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Kinetics of Pinane Oxidation to Pinane Hydroperoxide by Dioxygen

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Abstract—The liquid-phase oxidation of pinane to pinane hydroperoxide (PHP) by dioxygen is studied at 353–373 K and under dioxygen pressures ranging from 2 to 4 atm. The rate of pinane oxidation is described by the equation $w = w_{O_2} + w_{PHP}$, where the term w_{O_2} is independent of the PHP concentration, w_{PHP} is a function of the concentration $[PHP]^n$, and n ranges from 0.5 at low [PHP] to 1.0 at high [PHP]. The *cis*-isomer of 2-hydroperoxopinane generates free radicals during autooxidation. The ratio of the rate constants of *cis*- and *trans*-pinane oxidation is found ($k_{cis}/k_{trans} = 4.0$). The selectivity of the oxidation of pinane to PHP can reach 90–95%.

INTRODUCTION

Pinane hydroperoxide is a starting material for the preparation of pinanol—a valuable intermediate product in the synthesis of important perfumes, such as linalool, geraniol, and nerol [1, 2]. In addition, pinane hydroperoxide is used as an initiator of low-temperature radical polymerization of olefins [3].

Several papers [4–8] are devoted to the study of the preparation of pinane hydroperoxide (PHP) by the oxidation of pinane by molecular oxygen and identification of reaction products. The oxidation occurs via a radical mechanism and leads to the formation of many products. This is due to different routes for the transformation of *cis*- and *trans*-pinane isomers and hydroperoxide decomposition under the reaction conditions. A kinetics study of pinane oxidation is necessary for the development of a highly selective preparation procedure for PHP.

This study is devoted to the kinetics of pinane oxidation of by molecular oxygen.

EXPERIMENTAL

The liquid-phase oxidation of pinane was carried out in a stainless steel 150-ml reactor equipped with an electromagnetic stirrer (800–1000 rpm) and an automated system for the measurement and detection of the amount of absorbed oxygen. The autoclave was thoroughly washed with a solution of PHP and pinane. The armature of the electromagnetic stirrer was protected with Teflon. The calculated amount of pinane or a solution of hydroperoxide in pinane was loaded into the autoclave.

Pinane (the ratio of the *cis*- to *trans*-isomers was 2.54) was prepared by the hydrogenation of α-pinene on the Pd/C catalyst [9].

The total amount of the obtained pinane hydroperoxide was determined from the amount of hydrogen consumed for the catalytic hydrogenation of the pinane oxidation products (Pd/C catalyst, $T = 40°C$, and $P_{H_2} = 7$ atm). The composition of the products in the reaction mixture after hydroperoxide hydrogenation was determined by chromatography (flame-ionization detector, column 7 m × 3 mm packed with Silicone SE 30 (fraction 0.16–0.20 mm) on Chromaton N-AW). Nitrogen used as a carrier gas was passed with a velocity of 30 ml/min. The retention times of the main components were as follows: *trans*-pinane, 1780 s; *cis*-pinane, 1910 s ($T = 74°C$); *trans*-pinan-2-ol, 1140 s and *cis*-pinan-2-ol, 1190 s (temperature was increased from 100 to 200°C at a rate of 4°C/min). The products were identified by chromatography coupled with mass spectrometry on a VG-7070 instrument.

RESULTS AND DISCUSSION

General Regularities of the Process

A plot of the amount of absorbed dioxygen vs. reaction time is a monotonically ascending curve with a smooth initial region (Fig. 1). In a series of experiments with different durations of the reaction, we observed almost complete coincidence of oxygen absorption curves, indicating a good reproducibility of the results. A plot of the total amount of PHP vs. reaction time coincides with the curve of oxygen absorption at the initial region. When more than 0.4 mole oxygen per mole of pinane was absorbed, PHP accumulation is retarded. This indicates that almost all of the oxygen is

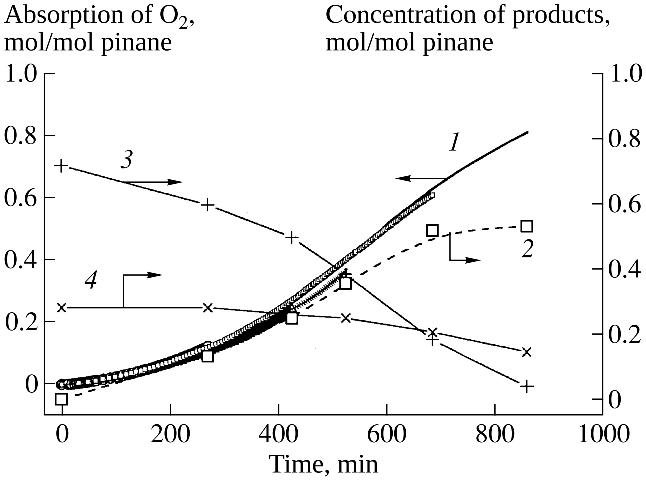


Fig. 1. Changes in the (*1*) amount of absorbed oxygen and concentrations of (*2*) PHP, (*3*) *cis*-pinane, and (*4*) *trans*-pinane during the reaction.

