Kinetics and mechanism of styrene hydrocarboalkoxylation catalyzed by Pd^0 complex in the presence of toluenesulfonic acid

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The kinetics of the catalytic reaction of styrene with CO and *n*-butanol in the $Pd(dba)_2$—TsOH—Ph_3P system in dioxane (383 K) was studied. The initial rates of accumulation of regioisomeric products (butyl 2- and 3-phenylpropionates) were measured as functions of the CO pressure, reactant concentrations, and the catalytic system components. A kinetic model of the process and a hydride mechanism with the $HPd(Ph_3P)_3^+$ cationic complex acting as a key intermediate were proposed.

Key words: carbonylation, styrene, palladium complexes, triphenylphosphine, toluenesulfonic acid, esters of phenylpropionic acids, kinetics, catalysis, reaction mechanism.

In recent years, palladium complexes with weakly basic acido ligands such as carboxylate or sulfonate anions have been used more and more extensively as homogeneous catalysts for carbonylation of unsaturated hydrocarbons.[1—4] The relatively weak coordination of these ligands to the central atom facilitates activation of the reactant molecules. The possibility of using these catalysts has been studied in relation to the synthesis of esters of 2-phenylpropionic acid, forming the basis of a number of nonsteroid antiinflammatory drugs,[5] by hydrocarboalkoxylation of styrene.[6] The catalytic activity and regioselective effect of palladium complexes in this reaction depend substantially on the nature of the acido ligand, which might be due to a change in the mechanism of the catalytic action.[7] In order to reveal these effects, we studied the kinetics of formation of butyl 3-phenylpropionate (**1**) and butyl 2-phenylpropionate (**2**) in the reaction of styrene with CO and *n*-butanol in the presence of a catalytic system consisting of the $Pd(dba)_2$ complex (**3**, dba is dibenzylideneacetone), triphenylphosphine (below referred to as L), and *p*-toluenesulfonic acid (TsOH).

$$PhCH{=}CH_2 + CO + BuOH \xrightarrow{Cat} \underset{\mathbf{1}}{PhC_2H_4COOBu} + \underset{\mathbf{2}}{PhCH(Me)COOBu} \qquad (1)$$

$$Cat = Pd(dba)_2/TsOH/L$$

The catalytically active species in this reaction are Pd^{II} complexes with a weakly bonded acido ligand, TsO, which are formed *in situ*. Previously,[8] we have studied a similar reaction using the $PdCl_2L_2$ complex (**4**) with a strongly coordinated acido ligand, the Cl^- anion.

Experimental

The reaction was carried out under a constant pressure of CO in an autoclave equipped with a stirrer and a sampler[9] in dioxane at 383 K in the presence of a catalytic system consisting of complex **3** and two components, toluenesulfonic acid monohydrate and PPh_3, both taken in an excess with respect to the complex. To prevent the contact with the autoclave internal surface, the reaction mixture was placed in a glass reactor. Complex **3** was synthesized similarly to a published procedure;[10] the other compounds were commercial preparations, which were purified by standard procedures. The CO pressure and the concentrations of the reactants and the catalytic system components are listed in Table 1. The course of the reaction was monitored using GLC analysis of samples.[7] The instant of styrene injection at a specified pressure and temperature was taken as the onset of the reaction. The rates of accumulation of regioisomeric esters **1** and **2** were determined from the slopes of the initial sections of kinetic curves. The target parameters of the kinetic models were calculated using a computer program by minimization of the sum of squares of the mismatch between the calculated and experimental reaction rates.

Results and Discussion

The results obtained (Table 1, Fig. 1) showed that under any conditions studied, reaction (1) gives predominantly linear regioisomer **1** (reaction regioselectivity $S \geq 65\%$) whose content virtually does not depend on the PPh_3 concentration (Table 1, runs 5, 18, 19). In this respect, the studied catalyst differs crucially from complex **4**, in whose presence branched isomer **2** is formed as the major product and the reaction regioselectivity markedly increases with an increase in the excess of L.[8,9]

In the range of *n*-butanol concentrations of 0.4—1.6 mol L^{-1}, the order of the reaction with respect

