Effect of temperature and CO pressure on the rate of cyclohexene hydrocarbomethoxylation catalyzed by the $Pd(OAc)_2$—PPh_3—TsOH system*

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The quantitative regularities of the effect of CO pressure and temperature on the rate of cyclohexene hydrocarbomethoxylation catalyzed by the $Pd(OAc)_2$—PPh_3—TsOH system were defined. Extremal dependences of the reaction rate on the CO pressure were revealed in the temperature range from 353 to 383 K. To interpret the obtained results, the catalytic cycle was constructed which included the hydride, alkyl, and acyl palladium complexes of the cationic type as intermediates. It was proposed that the catalyst is partially converted into an inactive form due to the exchange between ligands. The experiments on the effect of the CO pressure on the reaction rate made it possible to estimate the apparent rate constants for the kinetic reaction equation obtained earlier.

Key words: hydrocarbalkoxylation, palladium precursor, reaction rate, cyclohexene, methyl cyclohexanecarboxylate.

Hydrocarbalkoxylation of alkenes is a promising method for obtaining esters.[1—3] The possibilities of the synthesis of these products by the hydrocarbalkoxylation of linear alkenes C_6—C_9, cyclohexene, and styrene were described. An important information on the reaction mechanism can be obtained from the kinetic data, in particular, from the values of apparent activation energies. However, reports about the effect of temperature on the kinetics of these reactions are scarce and fragmentary. The hydrocarbalkoxylation of propylene by primary, secondary, and tertiary alcohols in the presence of the $Pd(PPh_3)Cl_2$ catalyst at 363—403 K gave[4] products in high yields with 40—50% selectivity for butanoic acid esters. The study of the catalytic hydrocarbalkoxylation of steroid androstene-16 by ethylene glycol and CO in the presence of $Pd(PPh_3)Cl_2$ showed[5] that the conversion increases from 27 to 92% with the temperature increase from 323 to 423 K. Analyzing values of apparent activation energy obtained for the catalytic mono- and polycarbonylation of ethylene to propionic acid derivatives and polyketones,[6] interesting conclusion about the reaction mechanism can be made. It was concluded that at temperatures >363 K the rate-determining step of the process is ethylene insertion at the Pd—Ac bond rather than the coordination of ethylene to the palladium center. The first attempts to study the temperature effect on the direction of the reaction in detail were made in works on the Pd-catalyzed hydrocarbalkoxylation of ethylene[7] and cyclohexene.[8] The study of the catalytic hydrocarbalkoxylation of ethylene to methyl propionate[7] in the presence of $Pd(PPh_3)_2(TsO)_2$ established that the turnover frequency of the catalyst (TOF) increases nonlinearly with increasing temperature iin the range 333—393 K. In addition, the palladium catalyst decomposes at temperatures >373 K. The extremal dependences of the TOF on the concentration of triphenylphosphine and hydride sources (*p*-toluenesulfonic acid (TsOH), water, and hydrogen) were obtained in the range 353—373 K. In all cases, the TOF increases with temperature; however, the activation parameters were not determined. The same groups of authors described the effect of the concentration of substances involved in cyclohexene hydrocarbmethoxylation[8] on the reaction rate in the temperature range 353—373 K.

Recently, we have conducted the study of the influence of the temperature, reagents (methanol, cyclohexanol, and CO), and components of the $Pd(PPh_3)Cl_2$—PPh_3—TsOH catalytic system on the rate of cyclohexene hydrocarbalkoxylation.[9—11] Based on the results of this study, we were able to estimate the apparent activation energies and to use the relevant values to derive the series of stability of the palladium complexes in the reaction medium.[9—11] This report is a continuation of our earlier works. We present herein the results of kinetic studies of the effect of the CO pressure and temperature on

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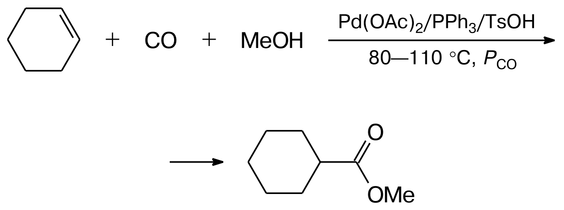
the rate of catalytic cyclohexene hydrocarbomethoxylation in the presence of the $Pd(OAc)_2$—PPh_3—TsOH system (Scheme 1).

