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Kinetics of the Hydrogenation of α-Pinene to *cis*- and *trans*-Pinanes on Pd/C

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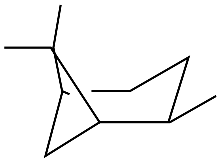
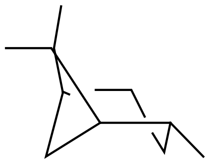
Abstract—The liquid-phase hydrogenation of α-pinene on a Pd/C catalyst at 0–100°C and hydrogen pressures of 1–11 atm was studied. It was found that the order of reaction with respect to pinene increased with hydrogen pressure and did not depend on temperature, whereas the selectivity of *cis*-pinane formation decreased with temperature and increased with hydrogen pressure. A mechanism was proposed for the hydrogenation of α-pinene. According to this mechanism, the selectivity of *cis*-pinane formation depends on the following two factors: (a) a temperature-dependent equilibrium between adsorbed α-pinene species, which are *cis*- and *trans*-pinane precursors, and (b) competition between the hydrogenation and β-H-elimination of surface σ-pinanyl complexes. The ratio between the rates of these reactions depends on the concentration of surface hydride species, and this concentration depends on the pressure of hydrogen.

INTRODUCTION

This work continues a series of studies on the kinetics of catalytic reactions of terpene hydrocarbon conversion into fragrance compounds. Terpene hydrocarbons, which are the constituents of turpentine, are valuable raw materials for fine organic synthesis [1]. In particular, pinane, which is produced by the hydrogenation of α-pinene, the main component of turpentine, is used for the synthesis of valuable fragrance compounds and drug components [2, 3]. The molecule of pinane exhibits a bicyclic structure and can exist as four spatial isomers of *cis*- and *trans*-pinane:



cis-Pinane



trans-Pinane

Either of them can occur as two optical isomers. This is due to the presence of three asymmetric carbon atoms. Moreover, a six-membered ring can occur as a chair or boat conformation.

Depending on reaction conditions, hydrogen addition to the double bond can result in the formation of two *cis*- and *trans*-pinane isomers; in this case, the asymmetry of two carbon atoms is retained. In the *in situ* reduction with hydrogen, the position of the double bond in a pinene molecule has no effect on the isomeric composition of the resulting pinane. For example, the reduction of either α-pinene or β-pinene in the lithium–ethylamine system resulted in a mixture containing 56–57% *cis*-pinane and 43–44% *trans*-pinane [4]. The reduction of β-pinene with lithium aluminum hydride gave a ratio between the *cis* and *trans* isomers equal to 89 : 11 [4]. This reaction occurs through the attachment of an H atom to a tertiary carbon atom and the formation of an Al–C bond at a methylene group. The steric effect of the AlH_3 group is favorable for the formation of the *trans* conformation of pinane. In the hydrogenation of α-pinene in the presence of catalysts (Pt/C, Pd/C, and Ni), the yield of *cis*-pinane can vary from 48.5 to 98.5% depending on reaction conditions [4]. The clarification of factors that are responsible for the selectivity of formation of a particular isomer is an important problem of stereoselective catalysis.

The aim of this work was to examine the formation of the *cis* and *trans* isomers of pinane in the liquid-phase hydrogenation of α-pinene on a Pd/C catalyst.

EXPERIMENTAL

α-Pinene prepared by the vacuum rectification of turpentine oil was used in this study. Composition: α-pinene, 92.0%; β-pinene, 3.0%; and Δ^3-carene, 5.0%.

The experiments on the liquid-phase hydrogenation of α-pinene were performed in a stainless steel reactor (150 ml) equipped with an electromagnetic stirrer (800–1000 rpm) and an automatic system for the measurement and detection of the amount of consumed hydrogen. The experimental conditions (catalyst weight, temperature, and hydrogen pressure) were chosen so that the observed rate of hydrogenation was not limited by the rate of hydrogen dissolution at the given intensity of stirring. The reaction was performed on a standard powdered 4%Pd/C catalyst with a particle size of 5–50 μm. The specific surface area of the carbon support (by Ar adsorption) was 480 m^2/g, and the total

