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Influence of Components of the $PdCl_2(PPh_3)_2$–PPh_3–*p*-Toluenesulfonic Acid Catalytic System on the Rate of Cyclohexene Hydrocarbalkoxylation with *m*-Cresol

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Abstract—Kinetic parameters were determined for the cyclohexene hydrocarbalkoxylation reaction catalyzed by the $PdCl_2(PPh_3)_2$–PPh_3–*p*-toluenesulfonic acid (TSA) catalyst system in the presence of *m*-cresol. It was shown that the reaction is first order in cyclohexene and a fractional order in $PdCl_2(PPh_3)_2$ and *m*-cresol and that the dependences of the reaction rate on P_{CO}, TSA and PPh_3 concentrations are nonmonotonic in character. The inhibitory effect of tosylate and chloride ions on the reaction was revealed. The results were rationalized in terms of a mechanism that involves hydride complexes of the cation type as intermediates. A rate equation for the reaction was derived in terms of the steady-state hypothesis to fit to experimental data.

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Hydrocarbalkoxylation of alkenes is a promising ester synthesis method [1–3]. Of catalytic systems used in this reaction, palladium phosphine complexes promoted with triphenylphosphine and strong protic acids are of particular interest [4–8]. Acting in combination, these compounds exert a stabilizing effect on the catalyst. At the same time, protic acids, serving as a hydride source during the formation of active forms of the catalyst, accelerate the reaction. The acid residues are weakly coordinated anions and, as such, make the palladium center of the catalytic complex more accessible, facilitating its interaction with reactants during catalytic cycles.

Despite the efficacy of the aforementioned catalyst systems, the number of works concerning their action is relatively small. This problem has been studied in some detail by Toniolo et al. [4, 6–8] and Petrov's group [9–11] using the hydrocarbalkoxylation of ethylene, cyclohexene, 1-heptene, styrene, and phenylacetylene as examples. The results of these studies show that the rate, as well as the selectivity, of reactions catalyzed by the "palladium phosphine complex–free phosphine–strong protic acid" system is a function of many factors whose influence is conjugate in character. In addition to the concentration of reactants and catalyst components, these factors include the nature of a protic acid, its anion, a catalyst precursor anion, and an alcohol as a reactant and a specific component of the reaction medium. The elucidation of these factors necessitates a broader variation in the concentrations of components of the reacting system and setting up special experiments on revealing the effect of the catalyst-precursor and protic acid anions. In connection with this, a systematic study of the kinetics of the model reaction of cyclohexene hydrocarbalkoxylation catalyzed by the $Pd(PPh_3)_2Cl_2$–PPh_3–*p*-toluenesulfonic acid system in the presence of *m*-cresol was attempted.

EXPERIMENTAL

The cyclohexene hydrocarbalkoxylation reaction with *m*-cresol was studied in a batch reactor described in [12]. Each experiment was carried out in toluene at a constant temperature and a constant CO pressure. In the course of kinetic experiments, the reaction mixture from the reactor was sampled at a certain intervals and analyzed by GLC on a Tsvet 162 chromatograph equipped with a flame-ionization detector. Glass columns of 3 mm in inner diameter packed with Chromaton N-AW-DMCS (0.16–0.20-mm fraction) coated 5% XE-60; the carrier gas was nitrogen or argon. The internal standard was *o*-xylene. The reactant and product concentrations were determined with an accuracy of ±3%. The confidence intervals of the kinetic parameters of interest are given in the text.

The reactants were cyclohexene, *m*-cresol, and carbon monoxide; the components of the catalyst system were dichlorobis(triphenylphosphine)palladium, triphenylphosphine, and *p*-toluenesulfonic acid; and the solvent was toluene.

Cyclohexene was prepared by cyclohexanol dehydration in the presence of concentrated phosphoric acid, according to a procedure described in [13], followed by drying over anhydrous calcium chloride and rectification.

$Pd(PPh_3)_2Cl_2$ was prepared from palladium(II) chloride and triphenylphosphine by the procedure described

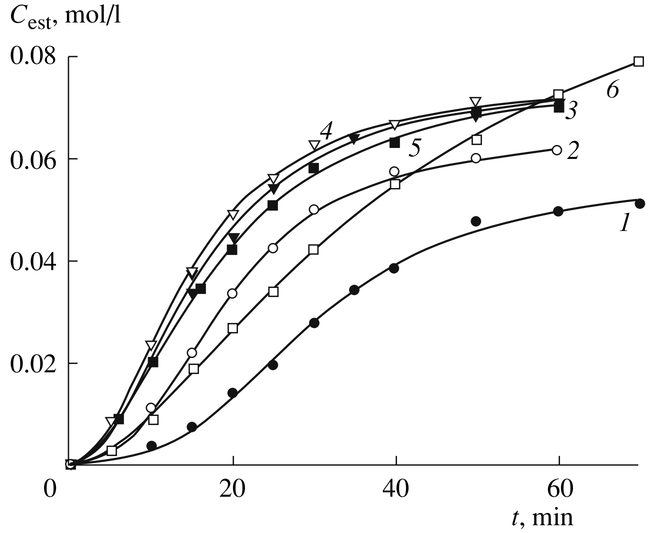


Fig. 1. Time dependence for ester concentration at different CO partial pressures in the cyclohexene hydrocarbalkoxylation reaction with *m*-cresol. T = 381K; concentrations, mol/l: $[CH_3C_6H_4OH] = 0.3$; $[C_6H_{10}] = 0.1$; $[Pd(PPh_3)_2Cl_2] = 2 \times 10^{-3}$; $[PPh_3] = 8 \times 10^{-3}$; $[p\text{-TSA}] = 2.4 \times 10^{-2}$; p_{CO}, MPa: (*1*) 1.1, (*2*) 2.1, (*3*) 3.1, (*4*) 4.1, (*5*) 5.1, and (*6*) 6.1.

