

# Kinetics and Mechanism of Cyclohexene Hydrocarbomethoxylation Catalyzed by a Pd(II) Complex

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**Abstract**—The kinetics of cyclohexene hydrocarbomethoxylation catalyzed by the  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2\text{--PPh}_3\text{--}p\text{-toluenesulfonic acid}$  (TSA) is reported. The reaction is first-order with respect to cyclohexene and TSA and of order 0.5 with respect to  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ . The reaction rate as a function of CO pressure or methanol or  $\text{PPh}_3$  concentration passes through an extremum. The chloride anion inhibits the reaction. A mechanism involving cationic hydride complexes as intermediates is suggested. A rate equation is set up by the quasi-steady-state treatment of experimental data.

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Alkene carbalkoxylation is a promising method for ester synthesis [1–3]. Among the catalytic systems employed in this reaction, palladium–phosphine complexes promoted with triphenylphosphines and strong protonic acids [4–8] are of special interest. The mutual effect of these compounds stabilizes the catalyst. At the same time, protonic acids accelerate the reaction, serving as a hydride source in the formation of active forms of the catalyst. Their acid residues, which are weakly coordinated anions, make the palladium center of the catalytic complex more accessible, favoring its interaction with reactants in the catalytic cycle.

Although these catalytic systems are effective, they have been the subject of a comparatively small number of studies. Nevertheless, rather detailed information is available on these catalysts [4, 6] and on their application to the hydrocarbalkoxylation of ethylene, cyclohexene, styrene, and phenylacetylene [7, 8]. Analysis of these studies demonstrates that the rate and selectivity of the reactions catalyzed by phosphinepalladium precursor–phosphine–strong acid systems depend on many interrelated factors. These factors are not only the concentrations of the reactants and catalytic components but also the natures of the protonic acid, its anion, the anion of the catalyst precursor, and the alcohol as a reactant and a specific component of the reaction medium. In order to elucidate the roles of these factors, it is necessary to vary, as widely as possible, the component concentrations in the reaction system and to study, by special experiments, the effects of different anions of the catalyst precursor.

Here, we report a systematic kinetic study of cyclohexene hydrocarbomethoxylation catalyzed by the  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2\text{--PPh}_3\text{--}p\text{-toluenesulfonic acid}$  system.

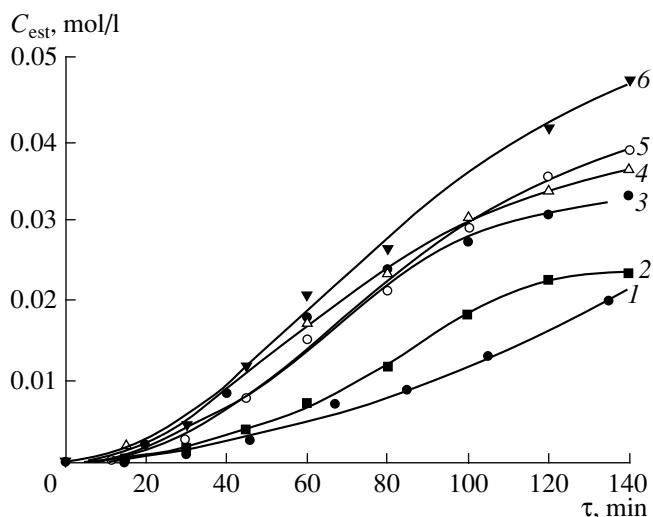
## EXPERIMENTAL

Cyclohexene hydrocarbomethoxylation was studied in a batch reactor [9]. The reaction was performed in toluene at a constant temperature and CO pressure. The reaction temperature was maintained by circulating a high-temperature heat carrier through the jacket of the reactor. In kinetic runs, the reaction mixture was sampled from the reactor at certain time intervals. The samples were analyzed by GLC on a Tsvet-162 chromatograph with a flame-ionization detector and glass columns with an inner diameter of 3 mm. The columns were packed with Chromaton NAW-DMCS (0.16–0.20 mm) loaded with 3%  $\text{H}_3\text{PO}_4$  and 10% Reoplex 400 (stationary phase). The carrier gas was nitrogen or argon. *o*-Xylene was used as the internal standard.

## RESULTS

In order to study the effects of the reactants and of the components of the catalytic system on the reaction rate, we carried out six series of experiments, varying one factor in each series. The typical results of these experiments are presented in Fig. 1 as methyl cyclohexanecarboxylate accumulation curves at various CO partial pressures ( $P_{\text{CO}}$ ). These curves indicate the existence of an autocatalytic period, which is evidence of the formation of active catalyst complexes responsible for the catalytic cycle.

Initial reaction rates were determined by differentiating the initial portions of the accumulation curves subsequent to their autocatalytic regions. The initial reaction rate as a function of the CO partial pressure (Fig. 2a) passes through an extremum at  $P_{\text{CO}} \approx 4$  MPa. This result is in agreement with earlier reports [4, 6, 8] on the effect of CO pressure on alkene hydrocarbalkoxylation in the presence of similar catalytic systems.



**Fig. 1.** Ester buildup in the course of cyclohexene hydrocarbomethylation at CO pressures of (1) 0.6, (2) 1.1, (3) 2.1, (4) 5.1, (5) 3.1, and (6) 4.1 MPa. Reaction conditions:  $T = 378$  K,  $[C_6H_{10}] = 0.1$  mol/l,  $[CH_3OH] = 0.15$  mol/l,  $[Pd(PPh_3)_2Cl_2] = 1 \times 10^{-3}$  mol/l,  $[PPh_3] = 4 \times 10^{-3}$  mol/l, and  $[TSA] = 1.2 \times 10^{-3}$  mol/l.

In a similar way, we studied the dependences of the reaction rate on the concentrations of the catalyst precursor  $Pd(PPh_3)_2Cl_2$ , triphenylphosphine (TPP), *p*-toluenesulfonic acid (TSA), cyclohexene, and methanol. The cyclohexene hydrocarbomethylation rate as a function of  $[Pd(PPh_3)_2Cl_2]$  (Fig. 2b) in logarithmic coordinates appears as a straight line with a slope of  $\sim 0.5$ , indicating that the formal order of the reaction with respect to the phosphine complex is 0.5. This result is at variance with the data obtained for cyclohexene hydrocarbomethylation in a 2.5 times narrower range of catalyst precursor  $(Pd(PPh_3)_2(TsO)_2)$  concentrations [6].

The initial reaction rate as a function of TPP concentration (Fig. 2c) peaks at  $[PPh_3] = 0.045$  mol/l. This kind of dependence is in good agreement with earlier data [4–7].

