ISSN 0965-5441, Petroleum Chemistry, 2016, Vol. 56, No. 1, pp. 38–43. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © N.V. Vereshchagina, T.N. Antonova, A.A. Il'in, Zh.B. Chirkova, 2016, published in Neftekhimiya, 2016, Vol. 56, No. 1, pp. 46–51.

Features of Dicyclopentene Formation during Hydrogenation of Dicyclopentadiene

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Received January 15, 2015

Abstracts—General trends and specific features of the reaction of dicyclopentadiene (tricyclo[5.2.1.0$^{2.6}$]decadiene-3,8) hydrogenation to dicyclopentene (tricycle[5.2.1.0$^{2.6}$]decene-3) with hydrogen in the liquid phase under mild conditions at atmospheric pressure over a finely divided 1% Pd/C catalyst have been studied. The kinetic parameters that characterize the effect of the solvent nature, catalyst concentration, and temperature on the rate of hydrogen uptake in the hydrogenation process have been determined. To substantiate the conclusion of the sequence of saturation of the dicyclopentadiene double bonds in terms of the mechanism of heterogeneous catalysis, their reactivity has been compared. It has been shown that in the presence of a number of functionalized aromatic compounds as a stabilizing additive, the yield of desired dicyclopentene increases to 98.5–99 mol % with the complete conversion of dicyclopentadiene. The structure of dicyclopentadiene and its hydrogenation product dicyclopentene has been confirmed using spectroscopic methods.

Keywords: dicyclopentadiene, dicyclopentene, liquid-phase hydrogenation, finely divided catalyst, double-bond reactivity

DOI: 10.1134/S0965544115080198

Dicyclopentene as the desired product of hydrogenation of dicyclopentadiene can be successfully used in the synthesis of various oxygenated products with various functional groups and individual structures, which is especially important for the production of biologically active substances and medicaments on their basis. Furthermore, oxygen-containing dicyclopentene derivatives are of interest for the fabrication of polymers, liquid crystals, and other materials [1–4].

The hydrogenation of dicyclopentadiene aimed to produce dicyclopentene (dihydrodicyclopentadiene) and dicyclopentane (tetrahydrodicyclopentadiene) was studied by many investigators using platinum group catalysts or nickel catalysts [4–12] in various solvents [5, 7, 8], primarily at an elevated hydrogen pressure (up to 10 MPa) [5–11]. For example, Ualikhanova et al. [5] noted that pressure elevation from 0.5 to 2.0 MPa during dicyclopentadiene hydrogenation on palladium black led to an increase in the rate of the process. The further increase in pressure to 4.0 MPa, conversely, reduced the rate by a factor of 4. As shown in the cited study and noticed by Behr et al. [6], an increase in the hydrogen pressure has a negative effect on the selectivity of the reaction. The ratio of the hydrogenation products dihydrodicyclopentadiene and tetrahydrodicyclopentadiene on a palladium catalyst with a particle size of 5–7 nm (nanocatalyst) may range from 7 : 1 to 1 : 8 depending on the pressure used.

At the same time, it was found [1] that in the case of dicyclopentadiene hydrogenation under atmospheric pressure over supported palladium catalysts, either finely divided or shaped, the yield of target dicyclopentene can be as high as 92 mol % and the dihydrodicyclopentadiene) (dicyclopentene) to tetrahydrodicyclopentadiene (dicyclopentane) ratio is 11.5 : 1. Finely divided catalysts are convenient for practical implementation of the process. By vigorous agitation, the three-phase gas–liquid–solid catalyst system is maintained in a pseudo-homogeneous state, which ensures the kinetic regime of the reaction [13, 14].

In this paper we present the results of studying the features of dicyclopentene formation during the hydrogenation of dicyclopentadiene at atmospheric pressure using a finely divided 1% Pd/C catalyst.

EXPERIMENTAL

Liquid-phase dicyclopentadiene hydrogenation with hydrogen was carried out in the presence of the finely divided 1% Pd/C catalyst, purchased from the All-Union Research and Design Institute for Monomers (VNIPIM), Tula, in a batch volumetric unit or a flow system in excess hydrogen. Experiments were evaluated by measuring the hydrogen uptake and the amount of products in the reaction mixture, which was analyzed by GLC. The data obtained made it possible to calculate the effective hydrogen uptake, the (degree of) conversion of dicyclopentadiene, and the yield of the products on a hydrogen absorbed or dicyclopentadiene consumed basis. The chromatographic analysis was performed on Chromatec Kristall 5000.2 instrument using a CR-5 capillary column of 30 m in length and 0.32 mm in diameter coated with 5% phenyl (95%) dimethylpolysiloxane, a film thickness of 0.5 μm. The evaporator temperature was 220°C, and the column temperature was programmed from 70 to 160°C at a heating rate of 10°C/min. The carrier gas (nitrogen) flow rate was 60 cm^3/min.