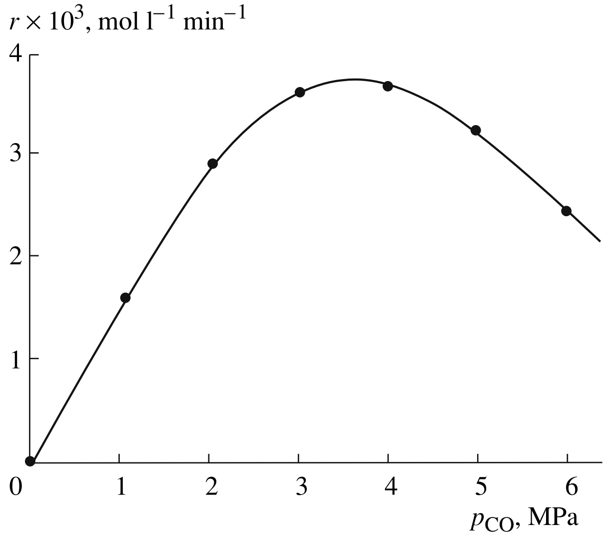


Fig. 2. Influence of p_{CO} on the initial rate of cyclohexene hydrocarbalkoxylation reaction with *m*-cresol. T = 381K; concentrations, mol/l: $[C_6H_{10}] = 0.1$, $[CH_3C_6H_4OH] = 0.3$, $[Pd(PPh_3)_2Cl_2] = 2 \times 10^{-3}$; $[PPh_3] = 8 \times 10^{-3}$; $[p\text{-TSA}] = 2.4 \times 10^{-2}$.

in [14]. According to IR, atomic-absorption, and elemental analysis data, the sample obtained corresponded to the structure of the $Pd(PPh_3)_2Cl_2$ complex.

The chromatographic standard *m*-cresyl cyclohexanecarboxylate was prepared according to the procedure described above for alkene hydrocarbalkoxylation, followed by neutralization of the reaction mixture with NaOH, drying over anhydrous calcium dichloride, and vacuum distillation.

The purification and isolation of desired products or chromatographic standards involved their distillation on a fractionating column with Fenske packing and a height of 20 theoretical plates. The purity criteria for the substances used were the boiling point and the refractive index. In chromatographic analysis, all substances gave one peak each on different phases.

Toluene (analytical grade) was preliminarily dried over anhydrous calcium dichloride and rectified.

RESULTS AND DISCUSSION

To elucidate the influence of the reactants and the components of the catalytic system on the reaction rate, we conducted six series of experiments, varying one of the factors within each series. Typical experimental results are represented as *m*-cresyl cyclohexanecarboxylate buildup curves at different partial pressures of CO (Fig. 1). It is seen that these curves are characterized by the autocatalytic portion, indicating the formation of active catalyst complexes responsible for the catalytic cycle.

The initial reaction rates were determined by differentiating the initial portions of the rate curves next to the autocatalytic portions. The plot of the initial rate versus the CO partial pressure given in Fig. 2 exhibits an extremum at a CO pressure of 3.5 MPa.

A similar dependence with a maximum at $[PPh_3] = 4 \times 10^{-3}$ mol/l was obtained for the influence of triphenylphosphine. The results agree with the data obtained by the Toniolo [4, 6], Petrov [9], and El'man [5] groups for alkene hydrocarbalkoxylation in the presence of analogous catalytic systems.

The results on the effect of $Pd(PPh_3)_2Cl_2$ on the cyclohexene hydrocarbalkoxylation rate are presented in Fig. 3 as the plot of the initial reaction rate versus the catalyst concentration. This dependence is nonlinear in character, indicating a decrease in the catalyst precursor activity with an increase in its concentration.

The results on the influence of TSA on the reaction rate are given in Fig. 4. This dependence has a maximum at $[TSA] = 4 \times 10^{-2}$ mol/l and differs from the data obtained by Toniolo et al. [4, 6] and the El'man group [5] for the cyclohexene hydrocarbalkoxylation reaction catalyzed by the $Pd(PPh_3)_2(TsO)_2$–PPh_3–TSA system. The cited authors revealed the S-shaped dependence of the reaction rates on [TSA], which saturated at high TSA values.

The results on the influence of *m*-cresol on the reaction rate, given in Fig. 5, show a fractional reaction order in this reagent, a feature that differs in our data from that of Toniolo et al. [6], who found the reaction to be first order in methanol for cyclohexene hydrocarbalkoxylation catalyzed by the $Pd(PPh_3)_2(TsO)_2$–PPh_3–

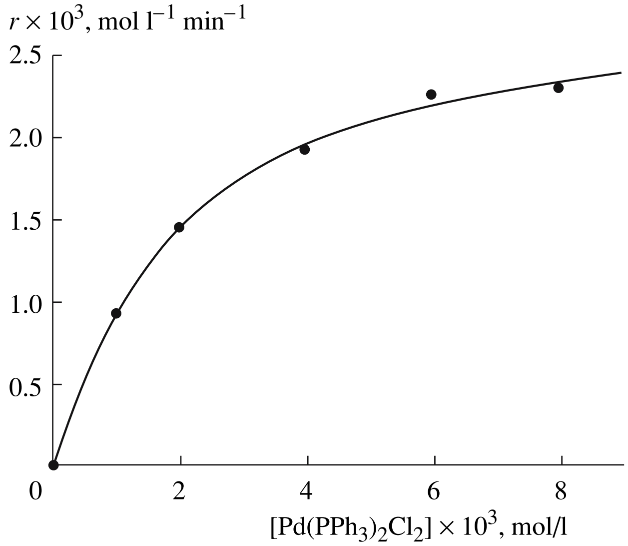


Fig. 3. Influence of $Pd(PPh_3)_2Cl_2$ on the initial rate of cyclohexene hydrocarbalkoxylation reaction with *m*-cresol. $T = 381$ K, $p_{CO} = 2.1$ MPa; concentrations, mol/l: $[C_6H_{10}] = 0.1$, $[CH_3C_6H_4OH] = 0.3$, $[PPh_3] = 4 \times 10^{-2}$; [*p*-TSA] = 0.12.