Scheme 1



Cyclohexene was chosen as an alkene for hydrocarbalkoxylation because its reaction sites are chemically equivalent and, hence, the hydrocarbomethoxylation of cyclohexene is accompanied by the formation of a single product, which makes it possible to use this reaction as a model one.

Experimental

The reaction was studied in a periodical reactor described earlier.[12]. Each experiment was carried out at constant temperature and CO pressure in toluene. Samples of the reaction mixture were analyzed by GLC. *o*-Xylene was used as an internal standard when determining the content of components. The procedures of kinetic experiments and analysis of the reaction mixture were described.[13] The reagents (toluene, cyclohexene, methanol, and *o*-xylene) were dried over calcium chloride and rectified. All components of the catalytic system ($Pd(OAc)_2$, PPh_3, and TsOH) were commercial grade materials (Sigma—Aldrich).

Results and Discussion

Five runs of experiments in the temperature range 353—383 K were carried out to study the effect of the CO pressure and temperature on the rate of cyclohexene hydrocarbomethoxylation. The typical kinetic curves describing the accumulation of the reaction product (methyl cyclohexanecarboxylate) are shown in Fig. 1.

The initial reaction rates were determined using the differentiation of the initial regions of the kinetic curves describing ester accumulation in the reaction mixture. The corresponding dependences of the initial reaction rate on the CO pressure in the temperature range 353—383 K are presented in Fig. 2. The dependences are described by curves with maxima in the range of CO pressures 0.9—2.1 MPa. These results are consistent with the earlier obtained data on the effect of the CO pressure on the hydrocarbalkoxylation of cyclohexene by methanol[9,10,14] and cyclohexanol.[11,15]

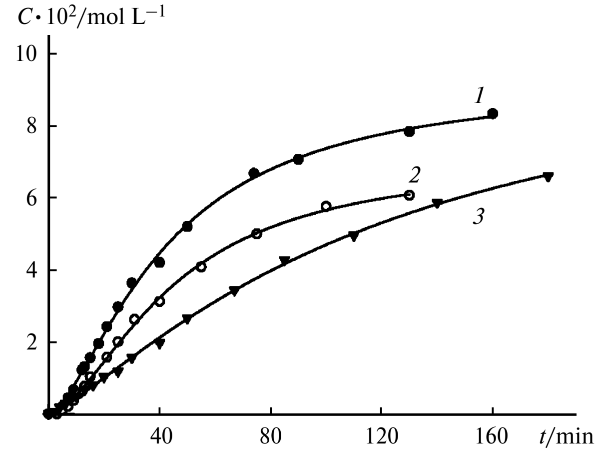


Fig. 1. Typical kinetic curves of methyl cyclohexanecarboxylate accumulation at P_{CO} = 1.6 (*1*), 1.1 (*2*), and 3.1 MPa (*3*); T = 373 K; concentrations, mol L^{-1}: [C_6H_{10}] = 0.10, [MeOH] = 0.45, [$Pd(OAc)_2$] = $2.0 \cdot 10^{-3}$, [PPh_3] = $1.2 \cdot 10^{-2}$, [TsOH] = $2.4 \cdot 10^{-2}$, and [*o*-xylene] = $5.0 \cdot 10^{-2}$.

