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Saturation Kinetics and Relative Reactivity of the Double Bonds of Alicyclic Dienes in Their Hydrogenation

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Abstract—The kinetics of the liquid-phase hydrogenation of cyclodienes with various structures (*endo*-tricyclo[5.2.1.0^{2,6}]decadiene-3,8 and *cis,cis*-1,5-cyclooctadiene) by hydrogen over a finely dispersed 1% Pd/C catalyst at atmospheric pressure has been studied. The catalyst provides the possibility for successive saturation of the double bonds of the dienes. The reactivities of the cyclodienes determined by their electron-donating properties have been compared. The solvent nature is the determining factor in the ratio of hydrogen absorption rates in the case of successive saturation of the double bonds of the hydrocarbons. The hydrogenation kinetics of cyclic dienes, including dicyclopentadiene, can be modeled using the Langmuir–Hinshelwood equation when the process is carried out in a perfectly mixed flow reactor.

Keywords: dicyclopentadiene, dicyclopentene, 1,5-cyclooctadiene, cyclooctene, liquid-phase hydrogenation, finely dispersed catalyst, reactivity of double bonds, differentiating properties of solvents

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INTRODUCTION

The hydrogenation of alicyclic dienes at one of the double bonds with the formation of cycloalkenes is essential for further synthesis of variously functionalized derivatives [1–7]. For example, dicyclopentene, a hydrogenated analogue of dicyclopentadiene, can be used to obtain oxygen-containing compounds with an individual structure. This feature is important for their use in the pharmaceutical industry (immunomodulating agent synthesis) and for the production of liquid crystal materials [8]. The efficiency of the use of cycloalkenes for practical purposes depends strongly on the selectivity of their formation in hydrogenation: selective hydrogenation can take place only in the case of successive saturation of the cyclodiene double bonds.

Here, we present the results of our kinetic studies of the hydrogenation of cyclooctadiene and dicyclopentadiene. These data make it possible to estimate the relative reactivity of the double bonds, the order in which they are saturated, and, hence, the selectivity of target cycloalkene formation.

Since dicyclopentadiene (*endo*-tricyclo[5.2.1.0^{2,6}] decadiene-3,8, DCPD) and *cis,cis*-1,5-cyclooctadiene (COD) are structurally different cyclodienes, studying the regularities of their hydrogenation in terms of the reactivity of their double bonds is of both practical and scientific interest. Alicyclic hydrocarbons with a medium-sized hydrocarbon ring that contain a double bond are characterized by a higher potential energy than their analogues with normal rings. This is due to the strain in the ring itself and, as a consequence, strain in the double bond. The results presented in this work make it possible to compare the double bonds of the hydrocarbons under consideration in terms of their reactivity and strain.

EXPERIMENTAL

Cyclodiene hydrogenation was performed in a gas–liquid–solid catalyst three-phase system using a closed-loop volumetric unit [9] and in a temperature-controlled flow reactor simulating a perfect-mixing reactor, which was fitted with a stirrer, a diffuser for hydrogen supply, a backflow condenser with an entrainment trap, and a thermometer.

The results of the experiments were assessed in terms of hydrogen uptake and the concentration of reaction products in the reaction mixture, which was analyzed using gas–liquid chromatography on a Khromatek-Kristall 5000.2 chromatograph (Russia) with a CR-5 capillary column (30 m × 0.32 mm, 5% phenyl 95% dimethylpolysiloxane stationary phase, film thickness of 0.5 μm). The injection port temperature was 220°C, the oven temperature was 70–160°C, and the heating rate was 10°C/min. The carrier gas (nitrogen) flow rate was 60 cm^3/min.