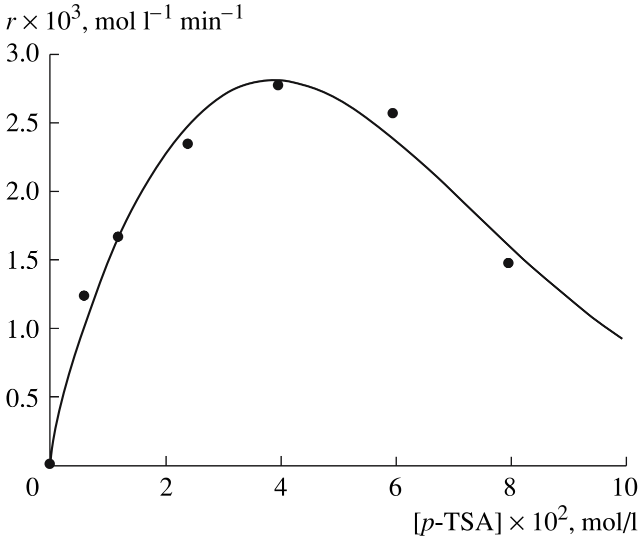


Fig. 4. Influence of [*p*-TSA] on the initial rate of cyclohexene hydrocarbalkoxylation reaction with *m*-cresol. $T = 381$ K, $p_{CO} = 2.1$ MPa; concentrations, mol/l: $[C_6H_{10}] = 0.1$, $[CH_3C_6H_4OH] = 0.3$, $[Pd(PPh_3)_2Cl_2] = 1 \times 10^{-3}$; $[PPh_3] = 8 \times 10^{-3}$.

TsOH system over a broad range of CH_3OH concentrations (0–7.5 mol/l). Note that the cited authors obtained their results under the conditions of reaction mixture dilution with acetone, whereas we used toluene as a dilutent in all runs.

We found that the reaction was also first order in cyclohexene over the concentration range examined (0–0.1 mol/l). These data are consistent with the results of the Petrov [10] and Toniolo [6] groups for the test alkenes (styrene and cyclohexene, respectively) in the catalysis by analogous systems, as well as with the data of these and other authors on alkene carbonylation in the presence of palladium phosphine complexes that did not contain a powerful hydride source [14–18].

In addition to the above experiments, we examined the influence of tosylate and chloride ions on the reaction rate. Sodium tosylate and rubidium chloride, respectively, were the sources of these ions. The experiments were carried out at different concentrations of these salts, but at a constant temperature and constant concentrations of other components: $T = 381$ K, $p_{CO} = 2.1$ MPa; concentrations, mol/l: $[C_6H_{10}] = 0.1$, $[CH_3C_6H_4OH] = 0.3$, $[Pd(PPh_3)_2Cl_2] = 2 \times 10^{-3}$; $[PPh_3] = 8 \times 10^{-3}$, $[p\text{-TSA}] = 2.4 \times 10^{-2}$. The results are given below as the dependence of the reaction rate on the concentration of the corresponding salt.

[TsONa], mol/l	0	0.05	0.1	0.15	0.2
$r \times 10^3$, mol l^{-1} min^{-1}	2.89	2.00	1.55	1.52	1.28

$[RbCl] \times 10^2$, mol/l	0	0.2	0.4	0.8	1.6	2.8
$r \times 10^3$, mol l^{-1} min^{-1}	2.89	2.30	1.46	1.17	0.83	0.15

It is seen that tosylate and chloride anions retard the reaction.

INTERPRETATION OF REACTION MECHANISM

Summarizing the obtained data and current ideas concerning the mechanism of the hydrocarbalkoxylation reaction catalyzed by palladium phosphine complexes [2, 4–10, 15–21], we may propose the following