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Table 1. Initial rates of accumulation of products **1** (r_1) and **2** (r_2) and regioselectivity (S) of reaction (1) under various CO pressures (P) and at various concentrations of styrene ([St]), Pd(dba)$_2$ ([Pd]), toluenesulfonic acid ([TsOH]), and Ph$_3$P ([L]) (383 K, dioxane, [BuOH] = 1.6 mol L^{-1})

Run	P /MPa	[St]	[Pd]	[TsOH]	[L]	$r_1 \cdot 10^3$		$r_2 \cdot 10^3$		S (%)
		mol L^{-1}				mol L^{-1} min^{-1}				
						Experiment	Calculation*	Experiment	Calculation*	
1	2.0	0.65	0.00163	0.0650	0.104	1.60	1.52	0.57	0.65	73.6
2	2.0	0.65	0.00325	0.0650	0.104	3.07	3.05	1.14	1.31	72.9
3	2.0	0.65	0.00650	0.0650	0.104	6.24	6.23	2.38	2.68	72.4
4	2.0	0.65	0.00325	0.0130	0.026	0.73	0.79	0.33	0.34	68.9
5	2.0	0.65	0.00325	0.0325	0.026	1.82	1.84	0.78	0.79	69.9
6	2.0	0.65	0.00325	0.0650	0.026	3.16	3.28	1.41	1.41	69.1
7	2.0	0.65	0.00325	0.1300	0.026	5.23	5.43	2.07	2.34	71.6
8	0.2	0.65	0.00325	0.0325	0.026	2.52	2.58	0.77	0.74	76.2
9	0.5	0.65	0.00325	0.0325	0.026	2.88	3.04	0.95	0.95	75.2
10	1.0	0.65	0.00325	0.0325	0.026	2.44	2.66	0.90	0.93	73.0
11	1.5	0.65	0.00325	0.0325	0.026	2.17	2.21	0.89	0.87	70.9
12	2.5	0.65	0.00325	0.0325	0.026	1.59	1.55	0.73	0.73	69.8
13	3.0	0.65	0.00325	0.0325	0.026	1.30	1.32	0.68	0.68	65.6
14	3.3	0.65	0.00325	0.0325	0.026	1.25	1.21	0.66	0.65	65.6
15	2.0	0.33	0.00325	0.0325	0.026	1.01	0.94	0.42	0.40	70.8
16	2.0	1.30	0.00325	0.0325	0.026	4.08	3.68	1.67	1.59	71.0
17	0.5	0.65	0.00325	0.0325	0.052	2.57	2.40	0.80	0.75	76.5
18	0.5	0.65	0.00325	0.0325	0.078	2.20	1.89	0.71	0.59	75.7
19	0.5	0.65	0.00325	0.0325	0.104	1.73	1.55	0.54	0.48	76.0

* The calculation was carried out according to the kinetic model proposed in this work.

to the concentration of n-butanol [BuOH] is close to zero (the total rate of styrene carbonylation r varies from 2.1 to 2.6 mmol L^{-1} min^{-1}). On further increase in the n-butanol content, the rate of styrene conversion increases exponentially to 24.6 mmol L^{-1} min^{-1} for [BuOH] = 9.1 mol L^{-1} (Fig. 1). The increase in the catalyst activity is accompanied by some decrease in the S value, which is 72% at 0.4 mol L^{-1} and 64% at 5 mol L^{-1}. The dependences of the rates of accumulation of products **1** and **2** on the CO pressure P (runs 5, 8—14) exhibit a feebly pronounced maximum in the region of 0.5 MPa (Fig. 2), and the S value somewhat decreases with an increase in the CO pressure.

Interpretation of the mechanism of olefin carbonylation is mainly based on analysis of these two dependences. Note in this connection that with complex **4**

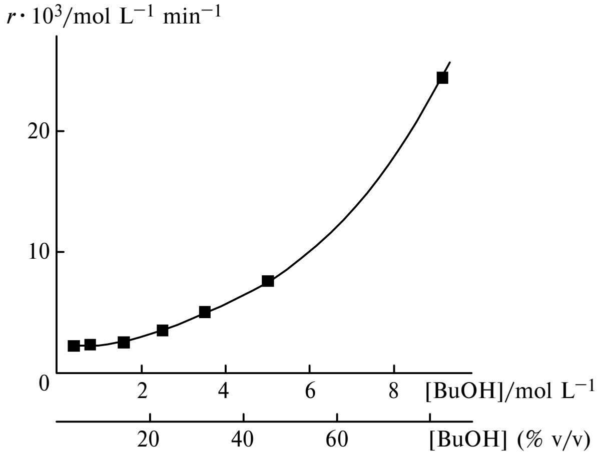


Fig. 1. Rate of styrene carbonylation by reaction (1) *vs.* the content of n-butanol (the conditions are presented in Table 1, run 5).