The structure of the reactant dicyclopentadiene (*endo*-tricyclo[5.2.1.$0^{2.6}$]decadiene-3,8) and its hydrogenation product dicyclopentene (tricyclo[5.2.1.$0^{2.6}$]decene-3) was confirmed using spectroscopic methods. ^1H NMR spectra were recorded on a Bruker DRX_500 instrument in DMSO-d_6 solutions at 30°C. As a reference standard for the chemical shift, the signals of residual solvent protons in the proton spectra ($\Delta\delta_H$ 2.50 ppm) were used.

Dicyclopentene (tricyclo[5.2.1.$0^{2.6}$]decene-3). ^1H NMR (500 MHz, DMSO-d_6): 1.26–1.16 (m, 4 H), 1.38 (1 H dt, $J = 9.1$ Hz, $J = 1.6$ Hz H-10’), 1.46 (1 H dt, $J = 9.1$ Hz, $J = 1.6$ Hz H-10), 2.11 (br. s, 1 H), 2.16 (2 H, ddd, $J = 9.3$ Hz, $J = 4.2$ Hz, $J = 2.2$ Hz, H-5), 2.27 (br. s., 1 H), 2.48 (1 H, ddd, $J = 9.3$, $J = 4.2$ Hz, $J = 1.6$Hz, H-6), 2.97 (1 H, ddd, $J = 2.4$ Hz, $J = 2.5$ Hz, $J = 4.6$ Hz, H-2), 5.56 (1 H, dddd, $J = 5.8$, $J = 4.6$ Hz, $J = 2.2$ Hz, $J = 0.8$ Hz H-3), 5.67 (1 H, ddd, $J = 5.8$, $J = 4.2$ Hz, $J = 2.2$ Hz, H-4).

RESULTS AND DISCUSSION

Figure 1 shows rate curves of hydrogen uptake during the hydrogenation of dicyclopentadiene in solvents of different natures (2-propanol, cyclooctane, toluene).

According to the data (Fig. 1), the dicyclopentadiene hydrogenation rate is the lowest in the toluene solution and the highest in the 2-propanol solution. The hydrogen uptake rate in 2-propanol is so high that it cannot be a differentiating solvent in the hydrogenation of double bonds. The dicyclopentadiene double bonds are hydrogenated successively, but continuously, almost at the same rate in this solvent (Fig. 1, curve *1*). At the same time, in the case of saturation of the double bonds of dicyclopentadiene in a cyclooctane or toluene solution, the hydrogen uptake rate curves exhibit distinct segments corresponding to the hydrogenation of a dicyclopentadiene double bond and then the double bond of dicyclopentene.

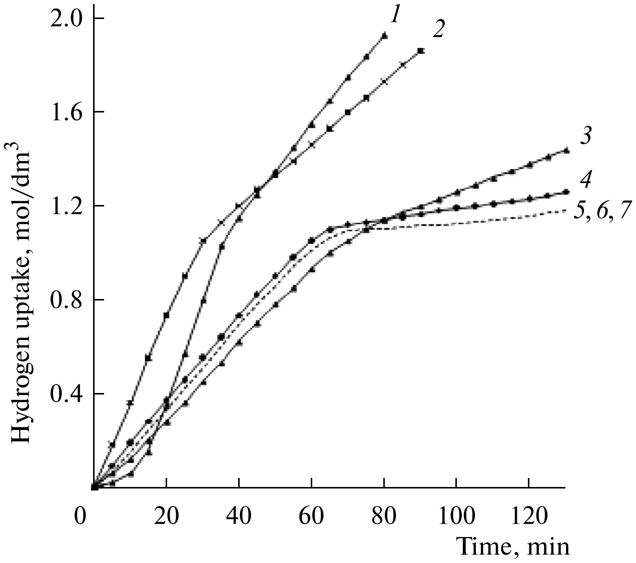


Fig. 1. Rate curves of hydrogen uptake during the hydrogenation of dicyclopentadiene.

$C_{cat} = 4$ g/dm^3; $C_{0,\ DCPD} = 1.04$ mol/dm^3; temperature, 333 K.

