Mendeleev Communications

Mendeleev Commun., 2025, **35**, 356–358

Dehydrogenation of *N*-ethyldodecahydrocarbazole over Pt/C catalyst in the hydrogen storage aspect

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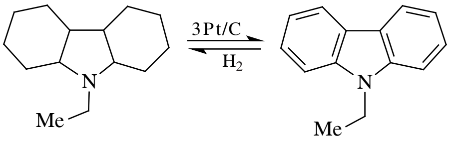
DOI: 10.71267/mencom.7652

The optimum conditions ($T = 210$ °C and $V_L = 1$ h^{-1}) were determined for the dehydrogenation of *N*-ethyldodecahydrocarbazole on a 3 wt% Pt/C catalyst in a flow-type catalytic unit at normal pressure. The kinetic parameters (conversion and selectivity) of the dehydrogenation process correlated well with the volumes of released hydrogen. High purity of the thus produced hydrogen was established by chromatography.

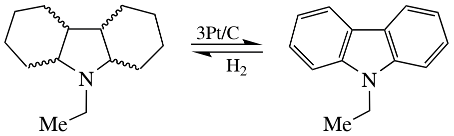


Keywords: hydrogen storage, hydrogenation, dehydrogenation, Pt/C catalyst, liquid organic hydrogen carriers, *N*-ethyldodecahydrocarbazole.

One of the promising directions of environmental energy of the future is based on the use of hydrogen fuel cells;[1] however, their wide application is impossible without the development of effective systems for storage and separation of chemically pure hydrogen. The most known systems have a number of disadvantages related to explosion safety, mass and dimensional characteristics of the systems and low capacity and purity of the released hydrogen.[2] The use of liquid organic hydrogen carriers for hydrogen storage and extraction, such as pairs of arene/naphthene compounds capable of cyclic processes of saturation (hydrogenation) and H_2 extraction (dehydrogenation), largely avoids these problems.[3–6] Since hydrogen is an element in the structure of naphthenic compounds, its density and content do not depend on external factors and determine complete explosion safety of storage and transportation of H_2 in naphthenes under normal conditions. However, high temperatures of dehydrogenation of hydrogen-containing naphthenes, at which hydrogen would release, are unfavorable for the operation of hydrogen fuel cells. At the same time, the calculation shows[7] that replacement of a carbon atom in carbocyclic aromatic hydrocarbons by nitrogen, sulfur or oxygen-containing groups contributes to lowering the standard enthalpy of hydrogenation $\Delta H^{\circ}_{H_2}$ of the formed heterocyclic compound. Together with this, fused molecules with alternating benzene rings and π-conjugated five-membered nitrogen-containing rings have a lower standard enthalpy of hydrogenation than molecules with other ring combinations. This means[7] that hydrogen extraction from the corresponding nitrogen-containing heterocyclic compounds should occur at lower temperatures than that in the dehydrogenation of their carbocyclic analogs.[8–10] At the same time, the enthalpies of dehydrogenation of systems based on such compounds as tetrahydropyrrole, tetrahydrothiophene and tetrahydrofuran, in the structure of which heteroatoms of nitrogen, sulfur or oxygen are present, increase in the series $[N] \ll [S] \sim [O]$ and are equal to 40, 50 and 51 kcal mol^{-1} H_2, respectively.[6] This indicates an increase in thermodynamic limitations in the dehydrogenation reaction of sulfur- and oxygen-containing compounds compared to nitrogen-containing compounds.

The simplest compound fitting this prerequisite is carbazole ($C_{12}H_9N$; mp = 246 °C, bp = 355 °C), the theoretical hydrogen capacity of which is 7.19 wt%. In particular, the complete conversion of carbazole during hydrogenation in autoclave on the Rh/C catalyst was achieved at a temperature of 150 °C,[8–10] and even at a temperature of 125 °C and a pressure of 69 bar,[7] which is noticeably lower than that required for benzene hydrogenation.[6,11,12] The disadvantage is the side formation of dicyclohexyl ($C_{12}H_{22}$), which is formed when the ring containing a heteroatom is eliminated.[8] In the hydrogenation of pyridine and its derivatives in the temperature range of 100–150 °C and pressure of 70 bar on Pd/Al_2O_3, Pd/C, PtO_2 and Rh/C catalysts, hydrogenolysis reaction products were also detected. To avoid such side reactions, shielding of the heteroatom with alkyl substituents can be employed, the presence of which contributes to the stability of substituted carbazoles to ring opening reactions; however, this leads to a decrease in the potential capacity of hydrogen stored in such compounds.

