Selective Catalytic Hydrogenation of Alicyclic Dienes with Hydrogen in a Liquid Phase

M. V. Bermeshev^{a, b, *}, T. N. Antonova^{c, **}, D. R. Shangareev^c, A. S. Danilova^c, and N. A. Pozharskaya^b

^aTopchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia ^bMendeleyev University of Chemical Technology of Russia, Moscow, 125047 Russia

^cYaroslavl State Technical University, Yaroslavl, 150023 Russia

*e-mail: bmv@ips.ac.ru **e-mail: antonovatn@ystu.ru Received March 13, 2018

Abstract—The hydrogenation behavior of a number of alicyclic dienes (5-vinyl-2-norbornene (5-vinyl-bicyclo[2.2.1]heptene-2), dicyclopentadiene (tricyclo[$5.2.1.0^{2.6}$]decadiene-3,8), and *cis,cis*-1,5-cyclooctadiene) to the corresponding cycloalkenes in the presence of a finely divided palladium catalyst suspended in the liquid phase has been studied. The reactivities of the double bonds of these dienes have been compared. The conversion of 5-vinyl-2-norbornene and selectivity of its hydrogenation to 2-vinylnorbornane depending on the reaction conditions have been evaluated. Conditions for the selective production of desired 2-vinylnorbornane are proposed for the further implementation of this process in practice.

Keywords: 5-vinyl-2-norbornene, 2-vinylnorbornane, dicyclopentadiene, 1,5-cyclooctadiene, liquid-phase hydrogenation, finely divided catalysts, double bond reactivity

DOI: 10.1134/S0965544118100031

The hydrogenation of one of the double bonds in alicyclic dienes to form corresponding cycloalkenes is of interest for further synthesis of derivatives with different functionalities, polymers for the fabrication of molded articles, and other materials with a set of valuable performance characteristics on their basis [1, 2]. The efficiency of the application of cycloalkenes for practical purposes largely depends on the selectivity of their formation in the hydrogenation process, which can take place only in the case of successive saturation of the double bonds of cyclodienes.

In this paper, we present the results of studying the basic features of hydrogenation of 5-vinyl-2-norbornene (VNB) to 2-vinylnorbornane using a finely divided catalyst (1% Pd/C) suspended in the liquid phase in comparison with the similar results of the saturation of double bonds of alicyclic dienes, such as dicyclopentadiene and 1,5-cyclooctadiene.

This catalyst is distinguished by high activity due to its structure, in which "amorphous carbon–Pd" thin composite layers provide the nanoscale dimensionality of the metal particles (20–900 nm) and allow carrying out the hydrogenation reaction at atmospheric pressure, moderate temperatures, and without preliminary activation according to published data [3]. As is shown in [4, 5], the application of a finely divided catalyst provides the selective formation of a number of cycloalkenes at a level of 92–98 mol % by hydrogenating the corresponding cyclodienes. In addition, its use under the conditions of vigorous stirring converts the three-phase gas/liquid/solid-catalyst system to the state of pseudohomogeneity, in which the reaction can be kinetically controlled mode and, hence, modeling of this process is possible [6].

The liquid-phase hydrogenation of VNB with hydrogen has been investigated earlier but mainly with the use of molded catalysts of the platinum group [7-9]. According to the data presented in [7], in the presence of silica gel-supported catalysts, such as Ru, Rh, Ir, and their mixtures, the *endo-* and *exo-*isomers of VNB taken at a 2 : 1 ratio are nonselectively hydrogenated at the double bond of the bicycloheptene moiety of the molecule and its vinyl group simultaneously. For this reason, endo-5-ethylnorbornene and endo-2vinylnorbornane, as well as their exo-isomers, are simultaneously formed as the main reaction products. According to Kohlman et al. [8], a high yield of 2-vinylnorbornane is achieved in the case of using 0.5% Pd/ γ -Al₂O₃ with a 15% CaO additive as the catalyst if the VNB hydrogenation process is performed under a hydrogen pressure of up to 10 atm in methanol as the solvent in the presence of poisoning additives (gaseous CO or pyridine). The introduction of poisoning additives undoubtedly decreases the technological effectiveness and environmental safety of such a process in the case of its practical implementation. It