At TSA concentrations of 0 to  $8 \times 10^{-2}$  mol/l, the reaction is first-order with respect to TSA. Beyond this concentration range, the reaction rate reaches its maximum and remains constant (Fig. 3a). This result is in agreement with the data reported for the effect of the TSA concentration on the rate of hydrocarbomethylation catalyzed by the  $Pd(PPh_3)_2(TsO)_2-PPh_3-TSA$  system [4–6].

The initial reaction rate as a function of methanol concentration passes through a maximum at  $[CH_3OH] = 0.15$  mol/l (Fig. 3b). By contrast, it was observed in an earlier study [6] that the rate of cyclohexene hydrocarbomethylation in the presence of the catalytic system  $Pd(PPh_3)_2(TsO)_2-PPh_3-TsOH$  increases linearly in a wide  $CH_3OH$  concentration range of 0–7.5 mol/l. This

difference arises from the fact that, in that study, the reaction mixture was diluted with acetone, while we used toluene as the diluent in all runs. Among the scarce data available on the effect of alcohols on the carbonylation rate, there is a single extremal dependence, which is observed for the ester yield as a function of alcohol concentration in the reaction



catalyzed by the  $PdCl_2-PPh_3-HCl$  system [10]. In the ethanol diluent order 1,2-dichloroethane–benzene–dioxane, the ester yield peak shifts to higher alcohol concentrations and weakens [10].

The reaction rate depends linearly on the cyclohexene concentration (Fig. 3c). Similar data were obtained for styrene and cyclohexene hydrocarbalkoxylation in the presence of similar catalytic systems [6, 8] and for alkene carbonylation in the presence of Pd–phosphine complexes containing no strong hydride source [11–14].

The catalyst precursor  $Pd(PPh_3)_2Cl_2$  contains chloride ions as ligands, which would be expected to be replaced by reactants in the catalytic cycle. If this were the case, the concentration of free  $Cl^-$  ions could affect the reaction rate. This assumption was verified by a series of experiments in which we evaluated the effect of the salts  $NaCl$ ,  $KCl$ , and  $RbCl$  on the hydrocarbomethylation rate (Fig. 4). The alkali metal chlorides slow down the reaction, and their inhibiting effect increases in the order



because of the increasing radius of the metal cation and the increasing capability of the ion pairs for dissociation. Thus, the chloride ion slows down the reaction.

## DISCUSSION

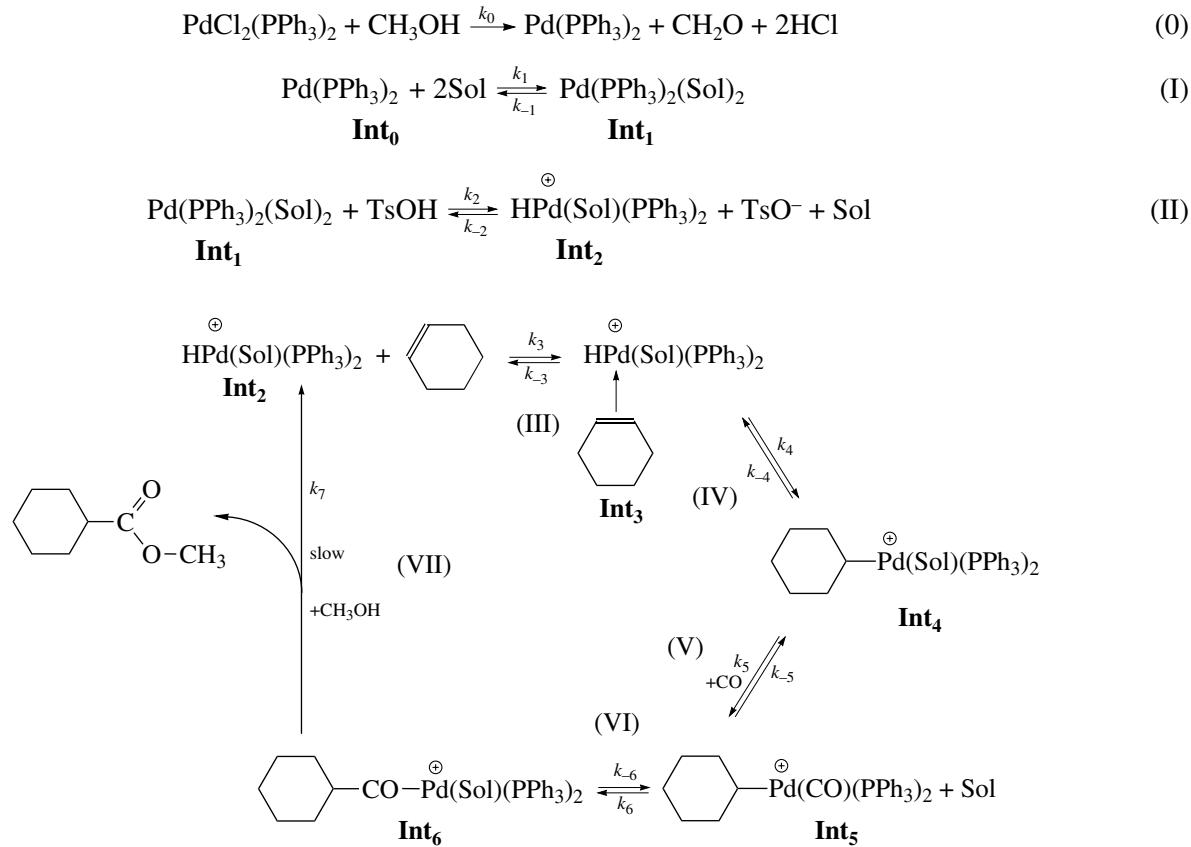
### *Mechanism of the Reaction*

From our data and the present notion of the mechanism of hydrocarbalkoxylation catalyzed by palladium–phosphine complexes [2, 4–8, 11, 13–17], we deduce that the key role in hydrocarbomethylation is played by hydride complexes (Scheme).

It might be assumed that raising the methanol concentration will change the rate-determining step. If this assumption were true, step (VI) would shift progressively from equilibrium with an increase in  $[CH_3OH]$  and in the rate of reaction (VII). At some alcohol concentration, this step could become an irreversible and slow step determining the overall reaction rate. However, this view is in conflict with some facts. First, if this change of the slow step took place, Michaelis–Menten-like kinetics would be observed, according to which, at some methanol concentration, the overall reaction rate would reach a constant maximum value instead of showing a clear-cut extremum. Second, the first order of this reaction with respect to methanol [6] indicates that, throughout an alcohol concentration

range similar to the range examined in our study, the overall reaction rate is determined by the same step,

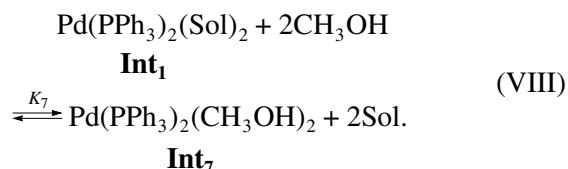
namely, the nucleophilic attack of an alcohol molecule on the acyl carbon atom of the intermediate **Int**<sub>6</sub>.