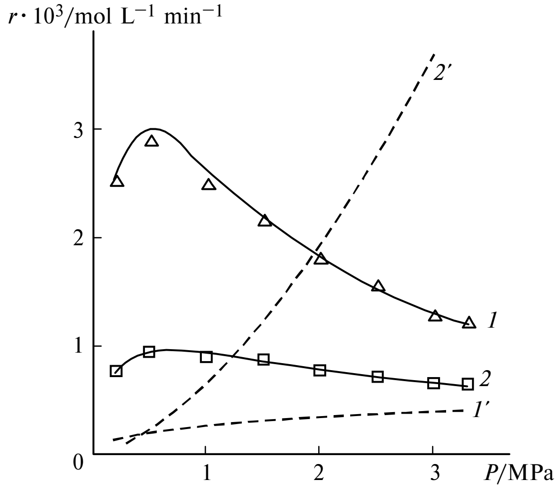


Fig. 2. Rates of accumulation of products **1** (*1*, *1′*) and **2** (*2*, *2′*) *vs.* CO pressure (P): *1*, *2*, Pd(dba)$_2$—10TsOH—8L catalyst, [Pd] = 0.00325 mol L^{-1}; *1′*, *2′*, PdCl$_2$L$_2$—6L catalyst, [Pd] = 0.0065 mol L^{-1} (the conditions are presented in Table 1, run 5).

used as the catalyst, the corresponding dependences look in a different way and, moreover, they are not the same for the two regioisomers.[8] Indeed, the dependence of the initial rate of formation of regioisomer **1** (r_1) on [BuOH] is described by the Michaelis equation, whereas the initial rate of formation of regioisomer **2** (r_2) passes through a maximum with an increase in [BuOH]. Both rates increase with an increase in P but, whilst the formal order of r_1 with respect to P is much less than unity (0.4), this value for r_2 is close to 1.5 (Fig. 2), and the order of the overall rate of styrene conversion is also greater than unity.

In the case of complex **3**, the reaction has the first order with respect to styrene (see Table 1, runs 5, 15, and 16, and Fig. 3). In addition, the first order with respect to complex **3** (runs 1—3), a fractional order (a Michaelis type dependence) with respect to the TsOH acid (runs 4—7), and a negative order with respect to Ph_3P (runs 9, 17—19) are observed. A change in the concentration of any of the above-listed components of the reaction mixture has virtually no influence on the process regioselectivity. The influence of excess concentrations of TsOH and Ph_3P differs somewhat from that found[6] for a similar catalytic system containing $Pd(OAc)_2$ instead of **3**, in the MeOH medium. In the system under comparison, the catalyst activity reached a limit (245 h^{-1}) at [TsOH]/[Pd] = 4 and increased only slightly upon further increase in the excess of the acid (*cf.* runs 4—7); the decrease in the activity upon an increase in the amount of Ph_3P is accompanied by an increase in the regioselectivity with respect to product **1** (*cf.* the change in S in runs 9, 17—19). These differences can be due to the change in the physicochemical properties of the medium caused by the replacement of the dioxane—butanol system by more polar methanol in which the catalyst activity and regioselectivity have been reported[6] to be higher than in *n*-butanol.

The results[7] of studies of the reaction systems in the dioxane—butanol solvent mixture and in the BuOH solvent by IR spectroscopy *in situ* indicate that complex **3** is converted under the reaction conditions into carbonyl phosphine complexes, $Pd(CO)L_2$ and $Pd(CO)_2L_2$ ($L = Ph_3P$); evidently, the PdL_n (n = 2, 3) complexes not detected in the IR spectra, are also present. The IR spectra do not exhibit ν(C=O) absorption bands, typical of Pd^{II} acyl and alkoxycarbonyl complexes. These data rule out the possibility that reaction (1) occurs by an alkoxide mechanism but does not contradict the hydride mechanism because Pd^0 complexes can form hydride intermediates in the presence of acids.[11] Direct detection of these intermediates is rather difficult due to the strong ν(C=O) absorption in the region of weak ν(H—Pd) mode. The steady-state concentration of the acyl complexes resulting from transformation of hydride intermediates may be too low to detect them by spectroscopy.