The standard enthalpy of hydrogenation of *N*-ethylcarbazole **1** ($C_{12}H_8$–N–C_2H_5; mp = 68 °C, bp = 270 °C) and dehydrogenation of *N*-ethyldodecahydrocarbazole **2** (Scheme 1) with respect to hydrogen is $\Delta H^{\circ}_{H_2} = -50.5 \pm 0.8$ kJ mol^{-1}, which is ~20 kJ mol^{-1} less than that for the benzene–cyclohexane



2
Mixture of stereoisomers

1

Scheme 1

system.[13,14] The above substrates are able to accumulate and release up to 5.0–6.0 wt% H_2 at a temperature of about 200 °C; however, the dehydrogenation reactions are rather slow.[8] Moreover, the maximum hydrogen recovery is usually achieved in the course of a prolonged reaction in a closed system. One of the main conditions for the use of mobile hydrogen storage systems is fast discharge. Thus, in the dehydrogenation of tetrahydrocarbazole in an autoclave on the 5 wt% Pd/Al_2O_3 catalyst at a temperature of 140 °C with 100% selectivity for carbazole, the maximum conversion does not exceed 81% even after 24 h of the reaction. When a homogeneous iridium complex was used as a catalyst, 100% conversion of *N*-ethyldodecahydrocarbazole **2** was achieved at 200 °C, but semi-hydrogenated compounds (*N*-ethylated octa- and tetrahydrocarbazoles) were also formed. Significant progress was achieved in the dehydrogenation of *N*-ethyldodecahydrocarbazole **2** in an autoclave on the 4 wt% Pd/SiO_2 catalyst, when 100% conversion and selectivity for *N*-ethylcarbazole **1** were obtained after 1.6 h of the reaction.[8]

It is known that rapid hydrogen evolution from reaction products is provided by processing in a flow catalytic unit.[6] At the same time, it is also known that the use of platinum-containing catalysts allows one to reduce the temperature of dehydrogenation of aromatic fused compounds. The aim of the present work is to select parameters and to estimate the hydrogen evolution rate in the dehydrogenation reaction of *N*-ethyldodecahydrocarbazole **2** in a flow-type catalytic unit on a heterogeneous catalyst of 3 wt% Pt/C.

The product of complete dehydrogenation of *N*-ethyldodecahydrocarbazole **2**($C_{14}H_{25}N$) is *N*-ethylcarbazole **1** ($C_{14}H_{13}N$) (see Scheme 1). Semi-hydrogenated compounds should be formed as intermediate products: *N*-ethylated tetrahydro ($C_{14}H_{17}N$), hexahydro ($C_{14}H_{19}N$) and octahydro ($C_{14}H_{21}N$) carbazoles. The chromatogram of the tested sample of *N*-ethyldodecahydrocarbazole **2** as the mixture of stereoisomers and the conditions of the reaction are given in Online Supplementary Materials.

The values of the volumes of hydrogen released in the course of the dehydrogenation of compound **2** over the 3 wt% Pt/C catalyst as a function of temperature and volumetric rate of substrate supply at normal pressure ($P = 1$ atm) are shown in Figure 1. It can be seen that at normal pressure the character of curves (panels *a* and *b*) changes at the inflection points corresponding to temperature $T = 210$ °C and volumetric rate of substrate feed $V_L = 1$ h^{-1}, where both lines go from convex to concave. Since at other points the character of kinetic parameters of the reaction changes differently, these conditions ($T = 210$ °C, $V_L = 1$ h^{-1} and $P = 1$ atm) are accepted as the main ones for further studies of the dehydrogenation reaction of *N*-ethyldodecahydrocarbazole **2**.

The time dependence of the volume of released hydrogen in the dehydrogenation reaction of compound **2** over the 3 wt% Pt/C catalyst in a flow reactor is shown in Figure 2. The uniform character of the variation of the values of the volume of released hydrogen as a function of time indicates the stability of the 3 wt% Pt/C catalyst with respect to the dehydrogenation process. The values of substrate conversion and selectivity for main reaction products as a function of time are summarized in Table S1 (see Online Supplementary Materials).

