Kinetics of the Hydrogenation of Pinane Hydroperoxide to Pinanol on Pd/C

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Abstract—The liquid-phase hydrogenation of pinane hydroperoxide (PHP) to pinanol on a Pd/C catalyst at 20–80°C and hydrogen pressures of 1–11 atm was studied. It was found that the rate of hydrogenation decreased with PHP concentration. The rate of PHP hydrogenation dramatically increased as the pressure of hydrogen was increased in a range of 2.5–3 atm. A mechanism was proposed for the hydrogenation of PHP. According to this mechanism, the step of hydrogen activation (homolytic or heterolytic addition) depends on the redox properties of the catalyst surface (the ratio between adsorbed PHP species and H_2). It was found that pinanol can be prepared with high selectivity by the hydrogenation of PHP on a Pd/C catalyst under mild conditions.

INTRODUCTION

This work continues a series of publications [1, 2] on the catalytic reactions of terpene hydrocarbon conversion into fragrance compounds. The catalytic hydrogenation of pinane hydroperoxide (PHP) opens the way to the easy preparation of pinanol [3, 4], which is used in the synthesis of linalool [5, 6] and other fragrance compounds. Preparative methods for obtaining pinanol by the hydrogenation of PHP in the presence of PtO_2 [7] and Pd/Al_2O_3 [8] are known. A special feature of the PHP hydrogenation reaction is that transition metals, which are hydrogenation catalysts, simultaneously catalyze the decomposition of peroxides [9, 10]. In particular, a side reaction of 1-acetyl-2,2-dimethyl-3-ethylcyclobutane formation was observed in the hydrogenation of PHP in the presence of a number of catalysts: Ni/Cr_2O_3, skeletal Ni, Co–Mn–Ag, and Pd/C [3]. The use of a Pd/C catalyst in the reaction of PHP hydrogenation resulted in the highest selectivity of pinanol formation [3].

The aim of this work was to study the kinetics of PHP hydrogenation into pinanol on a Pd/C catalyst.

EXPERIMENTAL

A PHP solution in pinane was prepared by pinane oxidation with atmospheric oxygen at 100°C [2] followed by the vacuum distillation of an excess of pinane to a PHP concentration of 4.3 mol/l.

The experiments on the liquid-phase hydrogenation of PHP 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 apparent rate of hydrogenation was not limited by the rate of hydrogen dissolution at a 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 m²/g, and the total pore volume (by moisture capacity) was 0.7 cm³/g. The average particle size of supported palladium (according to electron-microscopic data) was 3.5 nm.

The products of PHP reduction were identified by gas–liquid chromatography taking into account published data [8]. The concentrations of products in a reaction mixture were determined by chromatography (FID; 7 m × 3 mm column packed with Silicone SE 30 (15%) on Chromaton N-AW (particle size of 0.20–0.25 mm); $T = 100–200°C$; heating rate of 4 K/min). The retention times of the main components were the following: 1140 s for *trans*-pinanol and 1190 s for *cis*-pinanol.

RESULTS AND DISCUSSION

Product Composition

The catalytic hydrogenation of PHP resulted in the formation of a mixture of the following composition: 2-pinanol (88.0–90.5%), 1-acetyl-2,2-dimethyl-3-ethylcyclobutane (2.6–3.8%), isopinocamphone (0.7–1.8%), isopinocampheol and verbanol (4.9–5.7%), and isoverbanol and verbanone (1.5–1.9%).