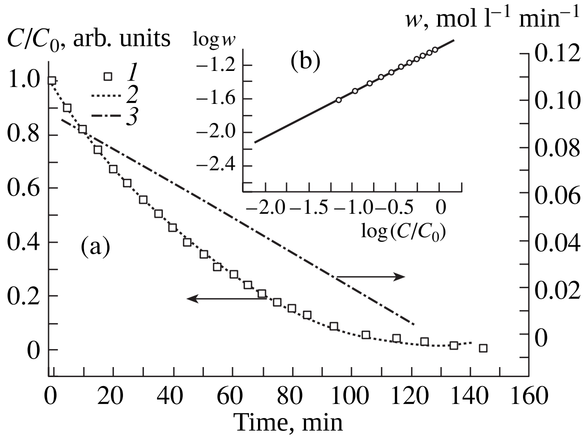


Fig. 1. Kinetic curves of α-pinene hydrogenation. (a) The time dependence of α-pinene concentration (C/C_0): (*1*) experimental data and (*2*) data calculated by Eq. (1). (b) The rate of hydrogenation (*w*) of α-pinene as a function of (*3*) time or concentration in logarithmic coordinates. Reaction conditions: $T = 40$°C; $P_{H_2} = 11$ atm; 4%Pd/C catalyst, 10.0 g/l; and α-pinene, 25 ml.

pore volume (by moisture capacity) was 0.7 cm^3/g. The average particle size of supported palladium (according to electron-microscopic data) was 3.5 nm.

The concentrations of products in the reaction mixture were determined by chromatography (FID; 7 m × 3 mm column packed with Silicone SE 30 on Chromaton N-AW (particle size of 0.16–0.20 mm)). The retention times of the main components were the following: 1450 s for α-pinene, 1780 s for *trans*-pinane, and 1910 s for *cis*-pinane. The products were identified by chromatography–mass spectrometry on a VG-7070 instrument.

RESULTS AND DISCUSSION

General Consideration

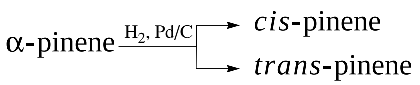
According to chromatographic analysis, the hydrogenation of α-pinene resulted in the formation of *cis*- and *trans*-pinane. By-products due to pinane ring opening were not detected. The consumption of hydrogen was consistent with the reaction stoichiometry. This fact allowed us to correctly convert the time dependence of the amount of consumed hydrogen into kinetic curves on the α-pinene concentration–time coordinates. For convenience in calculations, the concentration of α-pinene was expressed in arbitrary units as a ratio between current (*C*) and initial (C_0) concentrations.

Over the entire ranges of temperatures and hydrogen pressures examined, the curves of α-pinene concentration plotted as functions of time (*t*) (Fig. 1a) were adequately described by polynomials of the form

$$C/C_0 = 1 + at + bt^2. \qquad (1)$$

The reaction rate constant of hydrogenation, which was obtained by differentiating Eq. (1), linearly decreased with time. The rate of hydrogenation plotted against α-pinene concentration was also linear on logarithmic coordinates (Fig. 1b). The order of reaction with respect to α-pinene was found from the slope of this straight line, and the logarithm of the rate constant was found from an intercept on the axis of ordinates at $\log(C/C_0) = 0$. The initial rate of hydrogenation (w_0) at a given P_{H_2} and catalyst concentration was determined either from an initial portion of the curve or as the product of the initial concentration of α-pinene into the rate constant calculated from all experimental points. The obtained values were almost equal.

The ratio between the *cis* and *trans* isomers of pinane changed within the ranges $T = 0$–100°C and $P_{H_2} =$ 1–11 atm. However, under conditions of a particular experiment (at constant *T* and P_{H_2}), the selectivity (*S*) of formation of *cis*- and *trans*-pinane was independent of the conversion of α-pinene, and it remained almost constant ($S_{trans} = 41\%$ at $T = 90$°C and $P_{H_2} = 2$ atm, and $S_{trans} = 15\%$ at $T = 20$°C and $P_{H_2} = 11$ atm). This fact indicates that the formation of *cis*- and *trans*-pinane occurs via two parallel routes as follows:



Effect of Catalyst Concentration

The initial rate of reaction (w_0) was a linear function of catalyst concentration (Fig. 2a). The selectivity of *trans*-pinane formation and the order of reaction (*n*) with respect to α-pinene were independent of catalyst concentration (Fig. 2b). This fact suggests that the mass transfer of hydrogen from the gas phase to the liquid and the diffusion of dissolved hydrogen to catalyst grains occurred rapidly and did not limit processes that occurred at the catalyst surface.

Effect of Hydrogen Pressure

The initial rate of α-pinene hydrogenation as a function of hydrogen pressure has the shape of a monotonically increasing curve with a plateau at high hydrogen pressures (Figs. 3a, 3b). In the temperature range 0–100°C, experimental data are adequately described by the hyperbolic function (Figs. 3c, 3d)

$$w_0 = A_1 P_{H_2}/(A_2 + P_{H_2}), \qquad (2)$$

where A_1 and A_2 are empirical parameters, which are constant under particular experimental conditions.

