The images were taken by means of a JEM-2010 instrument (JEOL Ltd., Tokyo, Japan) operated at an accelerating voltage of 200 kV and a lattice resolution of 0.14 nm. Specific surface area (S_{BET}) measurements, using the BET method, were carried out by low-temperature nitrogen adsorption on an ASAP-2400 instrument (Micromeritics, Norcross, GA, USA). CO chemisorption was measured in a pulsed mode on an analyzer “Chemisorb” (MLE, Novosibirsk, Russia), equipped with a thermal conductivity detector. 50 mg of the catalyst were loaded into a U-shaped quartz reactor and treated with H₂ flow (100 cm³/min) at temperatures of 20 and 100 °C, with a heating rate of 10 °C/min. The reactor was kept at the final temperature for 20 min, then purged with argon and cooled to room temperature. After cooling, pulses of the CO (0.1 cm³) were applied to the reactor until the sample was saturated, and the amount of chemisorbed CO was estimated.

### 3.3. Thermostability Test of Heterocycles and Dehydrogenation Reaction

The initial hydrogenated heterocyclic substrates—tetradecahydrophenazine (14HP), decahydroquinoline (10HQ), and 1-methyl-octahydroindole (8HMI)—were synthesized from commercially available phenazine, quinoline, and 1-methylindole (all Sigma Aldrich, St. Louis, MO, USA). Synthesis procedures are given in the SM. ¹H-NMR and GC-MS methods confirmed the purity of the obtained compounds (over 99.7%).

To study the thermal stability of the heterocycles, 0.1 M solutions of 10HQ, 14HP, and 8HMI in tetraglyme were placed in sealed glass ampoules filled with argon, and subjected to thermolysis at temperatures (260–270 °C). Next, the ampoules were opened and the resulting mixtures were analyzed by the GC-MS method.

To study the process of dehydrogenation of the hydrogenated forms of the N-heterocycles, a reaction unit was prepared according to [27,29]. The setup consisted of a three-necked flask (50 mL, reflux condenser, Ar or H₂ supply line and reaction sampling line) immersed in a metal jacket with a temperature controller, and a hydrogen measuring system based on the displacement of water with increasing gaseous volume in the reactor formed by the dehydrogenation (Figure 7). The approach to the gravimetric measurement of the kinetics of H₂ release, that occurred during the reaction, was adopted from [30]. The error in measuring the rate of H₂ release according to the weight system was estimated as ±2 mL/h.
In a standard test to study the activity of the heterocycles, 50 mg of a catalyst were loaded into the reactor, the system was purged with argon (20 mL/min, 5 min, RT) and hydrogen (20 mL/min, 30 min, 100 °C). Upon completion of the reductive activation of the catalyst, the system was cooled to room temperature in an argon flow, and a suspension of 1 mmol of a nitrogenous heterocycle in 3 mL of a solvent (tetraethylene glycol dimethyl ether (tetraglyme), hexadecane, or decalin, Acros Organics, Geel, Belgium) was introduced. Next, the reactor was sealed, connected to the weight analysis line, stirred (500 rpm), and the reaction mixture was heated to the reaction temperature (140, 190, 220 or 240 °C) for 15 min (0–900 s). When using tetraglyme (3 mL) as a solvent, the increase in the gas volume of the reactor due to thermal expansion (up to 240 °C) was estimated as 19 ± 1 mL. The dehydrogenation process was carried out for 45 min (900–3600 s), followed by switching off the stirring and removing the reactor from the heating zone. A sample of the reaction mixture was separated from the catalyst particles by centrifugation and analyzed with GC or GC-MS methods to evaluate the amount of dehydrogenated forms of heterocycles and the hydrogen yield from the theoretical one (Y_{H_2}, %), demonstrated here:

\[
Y_{H_2}(10HQ \text{ dehydrogenation}) = Y_Q + 3/5Y_{4HQ}
\]

\[
Y_{H_2}(8HMI \text{ dehydrogenation}) = Y_{MI} + 3/4Y_{2HMI} + 1/2Y_{4HMI}
\]

\[
Y_{H_2}(14HP \text{ dehydrogenation}) = Y_P + 6/7Y_{2HP} + 5/7Y_{4HP} + 3/7Y_{8HP}
\]

where \(Y_{H_2}\) was the overall H_2 yield, defined as a percentage, and \(Y_i\) was the product/intermediate yield, defined as a percentage.