Note that the initial PHP was a set of isomers different in the positions of OOH groups. The process conditions of hydrogenation ($T = 20–80°C$, $P_{H_2} = 1–11$ atm, and $M_{Cat} = 0.01–1.20$ g) had almost no effect on the isomeric composition of reaction products. An analogous product composition was obtained by the quantitative reduction of PHP with Na_2SO_3 [8]. Evidently, the isomeric composition of hydrogenation products depends
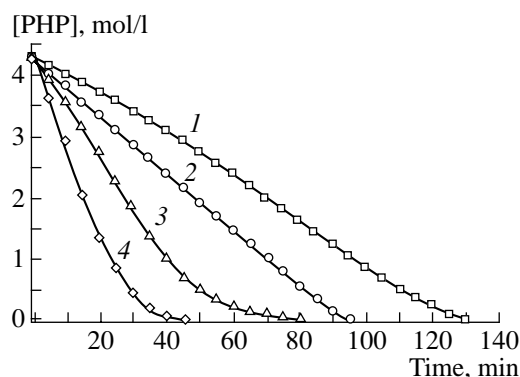
Fig. 1. Kinetic curves of PHP hydrogenation under various reaction conditions: (*1*) $T = 40°C$, $P_{H_2} = 1$ atm, and [4% Pd/C] = 9.6 g/l; (*2*) $T = 20°C$, $P_{H_2} = 3$ atm, and [4% Pd/C] = 48.0 g/l; (*3*) $T = 40°C$, $P_{H_2} = 6$ atm, and [4% Pd/C] = 1.6 g/l; and (*4*) $T = 40°C$, $P_{H_2} = 11$ atm, and [4% Pd/C] = 1.6 g/l. $[PHP]_0 = 4.3$ mol/l; solvent, pinane (25 ml); catalyst, 4% Pd/C.

Fig. 2. Rate of hydrogenation as a function of PHP concentration at $T = $ (*1*) 20, (*2*) 30, (*3*) 50, (*4*) 70, or (*5*) 80°C. Reaction conditions: $[PHP]_0 = 4.3$ mol/l; solvent, pinane (25 ml); [4% Pd/C] = 0.4–48.0 g/l; and $P_{H_2} = 3$ atm.

on the ratio between isomers in the parent PHP, because the hydrogenolysis of the peroxide O–O bond did not affect the configuration of the initial PHP molecule:
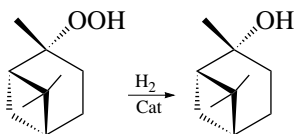
The intramolecular oxidation of cyclic hydroperoxides in the presence of palladium complexes resulted in the formation of α,β-unsaturated carbonyl compounds [3, 8]. It is likely that the formation of small amounts of 1-acetyl-2,2-dimethyl-3-ethylcyclobutane (2.64–3.79%) in the hydrogenation of PHP on a Pd/C catalyst in the tested ranges of temperatures and pressures occurred by the intramolecular oxidation of the PHP molecule followed by the hydrogenation of the C=C bond:
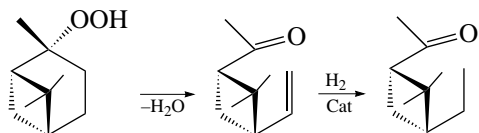
The formation of 1-acetyl-2,2-dimethyl-3-ethylcyclobutane occurred more intensely in the hydrogenation of PHP in the presence of Ni-containing catalysts [3]. Evidently, this is due to the greater ability of Ni (E^0(Ni/Ni^{2+})) = –0.25 V) to oxidize under the action of PHP, as compared with Pd (E^0(Pd/Pd^{2+}) = +0.987 V) [11].

Taking into account that the concentration of 1-acetyl-2,2-dimethyl-3-ethylcyclobutane was insignificant in comparison with the concentration of the target product (*cis* and *trans* isomers of 2-pinanol), the
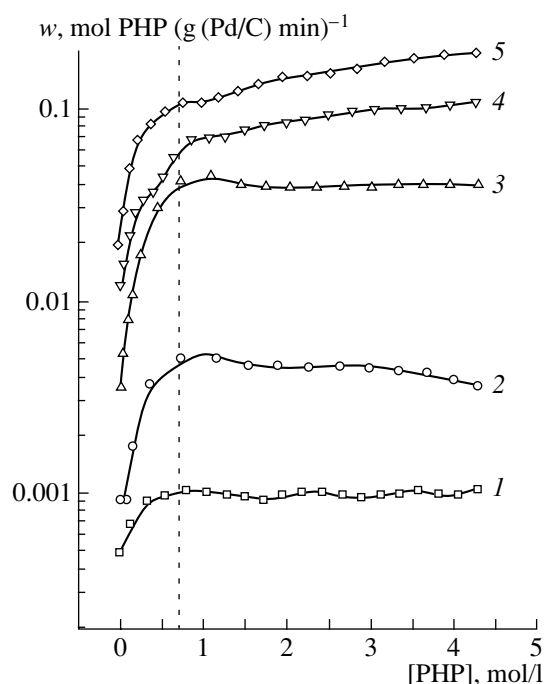
amounts of consumed hydrogen in all of the experiments can be considered as corresponding to the reaction stoichiometry. This fact allowed us to correctly transform the time dependence of the amount of consumed hydrogen into kinetic curves in the [PHP]–time coordinates (Fig. 1).