It should be borne in mind that the apparent rates of complex reactions depend on the occurrence of a great number of steps. Because of this, it is difficult to correlate the observed kinetics with the real mechanism. At the same time, it is our opinion that a number of justified assumptions on the concentrations of active reactant species at the surface of Pd can be made based on an analysis of the experimental data on α-pinene hydrogenation.

At low values of P_{H_2} (<6 atm), functions illustrated in Figs. 3a and 3b are close to a linear shape, which corresponds to a first-order reaction with respect to hydrogen pressure. This is observed in the case when the concentration of hydride species is much lower than the concentration of free adsorption sites on the surface. Evidently, a deviation from linearity at high values of P_{H_2} is due to the filling of the catalyst surface with adsorbed hydrogen.

The order of reaction with respect to α-pinene concentration monotonically increased with hydrogen pressure. This relationship (Fig. 4a) is adequately described by the function

$$n = B_1 P_{H_2}/(B_2 + P_{H_2}). \quad (3)$$

Note that these functions were in almost complete agreement in the temperature range 20–90°C. This fact indicates that the order of reaction with respect to α-pinene concentration primarily depends on hydrogen pressure rather than temperature. The extrapolation of linear anamorphosis (3) (Fig. 4b) to the value $P_{H_2} = 0$ gives the limiting value of the quantity $n = 0$. Evidently, at a low hydrogen pressure, the rate of hydrogenation of surface compounds is small compared with the rate of equilibration between α-pinene present in solution and its adsorbed forms, which occupy a significant portion of the free surface of the catalyst. As a result of this, the apparent rate of reaction is independent of changes in the concentration of α-pinene in solution over a wide range of α-pinene conversions (up to 90%). Moreover, equilibria are established in all reversible steps of α-pinene transformation, which occur at the catalyst surface. This results in a ratio between *cis*- and *trans*-pinane close to the thermodynamic equilibrium value. In this case, hydrogen adsorption on the surface (dissolution in the bulk of a particle) is a rate-limiting step of reaction, and the rate of this step linearly depends on P_{H_2} (Figs. 3a, 3b). At a sufficiently high hydrogen pressure, the value of n tends to 0.56–0.57 regardless of reaction temperature. The fractional order of reaction with respect to α-pinene concentration is indicative of a complex multistep mechanism including competition between α-pinene and hydrogen for free sites at the catalyst surface.

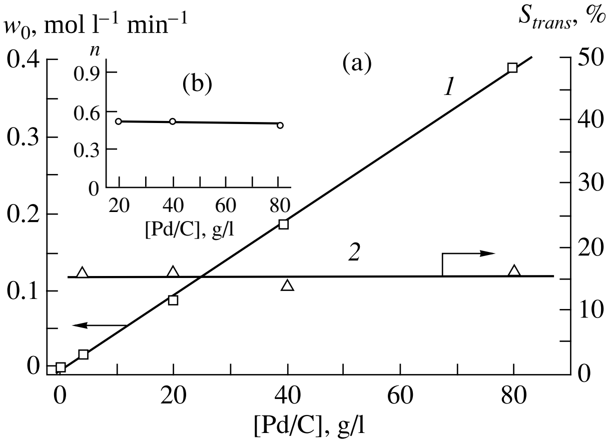


Fig. 2. (a) (*1*) Initial rate (w_0) of α-pinene hydrogenation and (*2*) the selectivity of *trans*-pinane formation as functions of catalyst concentration; (b) the order of reaction (n) with respect to α-pinene concentration. Reaction conditions: $T = 20°C$, $P_{H_2} = 11$ atm, and α-pinene, 25 ml.