RESULTS AND DISCUSSION

The order of hydrogenation of the cyclodiene double bonds can be affected by the nature of the catalyst

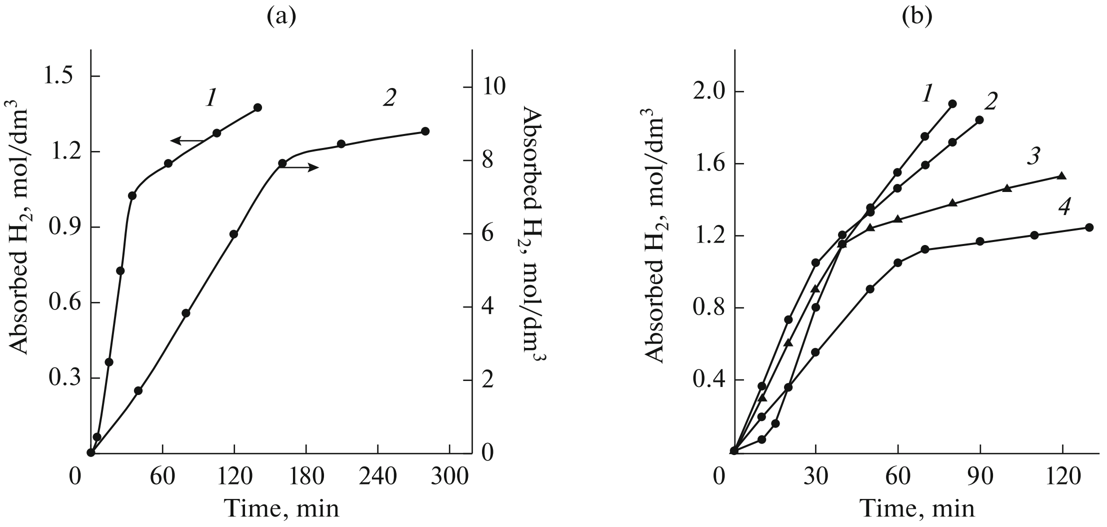


Fig. 1. Hydrogen uptake kinetics in the hydrogenation of the double bonds of (a) cyclooctadiene and (b) dicyclopentadiene. (a) $C_{\text{cat}} = 6$ g/dm^3, $T = 343$ K, and the solvent is (*1*) toluene, $C^0_{\text{COD}} = 1.0$ mol/dm^3 and (*2*) absent, $C^0_{\text{COD}} = 8.1$ mol/dm^3. (b) $C_{\text{cat}} = 4$ g/dm^3, $C^0_{\text{DCPD}} = 1.04$ mol/dm^3, and solvents are (*1*) 2-propanol ($T = 313$ K), (*2*) cyclooctane ($T = 333$ K), (*3*) toluene ($T = 333$ K), and (*4*) toluene ($T = 343$ K).

being used, specific features of the mechanism of heterogeneous catalysis, difference in reactivity between the double bonds, and reaction conditions, including the solvent nature.

The liquid-phase hydrogenation of cyclodienes by hydrogen was carried out over finely dispersed palladium supported on amorphous carbon (1% Pd/C catalyst)received from OOO VNIPIM (Tula, Russia). The high activity of this catalyst, which is apparently determined by its structure, makes it possible to carry out the hydrogenation reaction at atmospheric pressure and moderate temperatures without catalyst preactivation. According to the literature [10], thin amorphous C–Pd composite layers ensure that the metal particles are nanosized (20–900 nm) and, actually, the catalysts may be small (dinuclear or trinuclear) palladium clusters [11, 12]. In addition, use of a finely dispersed catalyst suspended in the liquid phase under vigorous stirring conditions makes the gas–liquid–solid catalyst three-phase system pseudohomogeneous, allowing kinetic control of the reaction.

An analysis of the composition of 1,5-cyclooctadiene hydrogenation products shows that the saturation of its double bonds proceeds successively (Fig. 1a). The hydrogen uptake kinetic curves have well-defined segments corresponding to the hydrogenation of the cyclooctadiene double bond followed by that of the cyclooctene double bond. The saturation rate of the first cyclooctadiene double bond exceeds the hydrogenation rate of the second bond by almost one order of magnitude both in cyclooctadiene hydrogenation in the absence of a solvent and in solution (table). Therefore, cyclooctadiene, an unsaturated hydrocarbon, is hydrogenated to cyclooctene at a rate that is ten times higher than the rate of cyclooctene hydrogenation to cyclooctane despite the fact that, supposedly, the double bonds in the eight-membered ring are equally strained.