To study the kinetics of the tetradecahydrophenazine dehydrogenation at similar substrate and solvent loadings, a reduced catalyst loading (25 mg) was used. After reaching the temperature in the reactor of 240 °C, over the next 2 h of the process, aliquots (20 μL) were taken from the reaction mixture every 20 min. The collected samples were diluted with acetone (1 mL), centrifuged to separate the catalyst particles, and analyzed using the GC method.

GC analysis was performed using an Agilent-7890A (Santa Clara, CA, USA) gas chromatograph equipped with a ZB-5HT column. Details of the analysis are given in the SM. GC-MS measurements were performed using an Agilent 7000B (Santa Clara, CA, USA) equipped with an HP-5 column. Mass spectra were taken at an electron ionization energy of 70 eV and a scan range of m/z 40–500.
3.4. Computational Details

Molecular geometries of the investigated compounds and intermediates were fully optimized in the gas phase in their respective ground states at the DFT level utilizing B3LYP [31], hybrid functionals coupled with 6-31+G* [32] basis sets, and GD3BJ [33] empirical dispersion. Subsequent calculation of the vibrational frequencies at harmonic approximation, utilizing previously obtained molecular geometries at the B3LYP/GD3BJ/6-31+G* level of theory, showed no presence of the imaginary frequencies. Studied thermodynamic potentials were calculated utilizing the aforementioned vibrational frequencies. All presented quantum chemical calculations were performed with the help of the ORCA 5.0.0 [34] computational package.

4. Summary

The study of the dehydrogenation of 1-methyl-octahydroindole (8HMI), tetradecahydrophenazine (14HP), and decahydroquinoline (10HQ) over Pd/Al₂O₃ and Pd/C catalysts was carried out. The alumina-supported Pd metal catalysts were prepared by adsorptive impregnation as well as wetness impregnation techniques using two different salts as a Pd source. The degree of experimental/theoretical hydrogen yield in the dehydrogenation of the N-heterocycles (after 3600 s at T = 240 °C) in the presence of both Pd alumina- and carbon-supported catalysts appeared to be in the following order: 10HQ ≈ 14HP < 8HMI. Thence, 1-methyl-octahydroindole appeared to be the most promising N-containing LOHC with the highest yield of hydrogen (~99 mol.%).

Computational study has shown that despite the lowest energetic barrier in the case of dehydrogenation of central nitrogen-containing heteroaromatic fragment, it is the slowest due to steric constrains, making dehydrogenation of a side ring a preferential reaction pathway. From the standpoint of thermodynamics, it was concluded that 1-methyl-octahydroindole was the most preferred of the studied compounds for hydrogen storage.

The 14HP had been chosen for further studies because of its three-ring structure. Varying the pathways of synthesis of the Pd catalysts supported by alumina allowed for augmentation of the hydrogen yield in the dehydrogenation of 14HP, compared to the carbon-supported catalytic system. The highest yield of hydrogen (~94 mol.%) was shown in the presence of a Pd/γ-Al₂O₃ sample (at 1 mmol of 14 HP in 3 mL of tetruglyme, 240 °C, 50 mg of catalyst) prepared through adsorptive impregnation of the alumina by a palladium nitrate salt solution.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12101260/s1, Figure S1: Influence of the reaction temperature on the composition of the dehydrogenation reaction products of 1-methyl-octahydroindole; Figure S2: Study of tetradecahydrophenazine dehydrogenation kinetics; Figure S3: Intermediate products detected at tetradecahydrophenazine dehydrogenation; Table S1–S14: The geometry coordinates of the optimized compounds.

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