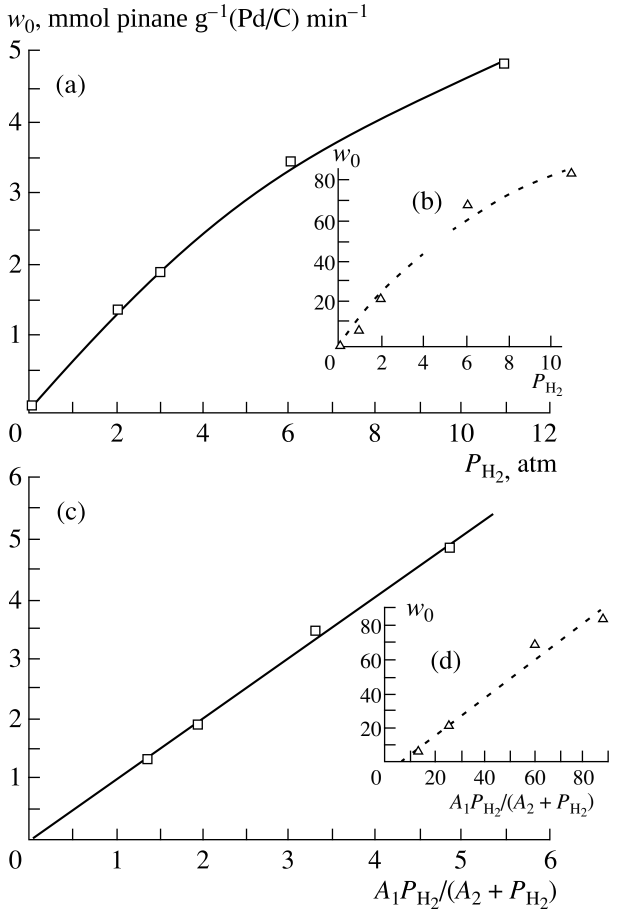


Fig. 3. (a, b) Initial rate (w_0) of α-pinene hydrogenation as a function of P_{H_2} and (c, d) linear anamorphoses (Eq. (2)) at T, °C: (a, c) 20 and (b, d) 90. Reaction conditions: 4%Pd/C catalyst, 2.0–80.0 g/l and α-pinene, 25 ml.

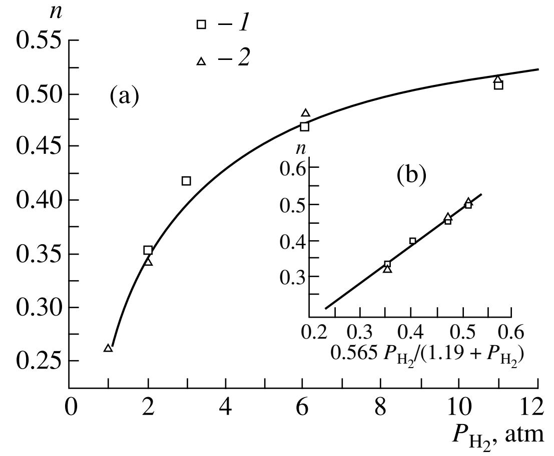


Fig. 4. (a) Order of reaction (*n*) with respect to α-pinene concentration as a function of P_{H_2} and (b) a linear anamorphosis (Eq. (3)). T = (*1*) 20 or (*2*) 90°C. Reaction conditions: 4%Pd/C catalyst, 2.0–80.0 g/l and α-pinene, 25 ml.

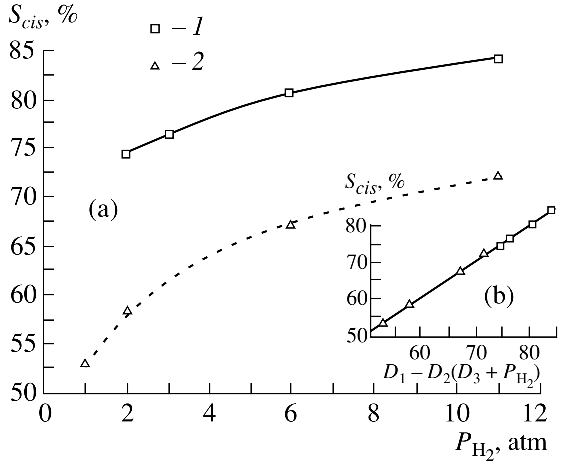
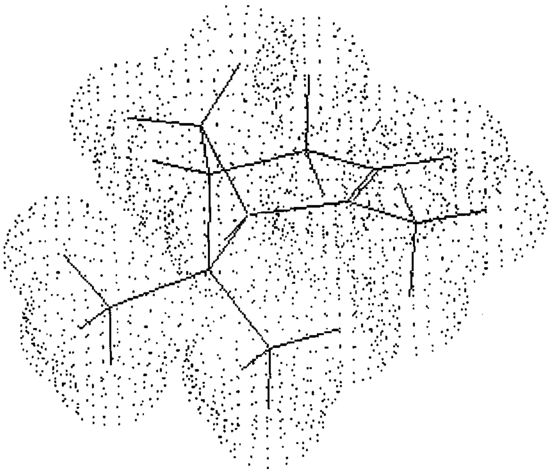


Fig. 5. (a) Selectivity of *cis*-pinane formation in the reaction of α-pinene hydrogenation as a function of P_{H_2} and (b) a linear anamorphosis (Eq. (4)). T = (*1*) 20 or (*2*) 90°C. Reaction conditions: 4%Pd/C catalyst, 2.0–80.0 g/l and α-pinene, 25 ml.