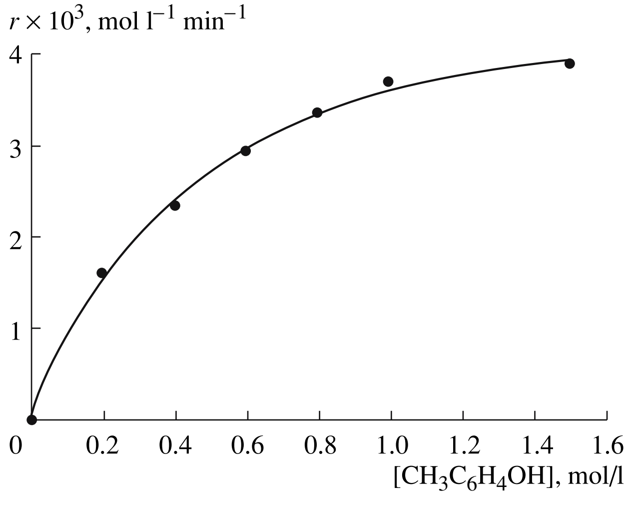
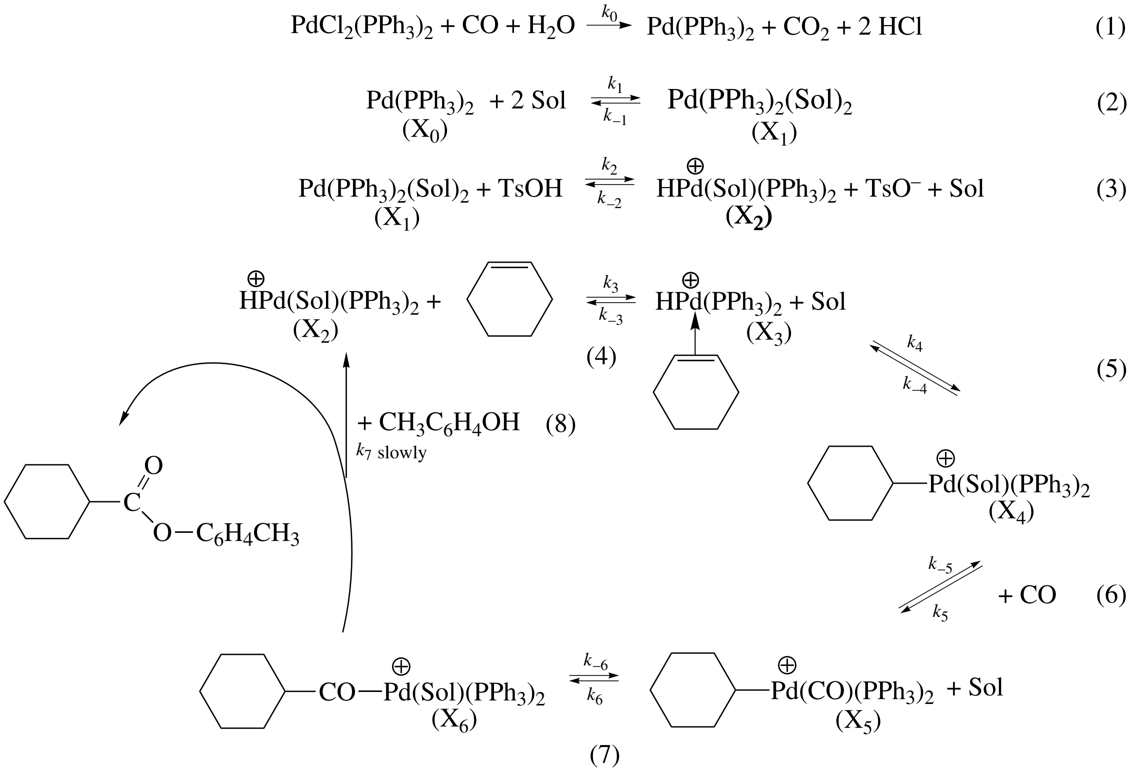


Fig. 5. Influence of $[CH_3C_6H_4OH]$ on the initial rate of cyclohexene hydrocarbalkoxylation reaction with *m*-cresol. $T = 381$ K; $p_{CO} = 2.1$ MPa; concentrations, mol/l: $[C_6H_{10}] = 0.1$, $[Pd(PPh_3)_2Cl_2] = 2 \times 10^{-3}$; $[PPh_3] = 8 \times 10^{-3}$; $[p\text{-TSA}] = 2.4 \times 10^{-2}$.



Scheme 1.

reaction route with a key role played by hydride complexes (Scheme 1):

The rate-determining character of step (8) is confirmed by the reaction sensitivity to the size of alcohol as a nucleophile [17, 22, 23] and its concentration [6, 18, 23], as well as by the feasibility of isolation of acylpalladium complexes of the X_6 type in a measurable amount from the reaction mixture [21, 24]. In this context, the fractional reaction order with respect to *m*-cresol can be explained in terms of the interplay of two factors. At low concentrations of *m*-cresol, this component prevalently functions as a reactant; at high concentrations, ligand-exchange reactions of *m*-cresol with intermediates of the catalytic cycle begin to play a progressively more significant role, leading to the withdrawal of a part of the catalyst from its reaction sphere. The most likely reaction of this type is reaction (9)

$$\underset{(X_1)}{Pd(PPh_3)_2(Sol)_2} + CH_3C_6H_4OH \xrightleftharpoons{K_7} \underset{(X_7)}{Pd(PPh_3)_2(CH_3C_6H_4OH)(Sol)} + Sol. \quad (9)$$

The cause of this behavior is the weak coordination of solvent molecules in complexes X_1, as well as a high concentration of these complexes due to a solvent excess and an expectedly high value of the equilibrium constant K_7.

In our opinion, the nonmonotonic character of the dependence of the reaction rate on p_{CO} is also the result of the interplay between two factors. At a pressure of up to 3–3.5 MPa, carbon monoxide predominantly acts as a reactant that is inserted in one of the intermediates of the catalytic cycle. However, as the pressure further grows the CO interaction with palladium-containing intermediates yielding less active or inactive complexes becomes progressively more significant. This process leads to the withdrawal of a part of the catalyst from the catalytic cycle and, as consequence, to a reduction in the reaction rate.