Solvents: (*1*) 2-propanol (313 K), (*2*) cyclooctane, (*3*) cyclooctane (323 K), (*4*) toluene, (*5–7*) toluene with (*5*) ionol, (6) *N*,*N*-dimethyl-*p*-phenylenediamine, and (*7*) hydroquinone additives in an amount of 1% of C_{cat}.

The rate of hydrogen uptake in the hydrogenation of the dicyclopentadiene double bond, as calculated from the data of Fig. 1, is greater than the rate of saturation of the dicyclopentene double bond in toluene (by a factor of 6.7) or cyclooctane (by a factor of 2.4) (Table 1).

It should be noted that in the case of hydrogenation in toluene, there was some period of time, during which hydrogen was actually not consumed (Fig. 1, curve *4*). This behavior shows toluene as a differentiating solvent that is a quite obviously preferred choice for the selective hydrogenation of dicyclopentadiene to dicyclopentene. The product formation sequence

Table 1. Ratio of rates of the double-bond hydrogenation reactions of dicyclopentadiene and dicyclopentene depending on the nature of the solvent

Solvent	T, K	Rate of hydrogenation of DCPD double bond ($W_{ef\,1}$), mol/(dm^3 min)	Rate of hydrogenation of DCP double bond ($W_{ef\,2}$), mol/(dm^3 min)	$W_{ef\,1}/W_{ef\,2}$
Cyclooctane	323	0.0163	0.0074	2.20
Cyclooctane	333	0.0343	0.0142	2.42
Toluene	333	0.0188	0.0028	6.71; 6.48*
Toluene	343	0.0333*	0.0050*	6.65*

* According to data in Fig. 3b.

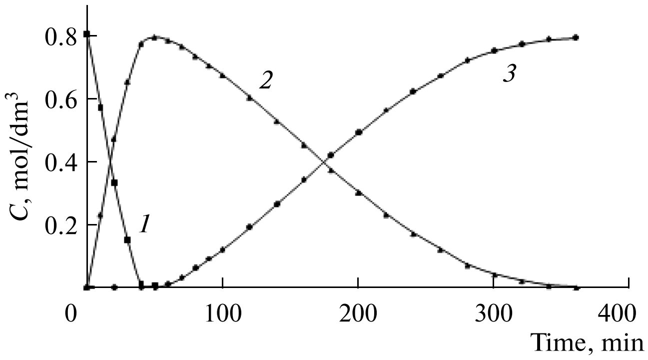


Fig. 2. Reactant consumption and product buildup rate curves in the dicyclopentadiene hydrogenation process.
Solvent: toluene; $C_{0\ DCPD} = 0.8$ mol/dm^3; $C_{cat} = 4$ g/dm^3; temperature, 338 K.
(*1*) dicyclopentadiene, (*2*) dicyclopentene, (*3*) dicyclopentane.

during the hydrogenation of dicyclopentadiene in the toluene solution is shown in Fig. 2.

The resulting ratio of the rates of hydrogenation of dicyclopentadiene double bonds is confirmed by the data on separate hydrogenation of dicyclopentadiene to dicyclopentene (dihydrodicyclopentadiene)) and dicyclopentene to dicyclopentane (tetrahydrodicyclopentadiene) over 1% Pd/C at their equal initial concentrations in the toluene solution (Figs. 3a, 3b; Table 1).

Thus, the ratio of the rate of double bond saturation in the bicycloheptene moiety of the dicyclopentadiene molecule to that in the five-membered ring of dicyclopentene depends on the solvent nature, but it is invariant to the initial concentration of the substrate in the feed solution and the reaction temperature.

To confirm the experimental data on the preferential hydrogenation of the double bond in the bicycloheptene moiety of the dicyclopentadiene molecule, we performed a comparative assessment of the reactivity of the double bonds of the hydrocarbons subject to hydrogenation using a quantum-chemical method (DFT simulation) with the ab initio/6-31 G** basis set. As a double-bond reactivity index, the electrostatic term of the Klopman equation ($I = |q_1 \cdot q_2|/l$) was used. It was calculated from the values of charge on carbon atoms at the double bonds with taking account of the bond lengths [15]. The simulation results describing the properties of the double bonds are presented in Table 2.