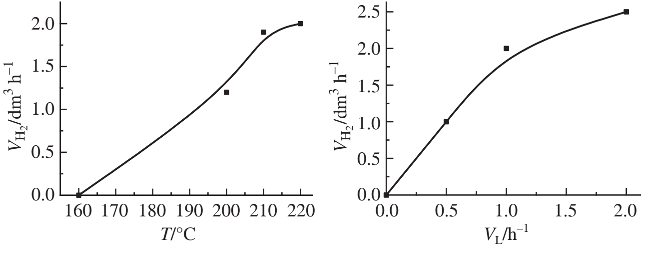


Figure 1 Dependence of the volume of hydrogen released in the dehydrogenation of *N*-ethyldodecahydrocarbazole **2** on (*a*) temperature and (*b*) substrate feed rate.

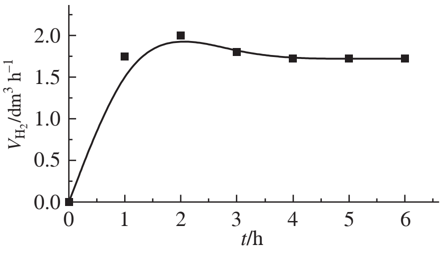


Figure 2 Time dependence of the volume of hydrogen released in the dehydrogenation reaction of dodecahydro-*N*-ethylcarbazole ($T = 210$ °C, $V_L = 1$ h^{-1} and $P = 1$ atm)

The theoretical calculated value of the hydrogen volume to be obtained in the course of dehydrogenation **2** → **1** at a substrate feed rate of 1 h^{-1} (linear feed rate 6 ml h^{-1}; catalyst volume 6 cm^3) should be 3.89 dm^3 h^{-1}. Taking into account the content of 77 wt% of *N*-ethyldodecahydrocarbazole **2** in the investigated sample, it corresponds to the maximum volume of hydrogen release, 3.00 dm^3 h^{-1}. However, Figure 2 shows that as a result of the dehydrogenation reaction of the investigated sample at $T = 210$ °C and $V_L = 1$ h^{-1} on the 3 wt% Pt/C catalyst in the flowing unit, the value of the volume of released hydrogen is 1.8–1.9 dm^3 h^{-1} within 6 h of the experiment. This corresponds to a conversion of about 60–65% of the calculated value or a hydrogen capacity of about 3.5 wt%.

Analysis of the reaction products of the experiment shows the absence of hydrogenolysis and cracking products. The analysis of gaseous reaction products showed the presence of only pure hydrogen in the sample without impurities of light hydrocarbons and carbon oxides. Taking into account the conversion and selectivity of the formed reaction products, the hydrogen release rate corresponds to the theoretically possible value. This indicates that the parameters $T = 210$ °C and $V_L = 1$ h^{-1} are optimal for the dehydrogenation reaction at normal pressure and provide a complete conversion of the substrate to the initial product (*N*-ethylcarbazole **1**) without loss of hydrogen capacity incorporated in this system. At the same time, it is known that for cycloalkanes the most efficient hydrogen extraction occurs at liquid-phase dehydrogenation, when under the conditions of distillation due to simultaneous boiling and evaporation of the substrate the latter is located between gas and ‘liquid film’. During the dehydrogenation, the thin ‘liquid film’ is superheated, which promotes the endothermic reaction. Hydrogen diffuses freely into the gas phase through the thin film of organic liquid without formation of bubbles. Relatively small differences between the boiling point of the substrate and the temperature of the dehydrogenation ($T = 210$ °C), in this case, apparently do not contribute to the formation of a ‘thin film’, and liquid-phase dehydrogenation is not realized quite effectively.

To summarize, dehydrogenation of *N*-ethyldodecahydrocarbazole **2** in a flow-type reactor under selected conditions occurs with high conversion rates. The selectivity for the main product, *N*-ethylcarbazole **1**, is higher than that in most previous studies in batch reactors. High purity of the thus released hydrogen is chromatographically established, which is important for fuel cell operation. However, due to the formation of semi-hydrogenated *N*-ethyl tetra-, hexa- and octahydrocarbazoles, the rate of hydrogen evolution and the hydrogen capacity of the investigated substrate are lower than those expected and noticeably inferior to carbocyclic analogs.

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (project 075-15-2023-585).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7652.

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Received: 16th October 2024; Com. 24/7652