This mode of deactivation was experimentally confirmed in works by Petrov et al. [16, 21], who not only kinetically substantiated a possible formation of palladium phosphine intermediates with two or more CO molecules in the coordination sphere, but also identified them. They assumed that the deactivating action of CO on the catalytic system can be interpreted in terms of its interaction with the coordination complex $Pd(PPh_3)_2(Sol)_2$.

$$\underset{(X_1)}{Pd(PPh_3)_2(Sol)_2} + 2\,CO \xrightleftharpoons{K_8} \underset{(X_8)}{Pd(PPh_3)_2(CO)_2} + 2\,Sol. \quad (10)$$

The character of the influence of triphenylphosphine on the rate of the test reaction also reflects the dual function of this component. In the concentration region to 0.004 mol/l, PPh_3 accelerates the reaction. This effect seems to be due to fact that PPh_3 increases the concentration of the intermediates responsible for the formation of reaction products. At higher concentrations, PPh_3 is involved in subsequent interactions with the intermediates of the catalytic cycle and converts a part of the catalyst into inactive and less active forms. The interplay between these factors is ultimately responsible for the nonmonotonic character of the dependence of the reaction rate on the PPh_3 concentration. The accelerating effect of the PPh_3 action on the reaction rate can be explained in terms of equilibria (11) and (12):

$$\underset{(X_1)}{Pd(PPh_3)_2(Sol)_2} + CO \xrightleftharpoons{K_9} \underset{(X_9)}{Pd(CO)(PPh_3)(Sol)_2} + PPh_3 \qquad (11)$$

$$\underset{(X_1)}{Pd(PPh_3)_2(Sol)_2} + CH_3C_6H_4OH \xrightleftharpoons{K_{10}} \underset{(X_{10})}{Pd(CH_3C_6H_4OH)(PPh_3)(Sol)_2} + PPh_3 \qquad (12)$$

which are shifted by the action of triphenylphosphine toward the complex $Pd(PPh_3)_2(Sol)_2$ responsible for the formation of $HPd^{\oplus}(Sol)(PPh_3)_2$, the key intermediate of the catalytic cycle. At the same time, the deactivating action of PPh_3, which prevails in the region of its high concentration, can be interpreted in terms of equilibrium (13)

$$\underset{(X_1)}{Pd(PPh_3)_2(Sol)_2} + 2\,PPh_3 \xrightleftharpoons{K_{11}} \underset{(X_{11})}{Pd(PPh_3)_4} + 2\,Sol \qquad (13)$$

whose shift toward the inactive form $Pd(PPh_3)_4$ is more sensitive to PPh_3 concentration than equilibria (11) and (12).

The retarding effect of tosylate anions seems to be due to the formation of hydrogen-bonded associates between these ions and *m*-cresol molecules, which leads to a decrease in the acting concentration of *m*-cresol. It is noteworthy that the reaction is not responsive to a change in the tosylate concentration when a low-acidity alcohol, such as cyclohexanol, is used as an esterifying agent. The additional argument in favor of the formation of these associates is a nonmonotonic dependence of the reaction rate on the TSA concentration: the formation of associates between TSA and *m*-cresol molecules must also lead to a decrease in the concentration of *m*-cresol and, hence, in the reaction rate.

In our opinion, the inhibiting effect of chloride anions is caused by a stronger coordinating power of these anions as compared with solvent molecules. This coordination leads to the formation of less active intermediates, such as X_{12}, in accordance with equilibria

$$HCl + Sol \xrightleftharpoons{K_{12}} Cl^- + \overset{\oplus}{H}Sol \qquad (14)$$

$$\underset{(X_1)}{Pd(PPh_3)_2(Sol)_2} + Cl^- \xrightleftharpoons{K_{13}} \underset{(X_{12})}{[Pd(PPh_3)_2(Sol)Cl]^-} + Sol. \qquad (15)$$

Complexes X_{12} can give rise to the alternative catalytic cycle, which involves neutral hydride complexes as intermediates (Scheme 2), by analogy with Scheme 1.

These hydride complexes are less reactive than the cationic complexes, thus causing a decrease in the total reaction rate.

Note that, in systems that mediate the reaction presumably via neutral hydride complexes and involve $PdCl_2$ or $Pd(PPh_3)_2Cl_2$ as a catalyst precursor, chloride anions have a promoting effect on the reaction [22, 25]. This makes us confident that the primary cause of the inhibiting effect of chlorine is formation by the action of chloride anions of alternative catalytic cycles, which proceed at a substantially lower rate with neutral chlorine-containing hydride intermediates. The existence of such cycles was clearly shown by Petrov et al. [2, 16, 21].

Since step (8) is rate determining, all its preceding steps, as well as reactions (9)–(15), can be considered equilibrium processes. Then, the reaction rate will be expressed by the equation

$$r = k_7[X_6][CH_3C_6H_4OH], \qquad (16)$$

and the concentrations of all components relevant to Scheme 1 and reactions (9)–(15) are defined by the equalities

$$K_1 = \frac{[X_1]}{[X_0]},\ K_2 = \frac{[X_2]}{[X_1][TsOH]},$$

$$K_3 = \frac{[X_3]}{[X_2][ol]},\ K_4 = \frac{[X_4]}{[X_3]}, K_5 = \frac{[X_5]}{[X_4][CO]},$$

$$K_6 = \frac{[X_6]}{[X_5]}, K_7 = \frac{[X_7]}{[X_1][CH_3C_6H_4OH]},$$

$$K_8 = \frac{[X_8]}{[X_1][CO]^2}, \quad K_9 = \frac{[X_9][PPh_3]}{[X_1][CO]},$$
$$K_{10} = \frac{[X_{10}][PPh_3]}{[X_1][CH_3C_6H_4OH]}, \quad K_{11} = \frac{[X_{11}]}{[X_1][PPh_3]^2}, \tag{17}$$
$$K_{12} = \frac{[Cl^-]}{[HCl]} = \frac{[Cl^-]}{2[C_M]}, \quad K_{13} = \frac{[X_{12}]}{[X_1][Cl^-]},$$

where [ol] is the olefin concentration.