Alicyclic diene	Solvent	<i>Т</i> , К	Cyclodiene hydrogenation rate (W_{effl}), mol 9dm ⁻³ min ⁻¹⁰	Cycloalkene hydrogenation rate (W_{eff2}), mol 9dm ⁻³ min ⁻¹⁰	$rac{W_{ m eff1}}{W_{ m eff2}}$
VNB	Pseudocumene*	323	0.0411	0.0092	4.47
	Toluene	333	0.0210	0.0080	2.63
DCPD	Cyclooctane	333	0.0343	0.0142	2.42
	Toluene	333	0.0188	0.0028	6.71
COD**	Toluene	343	0.0350	0.0031	11.2
	_	343	0.0536	0.0053	10.1

Table 1. Rate ratios in the successive hydrogenation of double bonds of alicyclic dienes depending on their structure. The catalyst (1% Pd/C) concentration is 4 g/dm^3

* The activating additive is ionol; ** the catalyst concentration is 6 g/dm³.

was also noted [9] that in the case of hydrogenation of VNB in a cyclohexane solution in the presence of barium sulfate-supported palladium for 6 h at 80°C and a hydrogen pressure of 2 atm, the yield of 2-vinylnorbornane of about 92% is provided with the complete conversion of the reactant diolefin. However, when methanol is used as the solvent, the selectivity for 2vinylnorbornane sharply decreases and does not exceed 40% despite the full conversion of VNB, a finding that is in contradiction with the data of the patent [8].

Since 5-vinyl-2-norbornene (5-vinyl-bicyclo [2, 2, 1]heptene-2) (VNB), dicyclopentadiene (tricyclo[$5.2.1.0^{2.6}$]decadiene-3,8) (DCPD), and *cis,cis*cyclooctadiene-1,5 (COD) are cyclodienes that differ in structure, a comparative investigation of the process of their liquid-phase hydrogenation with hydrogen with regard to double bond reactivity in the case of



Fig. 1. (a) Rate curve of hydrogen uptake in the VNB of hydrogenation process. The solvent is toluene, $C_{0, \text{VNB}} = 2.2 \text{ mol/dm}^3$, $C_{\text{cat}} = 4 \text{ g/dm}^3$, and the temperature is 333 K. (b) Chromatogram of the products of hydrogenation of COD at its conversion of 20%: (1) cyclooctene, (2, 3) intermediate products, and (4) COD.

using 1% Pd/C slurry is not only of practical, but also of scientific interest.

EXPERIMENTAL

The hydrogenation of cyclodienes was performed in a three-phase gas/liquid/solid-catalyst system in both a batch volumetric unit and a continuous-flow system in a thermostated reactor which modeled a perfectly mixed reactor and was equipped with a stirrer, a hydrogen feed diffuser, a reflux condenser with an entrainment separator, and a thermometer.

The experiments were assessed by the amount of absorbed hydrogen and concentration of the reaction products in the reaction mixture which were analyzed via gas-liquid chromatography on a Chromatec Kristall 5000.2 (Russia) chromatograph equipped with a CR-5 capillary column of a 30 m length and a 0.32 mm diameter coated with a mixture of 5% phenyl- and 95% dimethylpolysiloxane with 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 flow rate of the carrier gas (nitrogen) was $60 \text{ cm}^3/\text{min}$. Due to the absence of the hydrogenation byproducts, strict correspondence between the volumetrically measured amount of absorbed hydrogen and degree of reactant diene conversion calculated from the chromatographic analysis data is observed.

RESULTS AND DISCUSSION

The investigation of the hydrogenation reaction of VNB for the purpose of eliminating the possible process of its polymerization was performed in a solution, where aromatic hydrocarbons were used as a solvent.

It is known from published data [10] that these hydrocarbons are capable of differentiating the rates of hydrogenation of the double bonds of alicyclic dienes in the case of their successive saturation.

The successive character of the VNB process hydrogenation is evidenced by the results presented in Fig. 1a, showing that the rate curve of hydrogen uptake in the process under study has two rectilinear portions, which allow estimating the value of the hydrogen absorption rate at the first and the second step and then the ratio of the obtained values as well (Table 1). It is seen from the data of Table 1 that the ratio of the hydrogen uptake rates at the two steps is primarily determined by the structure of the alicyclic diene being hydrogenated.