As follows from the data in Table 2, the Klopman charge/charge term for tricyclo[5.2.1.0$^{2.6}$]decadiene-3,8 has a lesser value for the double bond of the bicycloheptene (norbornene) moiety (8–9 position). Therefore, this double bond has a lower order with respect to the electrons that form it (i.e., is rehybridized) and, hence, a higher reactivity in the hydrogenation reaction as compared with the double bond in the 3–4 position of this molecule or the dicyclopentene double bond (quantity $1/I$, Table 2).

The fact that the selective reduction leaves intact the double bond between the C_3–C_4 carbon atoms of the tricyclo[5.2.1.0$^{2.6}$]decadiene-3,8 molecule was confirmed by spectral data (NMR, COSY spectra).

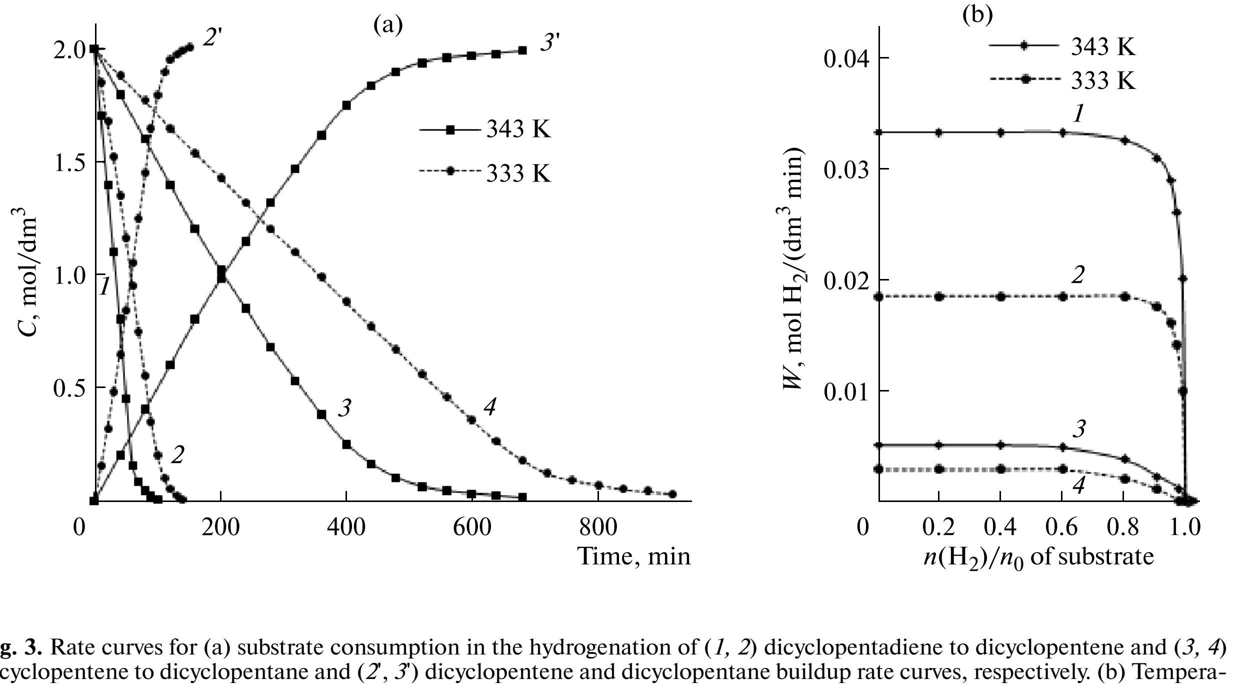
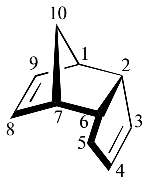
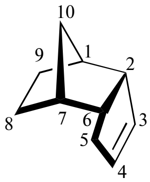


Fig. 3. Rate curves for (a) substrate consumption in the hydrogenation of (*1, 2*) dicyclopentadiene to dicyclopentene and (*3, 4*) dicyclopentene to dicyclopentane and (*2', 3'*) dicyclopentene and dicyclopentane buildup rate curves, respectively. (b) Temperature dependence of the rate of the process.
Solvent: toluene, $C_0 = 2.0$ mol/dm^3, $C_{cat} = 4$ g/dm^3.