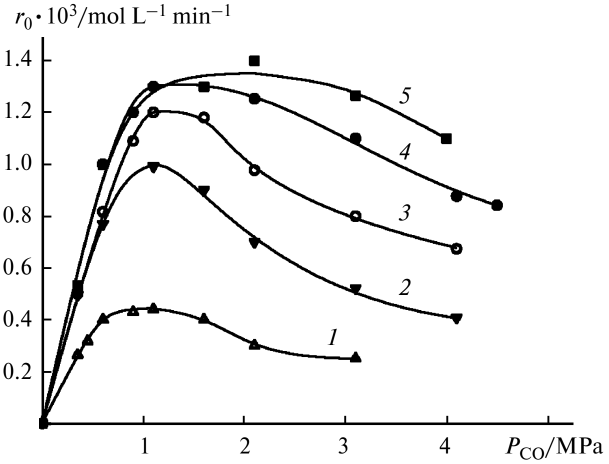


Fig. 2. Initial hydrocarbomethoxylation rate (r_0) *vs* CO pressure at 353 (*1*), 363 (*2*), 373 (*3*), 378 (*4*), and 383 (*5*) K; concentrations, mol L^{-1}: [C_6H_{10}] = 0.10, [MeOH] = 0.45, [$Pd(OAc)_2$] = = $2.0 \cdot 10^{-3}$, [PPh_3] = $1.2 \cdot 10^{-2}$, [TsOH] = $2.4 \cdot 10^{-2}$, and [*o*-xylene] = $5.0 \cdot 10^{-2}$.

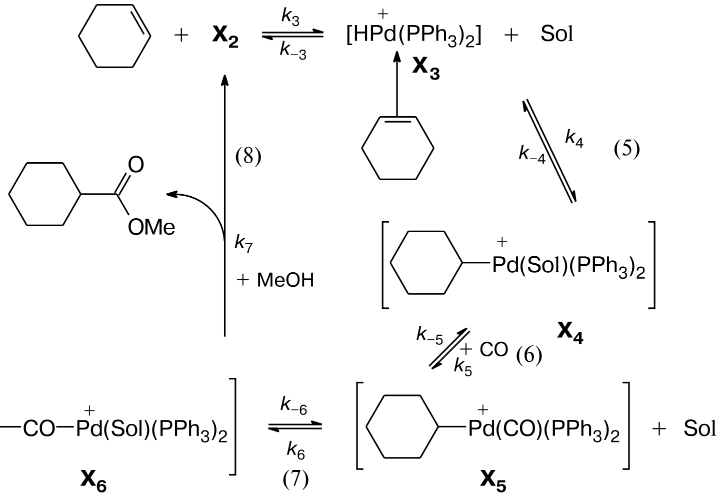
Earlier we found that, under the same conditions, hydrocarbalkoxylation is the first-order reaction with respect to cyclohexene[14–16] and $Pd(OAc)_2$ [16,17] and the dependences of the reaction rate on the concentration of alcohols (methanol and cyclohexanol),[10,11,14,15,18] PPh_3,[9,11,14–19] and TsOH[16,18,19] are described by curves with maxima. The following reaction mechanism can be proposed on the basis of the results described above and earlier obtained data (Scheme 2). Earlier the possibility of reduction of the Pd^{II} precursors with methanol to form zero-valence palladium complexes of the type $\mathbf{X_1}$ was demonstrated.[7,8] Complex $\mathbf{X_0}$ can add solvent (toluene) molecules: toluene is present in the reaction mixture in a significant excess over other components involved in the reaction (see Scheme 2, reaction (2)). At the same time, the

Scheme 2

$$\mathrm{Pd(OAc)_2 + 2\,PPh_3 + MeOH \xrightarrow{k_0} Pd(PPh_3)_2 + CH_2O + 2\,AcOH} \qquad (1)$$

$$\underset{\mathbf{X_0}}{\mathrm{Pd(PPh_3)_2}} + 2\,\mathrm{Sol} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{X_1}}{\mathrm{Pd(PPh_3)_2(Sol)_2}} \qquad (2)$$

$$\mathbf{X_1} + \mathrm{TsOH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{X_2}}{[\mathrm{H\overset{+}{P}d(Sol)(PPh_3)_2}]} + \mathrm{(Ts\overset{-}{O})Sol} \qquad (3)$$