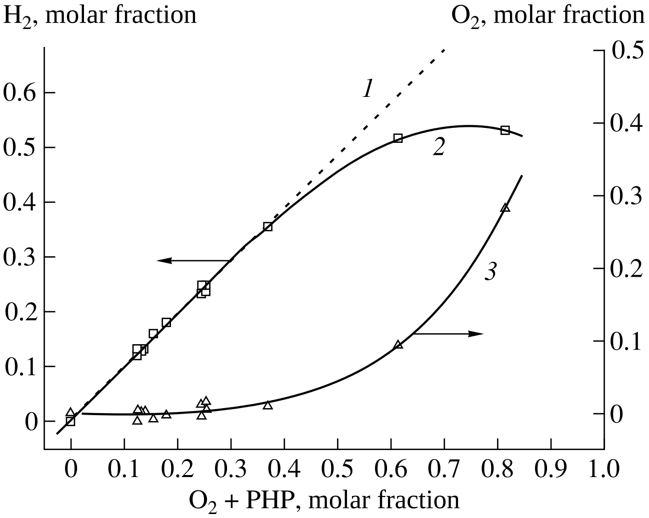


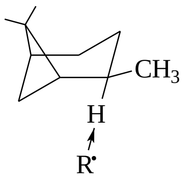
Fig. 2. Material balance of the oxidation of pinane by molecular oxygen: (*1*) calculated straight line (the ratio of absorbed O_2 and H_2 equals 1); (*2*) experimental curve of hydrogen absorption during the titration of PHP; and (*3*) curve obtained by the subtraction of curve *2* from straight line *1*. Reactions conditions: 50 ml of pinane, $T = 100°C$, $P_{O_2} = 2–4$ atm.

consumed for the formation of hydroperoxide at initial stages. The subsequent divergence of the curves is likely due to PHP decomposition during its long presence under the reaction conditions. To strike a material balance, the amount of reactants was expressed in molar fractions. For that purpose, the number of moles of absorbed oxygen, taking into account added PHP, and the number of moles of hydrogen consumed in PHP hydrogenation were divided by the total number of moles of the components in the initial mixture (Fig. 2).

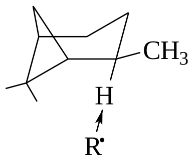
In an oxygen absorption interval of 0–0.25 molar fractions, the amount of hydrogen consumed for the titration of PHP corresponds to the calculated value (Fig. 2, curve *2*). The deviation of curve *2* from the calculated straight line determines the molar fraction of the products containing no active oxygen (the by-products of PHP decomposition). In this interval, the selectivity to PHP formation calculated as a ratio between the corresponding values in curve *2* and straight line *1* is 90–95%. This indicates the possibility for developing a highly selective process of pinane oxidation by molecular oxygen.

Specific Features of the Transformation of cis- and trans-Isomers of Pinane

The ratio of the *cis*- to *trans*-isomers in the starting pinane is 2.54. The concentration of *cis*-pinane decreases during oxidation from 0.72 to 0.04 molar fractions, whereas the concentration of *trans*-pinane changes insignificantly (from 0.28 to 0.15 molar fractions). This indicates that the hydroperoxide is mainly formed from *cis*-pinane. The lower reactivity of *trans*-pinane is a result of the steric effect of methyl groups, which hinder the attack of a free radical at the tertiary hydrogen atom.



cis-Pinane



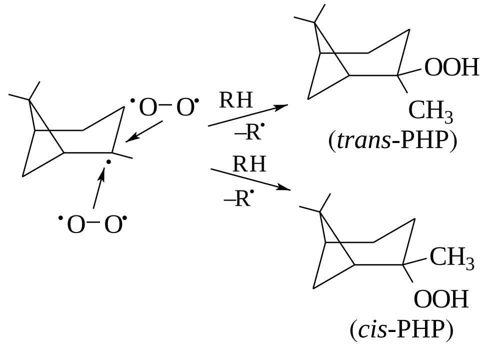
trans-Pinane

Since the oxidation of *cis*- and *trans*- pinane occurs under the same conditions involving the same radicals, the ratio of the apparent rate constants of these reactions can be estimated. The rates of isomer transformations found by differentiating the corresponding curves (Fig. 1, curves *3* and *4*) and divided by their concentrations remain almost unchanged during the whole experiment. The ratio of these values corresponds to that of the apparent rate constants of *cis*- (k_{cis}) and *trans*-pinane (k_{trans}) oxidation: $k_{cis}/k_{trans} = 4.0$, which is close to the published value [4].