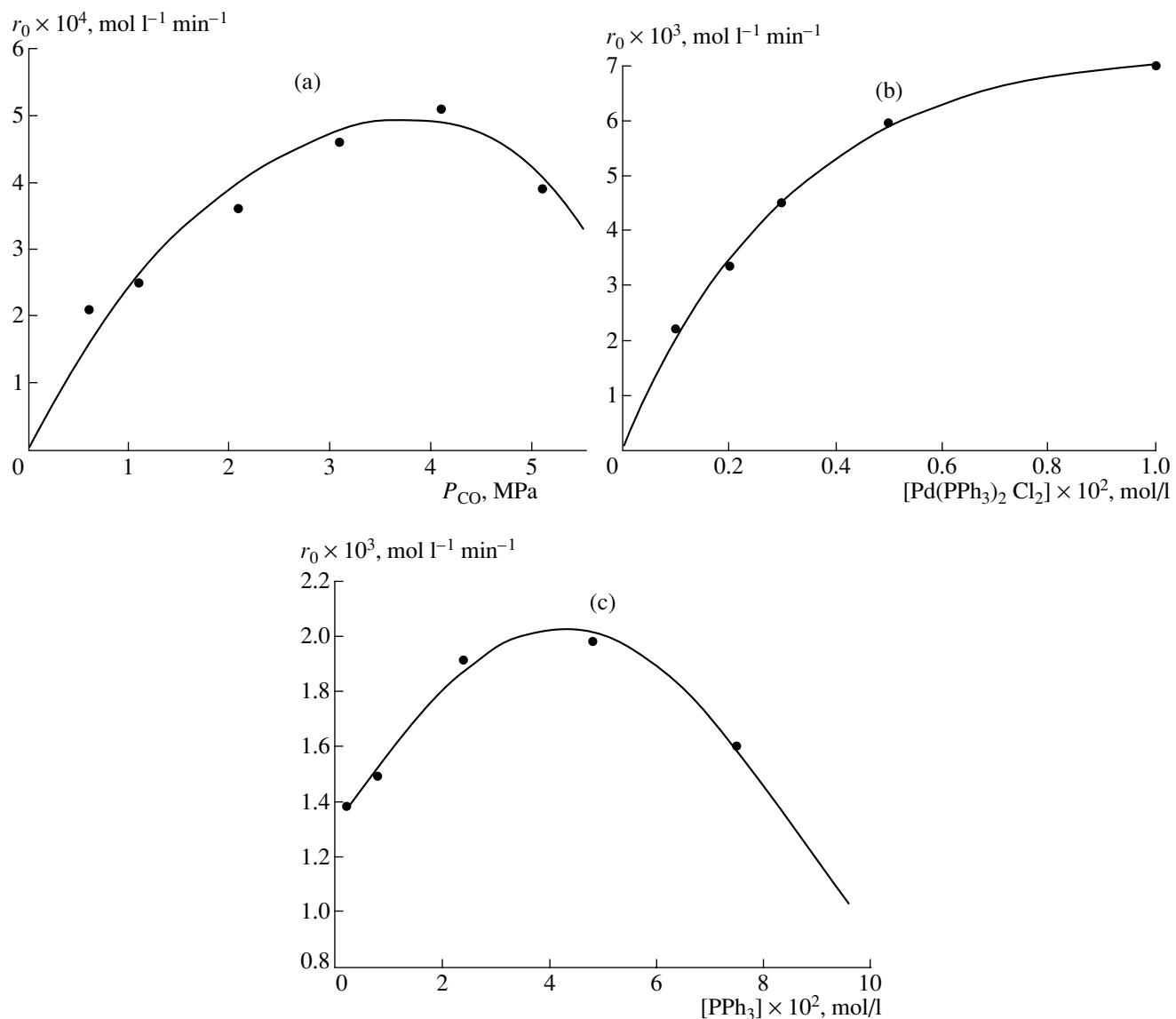
**Scheme.** Cyclohexene hydrocarbomethoxylation.

The difference between the effect of methanol concentration on the reaction rate observed in our study and the same effect reported in [6] arises from the fact that different reaction media were used. We believe that acetone, which is a rather strong electron donor and acceptor [18], is tightly coordinated to any intermediate, preventing methanol coordination. In this case, methanol performs a single function: it participates as a reactant in the slow step, making the reaction first-order with respect to  $\text{CH}_3\text{OH}$ . At the same time, toluene, which was used as the solvent, is a weaker ligand and can, therefore, be displaced by methanol from the coordination spheres of the intermediates in the catalytic cycle. Part of the catalyst can thus be withdrawn from the process. It is, apparently, the interplay between methanol participation in the reaction and the deactivation of the catalyst by methanol through ligand exchange that causes an extremum in the reaction rate as a function of methanol concentration. The deactivating effect of methanol on the catalyst may be due to the

following reaction:



This view is in agreement with data reported for vanillin carbonylation catalyzed by the system  $\text{PdCl}_2-\text{PPh}_3-\text{HCl}$  in ethanol-diluent solvents [10]. The finding that the ester yield peak shifts to higher alcohol concentrations in the diluent order 1,2-dichloroethane-benzene-dioxane, following the ascending order of electron-donating powers, provides a significant argument in favor of the view that the ligand exchange between alcohol molecules and intermediates in the carbonylation reactions is among the causes of the catalyst deactivation.