General Consideration

The initial reaction rate of PHP hydrogenation was a linear function of catalyst amount at temperatures of 20–80°C and hydrogen pressures of 1–11 atm. This fact indicates that the reaction was of first order with respect to catalyst concentration over the tested ranges of temperatures and pressures.

The obtained kinetic curves (Fig. 1) varied from linear to *S*-shaped depending on experimental conditions (temperature, hydrogen pressure, and catalyst amount). This can be due to the inhibition of reaction at high concentrations of PHP. Shutikova *et al.* [3] also reported on a decrease in the rate of hydrogenation with PHP concentration. Thus, the concentration of PHP is a key parameter responsible for the kinetics of hydrogenation.

Effect of Temperature

At a low temperature (20°C), the rate of reaction as a function of current PHP concentration, which was
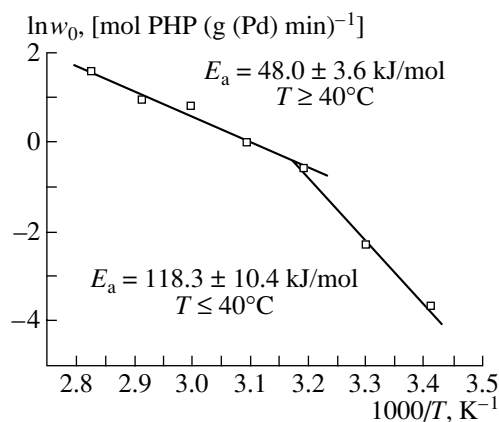
Fig. 3. Initial rate of hydrogenation as a function of temperature in Arrhenius coordinates. Reaction conditions: $[PHP]_0 = 4.3$ mol/l; solvent, pinane (25 ml); [4% Pd/C] = 0.4–48.0 g/l; and $P_{H_2} = 3$ atm.

Fig. 4. Initial rate of hydrogenation as a function of PHP concentration at $P_{H_2} = (1)$ 11, (2) 6, (3) 3, or (4) 1 atm. The positions of maximums are marked with asterisks. Reaction conditions: $[PHP]_0 = 4.3$ mol/l; solvent, pinane (25 ml); [4% Pd/C] = 1.6–9.6 g/l; and $T = 40°C$.

obtained by differentiating the time dependence of the PHP concentration, exhibits two portions (Fig. 2). At low concentrations (<0.6 mol/l), the rate of reaction dramatically increased with [PHP] and reached a plateau. At high PHP concentrations (0.6–4.3 mol/l), the rate of PHP hydrogenation remained almost unchanged. This fact is indicative of the zero order of hydrogenation with respect to PHP concentration in the region of high PHP concentrations.

At elevated temperatures (30–50°C), the functions exhibited extremums. As the concentration of PHP was increased, the rate of its hydrogenation increased, reached a maximum, and then gradually decreased. This fact is indicative of the inhibition of reaction at high concentrations of PHP.

At temperatures higher than 50°C, the rate of PHP hydrogenation at the second portion monotonically increased with PHP concentration.

A switch from the first portion to the second corresponds to a change in rate-limiting steps (the rate of PHP adsorption is limiting at the first portion; hydrogen adsorption is a rate-limiting step at the second portion). Note that the position of the border between the two portions of curves remained unchanged as the temperature was increased. It is likely that the ratio between the steady-state concentrations of PHP and hydrogen adsorbed on the catalyst surface depends on reaction temperature only slightly.