Thus, at the initial region of the curve of oxygen absorption at a [*cis*-pinane]/[*trans*-pinane] ratio of 2–2.5, the oxidation rate of *cis*-pinane is an order of magnitude higher than that of the *trans*-isomer, and the apparent kinetics largely refers to *cis*-pinane oxidation.

Isomeric Composition of Products

The selective oxidation of *cis*-pinane by molecular oxygen gives a set of isomers, which differ in the position of the OOH group [4]. Its reduction to the OH group must occur without a change in the positional and steric configuration of the product alcohol molecule. The main products of pinane oxidation (after reduction by hydrogen) are *cis*-pinan-2-ol (56.5–57.9%) and *trans*-pinan-2-ol (28.8–29.3%). In addition, pinan-3-ol and insignificant amounts of other oxygen-containing products (12.8–14.7%) are formed. The composition of products obtained by *cis*-pinane oxidation followed by the reduction of the hydroperoxide with Na_2SO_3 was similar [4]. The selectivity to a particular pinanol isomer remains about the same in the O_2 absorption interval from 0 to 0.25 moles per mole of pinane (Fig. 3). This indicates that the formation of pinane hydroperoxide isomers proceeds via parallel routes:



At a high oxygen absorption (>0.25 mol O_2 per mole of pinane), the selectivity of pinan-2-ol formation gradually decreases (Fig. 3). Analysis of the isomeric composition of pinan-2-ol shows that the concentration of *trans*-pinan-2-ol decreases insignificantly as the amount of absorbed oxygen increases, whereas the concentration of the *cis*-isomer decreases by a factor of ~1.5. This indicates that a decrease in the selectivity of pinane hydroperoxide, (pinan-2-ol) formation is mostly due to the decomposition of *cis*-2-hydroperoxopinane. It is known that chain initiation is due to the decomposition of a hydroperoxide molecule during autooxidation. Therefore, during pinane autooxidation, *cis*-pinane hydroperoxide generates free radicals.

Influence of the Pinane Hydroperoxide Concentration on the Reaction Rate

A series of experiments with different concentrations of initial PHP gave a family of plots of the amount of absorbed O_2 vs. reaction time (t) (Fig. 4), which are well described by polynomials of the type

$$N = A + Bt + Ct^2,$$

where N is the amount of absorbed O_2 (in moles per mole of pinane); A, B, and C are empirical parameters, and t is the reaction time (in min).

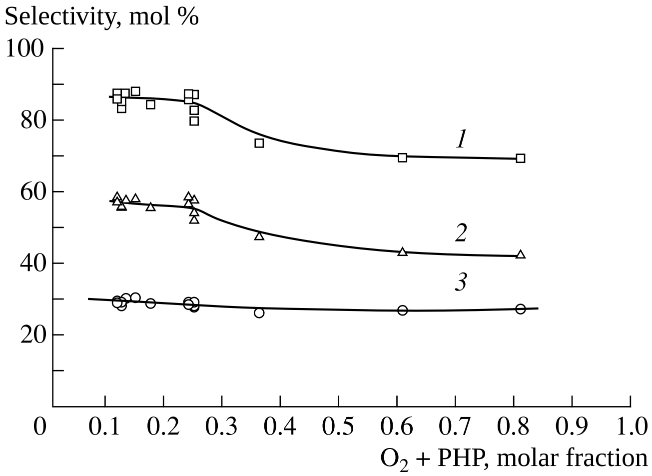


Fig. 3. Selectivities to pinanols vs. amount of absorbed oxygen (after PHP reduction): (*1*) pinan-2-ol; (*2*) *cis*-pinan-2-ol; and (*3*) *trans*-pinan-2-ol. Reaction conditions: pinane 50 ml, T = 80–100°C, P_{O_2} = 2–4 atm.