To explain this difference, we took into consideration the fact that the reactivity of an olefin double bond (π bond) in its saturation over a heterogeneous catalyst correlates with its electron-donating properties [13]. This property of the double bond ensures efficient adsorption of the molecule on the catalyst surface. The enhancement of the electron-donating properties of the 1,5-cyclooctadiene double bond may be due to transannular interactions (i.e., interactions between hydrogen atoms positioned on the opposite sides of the carbon ring), which are characteristic of medium-sized rings. In the cyclooctadiene molecule (a “tight” medium-sized ring), the double bonds on the opposite sides of the ring are brought closer together, and the electrons that form these bonds can interact. This interaction is similar to the interaction of the electrons of conjugated double bonds. The main characteristic feature of a conjugated system of double bonds is that it reacts as a single whole.

It is also known [14] that a conjugated system of double bonds in the 1,5-cyclooctadiene molecule undergoing hydrogenation can result from the migration of its double bonds during hydrogenation due to the isomerizing properties of the catalyst. As can be seen from the data presented in Fig. 2a, the products

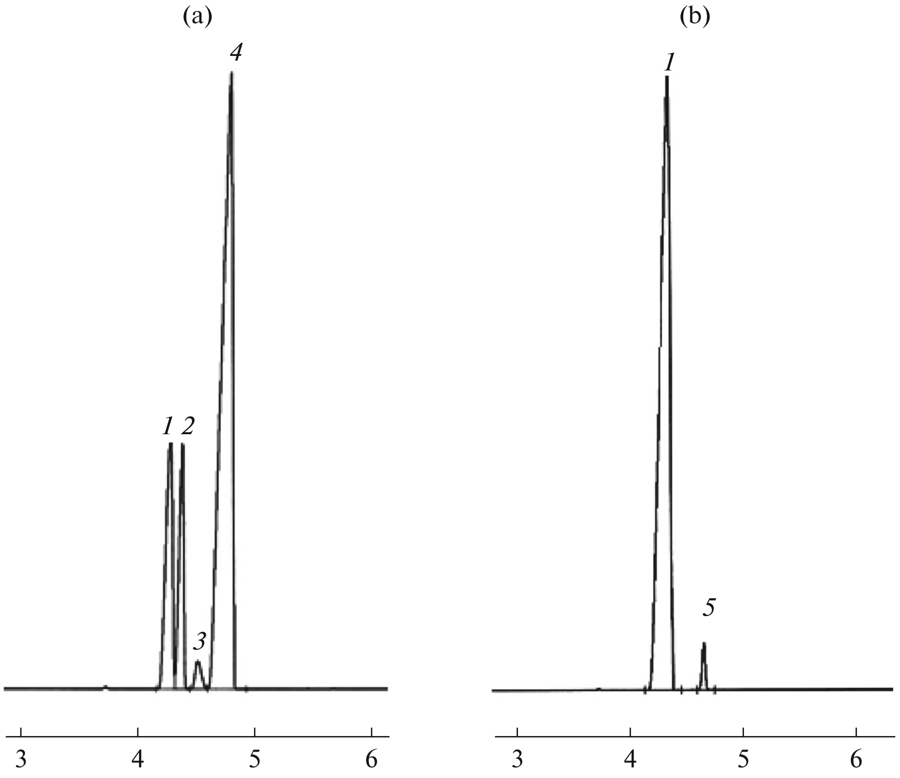


Fig. 2. Chromatogram of products of (a) complete and (b) partial 1,5-*cis,cis*-cyclooctadiene hydrogenation to *cis*-cyclooctene. (*1*) Cyclooctene, (*2*, *3*) intermediate products, (*4*) cyclooctadiene, and (*5*) cyclooctane.