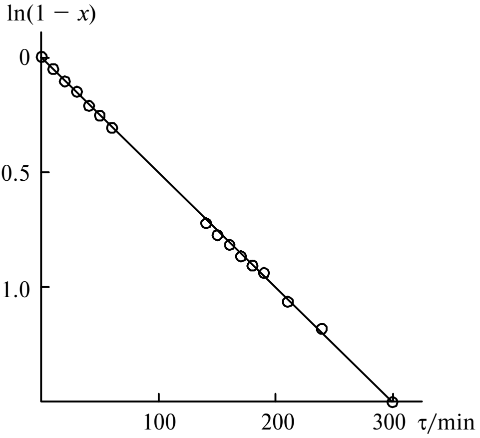
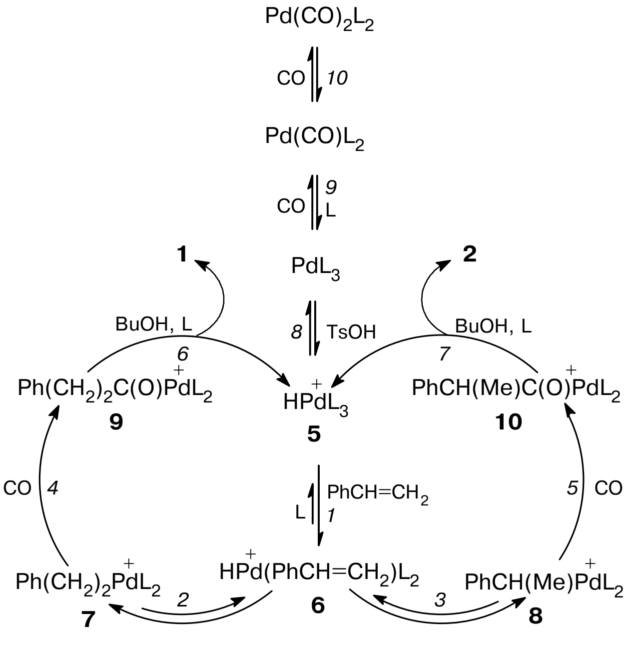


Fig. 3. Linearization of the kinetic curve for styrene conversion (x) in the coordinates of a first-order kinetic equation (for conditions, see Table 1, run 16).

According to some studies,[8,9] the high reaction order with respect to CO in the case of complex **4** and the difference between the dependences of r_1 and r_2 on P (see Fig. 2) are due to the substantial contribution of carbonyl-containing forms of Pd^0 to the catalysis of styrene conversion. Therefore, the negative order of the rates of accumulation of both regioisomers with respect to CO observed for reaction (1) at $P > 0.5$ MPa can be regarded as indicating that in the catalytic system under study, hydride intermediates are formed only from PdL_n complexes.

On the basis of these views, we developed a hydride reaction mechanism scheme in which the intermediate Pd^{II} complexes occur, as in a previous work,[6] in a cationic form (Scheme 1, the TsO^- counter-ion is omitted for the sake of simplicity). The role of a key

Scheme 1



intermediate is allotted to the cationic hydride complex $HPdL_3^+$ (**5**), which is produced in the presence of acids.[12] In the study cited,[6] complex **5** is regarded as one of the possible catalytically active initial species.