The total concentration of monomeric forms of the catalyst is expressed as

$$\begin{aligned} C_M = {} & [X_0] + [X_1] + [X_2] + [X_3] \\ & + [X_4] + [X_5] + [X_6] + [X_7] \\ & + [X_8] + [X_9] + [X_{10}] + [X_{11}] + [X_{12}]. \end{aligned} \tag{18}$$

With allowance for relations between X_0, X_1, …, X_{12}, as are determined by the sets of Eqs. (17) and (18), we obtain:

$$C_M = \frac{[X_6]}{K[ol][CO][TsOH]} \times \left\{ \begin{array}{c} 1 + \frac{1}{K_1} + K_2[TsOH] + (K_2K_3 + K_2K_3K_4)[ol][TsOH] + \left(\frac{K}{K_6} + K\right)[ol][CO][TsOH] \\ + K_7[CH_3C_6H_4OH] + K_8[CO]^2 + K_9\frac{[CO]}{[PPh_3]} + K_{10}\frac{[CH_3C_6H_4OH]}{[PPh_3]} + K_{11}[PPh_3]^2 + K_{13}[Cl^-] \end{array} \right\}, \tag{19}$$

where $K = K_2K_3K_4K_5K_6$.

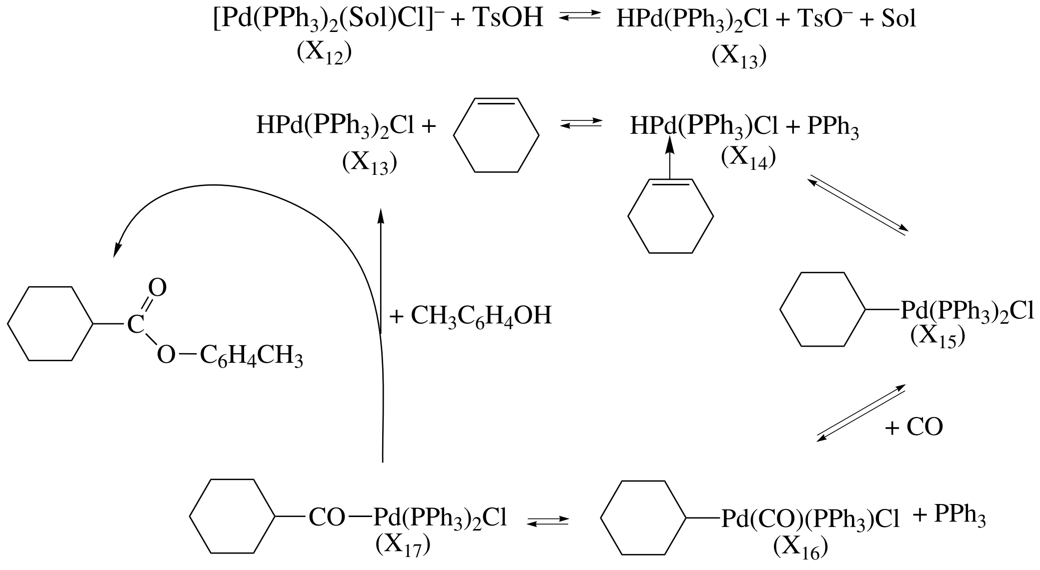
Solving Eq. (19) in $[X_6]$ and substituting this quantity into rate equation (16) for the rate-determining step, we obtain the expression for the reaction rate

$$r = \frac{k_7KC_M[ol][CO][TsOH][CH_3C_6H_4OH]}{\left\{ \begin{array}{c} 1 + \frac{1}{K_1} + K_2[TsOH] + (K_2K_3 + K_2K_3K_4)[ol][TsOH] + \left(\frac{K}{K_6} + K\right)[ol][CO][TsOH] \\ + K_7[CH_3C_6H_4OH] + K_8[CO]^2 + K_9\frac{[CO]}{[PPh_3]} + K_{10}\frac{[CH_3C_6H_4OH]}{[PPh_3]} + K_{11}[PPh_3]^2 + K_{13}[Cl^-] \end{array} \right\}}. \tag{20}$$

In view of the first reaction order observed with respect to cyclohexene, it may be assumed that the contribution of terms containing its concentration into the total balance of palladium complexes is negligible, and Eq. (20) will take a more compact form

$$r = \frac{k_7KC_M[ol][CO][TsOH][CH_3C_6H_4OH]}{\left\{ \begin{array}{c} 1 + \frac{1}{K_1} + K_2[TsOH] + K_7[CH_3C_6H_4OH] + K_8[CO]^2 + K_9\frac{[CO]}{[PPh_3]} + K_{10}\frac{[CH_3C_6H_4OH]}{[PPh_3]} \\ + K_{11}[PPh_3]^2 + K_{13}[Cl^-] \end{array} \right\}}. \tag{21}$$

The fitting of Eq. (21) to experimental data can be demonstrated using dependences of the reaction rate on p_{CO} and PPh_3, *m*-cresol, and catalyst-precursor concentrations. For example, by varying the *m*-cresol



Scheme 2.

concentration, this equation can be reduced to the form

$$r = \frac{k[\mathrm{CH_3C_6H_4OH}]}{\mathrm{A} + \mathrm{B}[\mathrm{CH_3C_6H_4OH}]}, \qquad (22)$$

where $k = k_7KC_M[\mathrm{ol}][\mathrm{CO}][\mathrm{TsOH}]$; $\mathrm{B} = K_7 + \dfrac{K_{10}}{[\mathrm{PPh_3}]}$; and $\mathrm{A} = 1 + \dfrac{1}{K_1} + K_2[\mathrm{TsOH}] + K_8[\mathrm{CO}]^2 + K_9\dfrac{[\mathrm{CO}]}{[\mathrm{PPh_3}]} + K_{11}[\mathrm{PPh_3}]^2 + K_{13}[\mathrm{Cl^-}]$.