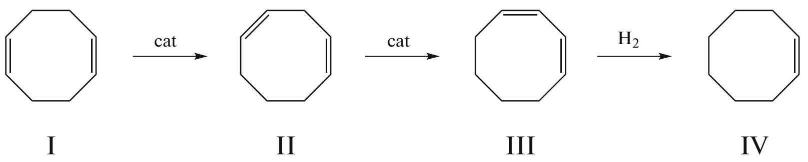
of incomplete 1,5-cyclooctadiene hydrogenation (20% conversion) contain, in addition to cyclooctene (peak *1*), two intermediate compounds (peaks *2* and *3*) that are absent in the case of equimolar cyclooctadiene saturation, when the products contain only target cyclooctene (Fig. 2b, peak *1*).

Solvent-dependent ratios of the hydrogenation rates of the double bonds of cyclooctadiene (W_{eff1}) and dicyclopentadiene (W_{eff2})

Solvent	Temperature, K	Double bond hydrogenation rate, mol/(dm^3 min)		$\frac{W_{\text{eff1}}}{W_{\text{eff2}}}$
		W_{eff1}	W_{eff2}	
1,5-Cyclooctadiene				
No solvent	343	0.0536	0.0053	10.1
Toluene	343	0.0350	0.0031	11.2
Dicyclopentadiene				
2-Propanol	313	0.0350	0.0225	1.56
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*
p-Xylene	333	0.0473	0.0090	5.26
o-Xylene	333	0.0380	0.0042	9.05

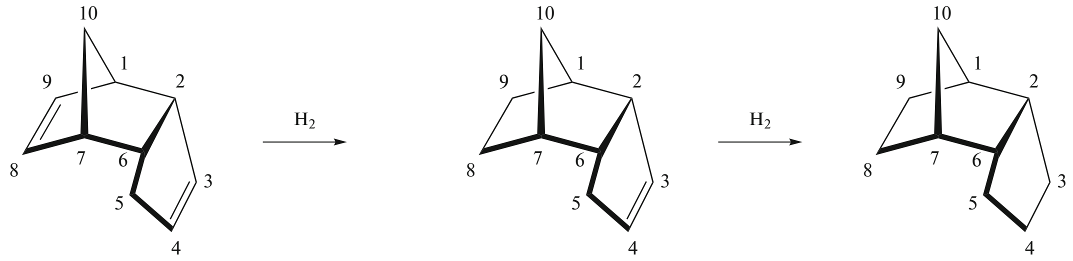
* According to the data of Fig. 4b.

In accordance with the presented experimental data, the formation of a conjugated system of double bonds in the 1,5-cyclooctadiene molecule may be due to their successive positional isomerization accompanied by the formation of intermediate compounds **II** and **III**:



Therefore, the enhancement of the electron-donating properties of one of the 1,5-cyclooctadiene double bonds is caused by the conjugation effect, and this is the reason why 1,5-cyclooctadiene is hydrogenated at a higher rate than cyclooctene (table).

As in the case of 1,5-cyclooctadiene, the saturation of the dicyclopentadiene double bonds proceeds successively iover finely dispersed 1% Pd/C, as distinct from the same process over nickel catalysts [6]. However, double bonds in the dicyclopentadiene (*endo*-tricyclo[5.2.1.$0^{2,6}$]decadiene-3,8) molecule are isolated and, according to the results of spectroscopic studies (^{1}H NMR and COSY spectroscopy), the double bond of the bicycloheptene moiety of the molecule is hydrogenated first [15]. There are no intermediate compounds among the reaction products during its saturation, and, in this case, the catalyst does not exhibit its isomerizing properties.



Tricyclo[5.2.1.$0^{2,6}$]decadiene-3,8 Tricyclo[5.2.1.$0^{2,6}$]decene-3 Tricyclo[5.2.1.$0^{2,6}$]decane

Dicyclopentadiene Dicyclopentene Dicyclopentane

According to conceptions of theoretical organic chemistry, the double bond of the bicycloheptene moiety of the dicyclopentadiene molecule is strained and rehybridized. Because of this, it possesses stronger electron-donating properties, so its reactivity in the hydrogenation process is fairly high.