The temperature dependence of the initial rate of hydrogenation plotted in Arrhenius coordinates (Fig. 3) exhibits two linear portions with apparent activation energies of 118.3 ± 10.4 kJ/mol for the low-temperature region and 48.0 ± 3.6 kJ/mol for $T = 50–80°C$. A decrease in the apparent activation energy by a factor of about 2 may be indicative of the switch of process to the intradiffusion region. The low concentration of the byproduct 1-acetyl-2,2-dimethyl-3-ethylcyclobutane, the
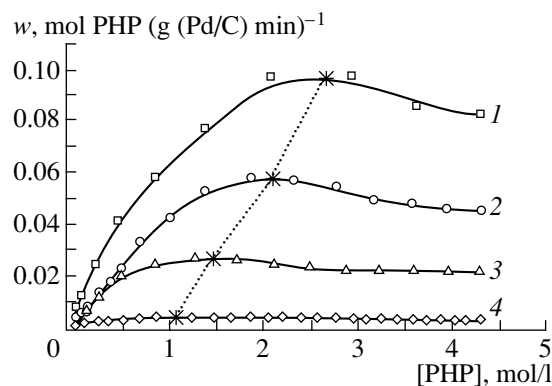
formation of which is aided by a deficit of hydrogen, indicates that the catalyst surface occurred in a reduced state at a high temperature. It is likely that the decrease in E_a was due to a change in the mechanism of PHP hydrogenation.

Effect of Hydrogen Pressure

The rate of the hydrogenation reaction was an extremal function of PHP concentration over the entire range of hydrogen pressures (1–11 atm) (Fig. 4). In this case, the position of a maximum was shifted toward higher PHP concentrations as the pressure of hydrogen was increased. This fact is indicative of a competition between PHP and H_2 for free adsorption sites on the surface of palladium. The right-hand branches of curves (toward increasing concentration of PHP from a maximum rate) form a family of curves, distances between which characterize the dependence of the rate of hydrogenation on hydrogen pressure. Analysis of these curves showed that the relationship between the rate of hydrogenation and the pressure of hydrogen is described by the same function over this range of PHP concentrations.

An analysis of the dependence of the initial rate of PHP hydrogenation (w_0) on the pressure of hydrogen allowed us to recognize two portions. At low hydrogen pressures (≤2 atm), w_0 linearly increased. As the pressure of hydrogen was further increased, w_0 sharply changed; then, it became a linear function with a slope much greater than that at the initial portion (Fig. 5). This fact suggests that two mechanisms of hydrogen activation on the surface of Pd can occur at different reactant ratios PHP/H_2 (mol/mol).

On the surface of Pd metal, the activation of hydrogen occurs via the reaction of oxidative addition by the homolytic cleavage of the H–H bond:
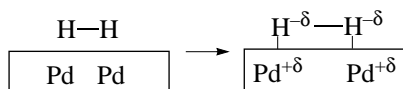
On an oxidized surface of Pd, the activation of hydrogen can occur via the heterolytic cleavage of the H–H bond:
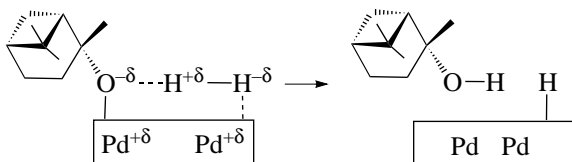
In the course of PHP hydrogenation, the catalyst surface can occur in both oxidized and reduced states. This is evidenced by data on the catalyst potential as a function of PHP concentration [3]. It is believed that, at a low pressure of H_2 and a high concentration of PHP, the surface of Pd occurs in an oxidized state and the activation of H_2 by oxidative addition is hindered. In this case, the likely mechanism is the heterolytic cleavage of the H–H bond. In the region of high hydrogen pressures, the catalyst surface primarily occurs in a
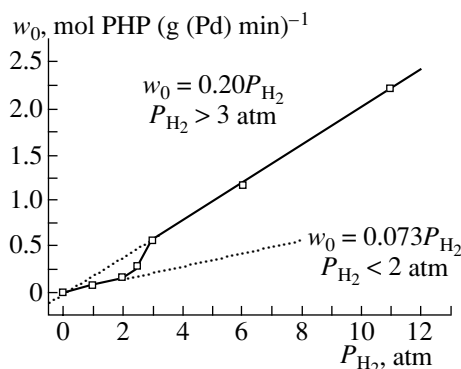
Fig. 5. Initial rate of hydrogenation as a function of hydrogen pressure. Reaction conditions: $[PHP]_0 = 4.3$ mol/l; solvent, pinane (25 ml); [4% Pd/C] = 1.6–9.6 g/l; and $T = 40°C$.