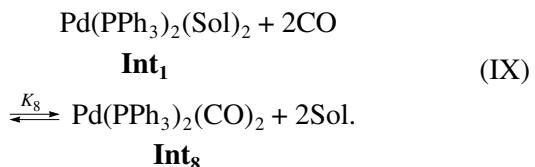


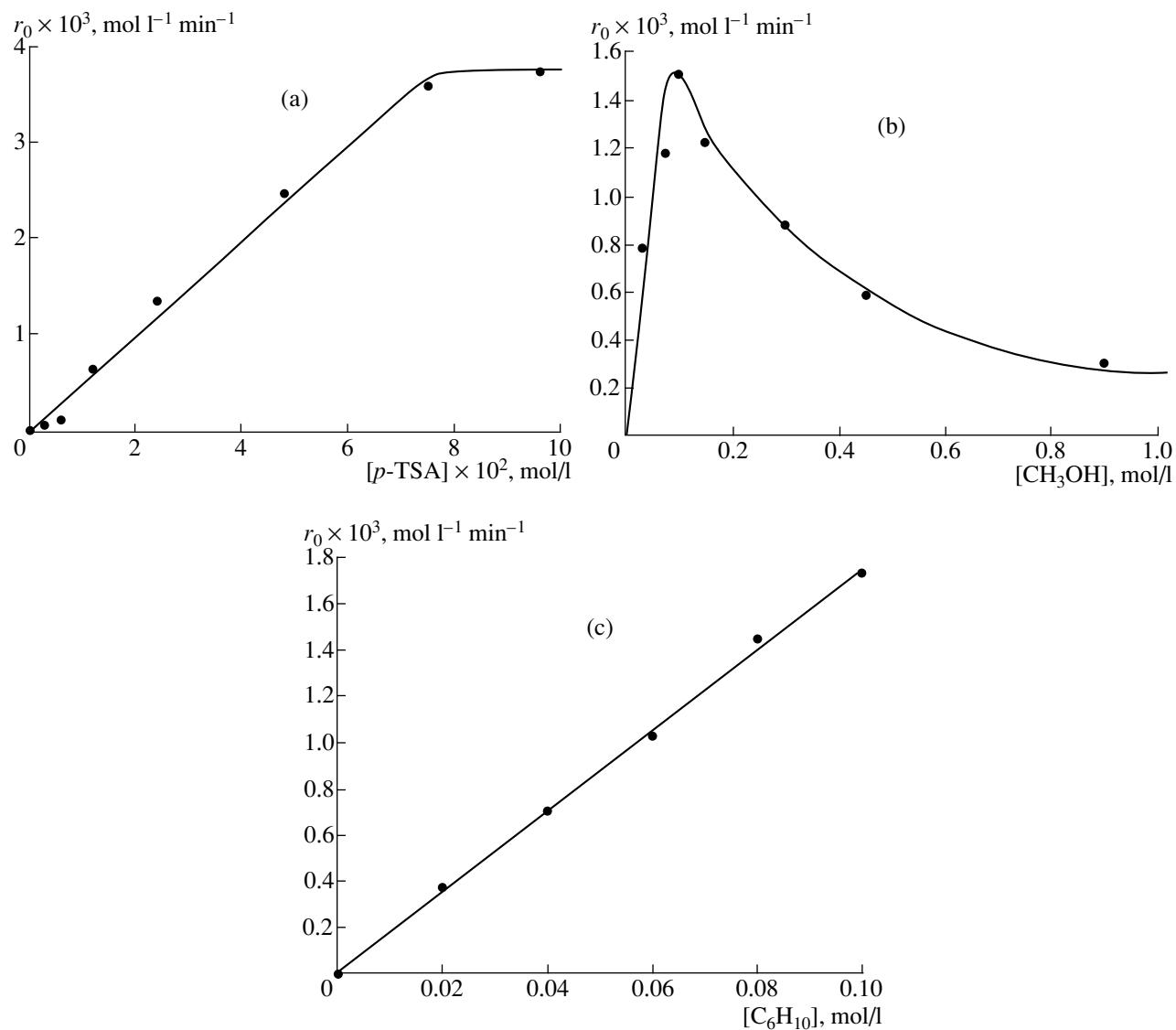
**Fig. 2.** Initial cyclohexene hydrocarbomethoxylation rate as a function of (a) CO pressure, (b)  $Pd(PPh_3)_2Cl_2$  concentration, and (c)  $[PPh_3]$  concentration at  $T = 378$  K,  $[C_6H_{10}] = 0.1$  mol/l, and  $[CH_3OH] = 0.15$  mol/l. (a)  $[Pd(PPh_3)_2Cl_2] = 1 \times 10^{-3}$ ,  $[PPh_3] = 4 \times 10^{-3}$ , and  $[TSA] = 1.2 \times 10^{-3}$  mol/l; (b)  $[TSA] = 0.120$  mol/l,  $[PPh_3] = 4 \times 10^{-2}$  mol/l, and  $P_{CO} = 2.1$  MPa; (c)  $[Pd(PPh_3)_2Cl_2] = 2 \times 10^{-3}$  mol/l,  $[TSA] = 0.120$  mol/l, and  $P_{CO} = 2.1$  MPa.

The fact that the reaction rate as a function of  $P_{CO}$  passes through an extremum (Fig. 2a), which is in agreement with data of other authors, is also believed to result from the interplay of two factors. Below 4 MPa, the main role is played by carbon monoxide incorporating into one of the intermediates of the catalytic cycle. As the CO pressure is further raised, CO reacts increasingly more rapidly with palladium-containing intermediates, yielding less active or inactive complexes. As a consequence, part of the catalyst is withdrawn from the catalytic cycle, thus slowing down the reaction.

This type of concentration dependence was experimentally corroborated by Noskov et al. [11, 17], who

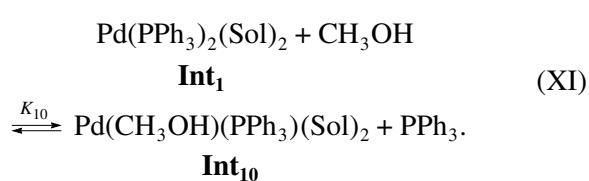
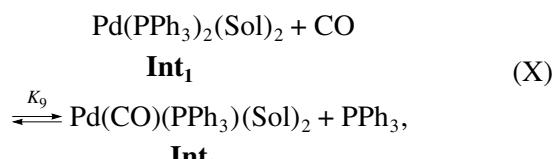
not only kinetically substantiated the formation of palladium–phosphine intermediates but also identified these intermediates. According to the conceptions developed in those studies, the deactivating effect of CO on the catalytic system is due to its interaction with  $Pd(PPh_3)_2(Sol)_2$ :