The double bond saturation rate in dicyclopentadiene hydrogenation to dicyclopentene exceeds the same parameter in cyclooctadiene hydrogenation to cyclooctene (Fig. 3a). Therefore, the electron-donating properties of the double bond of the bicycloheptene fragment of the dicyclopentadiene molecule exceed the same properties of the conjugated system of cyclooctadiene double bonds.

At the same time, the cyclooctene double bond of cyclooctene, remaining strained, is saturated at a higher rate in cyclooctene hydrogenation to cyclooctane compared to the dicyclopentene double bond in the five-membered, normal-sized, unstrained ring (Fig. 3b).

As distinct from what is observed for 1,5-cyclooctadiene, the ratio of the rates of dicyclopentadiene hydrogenation to dicyclopentene and further dicyclopentene hydrogenation to dicyclopentane is solvent-dependent. The hydrogen uptake rate during the hydrogenation of the first dicyclopentadiene double bond exceeds the saturation rate of its second bond by a factor of 9 in *o*-xylene, by a factor of 6.6 in toluene, by a factor of 2.4 in cyclooctane, and only by a factor of 1.5 in 2-propanol (Fig. 1b, table). This ratio does not depend on the reaction temperature, catalyst concentration, or substrate concentration in the solution.

According to the data obtained, use of aromatic solvents ensures that the double bonds of the initial diene are saturated in succession and differentiates them by saturation rate. This makes it possible to selectively obtain dicyclopentene via dicyclopentadiene hydrogenation.

Note that, in the process carried out in aromatic hydrocarbons, the hydrogen uptake rate is somewhat lower than in the same process conducted in cyclooctane and 2-propanol (Fig. 1b). This decrease in the hydrogenation rate is apparently due to the competition in the adsorption of electron-donating molecules

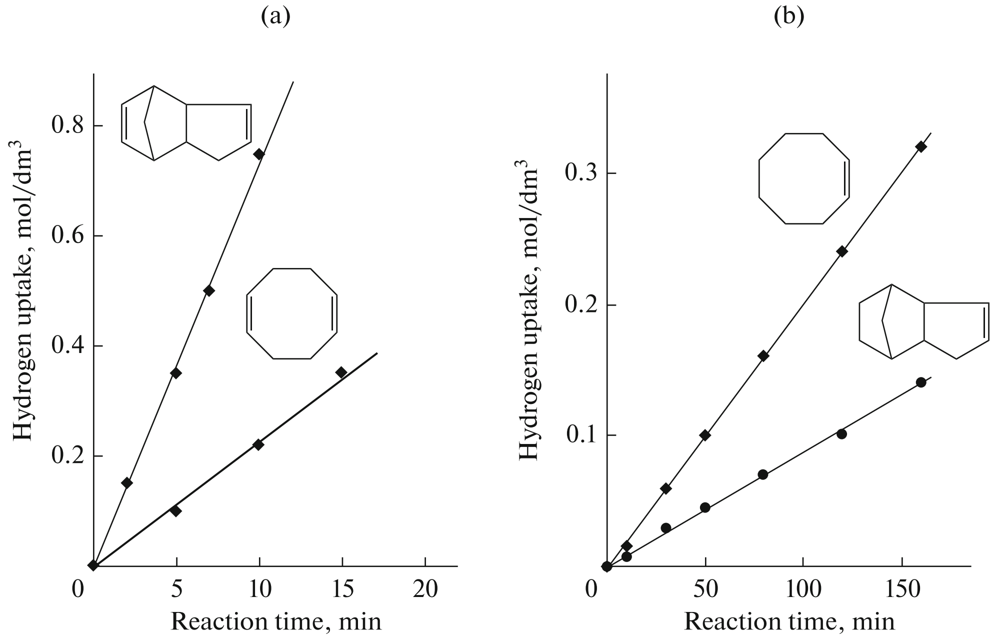


Fig. 3. Effect of the nature of cycloolefin on the reactivity of its double bonds in (a) diene and (b) monoolefin hydrogenation. The solvent is toluene, $C_{cat} = 4$ g/dm^3, $T = 338$ K, and $C^0 = 1.04$ mol/dm^3.