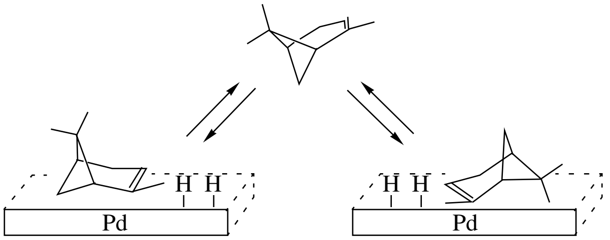
The selectivity of *cis*-pinane formation monotonically increased with increasing P_{H_2} (Fig. 5a), and it can be described by the equation

$$S_{cis} = D_1 - D_2/(D_3 + P_{H_2}). \quad (4)$$

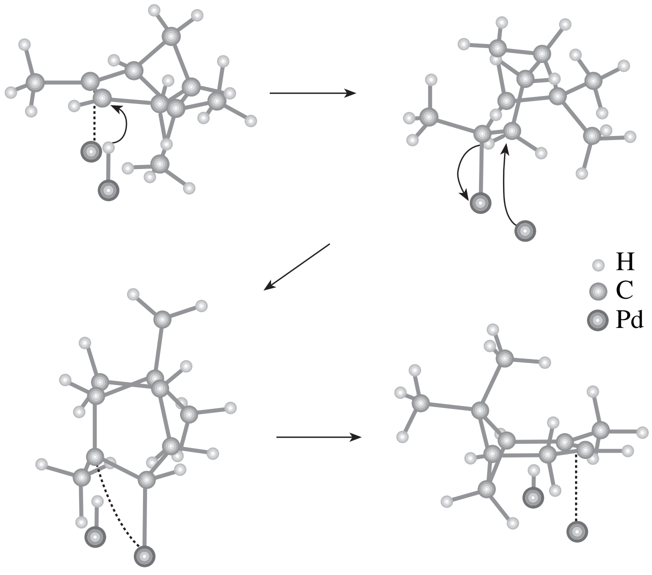
It is clear that S_{cis} depends on two terms: a constant D_1 and a hyperbolic function, which depends on hydrogen pressure. Thus, we can conclude that two factors affect the selectivity of reaction: the interaction of α-pinene with the catalyst surface and the concentration of surface hydride species.



Indeed, two sp^2-hybrid carbon atoms at the C=C bond in the α-pinene molecule form a plane in which all four substituents are located (two carbon atoms of a pinene ring, the carbon atom of a methyl group, and a hydrogen atom). The π orbital of the double bond is oriented perpendicularly to this plane. The >CH_2 unit is arranged on one side of the plane, whereas the much more bulky >$C(CH_3)_2$ unit is arranged on the other side. The α-pinene molecule is activated upon adsorption because of the formation of a π complex with a surface palladium atom.



The maximum overlapping of the π orbital and the *d* orbital of Pd is possible in the case when the steric effect of substituents arranged on the adsorption side of the α-pinene molecular plane is minimum. Thus, the most favorable form of adsorbed α-pinene is a structure in which the bulky >$C(CH_3)_2$ unit is directed oppositely to the surface of Pd. In the adsorbed complex, the methyl group is also deflected from the catalyst surface for steric reasons. Because of this, the >$C(CH_3)_2$ unit and the methyl group occur on the side of the plane formed by the sp^2-hybrid carbon atoms of the C=C bond, and this structure is responsible for the formation of *cis*-pinane. The adsorption of the α-pinene molecule on the opposite side will result in the formation of a surface structure responsible for the formation of *trans*-pinane. An equilibrium between these two forms of adsorption of the α-pinene molecule on the surface of Pd depends on the Gibbs energies of these adsorption processes. This Gibbs energy is a function of temperature, and it is independent of the concentration of free adsorption sites, that is, of the pressure of hydrogen. The insertion of an activated α-pinene molecule into the Pd–H bond results in the formation of a surface Pd–σ-pinanyl complex, in which the conformation of the pinane ring (*cis* or *trans*) corresponds to the form of adsorbed α-pinene. It was found using deuterium–hydrogen exchange that the insertion of an olefin into the Pd–H bond is a reversible process for cycloalkenes under analogous conditions on a Pd catalyst [5]. The commonly accepted mechanism of olefin isomerization includes the steps of insertion of a coordinated olefin into the Me–H bond, rotation about a C–C bond, and β-elimination of a hydrogen atom. In cyclic hydrocarbons, starting from a five-membered ring, rotation about a C–C bond takes place on changing the ring conformation. The rotation angle is 56.44° for five-membered rings, whereas this angle can be as great as 120° for six-membered rings (conformations: chair ⟷ boat; chair ⟷ boat ⟷ chair). For a pinane ring, the rotation angle is 85°. Taking into account that the torsion angle between the Pd–C and C–H bonds (attached H atom) in the σ-pinanyl complex is 42.5°, the change in the conformation of the pinane ring will result in rotation about the C–C axis through 85°. Because of this, the plane that goes through the Pd–C and C–C bonds will be located between the C–H bonds of the CH_2 group. Thus, either of the hydrogen atoms of the CH_2 group can participate in the reaction of β-elimination. The elimination of an attached hydrogen atom will result in the formation of the initial π complex, whereas the elimination of another hydrogen atom will result in the formation of a π complex in which α-pinene is oriented on the opposite side. This process can be represented by the following scheme:



In the newly formed Pd–σ-pinanyl complex, the conformation of the pinane ring is correspondingly changed. An equilibrium between the *cis* and *trans* conformations of the pinanyl ligand in the surface σ complex is attained upon repeating the steps of hydrogen attachment and elimination many times. The hydrogenolysis of the Pd–C bond in the Pd–σ-pinanyl complex gives the pinane molecule without changing its conformation.

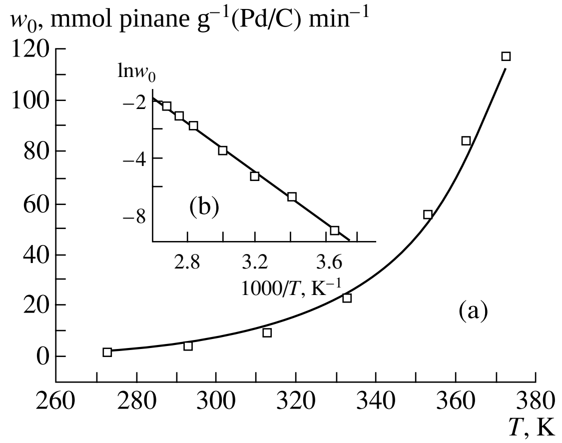
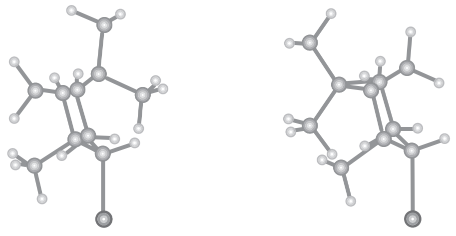


Fig. 6. Temperature dependence of the initial rate of reaction (w_0) in (a) linear and (b) Arrhenius coordinates. Reaction conditions: P_{H_2} = 11 atm; 4%Pd/C catalyst, 1.6–80.0 g/l; and α-pinene, 25 ml.

The extrapolation of linear anamorphosis (4) to $P_{H_2} = 0$ gives the selectivity $S_{0,\,cis} = D_1 - D_2/D_3$, which corresponds to the conditions of equilibration between the *cis* and *trans* conformations of surface complexes (Fig. 5b). The *cis*- and *trans*-σ-pinanyl complexes exhibit identical structures of their reaction centers and nearest environments, whereas they differ in the mutual orientations of methyl groups separated from their reaction centers by three C–C bonds.



trans-σ-pinanyl *cis*-σ-pinanyl

It is believed that changes in the standard Gibbs energies for the reaction of Pd–C bond hydrogenolysis in the *cis*-σ-pinanyl and *trans*-σ-pinanyl complexes are similar. Then, the ratio between the equilibrium concentrations of the *cis* and *trans* conformations of surface complexes at $P_{H_2} \longrightarrow 0$ corresponds to the ratio between the *cis* and *trans* isomers of pinane in a thermodynamic equilibrium mixture.