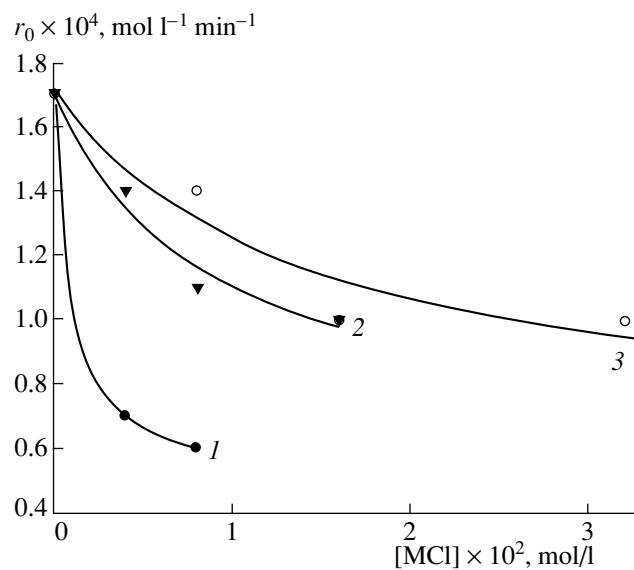


**Fig. 3.** Initial cyclohexene hydrocarbomethoxylation rate as a function of (a) TSA, (b) methanol, and (c) cyclohexene concentrations at  $T = 378$  K and  $P_{\text{CO}} = 2.1$  MPa. (a)  $[\text{C}_6\text{H}_{10}] = 0.1$  mol/l,  $[\text{CH}_3\text{OH}] = 0.15$  mol/l,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2] = 1 \times 10^{-3}$  mol/l, and  $[\text{PPh}_3] = 6 \times 10^{-3}$  mol/l; (b)  $[\text{C}_6\text{H}_{10}] = 0.1$  mol/l,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2] = 2 \times 10^{-3}$  mol/l,  $[\text{PPh}_3] = 8 \times 10^{-3}$  mol/l, and  $[\text{TSA}] = 2.4 \times 10^{-2}$  mol/l; (c)  $[\text{CH}_3\text{OH}] = 0.3$  mol/l,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2] = 2 \times 10^{-3}$  mol/l,  $[\text{PPh}_3] = 8 \times 10^{-3}$  mol/l, and  $[\text{TSA}] = 2.4 \times 10^{-2}$  mol/l.

The effect of TPP on the reaction rate indicates that this component also acts in a dual way. At concentrations below 0.04 mol/l, it accelerates the reaction. This effect is apparently due to TPP favoring the buildup of intermediates responsible for the formation of the reaction products. At higher concentrations, TPP reacts with intermediates of the catalytic cycle, resulting in the conversion of some catalyst to inactive or low-activity forms. The interplay of these factors is the reason why the reaction rate as a function of TPP concentration passes through an extremum. The accelerating effect of TPP is explicable in terms of the following equilibria:

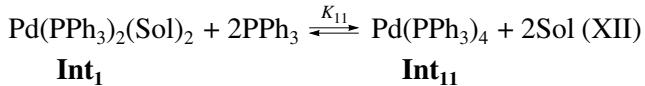


At low TPP concentrations, these equilibria are shifted to the  $\text{Pd}(\text{PPh}_3)_2(\text{Sol})_2$  complex, which is



**Fig. 4.** Cyclohexene hydrocarbomethoxylation rate as a function of (1)  $\text{RbCl}$ , (2)  $\text{KCl}$ , and (3)  $\text{NaCl}$  concentrations. Reaction conditions:  $T = 381 \text{ K}$ ,  $P_{\text{CO}} = 2.1 \text{ MPa}$ ,  $[\text{C}_6\text{H}_{10}] = 0.375 \text{ mol/l}$ ,  $[\text{CH}_3\text{OH}] = 0.3 \text{ mol/l}$ ,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2] = 2 \times 10^{-3} \text{ mol/l}$ ,  $[\text{PPh}_3] = 2.0 \times 10^{-2} \text{ mol/l}$ , and  $[\text{TSA}] = 6.0 \times 10^{-2} \text{ mol/l}$ .

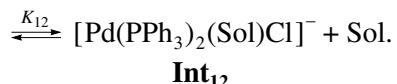
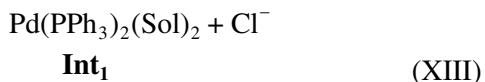
responsible for the formation of  $\text{HPd}^{\oplus}(\text{Sol})(\text{PPh}_3)_2$ , the key intermediate in the catalytic cycle. At high TPP concentrations, the equilibrium



is shifted to the inactive species  $\text{Pd}(\text{PPh}_3)_4$ , resulting in catalyst deactivation. Equilibrium (XII) is more sensitive to the TPP concentration than equilibria (X) and (XI).

The fact that the reaction is first-order with respect to TSA is evidence that this acid plays a significant role in the generation of hydride intermediates responsible for the formation of the ester. The plateau in the rate curve shown in Fig. 3a can be due to either TSA reaching its solubility limit in the reaction mixture or the stoichiometric formation of hydride complexes in excess TSA.

We believe that the inhibiting effect of the chloride anion is due to the fact that this anion has a greater coordinating power than the solvent molecules. In other words, this effect can be due to the equilibrium



The view that step (VII) determines the overall reaction rate is supported by various facts, including the first order of the reaction with respect to alcohol [6, 13], the sensitivity of the reaction rate to the molecular size of the nucleophilic alcohol [6, 13, 19], and the possibility of separating measurable amounts of acylpalladium complexes such as  $\text{Int}_6$  from the reaction mixture [17, 20]. The other steps can be considered to be equilibrium. The reaction rate will be given by the equation

$$r = k_7[\text{Int}_6][\text{CH}_3\text{OH}], \quad (1)$$

and the concentrations of all components appearing in the reaction scheme and in Eqs. (VIII)–(XIII) will be determined by the following equilibrium constants:

$$\begin{aligned} K_1 &= \frac{[\text{Int}_1]}{[\text{Int}_0]}, & K_2 &= \frac{[\text{Int}_2]}{[\text{Int}_1][\text{TsOH}]}, \\ K_3 &= \frac{[\text{Int}_3]}{[\text{Int}_2][\text{Ol}]}, & K_4 &= \frac{[\text{Int}_4]}{[\text{Int}_3]}, \\ K_5 &= \frac{[\text{Int}_5]}{[\text{Int}_4][\text{CO}]}, & K_6 &= \frac{[\text{Int}_6]}{[\text{Int}_5]}, \\ K_7 &= \frac{[\text{Int}_7]}{[\text{Int}_1][\text{CH}_3\text{OH}]^2}, & K_8 &= \frac{[\text{Int}_8]}{[\text{Int}_1][\text{CO}]^2}, \\ K_9 &= \frac{[\text{Int}_9][\text{PPh}_3]}{[\text{Int}_1][\text{CO}]}, & K_{10} &= \frac{[\text{Int}_{10}][\text{PPh}_3]}{[\text{Int}_1][\text{CH}_3\text{OH}]}, \\ K_{11} &= \frac{[\text{Int}_{11}]}{[\text{Int}_1][\text{PPh}_3]^2}, & K_{12} &= \frac{[\text{Int}_{12}]}{[\text{Int}_1][\text{Cl}^-]}, \end{aligned} \quad (2)$$

where  $[\text{Ol}]$  is the olefin concentration.