In turn, Eq. (22) is easy to reduce to the form

$$\frac{1}{r} = \frac{\mathrm{A}}{k}\frac{1}{[\mathrm{CH_3C_6H_4OH}]} + \frac{\mathrm{B}}{k}. \qquad (23)$$

The linear character of the $\dfrac{1}{r} - \dfrac{1}{[\mathrm{CH_3C_6H_4OH}]}$ plots presented in Fig. 6 indicates the validity of the kinetic derived model and the proposed reaction mechanism concerning the influence of *m*-cresol on the reaction rate.

Under the conditions of a one-factor experiment on the influence of triphenylphosphine on the reaction rate, Eq. (21) is reduced to the form

$$r = \frac{k}{D + \dfrac{E}{[\mathrm{PPh_3}]} + K_{11}[\mathrm{PPh_3}]^2}, \qquad (24)$$

where $k = k_7KC_M$ [ol] [CO] [TsOH] $[\mathrm{CH_3C_6H_4OH}]$; $E = K_9[\mathrm{CO}] + K_{10}[\mathrm{CH_3C_6H_4OH}]$; and $D = 1 + \dfrac{1}{K_1}K_2[\mathrm{TsOH}] + K_7[\mathrm{CH_3C_6H_4OH}] + K_8[\mathrm{CO}]^2 + K_{13}[\mathrm{Cl^-}]$.

The latter equation is readily transformed into the relationship

$$\frac{[\mathrm{PPh_3}]}{r} = \frac{E}{k} + \frac{D}{k}[\mathrm{PPh_3}] + \frac{K_{11}}{k}[\mathrm{PPh_3}]^3. \qquad (25)$$

The dependence of the ratio $\dfrac{[\mathrm{PPh_3}]}{r}$ on the $\mathrm{PPh_3}$ concentration is given in Fig. 7.

The evaluation of the parameters of Eq. (25) by the least squares method and the subsequent verification of its adequacy demonstrated agreement between the calculated (curve) and the experimental (symbols) data.

Thus, the proposed mechanism and the corresponding kinetic model describe the experimental data well on the influence of the $\mathrm{PPh_3}$ concentration on the reaction rate.

Under the conditions of a one-factor experiment on the influence of CO pressure on the rate of cyclohexene hydrocarbalkoxylation reaction, Eq. (21) is reduced to the form

$$r = \frac{kp_{\mathrm{CO}}}{G + aP_{\mathrm{CO}}^2 + bp_{\mathrm{CO}}}, \qquad (26)$$

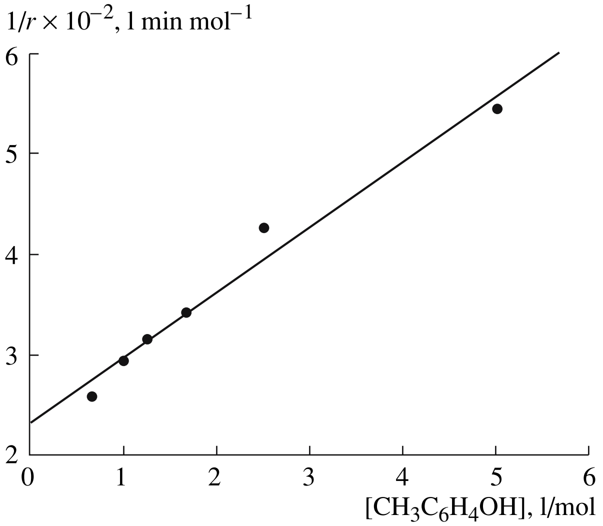


Fig. 6. Fitting Eq. (23) to experimental data. T = 381K; p_{CO} = 2.1 MPa; concentrations, mol/l: [C_6H_{10}] = 0.1, [$Pd(PPh_3)_2Cl_2$] = 2×10^{-3}, [PPh_3] = 8×10^{-3}; [p-TSA] = 2.4×10^{-2}.

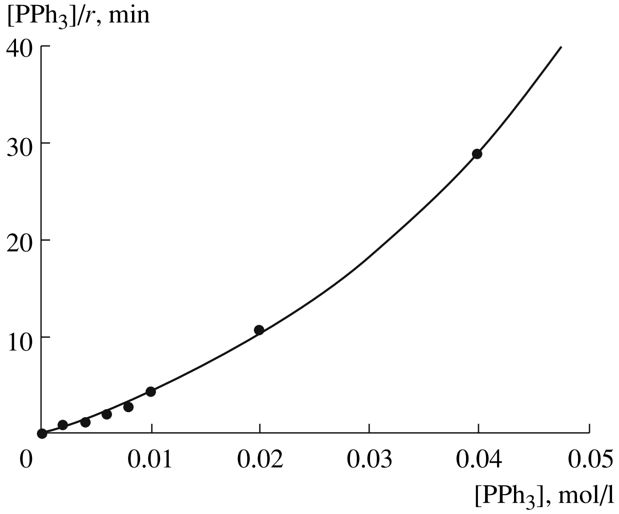


Fig. 7. Fitting Eq. (25) to experimental data. T = 381K; p_{CO} = 2.1 MPa; concentrations, mol/l: [C_6H_{10}] = 0.1; [$CH_3C_6H_4OH$] = 0.3; [$Pd(PPh_3)_2Cl_2$] = 2×10^{-3}, [p-TSA] = 2.4×10^{-2}.

where $k = \frac{k_7 K C_M}{H}$ [ol] [TsOH] [$CH_3C_6H_4OH$]; $a = \frac{K_8}{H^2}$; $b = \frac{K_9}{H[PPh_3]}$; $G = 1 + \frac{1}{K_1} + K_2[TsOH] + K_7[CH_3C_6H_4OH] + K_{10}\frac{[CH_3C_6H_4OH]}{[PPh_3]} + K_{11}[PPh_3]^2 + K_{13}[Cl^-]$; and H is the Henry constant for CO.