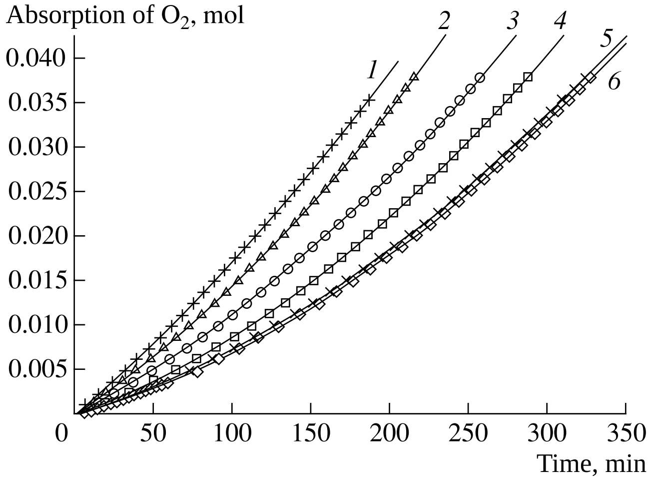


Fig. 4. Oxygen absorption vs. time at the initial PHP concentration, mol/l: (*1*) 0, (*2*) 0.039, (*3*) 0.078, (*4*) 0.156, (*5*) 0.312, and (*6*) 0.784. Reaction conditions: pinane 50 ml, T = 100°C, P_{O_2} = 2 atm.

The initial rates of oxygen absorption were found by the differentiation of these curves at the zero-time limit. In this experimental series, at the initial instant, the concentration of *cis*-pinane was approximately the same (3.8–4.4 mol/l). This enables the determination of the reaction order with respect to the PHP concentration. The initial rate of oxygen absorption as a function of the PHP concentration is well described by the function

$$w = w_{O_2} + w_{PHP},$$

where the term w_{O_2} 2 = 0.7 mmol l^{-1} min^{-1} is independent of the PHP concentration, and w_{PHP} is a function of $[PHP]^{05}$ (Fig. 5).

Note that $w_{PHP} = 0$ in the absence of PHP, but the overall reaction rate w differs from zero ($w = w_{O_2}$ = 0.7 mmol l^{-1} min^{-1}) (Fig. 5). It is reasonable to assume

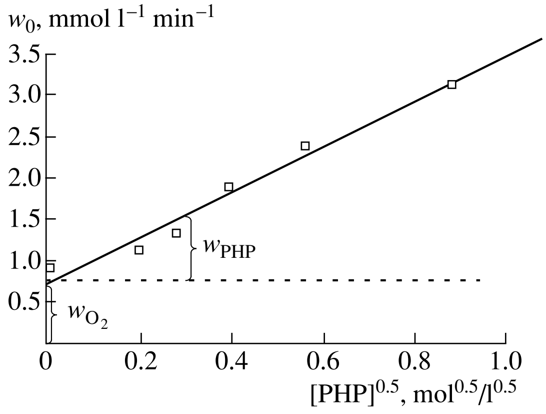


Fig. 5. Initial reaction rate vs. PHP concentration. Reaction conditions: pinane 50 ml, $T = 100°C$, $P_{O_2} = 2$ atm.

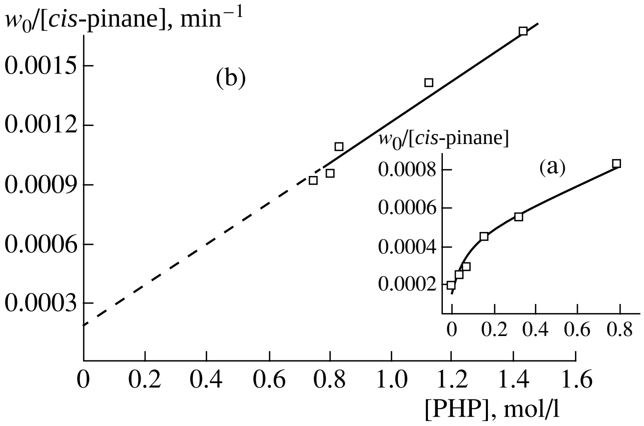


Fig. 6. Initial reaction rate dirided by the *cis*-pinane concentration as a function of the PHP concentration in the [PHP] intervals of (a) 0–0.8 and (b) 0.8–1.5 mol/l. Reaction conditions: pinane 50 ml, $T = 100°C$, $P_{O_2} = 2$ atm.

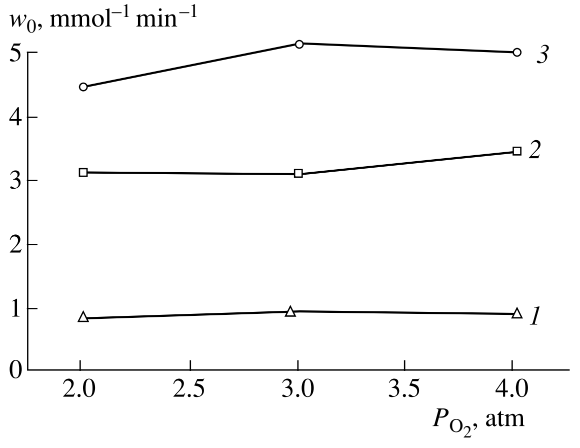


Fig. 7. Initial reaction rate as a function of the oxygen pressure at the initial PHP concentrations, mol/l: (*1*) 0; (*2*) 0.784; and (*3*) 1.490. Reaction conditions: pinane 50 ml, $T = 100°C$.