Table 2. Energy characteristics of dicyclopentadiene and dicyclopentene and reactivity indices of their double bonds

Hydrocarbon to be hydrogenated	Total energy, kcal/mol	Bond length, l, nm	Charge on carbon atoms, q	$I \times 10^3$	$1/I \times 10^{-3}$
	−241180.4	**$-C_8{=}C_9-$** 0.13221	**C_8**. 0.009 **C_9**. 0.015	**$-C_8{=}C_9-$** 1.021	**$-C_8{=}C_9-$** 0.9793
Dipole moment (total) 0.1020	(−384.345)	**$-C_3{=}C_4-$** 0.13194	**C_3**. −0.024 **C_4**. 0.007	**$-C_3{=}C_4-$** 1.273	**$-C_3{=}C_4-$** 0.7854
	−242732.2	**$-C_3{=}C_4-$** 0.13223	**C_3**. −0.0125 **C_4**. −0.0125	**$-C_3{=}C_4-$** 1.1816	**$-C_3{=}C_4-$** 0.8463
Dipole moment (total) 0.1396	(−386.818)				

Similar quantum-chemical calculations using the B3LYP/6-31G* basis set were performed earlier by Zou et al. [10] to explain the specifics of dicyclopentadiene hydrogenation to dicyclopentane (tetrahydrodicyclopentadiene) on a skeletal nickel catalyst (SRNA-4) at a hydrogen pressure of 1.5 MPa. The set of their calculation results allowed the cited authors to conclude that the double bond of the norbornene moiety of the dicyclopentadiene molecule is superior in reactivity. However, they found that both 3,4-dihydrodicyclopentadiene and 8,9-dihydrodicyclopentadiene are formed as hydrogenation intermediates, which are then hydrogenated to tetrahydrodicyclopentadiene in the parallel reactions, but the double bond in the norbornene moiety of dihydrodicyclopentadiene disappears at a higher rate. According to the reported data [10], the nickel catalyst is not selective in the hydrogenation of the dicyclopentadiene double bonds, unlike the palladium catalyst (1% Pd/C) used in this work.

Figure 4a shows the dependence of the rate of hydrogen uptake during the hydrogenation of dicyclopentadiene to dicyclopentene upon the catalyst concentration. Its change in the range of 2–7 g/dm^3 leads to a proportional increase in the reaction rate, irrespective of the nature of the solvent (toluene, 2-propanol), thereby indicating that the test reaction is first order with respect to the catalyst. On the other hand, the hydrogenation rate of dicyclopentadiene does not depend on its initial concentration in the solution (Fig. 4a) and, hence, the reaction is zero order in the reactant. The time taken by a zero-order reaction for completion is proportional to the initial concentration of the substrate in the solution. Nonetheless, in order to obtain dicyclopentene, it is reasonable to use rather concentrated solutions of dicyclopentadiene in toluene (30 wt %; 2.10 mol/dm^3). Thus, the productivity of equipment can be enhanced in the case of possible implementation of the process.

The hydrogenation rate is affected by the partial pressure of hydrogen in the system and the mixing efficiency of the reaction components. As the partial pressure of hydrogen in the nitrogen–hydrogen mixture increases in the range of 0.06–0.090 MPa, the rate of hydrogenation increases proportionally (Fig. 4b). The proportionality saturates at a hydrogen pressure of 0.095–0.11 MPa, i.e., when the pressure in the system is close to atmospheric. Apparently, the dicyclopentadiene hydrogenation process over the finely divided catalyst at atmospheric pressure occurs in the absence of not only internal, but also external diffusion constraints, i.e., in the kinetic region.

The calculated value of the effective activation energy for the reaction of dicyclopentadiene hydrogenation to dicyclopentene depends on the nature of the solvent and lies within 52–64 kJ/mol (Table 3). The finding suggests that the hydrogenation of dicyclopentadiene to dicyclopentene under the given conditions can be assigned in terms of its kinetic parameters to type III hydrogenation reactions (by Sokol'skii's classification) [16, 17], in which the rate-limiting step is hydrogen activation on the catalyst surface.