Since the reaction is first-order with respect to TSA and cyclohexene, the contribution from  $\text{Int}_2$ ,  $\text{Int}_3$ ,  $\text{Int}_4$ ,  $\text{Int}_5$ , and  $\text{Int}_6$  to the total amount of palladium complexes can be neglected. The total concentration of monomeric catalyst species will then appear as

$$C_m = [\text{Int}_0] + [\text{Int}_1] + [\text{Int}_7] + [\text{Int}_8] + [\text{Int}_9] + [\text{Int}_{10}] + [\text{Int}_{11}] + [\text{Int}_{12}].$$

Using the equilibrium constant equations (Eq. (2)), we obtain

$$\begin{aligned} C_m &= \frac{[\text{Int}_6]}{K[\text{Ol}][\text{CO}][\text{TsOH}]} \left\{ 1 + a[\text{CH}_3\text{OH}]^2 \right. \\ &\quad + b[\text{CO}]^2 + c\frac{[\text{CO}]}{[\text{PPh}_3]} + d\frac{[\text{CH}_3\text{OH}]}{[\text{PPh}_3]} \\ &\quad \left. + e[\text{PPh}_3]^2 + f[\text{Cl}^-] \right\}, \end{aligned} \quad (3)$$

where  $a = \frac{K_1 K_7}{1 + K_1}$ ,  $b = \frac{K_1 K_8}{1 + K_1}$ ,  $c = \frac{K_1 K_9}{1 + K_1}$ ,  $d = \frac{K_1 K_{10}}{1 + K_1}$ ,  $e = \frac{K_1 K_{11}}{1 + K_1}$ ,  $f = \frac{K_1 K_{12}}{1 + K_1}$ ,  $K = \frac{K_1 K_2 K_3 K_4 K_5 K_6}{1 + K_1}$ .

$$r = \frac{k C_m [OI][CO][TsOH][CH_3OH]}{\left\{1 + a[CH_3OH]^2 + b[CO]^2 + c\frac{[CO]}{[PPh_3]} + d\frac{[CH_3OH]}{[PPh_3]} + e[PPh_3]^2 + f[Cl^-]\right\}}, \quad (4)$$

where  $k = k_7 K$ .

The adequacy of Eq. (4) to experimental data is proved by the dependence of the reaction rate on  $P_{CO}$  and the methanol and TPP concentrations. In the case of a variable methanol concentration, this equation can be reduced to

$$r = \frac{\frac{k^*}{A}[CH_3OH]}{1 + \frac{a}{A}[CH_3OH]^2 + \frac{d'}{A}[CH_3OH]}, \quad (5)$$

where  $k^* = k C_m [OI][CO][TsOH]$ ;  $d' = \frac{d}{[PPh_3]}$ ;  $A = 1 + b[CO]^2 + c\frac{[CO]}{[PPh_3]} + e[PPh_3]^2 + f[Cl^-]$ .

In turn, Eq. (5) is readily reducible to

$$\frac{\frac{k^*}{A}[CH_3OH]}{r} - 1 = \frac{d'}{A}[CH_3OH] + \frac{a}{A}[CH_3OH]^2$$

or, eventually,

$$\frac{\left\{\frac{k^*[CH_3OH]}{Ar} - 1\right\}}{[CH_3OH]} = \frac{d'}{A} + \frac{a}{A}[CH_3OH]. \quad (6)$$

The coefficient  $\frac{k^*}{A}$  can be estimated from the initial slope of the  $r_0$  versus  $[CH_3OH]$  curve (Fig. 3b), since, at  $[CH_3OH] \rightarrow 0$ , the second and third terms in the denominator of Eq. (5) can be neglected. This yields  $\frac{k^*}{A} = 2.64 \times 10^{-2} \text{ min}^{-1}$ . Using this value, it is possible

$$\left\{\frac{k^*[CH_3OH]}{Ar} - 1\right\}$$

to plot  $\frac{k^*[CH_3OH]}{Ar}$  as a function of  $[CH_3OH]$  (Fig. 5a).

The linearity of this plot is evidence that the above kinetic model and mechanism are true in respect of the dependence of the reaction rate on the methanol concentration.

By solving Eq. (3) for  $[Int_6]$  and substituting the result into the rate equation for the slow step (Eq. (1)), we arrive at the following expression for the reaction rate:

In the one-factor study of the effect of TPP on the reaction rate, Eq. (4) was reduced to

$$r = \frac{k^*}{A' + \frac{c^*}{[PPh_3]} + e[PPh_3]^2}, \quad (7)$$

where  $k^* = k C_m [OI][CO][TsOH][CH_3OH]$ ;  $A' = 1 + a[CH_3OH]^2 + b[CO]^2 + f[Cl^-]$ ;  $c^* = c[CO] + d[CH_3OH]$ .

Equation (7) is readily reducible to

$$\frac{[PPh_3]}{r} = \frac{c^*}{k^*} + \frac{A'}{k^*}[PPh_3] + \frac{e}{k^*}[PPh_3]^3. \quad (8)$$

Thus, according to Eq. (8),  $\frac{[PPh_3]}{r}$  is a cubic polynomial function of  $PPh_3$  concentration. The parameters of Eq. (8) were estimated by least squares to be  $\frac{c^*}{k^*} = 3.52 \text{ min}$ ,  $\frac{A'}{k^*} = 2.06 \times 10^2 \text{ min}^{-1} \text{ mol}^{-1}$ , and  $\frac{e}{k^*} = 7.8 \times 10^4 \text{ min}^{-1} \text{ mol}^{-3}$ . It is clear from Fig. 5b that the calculated and observed data are in good agreement.