reduced state, which is favorable for the mechanism of homolytic H–H cleavage.

Mechanism of PHP Hydrogenation

The results obtained in the course of kinetic studies allowed us to propose the following scheme of PHP conversion:
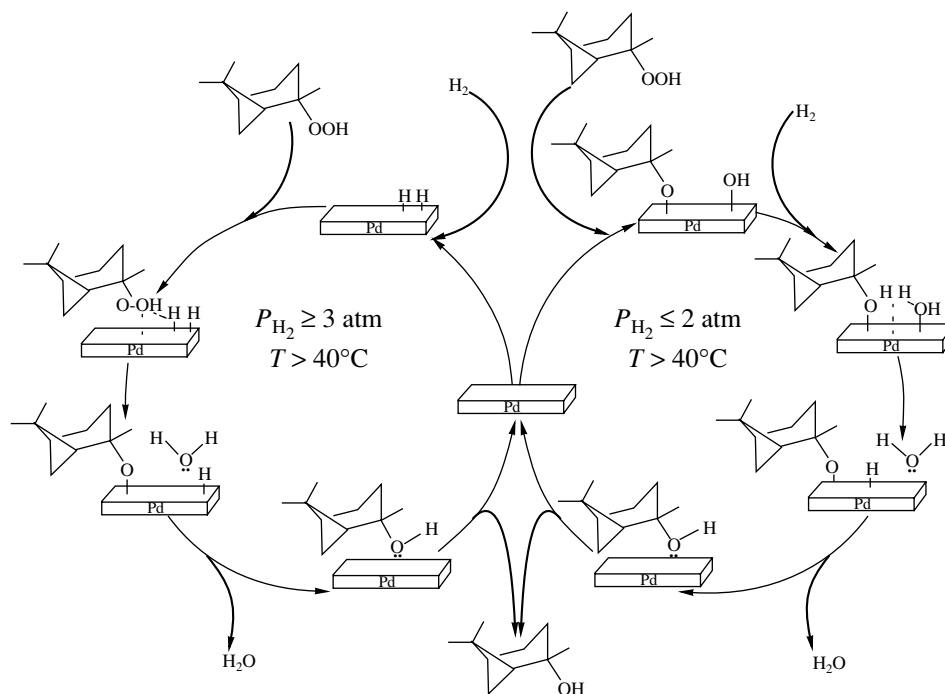
(1) At a high pressure of hydrogen, surface hydride species are readily formed in the reaction of oxidative addition by the homolytic cleavage of the H–H bond. The chemisorption of PHP on the reduced surface of Pd results in the formation of the water molecule and a surface pinoxyl species. Reductive elimination because of an attack of a surface hydride at the oxygen atom of the adsorbed pinoxyl group results in the formation of the pinanol molecule and in the regeneration of the Pd surface.

(2) Under conditions of a low pressure of hydrogen, the chemisorption of PHP occurs via an oxidative addi-

tion reaction by the cleavage of the peroxide O–O bond with the formation of surface –OR and –OH species. The heterolytic cleavage of the H–H bond with the participation of surface nucleophilic oxygen atoms (OR or OH groups) and the Pd atom results in the formation of the H_2O (ROH) molecule and the H adatom. As a result of reductive elimination, the pinanol molecule is formed followed by the regeneration of the surface of the metallic Pd.

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