Moreover, the rate constants of Pd–C bond hydrogenolysis in these structures are insignificantly different. Consequently, the value of $S_{0,\,cis}$ reflects the thermodynamic equilibrium composition of *cis*- and *trans*-

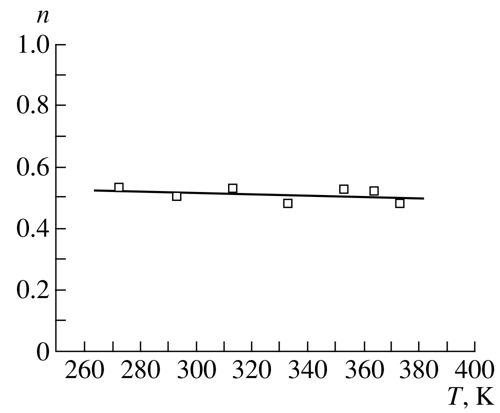


Fig. 7. Temperature dependence of the order of reaction with respect to α-pinene concentration. Reaction conditions: P_{H_2} = 11 atm; 4%Pd/C catalyst, 1.6–80.0 g/l; and α-pinene, 25 ml.

pinanes at a given temperature. Note that the selectivity of *cis*-pinane formation was 56–57% in the *in situ* nonstereoselective reduction of α-pinene with hydrogen in the Li + ethylamine system at 20°C [4]. This value falls within the range $S_{0,\,cis}$ = 68–46.6% for a temperature range of 20–90°C.

The extrapolation of linear anamorphosis (4) to the infinitely high pressure of hydrogen gives the selectivity $S_{\infty,\,cis} = D_1$, which corresponds to conditions under which the step of elimination of a β-hydrogen atom is suppressed. In this case, $S_{\infty,\,cis}$ reflects the concentration ratio between two adsorbed α-pinene species—the precursors of *cis* and *trans* conformations of a pinane ring. It is likely that a decrease in the value of $S_{\infty,\,cis}$ from 93 to 80% as the temperature was increased from 20 to 90°C is due to a shift in the equilibrium toward the formation of *trans*-pinane.

Effect of Temperature

The apparent reaction rate of α-pinene hydrogenation increased with temperature (Fig. 6a), and the temperature dependence of the rate was linear in Arrhenius coordinates (Fig. 6b). The found value of the apparent activation energy (37.5 ± 1.0 kJ/mol) is comparable to the activation energy (38.9 kJ/mol) of cyclohexene hydrogenation on a Pd/Al_2O_3 catalyst [5].

The order of reaction with respect to pinene concentration was constant at a constant pressure of hydrogen, and it remained unchanged as the temperature was increased (Fig. 7). It is likely that under these conditions an increase in the temperature accelerated all steps of a catalytic cycle, but it did not change the concentration ratio between adsorbed α-pinene species and hydrogen on the catalyst surface.

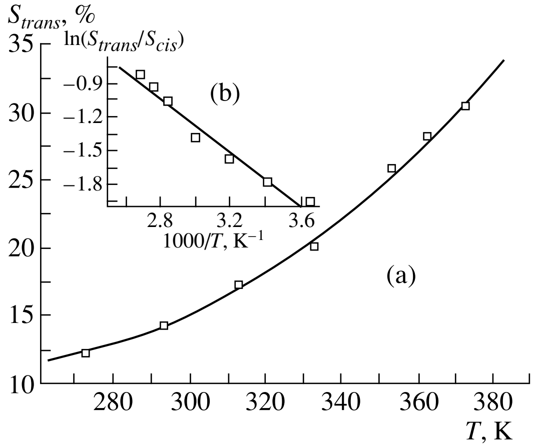


Fig. 8. (a) Temperature dependence of the selectivity of *trans*-pinane formation (S_{trans}); (b) the temperature dependence of the ratio S_{trans}/S_{cis} in Arrhenius coordinates. Reaction conditions: P_{H_2} = 11 atm; 4%Pd/C catalyst, 1.6–80.0 g/l; and α-pinene, 25 ml.

The selectivity of *trans*-pinane formation monotonically increased with temperature (Fig. 8). The hydrogenation of α-pinene to *cis*- and *trans*-pinanes occurred via two parallel routes, and the selectivity of *trans*-pinane formation can be expressed as the ratio between constants

$$S_{trans} = k_{trans}/(k_{trans} + k_{cis}) = k_{trans}/k,$$

where k is the apparent rate constant of α-pinene hydrogenation, and k_{trans} and k_{cis} are the apparent rate constants of formation of *trans*-pinane and *cis*-pinane, respectively.