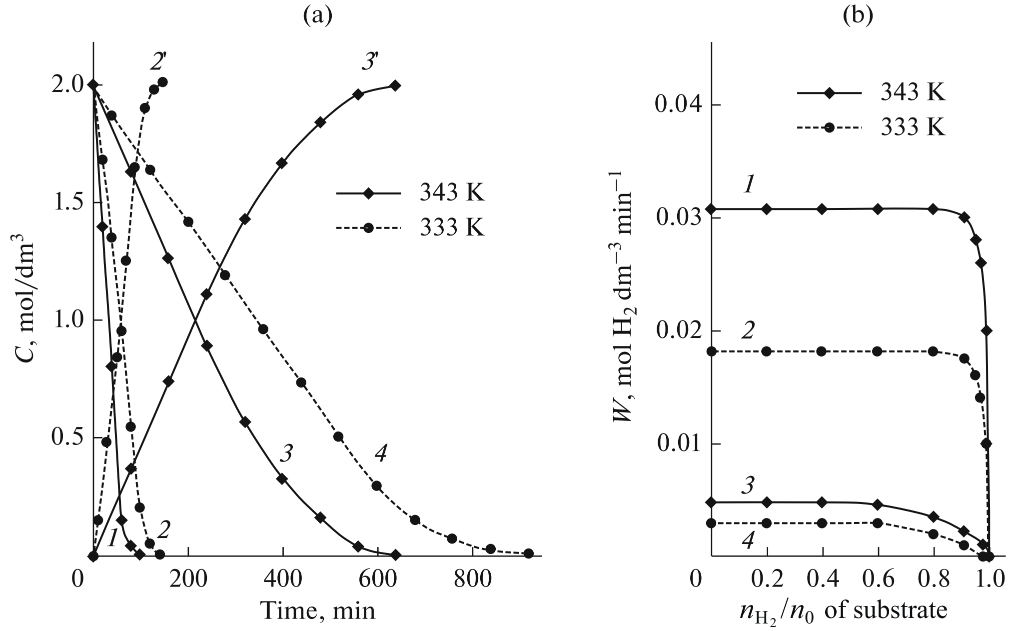


Fig. 4. (a) Kinetics of substrate consumption during the hydrogenation of (*1*, *2*) dicyclopentadiene to dicyclopentene and (*3*, *4*) dicyclopentene to dicyclopentane and the kinetics of accumulation of (*2'*) dicyclopentene and (*3'*) dicyclopentane. (b) Reaction rate depending on the reaction temperature. The solvent is toluene, $C^0 = 2.0$ mol/dm^3, and $C_{cat} = 4$ g/dm^3.

of aromatic hydrocarbons and dicyclopentadiene on the catalyst surface.

The observed ratio of double bond hydrogenation rates in the case of toluene used as the solvent is confirmed by the results of separate hydrogenation of dicyclopentadiene to dicyclopentene (dihydrodicyclopentadiene) and dicyclopentene to dicyclopentane (tetrahydrodicyclopentadiene) at equal initial substrate concentrations in the solution (Figs. 4a, 4b, table).