$$\mathbf{X_1} + 2\,\mathrm{MeOH} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \underset{\mathbf{X_7}}{\mathrm{Pd(MeOH)_2(PPh_3)_2}} + 2\,\mathrm{Sol} \qquad (9)$$

$$\mathbf{X_1} + 2\,\mathrm{CO} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \underset{\mathbf{X_8}}{\mathrm{Pd(CO)_2(PPh_3)_2}} + 2\,\mathrm{Sol} \qquad (10)$$

$$\mathbf{X_1} + \mathrm{CO} \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} \underset{\mathbf{X_9}}{\mathrm{Pd(CO)(PPh_3)(Sol)_2}} + \mathrm{PPh_3} \qquad (11)$$

$$\mathbf{X_1} + \mathrm{MeOH} \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} \underset{\mathbf{X_{10}}}{\mathrm{Pd(MeOH)(PPh_3)(Sol)_2}} + \mathrm{PPh_3} \qquad (12)$$

$$\mathbf{X_1} + 2\,\mathrm{PPh_3} \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\mathbf{X_{10}}}{\mathrm{Pd(PPh_3)_4}} + 2\,\mathrm{Sol} \qquad (13)$$

Sol are solvent (toluene) molecules.

reaction of the palladium complexes with *p*-toluenesulfonic acid, which is a strong hydride source, affords the key intermediate of the catalytic cycle $\mathbf{X_2}$ (reaction (3)).[1,7,8]

The following arguments support the mechanism presented in Scheme 2. The types of intermediates shown in Scheme 2 have earlier been isolated, spectrally characterized, and tested for participation in the catalytic cycle.[20—24] The hydride intermediate $\mathrm{HPd(PPh_3)_2Cl}$ assigned to the type $\mathbf{X_2}$ and synthesized from $\mathrm{Pd(PPh_3)_4}$ and HCl affords the corresponding carboxylic acids upon the addition of hex-1-ene, HCl, CO, and water.[20] In turn, the hydride complex, which was isolated from the

$Pd(OAc)_2$—$P(C_6H_4SO_3Na\text{-}m)_3$ system in a medium of aqueous CF_3COOH, in the presence of ethylene gives alkylpalladium complexes of the type $\mathbf{X_4}$ reacting with CO to form acyl complex $\mathbf{X_6}$. The hydrolysis of the latter affords propionic acid and regenerates complex $\mathbf{X_2}$.[21] At the same time, for a series of Pd-containing catalytic systems, including those based on $Pd(PPh_3)_2Cl_2$, acyl complexes of the type $\mathbf{X_6}$ were isolated. The treatment of the complexes with aqueous solutions of acids (for example, HCl) gives the corresponding carboxylic acids, while the treatment with alcohols affords esters.[22—24]

The extremal pattern of the dependences of the reaction rate on the CO pressure obtained in this work and the earlier found dependences of the cyclohexene cyclocarbalkoxylation rate on the concentration of alcohols (methanol and cyclohexanol)[10,11,14,15,18] is caused, in our opinion, by two factors. The increase in the reaction rate with an increase in the alcohol concentration and CO pressure in the region of their low values observed in several works obeys the law of acting masses and, hence, an increase in the reagent concentration leads to an increase in the reaction rate. At the same time, excessive amounts of these reagents are involved in ligand exchange reactions (see Scheme 2, reactions (9)—(12)) with intermediates of the catalytic cycle. As a result, the formation of inactive palladium forms and withdrawal of a portion of the catalyst from the catalytic cycle are observed. Consequently, the hydrocarbalkoxylation rate decreases in the region of high alcohol concentrations and high CO pressures.

An explanation for the extremal pattern of the dependence of the hydrocarbalkoxylation rate on the PPh_3 concentration found earlier[9,11,14—19] is that the rates of ligand exchange reactions (11) and (12) and reaction (13) oppose one another in influencing the rate of hydrocarboxylation. The former two reactions are responsible for the generation of the active Pd complexes, and the latter is responsible for the withdrawal of a portion of the catalyst from the catalytic cycle.