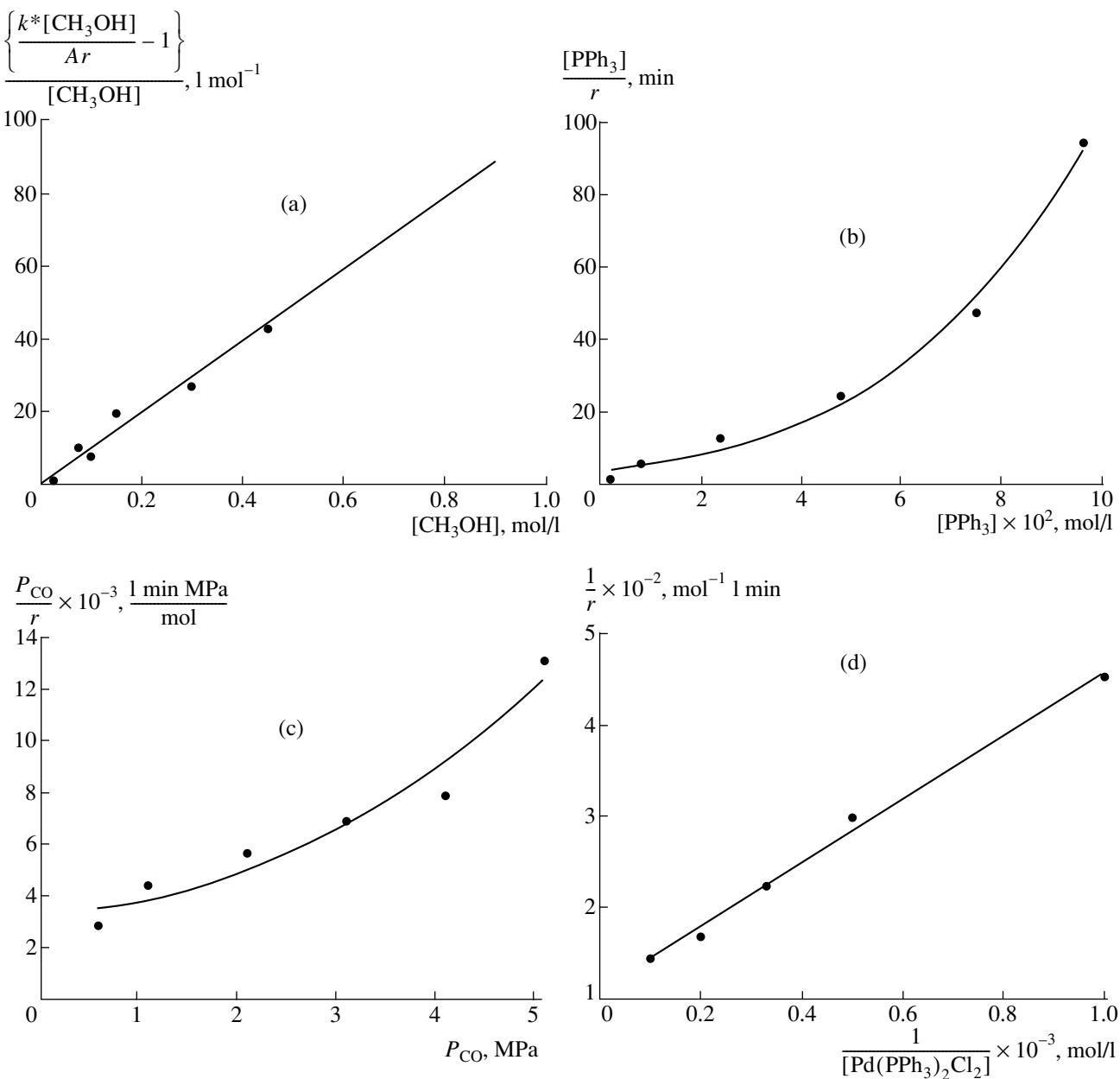
In the one-factor study of the effect of CO on the cyclohexene hydrocarbomethoxylation rate, Eq. (4) was reduced to

$$r = \frac{k^* P_{CO}}{A'' + b' P_{CO}^2 + c' P_{CO}}, \quad (9)$$

where  $A'' = 1 + a[CH_3OH]^2 + d\frac{[CH_3OH]}{[PPh_3]} + e[PPh_3]^2 + f[Cl^-]$ ,  $k^* = \frac{k C_m}{H} [OI][TsOH][CH_3OH]$ ,  $b' = \frac{b}{H^2}$ ,  $c' = \frac{c}{H[PPh_3]}$ , and  $H$  is the Henry constant for CO.

Equation (9) can be rearranged to obtain

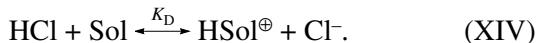
$$\frac{P_{CO}}{r} = \frac{A''}{k^*} + \frac{c'}{k^*} P_{CO} + \frac{b'}{k^*} P_{CO}^2. \quad (10)$$



**Fig. 5.** Validation of Eq. (4) against experimental data for the effects of (a)  $[\text{CH}_3\text{OH}]$ , (b)  $[\text{PPh}_3]$ , (c)  $P_{\text{CO}}$ , and (d) the catalyst precursor concentration on the cyclohexene hydrocarbomethylation rate at  $T = 378$  K and  $[\text{C}_6\text{H}_{10}] = 0.1$  mol/l. The points represent experimental data, and the solid lines represent the data calculated using Eq. (4). (a)  $P_{\text{CO}} = 2.1$  MPa,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2] = 2 \times 10^{-3}$  mol/l,  $[\text{PPh}_3] = 8 \times 10^{-3}$  mol/l, and  $[\text{TSA}] = 2.4 \times 10^{-2}$  mol/l; (b)  $P_{\text{CO}} = 2.1$  MPa,  $[\text{CH}_3\text{OH}] = 0.15$  mol/l,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2] = 2 \times 10^{-3}$  mol/l, and  $[\text{TSA}] = 0.120$  mol/l; (c)  $[\text{CH}_3\text{OH}] = 0.15$  mol/l,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2] = 1 \times 10^{-3}$  mol/l,  $[\text{TSA}] = 1.2 \times 10^{-2}$  mol/l, and  $[\text{PPh}_3] = 4 \times 10^{-3}$  mol/l; (d)  $P_{\text{CO}} = 2.1$  MPa,  $[\text{CH}_3\text{OH}] = 0.15$  mol/l,  $[\text{TSA}] = 1.2 \times 10^{-2}$  mol/l, and  $[\text{PPh}_3] = 4 \times 10^{-3}$  mol/l.

The least-squares estimation of the parameters of Eq. (10) yields  $\frac{A''}{k^*} = 3.4$  1 min MPa mol<sup>-1</sup>,  $\frac{c'}{k^*} = 5.45 \times 10^{-5}$  1 min mol<sup>-1</sup>, and  $\frac{b'}{k^*} = 3.35 \times 10^{-3}$  1 min mol<sup>-1</sup> MPa<sup>-1</sup>. It is clear from Fig. 5c that the data calculated using Eq. (10) are in good agreement with the observed data.