The observed difference between the hydrogenation rates of the first and second double bonds of cyclodienes (1,5-cyclooctadiene and dicyclopentadiene)

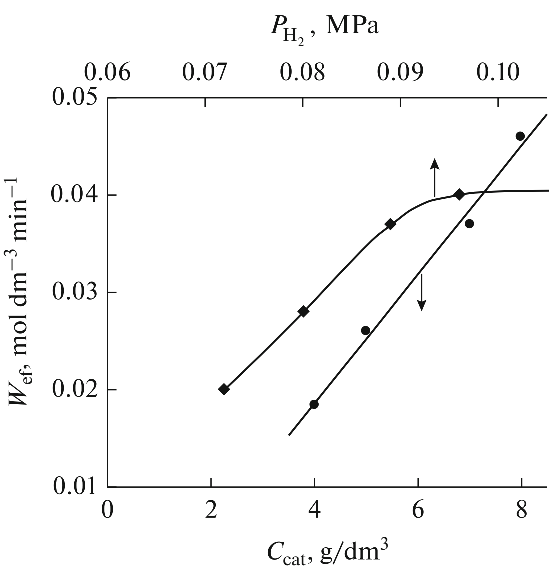


Fig. 5. Hydrogen uptake rate in dicyclopentadiene hydrogenation as a function of the catalyst concentration and hydrogen partial pressure. The solvent is toluene, T = 333 K, and C^0_{DCPD} = 1.04 mol/dm^3.

provides an opportunity to selectively synthesize the corresponding cycloalkenes (cyclooctene and dicyclopentene) by their hydrogenation, and the greater this difference the higher the process selectivity. As a consequence, the yield of target dicyclopentene is 98.5–99% at complete dicyclopentadiene conversion in the case of dicyclopentadiene hydrogenation in toluene solution, while in the case of 1,5-cyclooctadiene hydrogenation in the presence of finely dispersed 1% Pd/C, an equally high yield of cyclooctene is achieved when carrying out the process in the absence of a solvent. Insignificant amounts of the saturated cycloalkane form as a by-product.

The consumption rate of the initial cyclodiene, as well as that of cycloalkane, in hydrogenation (effective hydrogenation rate) is constant in time (Fig. 4), and, therefore, the reaction is zeroth-order with respect to the compound being hydrogenated. The proportionality of the reaction rate to the catalyst concentration (Fig. 5) is evidence that the reaction is first-order with respect to the catalyst. It was also found that the hydrogenation rate increases proportionally to the increase in the partial pressure of hydrogen in the nitrogen–hydrogen mixture within the 0.06–0.09 MPa range (Fig. 5). As the partial pressure is further raised to 0.11 MPa, the reaction order with respect to hydrogen changes from zero to unity because the hydrogen uptake rate stops depending on this factor. The activation energy of the hydrogenation of 1,5-*cis,cis*-cyclooctadiene (63.5 ± 2.5 kJ/mol) and dicyclopentadiene (52.1 ± 2.6 kJ/mol in toluene solution and 63.8 ± 3.2 kJ/mol in cyclooctane solution) was calculated from the Arrhenius dependence of the apparent reaction rate on temperature. According to these data, the hydrogenation reaction has neither external nor internal diffusion limitations; i.e., it is kinetically controlled.

Therefore, kinetically, the cyclodiene hydrogenation reaction belongs to type III hydrogenation reactions, according to Sokol'skii's classification [16]. The rate-limiting step of this type of reaction is the activation of hydrogen on the catalyst surface, which becomes possible when hydrogen and the substrate are adsorbed on different sites of the catalyst surface.

In heterogeneous catalysis, the key kinetic law is the law of active surfaces:

$$W = k\Theta_{DCPD}\Theta_{H_2}, \quad (1)$$

where W is the reaction rate, k is the rate constant, and Θ_{DCPD} and Θ_{H_2} are the fractions of the active sites occupied by dicyclopentadiene and hydrogen molecules, respectively (surface coverages).