Transformation of Eq. (26) leads to the expression

$$\frac{P_{CO}}{r} = \frac{G}{k} + \frac{b}{k}p_{CO} + \frac{a}{k}p_{CO}^2. \qquad (27)$$

The evaluation of the parameters of Eq. (27) by the least squares method and the subsequent verification of its adequacy demonstrated the fitting of the calculated to the experimental data.

Equation (21) also gives qualitative substantiation of the fractional reaction order with respect to the catalyst precursor $Pd(PPh_3)_2Cl_2$. It can be shown that the concentration of chloride anions in the denominator of this equation is linearly related to the initial catalyst concentration C_M. Thus, the amount of hydrochloric acid produced in reaction (1) is equal to double the amount of the initial catalyst form, [HCl] = $2C_M$. The resulting hydrochloric acid is a source of chloride anions in accordance with acid–base equilibrium (14).

Under the conditions of a significant excess of TSA over the catalyst with allowance for its higher acidity in comparison with HCl, the concentration of $HSol^{\oplus}$– ions can be considered to be constant.

$$\mathrm{TsOH + Sol} \xrightarrow{K_D} \mathrm{H}\overset{\oplus}{\mathrm{Sol}} + \mathrm{TsO}^-. \qquad (28)$$

Then, in accordance with Eq. (14), the Cl^- concentration is expressed by

$$[Cl^-] = K'_{12}[HCl] = 2K'_{12}C_M, \qquad (29)$$

where $K'_{12} = K_{12}[Sol]$.

Substituting Eq. (29) into Eq. (21), we can obtain the following expression for the reaction rate:

$$r = \frac{kC_M}{L + dC_M}, \qquad (30)$$

where $k = k_7K$[ol][CO][TsOH][$CH_3C_6H_4OH$], and $d = 2K_{13}K'_{12}$, $L = 1 + \frac{1}{K_1} + K_2[TsOH] + K_7[CH_3C_6H_4OH] + K_8[CO]^2 + K_9\frac{[CO]}{[PPh_3]} + K_{10}\frac{[CH_3C_6H_4OH]}{[PPh_3]} + K_{11}[PPh_3]^2$.

Reducing Eq. (30) to the linear form

$$\frac{1}{r} = \frac{d}{k} + \frac{L}{k}\frac{1}{C_M}, \qquad (31)$$

we represent the data on the influence of the catalyst concentration on the reaction rate in $\frac{1}{r} - \frac{1}{C_M}$ coordinates (Fig. 8). The linear character of this dependence corroborates the given interpretation of the role of the catalyst precursor in the reaction under investigation.

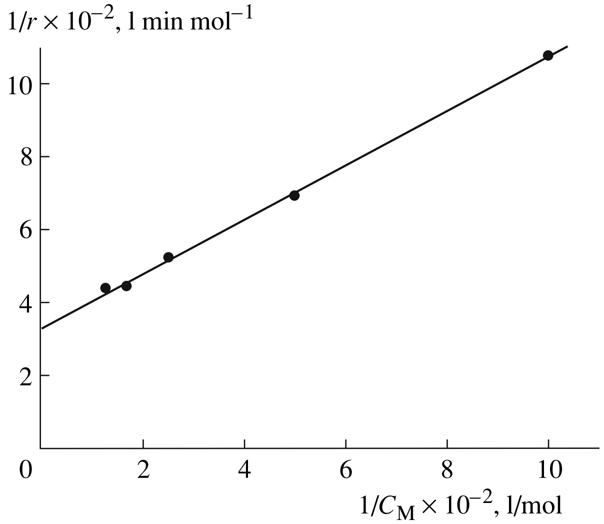


Fig. 8. Fitting Eq. (31) to experimental data. p_{CO} = 2.1 MPa; concentrations, mol/l: $[C_6H_{10}]$ = 0.1, $[CH_3C_6H_4OH]$ = 0.3, $[PPh_3] = 4 \times 10^{-2}$; [p-TSA] = 0.12.

CONCLUSIONS

Kinetic relationships for the cyclohexene hydrocarbalkoxylation reaction in the presence of *m*-cresol catalyzed with the $Pd(PPh_3)_2Cl_2$–PPh_3–TSA system were established. It was shown that the reaction is first order in cyclohexene and fractional order in both $Pd(PPh_3)_2Cl_2$ and *m*-cresol and that the dependences of the reaction rate on p_{CO}, TSA, and PPh_3 concentrations are nonmonotonic in character.

The data obtained were interpreted in terms of the mechanism comprising hydride complexes of the cationic type as intermediates. It was assumed that the cause of the fractional order in the catalyst is the formation of chlorine atoms from the precursor $Pd(PPh_3)_2Cl_2$, which withdraws a part of the catalyst from the main catalytic cycle. The nonmonotonic dependences of the reaction rate on p_{CO} and the triphenylphosphine concentration were interpreted as the interplay of two factors: the formation and consumption of the intermediates in the catalytic cycle under the action of these components. It was supposed that the break in the reaction rate–TSA concentration dependence and the retardation effect of the tosylate anion are due to the formation of associates via hydrogen bonding between the *m*-cresol hydroxyl group and TSA oxygen atoms. On the basis of the steady-state concept, a rate equation adequate to the experimental data was derived.

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