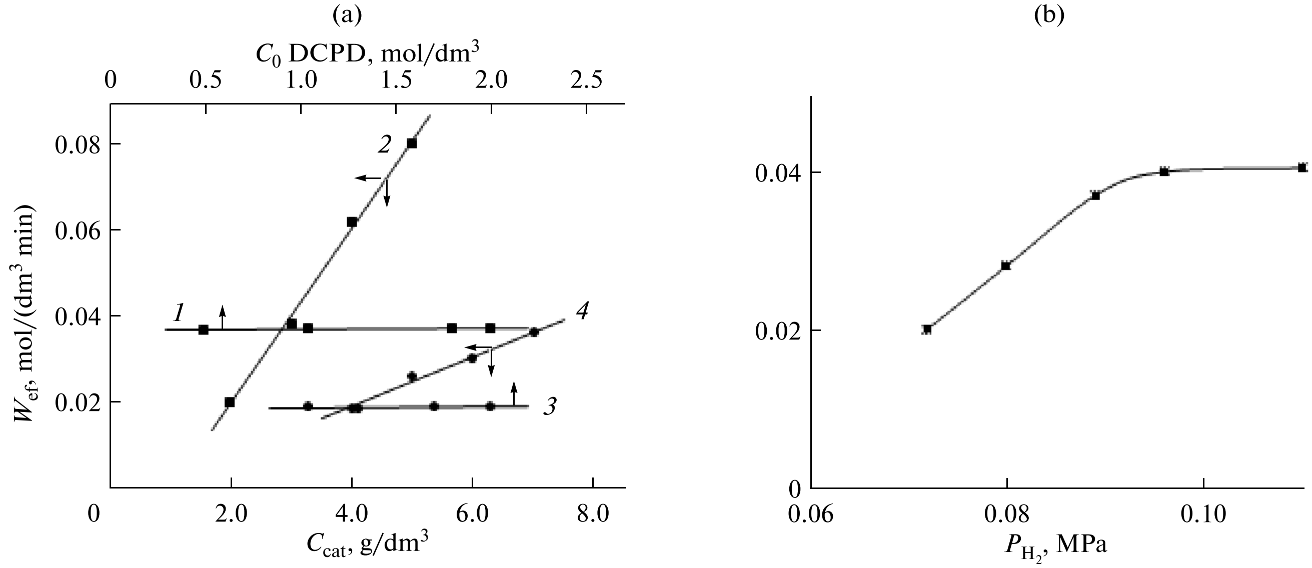


Fig. 4. Dependence of the hydrogen uptake rate on (a) the initial concentration of dicyclopentadiene and catalyst concentration and (b) the partial pressure of hydrogen.
Solvents: (*1, 2*) 2-propanol, (*3, 4*) toluene.

In some studies on the hydrogenation of dicyclopentadiene [7–10], the effective activation energy of saturation of its double bonds was found to be noticeably lower: E_{1st} = 3.19–24.7 kJ/mol, E_{2st} = 12.20–40.9 kJ/mol. As noted by Sokol'skii [16], a significant difference in the values of the activation energy of the hydrogenation reaction is quite acceptable since the hydrogenation of the same compound under widely varying conditions (catalyst, reaction temperature, solvent, hydrogen pressure) can follow different, often related mechanisms.

Since dicyclopentadiene is an unsaturated hydrocarbon capable of polymerizing, several functionalized aromatic compounds taken in an amount of 1–5% of 1% Pd/C catalyst mass were used for its stabilization under hydrogenation conditions in a toluene solution with the aim to increase the yield of the desired product dicyclopentene. These compounds were *p*-hydroxydiphenylamine, hydroquinone, β-naphthylamine, *N*,*N*-dimethyl-*p*-phenylenediamine, 2,6-di-*tert*-butyl-4-methylphenol (ionol), which are inhibitors of radical chain processes. The stabilizing additives, regardless of their structure, do not affect the rate of hydrogenation of the dicyclopentadiene and, next, the dicyclopentene double bond (Fig. 1, curves *5–7*), but they can increase the selectivity for dicyclopentene (tricyclo[5.2.1.0$^{2.6}$]decene-3) from 92% [1] to 98.5–99 mol % with the almost complete conversion of dicyclopentadiene [2]. Apparently, the additives are able to modify the catalyst surface and, consequently, enhance the differentiating properties of toluene in the sequential saturation of double bonds.

Table 3. Kinetic parameters of dicyclopentadiene hydrogenation to dicyclopentene

T, K	W_{ef}, mol/(dm^3 min)	E_{eff}, kJ/mol	Y
Cyclooctane			
313	0.008	63.8 ± 3.2	2.09
323	0.016		
333	0.035		
Toluene			
323	0.0096	52.1 ± 2.6	1.76
328	0.0134		
333	0.0184		
338	0.0216		

To summarize, the successive saturation of double bonds during the hydrogenation of dicyclopentadiene (*endo*-tricyclo[5.2.1.0$^{2.6}$]decadiene-3,8) over 1% Pd/C with differentiation of their saturation rates ensures the selective formation of dicyclopentene (tricyclo[5.2.1.0$^{2.6}$]decene-3).

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Translated by S. Zatonsky