The above complex and the π-olefinic intermediate **6** formed from this complex on treatment with styrene are common to the cycles of formation of regioisomers **1** and **2**. Only at this step, which is common to both routes, can the inhibitory effect of triphenylphosphine be identical for r_1 and r_2; therefore, it is reasonable to consider step *1* to be reversible. The process regioselectivity is determined at the step of transformation of π-complex **6** into coordinatively unsaturated σ-alkyl intermediates **7** and **8**. The variation in the r_2/r_1 ratio with an increase in P described by Eq. (2) provides grounds to believe that step *2* is reversible and step *3* is quasi-equilibrium, which is consistent with the data on deuterium exchange in styrene in the presence of hydride metal complexes.[13,14]

$$r_2/r_1 = 0.29 + 0.071P \tag{2}$$

The addition of CO followed by insertion into the C—Pd bond is presented in Scheme (1) as steps *4* and *5* of carbonylation of complexes **7** and **8**. The nearly zero order of reaction (1) with respect to *n*-butanol in the region of low [BuOH] values implies that the process rate does not depend on the rate of butanolysis of acyl intermediates **9** and **10**. Therefore, steps *6* and *7* are not included in the kinetic model, and the preceding steps *4* and *5* are assumed to be reversible.

Complex **5** and the ballast carbonyl-containing Pd^0 species equilibrated with it (steps *8—10*) are included in the catalyst material balance

$$[Pd] = [HPdL_3^+] + [Pd(CO)L_2] + [Pd(CO)_2L_2]. \tag{3}$$

As shown by preliminary calculations, the quasi-steady-state concentrations of PdL_n complexes and of other palladium-containing species are negligibly low. The allowance made for material balance (3) and the assumption of a quasi-steady-state character of the concentrations of the palladium-containing intermediates shown in Scheme (1) gave the following equations

$$r_1 = Z_1 \cdot Z_2, \tag{4}$$

$$Z_1 = \frac{A_4[\mathrm{St}]P}{([L]' + A_1P)(1 + A_2P) + A_3P},$$

$$Z_2 = \frac{[\mathrm{Pd}][\mathrm{TsOH}]'}{[\mathrm{TsOH}]' + A_5P/[L]' + A_6P^2/[L]'},$$

$$r_2 = r_1A_1(1 + A_2P)/A_3, \tag{5}$$

which describe the kinetics of reaction (1) at a constant alcohol concentration. The second factor (Z_2) in Eq. (4) is the quasi-steady-state concentration of the key complex **5**; [St] and [Pd] are the concentrations of styrene and complex $Pd(dba)_2$, respectively; [TsOH]′ and [L]′ are the quasi-steady-state concentrations of toluenesulfonic acid and PPh_3 calculated from the [TsOH] and [L] values given in Table 1 using the equations

$$[\mathrm{TsOH}]' = [\mathrm{TsOH}] - \frac{[\mathrm{Pd}][\mathrm{TsOH}]'}{[\mathrm{TsOH}]' + A_5P/[\mathrm{L}]' + A_6P^2/[\mathrm{L}]'}, \tag{6}$$

$$[\mathrm{L}]' = [\mathrm{L}] - 2\,[\mathrm{Pd}] - ([\mathrm{TsOH}] - [\mathrm{TsOH}]'). \tag{7}$$

The A_i parameters are expressed *via* the rate constants of steps given in Scheme (1): $A_1 = K_3k_5/k_{-1}$, $A_2 = k_4/k_{-2}$, $A_3 = k_2k_4/k_{-1}k_{-2}$, $A_4 = k_1A_3$, $A_5 = K_8K_9$, $A_6 = K_8K_9K_{10}$. Steps *3* and *8—10* are assumed to be quasi-equilibrium, steps *1* and *2* are taken to be reversible, and the other steps are irreversible. Processing of the kinetic data obtained for a constant *n*-butanol concentration (1.6 mol L^{-1}) gave the following values: A_1 = 0.0031 mol L^{-1} MPa^{-1}; A_2 = 0.29 MPa^{-1}; A_3 = 0.0114 mol L^{-1} MPa^{-1}; A_4 = 0.235 MPa^{-1} min^{-1}; A_5 = 0.0021 mol^2 L^{-2} MPa^{-1}; A_6 = 0.00012 mol^2 L^{-2} MPa^{-2}. With these A_i values, the set of equations (4)—(7) describes the experimental data with a mean relative error of ~6% (*cf.* experimental and calculated data in Table 1), which is comparable with the error of determination of the r_1 and r_2 values. Substitution of the parameters A_1—A_3 into Eq. (5) gives the ratio