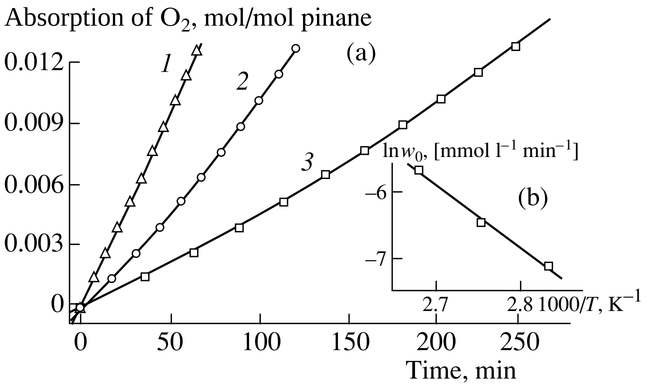


Fig. 8. Temperature effect on the (a) oxygen absorption during oxidation and (b) initial reaction rate in the Arrhenius coordinates: (*1*) 100, (*2*) 90, and (*3*) 80°C. Reaction conditions: pinane 50 ml, $P_{O_2} = 4$ atm, $[PHP]_0 = 0.784$ mol/l.

that the term w_{O_2} (independent of [PHP]) is determined by the route in which the chain is initiated due to the direct interaction of pinane with the O_2 molecule:

$$RH + O_2 \longrightarrow R^{\bullet} + OOH^{\bullet}. \qquad (I)$$

The second term w_{PHP} characterizes the contribution of the route of chain initiation by the monomolecular decomposition of pinane hydroperoxide:

$$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH. \qquad (II)$$

At the initial region, both routes make comparable contributions to the overall rate of pinane oxidation (Fig. 5).

The recombination of free radicals formed in reactions (I) and (II) results in the formation of initial reactants. This is most likely a reason for the high selectivity in pinane oxidation at a low PHP concentration (Fig. 2).

The reaction order with respect to the PHP concentration increases with an increase in [PHP] and reaches 1.0 (Fig. 6). This is characteristic of autooxidation kinetics with a bimolecular initiation step:

$$2ROOH \longrightarrow RO^{\bullet} + ROO^{\bullet} + H_2O. \qquad (III)$$

The yield of by-products increases in this region (Fig. 2). This phenomenon is probably the result of the formation of various products in radical recombination, for example, by the reaction:

$$RO^{\bullet} + ROO^{\bullet} \longrightarrow ROR + O_2.$$

Influence of the Oxygen Pressure on the Reaction Rate

In a series of experiments with different initial PHP concentrations, the initial rate of pinane oxidation was independent of the oxygen pressure in the studied pressure interval (Fig. 7). This implies that the rate of pinane oxidation via routes (I) and (II) has a zero order with respect to the oxygen pressure.

The selectivity to PHP (85.3–87.2%) and the *cis*-to-*trans* isomeric ratio (1.96–1.98) are independent of the oxygen pressure at 2–4 atm. Most likely, in pinane oxidation, the steps involving molecular oxygen are not limiting. The almost zero reaction order with respect to the oxygen pressure is typical of hydrocarbon autooxidation [10].

Temperature Effect

An increase in the temperature of the process (from 80 to 100°C) leads to an increase in the rate of oxygen absorption (Fig. 8), whereas the reaction rate order with respect to PHP (0.5), selectivity to pinan-2-ol (83–86%), and the *cis*/*trans* ratio of the pinan-2-ol isomers (1.90–1.95) remain unchanged. The pinane *cis*-isomer is predominantly oxidized in the reaction, whereas the concentrarion of the *trans*-isomer changes insignificantly in this temperature interval. Thus, the found temperature function is in fact related to the rate of *cis*-pinane oxidation. The activation energy of *cis*-pinane oxidation (~80 kJ/mol) corresponds to those of the known processes of radical oxidation, for example, the oxidation of dibenzyl ether initiated by azoisobutyronitrile (E_{act} = 93.66 kJ/mol [11]).

CONCLUSIONS

Thus, the study of the specific features of autocatalytic pinane oxidation helped to find the conditions for the highly selective preparation of pinane hydroperoxide, a valuable key product of organic synthesis.

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