For example, COD is hydrogenated to cyclooctene at a rate that is ten times rate of cyclooctene hydrogenation to cyclooctane despite the fact that the double bonds in the eight-membered cycle are supposedly equivalent in strain. The observed enhanced reactivity of the first double bond in hydrogenation can be associated with the fact that in the COD molecule (a "tight" medium-sized cycle), the double bonds of the opposite sides of the cycle are brought closer together, and their electrons are capable of interacting with each other through the ring, which becomes similar to the interaction of the electrons of conjugated double bonds, and the main characteristic feature of a system of conjugated double bonds is that it reacts as a whole. It was noted [11] that the conjugated system of double bonds in the COD molecule can be organized as a result of the migration of double bonds, i.e., successive positional isomerization of these bonds in the hydrogenation process due to the isomerizing properties of the palladium catalyst (Scheme 1):



Scheme 1. Hydrogenation of cyclooctadiene-1,5.

The obtained data on the composition of the COD hydrogenation products (Fig. 1b) are the confirmation of this route of formation of the conjugated system of double bonds. Thus, the products of partial hydrogenation of COD (a conversion of 20%) contain, together with cyclooctene (compound 1, Fig. 1b), two new products (compounds 2 and 3) which are apparently intermediates II and III in Scheme 1. These compounds are absent in the case of equimolar saturation of COD with hydrogen, where the products contain only desired cyclooctene. The effect of conjugation promotes the enhancement of the electrondonating properties of the double bond of COD and, as a result, an increase in the rate of its hydrogenation in comparison with cyclooctene (Table 1).

In the case of successive saturation of the DCPD double bonds (Scheme 2), the double bond of the bicycloheptene (norbornene) moiety of its molecule is hydrogenated first as the most strained and possessing



Fig. 2. Chromatograms of VNB hydrogenation products at different conversions: (a) 30%, (b) 110%, (c) 140%. (*1*) Reactant 5-vinyl-2-norbornene, (*2*) *endo*-2-vinilnorbornane, (*2*) *exo*-2-vinilnorbornane, and (*3*, *3*) *exo*- and *endo*-isomers of 2-ethylnorbornane.

stronger electron-donating properties. The rate of hydrogenation of the norbornene double bond is higher by a factor of 6.7-fold than that of saturation of the double bond of dicyclopentene in the cyclopen-

tene moiety of the molecule (Table 1, Scheme 2). It was found that there is no isomerization of the double bonds in the case of hydrogenation of this diene under the given conditions.



Scheme 2. Hydrogenation of dicyclopentadiene.

The double bonds of the VNB molecule, like those in DCPD, are not equivalent in their strain, and the hydrogenation rate of the double bond in the bicycloheptene part of the VNB molecule is greater by a factor of 2.6 than that of the double bond of the vinyl group (Table 1, Scheme 3). It should be noted that under similar conditions of hydrogenation, the rates of saturation of the double bond in the bicycloheptene moiety of VNB and DCPD molecules are almost the same (0.021 and 0.019 mol dm⁻³ min⁻¹, Table 1), i.e., the reactivity of the double bond is primarily determined by its nature, not by the structure of the molecule as a whole. Vinylnorbornadiene used in the work was a mixture of the *exo*- and *endo*-isomers, with the *endo*-isomer being predominant. The products of partial saturation of VNB (molar ratio H_2 : VNB = 0.3 : 1.0–1.1 : 1.0) contain two isomers of dihydrovinylnor-bornene, namely, *endo*-2-vinylnorbornane (Fig. 2, compound 2) and *exo*-2-vinylnorbornane (Fig. 2, compound 2'). The products of deeper hydrogenation of VNB (Fig. 2c) obtained at a molar ratio of H_2 : VNB = 1.4 : 1.0 contain the dihydrovinylnorbornene isomers (compounds 2 and 2') and two isomers of tetrahydrovinylnorbornene (compounds 3 and 3', the isomers of 2-ethylnorbornane). The isomerization of the vinyl group to the ethylidene group to form 5-

Modifying additive	Solvent	Т, К	Time, min	2-Vinylnorbornane yield, %
No additives	Toluene	333	90	85.3
Ionol	Toluene	313	250 (diff. mode)	88.7
		323	90	89.0
		333	70	88.0
No additives	Pseudocumene	333	120	85.5
Ionol	Pseudocumene	323	110	88.1

Table 2. Yield of desired 2-vinylnorbornane depending on VNB hydrogenation conditions. The catalyst concentration is 4 g/dm^3 , and the VNB conversion is 100%

ethylidene-2-norbornene or 2-ethylidenenorbornane could have proceeded during the hydrogenation process (Scheme 3). However, the absence of noticeable amounts of 2-ethylidenenorbornane (less than 1%) among the hydrogenation products suggests that either this process did not occur at all (5-ethylidene-2norbornene is present in insignificant amounts in initial VNB) or its contribution was insignificant.