$$r_2/r_1 = 0.27 + 0.079P, \tag{8}$$

close to empirical relation (2). This evidence for the adequacy of the kinetic model supports the mechanism suggested for reaction (1). When comparing this mechanism with the mechanism of the catalys by complex **4**, it is noteworthy, first of all, that the pathway to the key intermediate changes on passing from a strongly coordinated acido ligand (Cl^-) to a weakly bound one (TsO^-). In the former case, the oxidative addition of HCl to Pd^0 results in the neutral $HPdClL_2$ complex and its carbonyl-containing analogs,[8,9] whereas in the latter case, cation **5** is formed upon protonation of PdL_3. The less basic mono- and dicarbonyl forms of Pd^0 do not give apparently the corresponding cations; these complexes constitute an inactive part of the catalyst, whose fraction increases with an increase in the CO pressure. This accounts for the adverse influence of the pressure on the rate of reaction (1). The presence of these complexes decreases substantially the efficiency of utilization of the palladium present in the reaction system. According to an estimate of the concentration of complex **5** from Eq. (4) using the A_5 and A_6 values found, the content of the active component under the standard conditions of run 5 (Table 1) is equal to ~12%.

Since in the case of the Pd^0/TsOH/L system, no carbonyl-containing neutral hydride complexes responsible for the predominant accumulation of the branched product are formed,[8] the formation of linear isomer **1** becomes the prevailing reaction route. However, the insertion of styrene into the H—Pd bond of cation **5** occurs less regioselectively ($S < 80\%$) than that in the case of the neutral $HPdClL_2$ complex ($S \approx 100\%$).

A weighty contribution to the differences between the mechanisms discussed is made by the ionic nature of the catalytically active complexes with weakly bound acido ligands. Since the dielectric constant of the medium ε is less than 5.7 (in the region of $[BuOH] \le 5$ mol L^{-1}),[15] the majority of these complexes form, apparently, ion pairs with the TsO^- counter-ion.[16] In this system, specific solvation of the anion by *n*-butanol is possible. Therefore, it can be assumed that solvent-separated ion pairs are mainly formed. The coordinatively unsaturated Pd^{II} cationic complexes contained in these ion pairs appear to be more reactive than neutral intermediates; this is the reason for the increase in the catalytic activity (from 16 h^{-1} for complex **4** to 78 h^{-1} for complex **3** under conditions of run 2). The ionization accelerates butanolysis of the acyl complexes; as a consequence, this final step no longer determines the rate of accumulation of the corresponding products. In this case, the quasi-steady-state concentrations of intermediates **7** and **8** are, apparently, too low to be detected *in situ* by IR spectroscopy, whereas in the case of **4**, the $PhC_2H_4C(O)PdClL_2$ complex can even be isolated from the reaction mixture.[8]

The exponential dependence of the reaction rate on the content of *n*-butanol in the $Pd(dba)_2/TsOH/L$ system (Fig. 1) suggests that the influence of the alcohol is related to the change in the physicochemical properties of the medium, first of all, the ε value, which increases with an increase in the volume fraction of BuOH in the reaction mixture, rather than to the kinetic factor.[15] This may induce an increase in the catalyst activity due to the enhancement of dissociation of both ion pairs of catalytically active intermediates and TsOH with a shift of equilibria *8—10* toward complex **5**, whose steady-state concentration increases at the cost of the $Pd(CO)L_2$ and $Pd(CO)_2L_2$ ballast species (the proportion of these species in standard experiment 5 is ~90%). This is supported by the dependence that we found between $\ln(r)$ and ε of the corresponding dioxane—*n*-butanol mixtures[15] (the linear correlation coefficient is 0.99)

$$-\ln(r) = 3.22 + 8.11/\varepsilon, \tag{9}$$

whose pattern is similar to that of the dependence describing the effect of the dielectric constant on the dissociation constants of electrolytes.[17] However, the basicity of the solvent might also play a role. Thus when dioxane is replaced by equally non-polar but less basic toluene, the catalyst activity increases by almost an order of magnitude.[7]

Thus, the results of this study demonstrate that on weakening of the coordination of the acido ligand to the central atom in palladium phosphine complexes, the hydride mechanism of the carbonylation catalysis of unsaturated hydrocarbons is retained. However, in this case, due to the ionic character of catalytically active intermediates with the weakly bound acido ligand, the mechanism somewhat changes, which influences the process kinetics.

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