If dicyclopentadiene and hydrogen are adsorbed on different sites of the catalyst surface, the Langmuir–

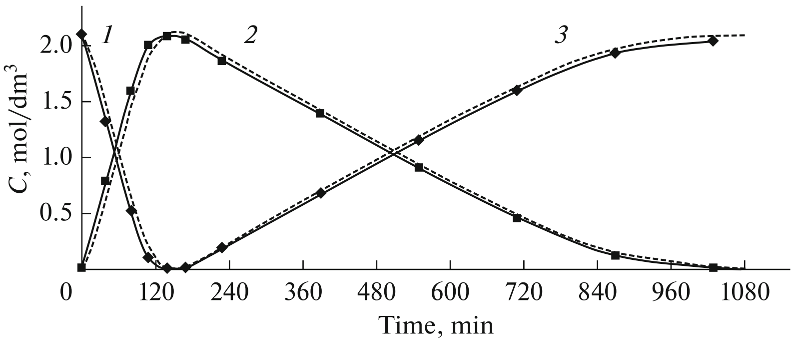


Fig. 6. Kinetics of the consumption and accumulation of products in dicyclopentadiene hydrogenation: (- - -) calculated and (—) experimental vdata; (*1*) dicyclopentadiene, (*2*) dicyclopentene, and (*3*) dicyclopentane. The solvent is toluene, C_{cat} = 4 g/dm^3, and T = 338 K.

Hinshelwood equation relating the surface coverage (Θ) to the concentration of reagents (C) appears as

$$\Theta_{\mathrm{DCPD}} = \frac{b_{\mathrm{DCPD}}C_{\mathrm{DCPD}}}{1 + b_{\mathrm{DCPD}}C_{\mathrm{DCPD}}},\quad \Theta_{\mathrm{H}_2} = \frac{b_{\mathrm{H}_2}C_{\mathrm{H}_2}}{1 + b_{\mathrm{H}_2}C_{\mathrm{H}_2}},\quad (2)$$

where b_{DCPD} and b_{H_2} are the equilibrium constants of dicyclopentadiene and hydrogen adsorption processes, respectively.

The reaction is zeroth-orders with respect to cyclodiene and hydrogen at the highest cyclodiene and hydrogen coverages on the catalyst surface, i.e., when their adsorption equilibrium constant (b) is sufficiently large. At large values of the adsorption equilibrium constant, $bC \gg 1$. In this case, Θ becomes unity 1 for both diene and hydrogen adsorption and $W_{\mathrm{ef}} = k_{\mathrm{eff}}$, where $k_{\mathrm{eff}} = kC_{\mathrm{cat}}$.

These kinetic regularities of dicyclopentadiene hydrogenation are observed both in the closed-loop volumetric unit and in the perfectly mixed flow reactor. This fact is important for developing a dicyclopentene production technology [15].

CONCLUSIONS

When a finely dispersed palladium catalyst (1% Pd/C) suspended in a liquid phase is used in the hydrogenation of cyclodienes, such as 1,5-*cis,cis*-cyclooctadiene and *endo*-tricyclo[5.2.1.0^{2,6}]decadiene-3,8 (dicyclopentadiene), at atmospheric pressure, successive saturation of the double bonds of their molecules takes place. In the dicyclopentadiene molecule, the double bond of the bicycloheptene moiety is hydrogenated first. Cyclooctadiene hydrogenation to cyclooctene proceeds via the formation of a conjugated system of double bonds.

The ratio of the hydrogenation rates of the double bonds of the bicycloheptene and cyclopentene moieties of the dicyclopentadiene molecule is solvent-dependent. This ratio is 7–9 : 1 for aromatic solvents (toluene and xylenes), which exert the strongest differentiating effect. The ratio of the hydrogenation rates of cyclooctadiene double bonds is 10.6 for the process carried out both in a solution and in the absence of a solvent. This makes it possible to obtain target cyclooctene, as well as dicyclopentene, in 98.5–99% yield at the complete conversion of the initial cyclodiene.

The kinetics of the hydrogenation of cyclooctadiene to cyclooctene and dicyclopentadiene to dicyclopentene has been studied. The reaction orders with respect to individual reactants and the apparent activation energy have been determined, and the mechanism of the process has been discussed. The kinetic parameters determined indicate that the reaction examined is a type III hydrogenization reaction. The cyclic diene hydrogenation kinetics obeys the Langmuir–Hinshelwood equation.

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