Z- and E-isomers of 5-ethylidene-2-norbornene Scheme

bornene *Z*- and *E*-isomers of 2-ethylidene-norbornane **Scheme 3.** Hydrogenation of 5-vinyl-2-norbornene.

The process of VNB hydrogenation of under atmospheric pressure over a finely divided palladium catalyst sharply slows down when the initial cyclodiene is completely consumed and degree of conversion of the dihydrovinylnorbornene isomers becomes 40-50% (the conversion with respect to VNB is $\geq 140\%$). Such a characteristic feature of this process can be explained if we assume that the isomerizing properties of the palcatalyst promote the formation ladium of 2-ethylidenenorbornane as one of the products of the reaction under study. It is known from the literature [7] that a trisubstituted double bond of 2-ethylidenenorbornane is difficult to hydrogenate, if at all. In this case, 2-ethylidenenorbornane formed in the minimum (trace) amount can serve as a catalytic poison by adsorbing on the surface of the catalyst and deactivating its catalytic sites.

Figure 3 presents VNB consumption and product buildup rate curves for the VNB hydrogenation process. Analysis of the data presented in Figs. 2 and 3 shows that this process is complex, comprising a number of consecutive and parallel reactions (Scheme 3). To achieve a high yield of desired 2-vinylnorbornane in the case of implementation of the VNB hydrogenation process and get more clear differentiation of the rates of saturation of its double bonds, we studied the influence of the nature of the solvent and some activating additives on the parameters of this process. The obtained results are presented in Figs. 4a and 4b, and in Tables 1 and 2.

As is seen from the data presented in Fig. 4a, the rate of hydrogen uptake in the VNB hydrogenation process depends on the nature of the solvent. In toluene and pseudocumene, it is almost the same, being quite high to exceed the rate of the process in the case of other solvents. The rate of hydrogenation of VNB to 2-vinylnorbornane in aromatic solvents does not depend on the concentration of VNB in the initial solution, and the duration of the reaction under the specified conditions is 100-120 min.

Pseudocumene is the most preferable solvent for the process of VNB hydrogenation to 2-vinylnorbornane. Its boiling point (168°C) is higher than that of VNB or VNB derivatives. As a result, during the isola-



Fig. 3. Rate curves for the consumption of VNB and the buildup of products in the VNB hydrogenation process. The solvent is toluene, $C_{\text{cat}} = 4 \text{ g/dm}^3$, $C_{0 \text{ VNB}} = 2.2 \text{ mol/dm}^3$, and temperature is 333 K. (1) 5-vinyl-2-norbornene, (2) endo-2-vinylnorbornane, (2) exo-2-vinylnorbornane, (3, 3') exo- and endo-isomers of 2-ethylnorbornane.

tion of 2-vinylnorbornane from the hydrogenation products by fractional distillation for further use, pseudocumene will prevent its possible polymerization in the column still.

To stabilize VNB, an unsaturated hydrocarbon capable of polymerizing during hydrogenation, we used some functionally substituted aromatic compounds, such as *N*,*N*-dimethyl-*p*-phenylenediamine,

hydroquinone, and 2,6-di-*tert*-butyl-4-methylphenol (ionol) which are inhibitors of radical chain processes (including the polymerization process), in an amount of 5% of the taken catalyst mass.

As is seen from the data presented in Fig. 4b, the use of N, N-dimethyl-p-phenylenediamine and ionol in the VNB hydrogenation process in aromatic solvents leads to an unexpected increase in the hydrogen uptake rate, which can result from either the activation of the catalyst as a result of the modification of its surface or activation of the double bond to be hydrogenated. The activating properties of the additives introduced in the specified amount promote an almost twofold increase in the reaction rate, and, in this case, the time of VNB hydrogenation to 2-vinylnorbornane decreases to 60–70 min (Fig. 4b).

Since fast processes are not always selective, the influence of the activating additives on the selectivity for the target product 2-vinylnorbornane was also studied at 313–323 K. It was found that at this temperature, the use of activating additives, in particular, ionol, in the VNB hydrogenation process in a pseudocumene solution with an initial VNB concentration of 30 wt % made it possible to increase the ratio of the rates of saturation of the double bonds in the bicycloheptene moiety of VNB and the ethylene bond of 2-vinylnorbornane from 2.63 to 4.47 (Table 1).