Equation (4) explains why the reaction is of order 0.5 with respect to the catalyst precursor  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ . It can be demonstrated that the chloride anion concentration, which appears in the denominator of this equation, is linearly related to the initial catalyst concentration  $C_m$ . According to the reaction equation (0),  $[\text{HCl}] = 2C_m$ . Chloride anions result from the acid–base equilibrium



When TSA is in considerable stoichiometric excess over the catalyst, the concentration of  $\text{HSol}^+$  ions is virtually constant considering that the acidity of TSA is higher than the acidity of HCl. Therefore, according to equilibrium (XIV), the concentration of chloride ions is

$$[\text{Cl}^-] = K'_D [\text{HCl}] = 2K'_D C_m, \quad (11)$$

$$\text{where } K'_D = \frac{K_D [\text{Sol}]}{[\text{HSol}^+]}.$$

Substituting Eq. (11) into Eq. (4), we obtain the following expression for the reaction rate:

$$r = \frac{k^* C_m}{A''' + f' C_m}, \quad (12)$$

where  $k^* = k[\text{CO}][\text{Ol}][\text{TsOH}][\text{CH}_3\text{OH}]$ ,  $f' = 2fK'_D C_m$ , and  $A''' = 1 + a[\text{CH}_3\text{OH}]^2 + b[\text{CO}]^2 + c \frac{[\text{CO}]}{[\text{PPh}_3]} + d \frac{[\text{CH}_3\text{OH}]}{[\text{PPh}_3]} + e[\text{PPh}_3]^2$ .

Equation (12) can be linearized to obtain

$$\frac{1}{r} = \frac{f'}{k^*} + \frac{A'''}{k^*} \frac{1}{C_m},$$

and the reaction rate as a function of catalyst concentration (Fig. 2b) can be plotted as  $\frac{1}{r}$  versus  $\frac{1}{C_m}$  (Fig. 5d).

The linearity of this plot is evidence in favor of our view of the role of the catalyst precursor in the reaction.

Thus, the above reaction mechanism and the kinetic model that it implies adequately describe the experimental data concerning the dependence of the cyclohexene hydrocarbomethoxylation rate on the methanol, TPP, and catalyst precursor concentrations and CO pressure.

The inhibiting effect of the chloride anion may result from the fact that part of the catalyst is involved in an alternative catalytic cycle generated by complexes of the  $\text{Int}_{12}$  type. The intermediates in this cycle may be neutral hydride complexes such as  $\text{HPd}(\text{PPh}_3)_2\text{Cl}$ ,  $\text{C}_6\text{H}_{11}\text{Pd}(\text{PPh}_3)_2\text{Cl}$ , and  $\text{C}_6\text{H}_{11}(\text{CO})\text{Pd}(\text{PPh}_3)_2\text{Cl}$ , which are less reactive than cationic complexes. The low reactivity of these complexes is due to their weaker accepting power and to the low mobility of the chloride anions in their coordination spheres.

Note that, in the systems in which the reaction is most likely to proceed via neutral hydride complexes and the catalyst precursor is  $\text{PdCl}_2$  or  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ , the chloride anion promotes the reaction [17, 21] or does not exert any effect on it [22]. This strengthens our

belief that the primary cause of the inhibiting effect of chloride is that the chloride anion gives rise to alternative catalytic cycles involving neutral chlorine-containing hydride intermediates. The reactions proceeding by these mechanisms are much slower than the main reaction. The existence of such cycles is clearly demonstrated in earlier works [2, 11, 17].

## REFERENCES

1. Lapidus, A.L. and Pirozhkov, S.D., *Usp. Khim.*, 1989, vol. 58, no. 2, p. 197.
2. Petrov, E.S., *Zh. Fiz. Khim.*, 1988, vol. 62, no. 10, p. 2858.
3. Yan, Yu.B. and Nefedov, B.K., *Sintezы на основе оксидов углерода* (Syntheses Using Carbon Oxides), Moscow: Khimiya, 1987.
4. Vavasori, A., Cavinato, G., and Toniolo, L., *J. Mol. Catal. A*, 2001, vol. 176, p. 11.
5. Zherbaev, Kh.A., Tsukanov, I.A., El'man, A.R., and Zhubanov, K.A., *Zh. Org. Khim.*, 1994, vol. 64, no. 7, p. 1189.
6. Vavasori, A., Toniolo, L., and Cavinato, G., *J. Mol. Catal. A*, 2003, vol. 191, p. 9.
7. Kron, T.E., Terekhova, M.I., Noskov, Yu.G., and Petrov, E.S., *Kinet. Katal.*, 2001, vol. 42, no. 2, p. 204.
8. Noskov, Yu.G. and Petrov, E.S., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 10, p. 1756.
9. El'man, A.R., Matveev, V.A., Slivinskii, E.V., and Lektev, S.M., *Khim.-Farm. Zh.*, 1990, no. 3, p. 47.
10. Cavinato, G. and Toniolo, L., *J. Mol. Catal.*, 1991, vol. 69, p. 283.
11. Noskov, Yu.G., Simonov, A.I., and Petrov, E.S., *Kinet. Katal.*, 2000, vol. 41, no. 4, p. 564.
12. Fenton, D.M., *J. Org. Chem.*, 1973, vol. 38, no. 18, p. 3192.
13. Knifton, J.F., *J. Org. Chem.*, 1976, vol. 41, no. 17, p. 2885.
14. Yoshida, H., Sugita, N., Kudo, K., and Takezaki, Y., *Bull. Chem. Soc. Jpn.*, 1976, vol. 49, no. 8, p. 2245.
15. Karpyuk, A.D., Kolosova, N.D., Terekhova, M.P., Chernoplekova, V.A., Petrov, E.S., and Beletskaya, I.P., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, no. 10, p. 2291.
16. Verspui, G., Moiseev, I.I., and Sheldon, R.A., *J. Organomet. Chem.*, 1999, vol. 586, p. 196.
17. Petrov, E.S. and Noskov, Yu.G., *Ross. Khim. Zh.*, 1998, vol. 42, no. 4, p. 149.
18. Schmid, R. and Sapunov, V., *Non-Formal Kinetics*, Weinheim: Chemie, 1982.
19. Cavinato, G. and Toniolo, L., *J. Mol. Catal.*, 1979, vol. 6, p. 111.
20. Protchenko, A.V., Shifrina, R.R., and Petrov, E.S., *Neftekhimiya*, 1988, vol. 28, no. 2, p. 200.
21. Blazer, H.U., Indolese, A., Schyder, A., Steiner, H., and Studer, M., *J. Mol. Catal. A*, 2001, vol. 123, p. 3.
22. Terekhova, M.N., Kron, T.E., Noskov, Yu.G., and Petrov, E.S., *Neftekhimiya*, 1996, vol. 36, no. 4, p. 3303.