Note that

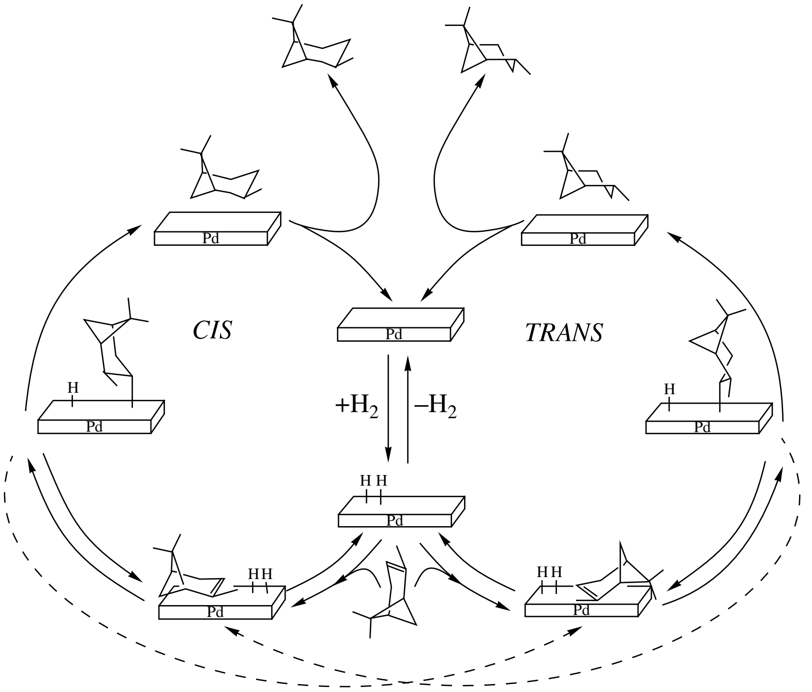
$$\ln k_{trans} = \ln(kS_{trans}); \quad \ln k_{cis} = \ln(kS_{cis});$$

$$S_{trans}/S_{cis} = k_{trans}/k_{cis}.$$

Then, the activation energy of formation of either of the isomers can be estimated from the $\ln(kS_{trans}) - 1/T$ or $\ln(kS_{cis}) - 1/T$ temperature dependence, respectively, and the difference (E_a(*trans*) – E_a(*cis*)) can be determined to sufficient accuracy based on the $\ln(k_{trans}/k_{cis}) - 1/T$ relationship (Fig. 8b). We estimated the activation energies as E_a(*trans*) = 47.0 ± 2.5 and E_a(*cis*) = 35.5 ± 1.4 kJ/mol; (E_a(*trans*) – E_a(*cis*)) = 9.8 ± 0.8 kJ/mol.

Mechanism of Formation of cis-Pinane and trans-Pinane

Based on the studies performed, we propose the following mechanism of α-pinene hydrogenation, which includes two catalytic cycles:



The reversible adsorption of hydrogen resulted in the formation of hydride species on the surface of palladium. The subsequent adsorption of α-pinene resulted in the precursors of the *cis* (*CIS* cycle) or *trans* (*TRANS* cycle) conformation of pinane. The insertion of adsorbed α-pinene into the Pd–H bond resulted in the formation of σ-*cis*- and σ-*trans*-pinanyl complexes. The reverse process (the elimination of hydrogen) can afford π-olefinic complexes with both initial and inverted conformations. The pinane molecule resulted from the hydrogenolysis of the Pd–C bond in the σ-pinanyl complex. Its conformation corresponds to the structure of the pinanyl ligand in the σ complex. The desorption of pinane from the palladium surface makes room for the subsequent cycles of the catalytic reaction. The ratio between the *cis* and *trans* isomers of pinane depends on the ratio between reaction rates in the corresponding cycles.

The concentration ratio between adsorbed α-pinane species is the key parameter responsible for the ratio between these rates. In turn, this parameter depends on the ratio between the equilibration rates of α-pinene sorption–desorption and hydrogen-atom attachment–elimination. An increase in the pressure of hydrogen suppresses the elimination, and the selectivity of *cis*-pinane formation depends on the ratio between the constants of α-pinene adsorption as *cis* and *trans* precursors. In this case, a decrease in the temperature shifts the equilibrium toward the *cis* form. A decrease in the pressure of hydrogen is favorable for the equilibration of all adsorbed species. In this case, the ratio between the *cis* and *trans* isomers of pinane approaches the thermodynamic equilibrium composition, which, in turn, is also temperature dependent. An increase in the reaction temperature is favorable for an increase in the number of free adsorption sites without considerable changes in the ratio of the total concentration of adsorbed α-pinene species to the concentration of palladium hydride species. Because of this, the selectivity of *cis*-pinane formation decreases without changes in the order of reaction with respect to α-pinene concentration or hydrogen pressure.

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