The result of using the activating additives is an increase in the total yield of isomeric 2-vinylnorbornanes to 88-89 mol % with the predominant formation of *endo*-2-vinylnorbornane and the complete conversion of reactant VNB (Table 2). The weight ratio of desired *endo*- and *exo*-2-vinylnorbornanes was about 4 : 1; i.e., *endo*-2-vinylnorbornane is the main product of selective hydrogenation.



Fig. 4. Rate curve of hydrogen uptake in the VNB hydrogenation process depending on the nature of (a) solvent ((1) toluene, (2) pseudocumene, (3) phenylcyclohexane, and (4) 2-propanol) and (b) activating additives ((1) without additives, (2) ionol (solvent pseudocumene), (3) ionol, and (4) N,N-dimethyl-p-phenylenediamine (solvent toluene)). $C_{\text{cat}} = 4 \text{ g/dm}^3$, $C_{0, \text{ VNB}} = 2.3 \text{ mol/dm}^3$, 333 K.

Thus, as a result of the study, the kinetic parameters and quantitative characteristics of the hydrogenation of 5-vinyl-2-norbornene over finely divided 1% Pd/C suspended in the liquid phase have been evaluated in comparison with those of the hydrogenation of its cyclic analogues, namely, dicyclopentadiene and 1,5-cyclooctadiene.

It has been found that the strained double bond of the bicycloheptene moiety of 5-vinyl-2-norbornene is saturated with hydrogen at the same rate as the double bond of the same moiety of dicyclopentadiene. However, in the case of successive saturation of the double bonds of 5-vinyl-2-norbornene, the ratio of the hydrogenation rates of the first and second double bonds has a relatively low value (4.47) in comparison with dicyclopentadiene (6.7) and 1,5-cyclooctadiene (10–11), a situation that requires the amount of hydrogen absorbed in the hydrogenation process to be controlled.

It has been shown that carrying out the 5-vinyl-2norbornene hydrogenation process in pseudocumene solution at a VNB concentration of 30 wt % under atmospheric pressure in the presence of activating additives, in particular, ionol, in an amount of 5% of catalyst mass ensures the selectivity for target 2-vinylnorbornane at a level of 88–89% in the case of complete conversion of the initial diene in a reactor modeling a perfectly mixed reactor.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation (unique project identifier RFMEFI60417X0181, agreement no. 14.604.21.0181 of September 26, 2017).

REFERENCES

- 1. V. Sh. Fel'dblyum, *Synthesis and Application of Unsaturated Hydrocarbons* (Khimiya, Moscow, 1982) [in Russian].
- 2. N. V. Vereshchagina, T. N. Antonova, I. G. Abramov, and G. Yu. Kopushkina, Pet. Chem. **54**, 207 (2014).
- 3. A. A. Nechitailov, T. K. Zvonareva, A. D. Remenyuk, et al., in *Proceedings of XVIII Mendeleev Congress on General and Applied Chemistry: Abstracts of Papers* (Nauka, Moscow, 2007), Vol. 3, p. 211 [in Russian].
- 4. T. N. Antonova, I. A. Abramov, V. Sh. Fel'dblyum, et al., Pet. Chem. **49**, 366 (2009).
- N. V. Vereshchagina, G. B. Zakharova, T. N. Antonova, and I. G. Abramov, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. 56 (12), 79 (2013).
- Stefoglo, E.F., *Catalytic Slurry Reactors* (Nauka, Novosibirsk, 1990) [in Russian].
- Yu. G. Osokin, V. A. Mikhailov, I. A. Zubovich, and V. Sh. Fel'dblyum, Dokl. Akad. Nauk SSSR 220, 851 (1975).
- 8. M. Kohlman, G. Esser, H. Hauthal, and W. Pritzkow, DD Patent No. 106343 (1974).
- 9. Sh. Hayashi and H. Ito, JP Patent No. 07109232 (1995).
- N. V. Vereshchagina, T. N. Antonova, A. A. Il'in, and Zh. V. Chirkova, Pet. Chem. 56, 38 (2016).
- 11. V. Sh. Fel'dblyum and Yu. A. Moskvichev, *Unsaturated Hydrocarbons and Their Derivatives: New Opportunities in Synthesis, Catalysis, and Technology* (Mir, Moscow, 2003) [in Russian].

Translated by E. Boltukhina