An extremal character of the dependences of the cyclohexene hydrocarbalkoxylation rate on the concentration of TsOH monohydrate is caused by several factors.[16,18] An increase in the TsOH concentration in the system shifts the equilibrium of reaction (3) toward hydride intermediate $\mathbf{X_2}$ and increases its concentration in the system. That, in turn, results in an increase in the concentration of the reaction products and the observed increase in the rate because the catalytic cycle proceeds as a sequence of several steps (4)—(8). At the same time, the hydrocarbalkoxylation rate can decrease in the region of high acid concentration due to the decomposition of the Pd precursor to form palladium black (Pd_s) in the reaction with water vapor[1]

$$Pd(OAc)_2 + CO + H_2O \longrightarrow Pd_s + CO_2 + 2\,AcOH. \qquad (14)$$

Thus, the water concentration increases with an increase in the concentration of *p*-toluenesulfonic acid monohydrate in the system, which induces an increase in the rate of reaction (14) and, as a consequence, a decrease in the hydrocarbalkoxylation rate observed in a series of works.

It can be assumed that reaction (8) is the rate-determining step of the catalytic cycle. This assumption can be supported by the following arguments. The sensitivity of the reaction rate to the concentration and size of an alcohol molecule has earlier been established.[8,22] In the chain of reactions (1)—(8), alcohol participates in the first and last steps only. If none of these two steps is rate-determining, the rate of the whole process should be insensitive to the alcohol concentration and the size of its molecule and the reaction order with respect to alcohol should be zero. However, the kinetic studies demonstrate the first order of the hydrocarbalkoxylation reactions with respect to alcohol in the region of its low concentrations.[10,11,14,15] In addition, intermediates of the type $\mathbf{X_6}$ were isolated from the reaction systems of alkene hydrocarbalkoxylation containing all three reagents (alkene, CO, and alcohol),[3,4,20,23] which indicates their higher concentration in the system compared to preceding intermediates $\mathbf{X_0}$—$\mathbf{X_5}$. This suggests that reactions (1)—(7) are fast, whereas reaction (8) is the slowest step of the process and, hence, intermediates $\mathbf{X_6}$ are accumulated in the system. Thus, all established facts of sensitivity of the reaction rate to the concentration and size of the alcohol molecule and the accumulation of intermediates $\mathbf{X_6}$ in the reaction mixture indicate the rate-determining character of step (8).

Earlier[25] we obtained the kinetic equation for the hydrocarbomethoxylation of cyclohexene catalyzed by the $Pd(OAc)_2$—PPh_3—TsOH system. Under the conditions of one-factor experiment on studying the effect of the CO pressure, this equation takes the form

$$r = \frac{k_{\mathrm{app}} P_{\mathrm{CO}}}{A + bP_{\mathrm{CO}}^2 + cP_{\mathrm{CO}}}, \qquad \text{(I)}$$

where $k_{\mathrm{app}} = \dfrac{K_1K_2K_3K_4K_5K_6k_7}{1+K_1} \cdot$

$$\cdot \frac{C_{\mathrm{M}}[C_6H_{10}][\mathrm{TsOH}]^2[\mathrm{MeOH}]}{H_{\mathrm{CO}}},$$

$$A = 1 + \frac{K_1K_8}{1+K_1}\cdot[\mathrm{MeOH}]^2 + \frac{K_1K_{11}}{1+K_1}\cdot$$

$$\cdot\frac{[\mathrm{MeOH}]}{[\mathrm{PPh_3}]} + \frac{K_1K_{12}}{1+K_1}\cdot[\mathrm{PPh_3}]^2,$$

C_{M} is the analytical concentration of all monomeric palladium forms, $[C_6H_{10}]$ is the cyclohexene concentration, H_{CO} is Henry constant for CO, and $[PPh_3]$ is the concentration of free PPh_3 determined by the difference of its analytical concentration and the doubled concentration of $Pd(OAc)_2$ according to the stoichiometry of the Pd phosphine complexes.

We obtained the kinetic equations similar to Eq. (I) for the hydrocarbalkoxylation of cyclohexene by methanol and cyclohexanol in a series of our earlier works.[9—11,14,15] The agreement of Eq. (I) with the experimental data can be confirmed by the values of the initial reaction rate r_0 as a function of P_{CO}. The transformation of Eq. (I) gives

$$P_{CO}/r = A/k_{app} + (c/k_{app})P_{CO} + (b/k_{app})P^2{}_{CO}. \qquad \text{(II)}$$

The estimation by the least-squares method of the parameters of Eq. (II) gave the values presented in Table 1. It is seen that parameter c/k_{app} is statistically insignificant in the whole studied temperature range. Therefore, Eq. (II) can be reduced to the following form:

$$P_{CO}/r = A/k_{app} + (b/k_{app})P^2{}_{CO}. \qquad \text{(III)}$$

The dependences of P_{CO}/r on $P^2{}_{CO}$ corresponding to Eq. (III) are shown in Fig. 3. The values of the parameters of Eq. (III) obtained by the least-squares method are listed in Table 2. The values calculated by Eq. (III) taking into account confidence intervals are close to the values obtained using Eq. (II) and presented in Table 1. The plots (see Fig. 3) constructed using Eq. (III) demonstrate a good agreement between the experimental and calculated data. This confirms the statistical insignificance of parameter c/k_{app}.

Thus, the kinetic regularities of the effect of the CO pressure in the cyclohexene hydrocarbomethoxylation rate catalyzed by the $Pd(OAc)_2$—PPh_3—TsOH system were considered in the temperature range from 353 to 383 K. An extremal pattern of the dependences of the reaction rate on the CO pressure was established in the temperature range studied. The data obtained were interpreted in the framework of the hydride mechanism of hydrocarbalkoxylation. The apparent constants of the earlier obtained kinetic equation for the reaction were estimated by varying the CO pressure.

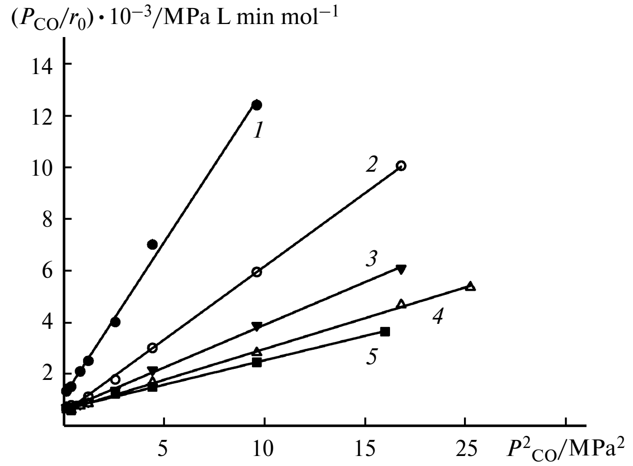


Fig. 3. Fitting the kinetic equation to experimental data at temperatures 353 (*1*), 363 (*2*), 373 (*3*), 378 (*4*), and 383 K (*5*).

Table 1. Parameters in Eq. (II)

T/K	$A/k_{app} \cdot 10^{-8}$ /Pa L min mol^{-1}	$c/k_{app} \cdot 10^{-2}$ /L min mol^{-1}	$b/k_{app} \cdot 10^4$ /L min Pa^{-1} mol^{-1}
353	10±7	3±10	11±2.0
363	7±2	−2±2	6.0±0.5
373	6±2	0±2	3.0±0.5
378	6±2	0±2	2.0±0.4
383	5±2	1±2	2.0±0.5

Table 2. Parameters in Eq. (III)

T/K	$A/k_{app} \cdot 10^{-8}$ /Pa L min mol^{-1}	$b/k_{app} \cdot 10^4$ /L min Pa^{-1} mol^{-1}
353	12±2.0	11.9±0.7
363	5±1.0	5.7±0.2
373	6.0±0.8	3.3±0.1
378	5.8±0.7	2.38±0.07
383	6±1.0	1.9±0.1

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