Kinetics and Mechanism of Styrene Hydroalkoxycarbonylation Catalyzed by the Complex PdCl$_2$(Ph$_3$P)$_2$ in the Presence of Butanol
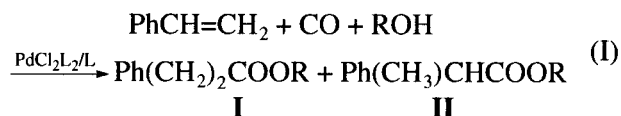
Yu. G. Noskov, A. I. Simonov, and E. S. Petrov

*Karpov Research Institute of Physical Chemistry (Russian State Scientific Center),
ul. Vorontsovo pole 10, Moscow, 103064 Russia*

Received December 17, 1998

Abstract—The single-factor experiment method was used to study the kinetics of styrene hydrobutoxycarbonylation catalyzed by the complex PdCl$_2$(Ph$_3$P)$_2$ in dioxane (383 K, [BuOH] = 1–8 mol/l). The rates of accumulation of the regioisomeric reaction products as empirical functions of CO pressure and concentrations of styrene, triphenylphosphine, and the catalyst were found. The acyl complex (PhC$_2$H$_4$CO)PdCl(Ph$_3$P)$_2$ was isolated from the reaction mixture. The assumed intermediate of an alcoholate mechanism, the (BuOOC)PdCl(Ph$_3$P)$_2$ complex, is not formed by the reaction of PdCl$_2$(Ph$_3$P)$_2$ with CO and butanol. The set of data generally corresponds to a hydride mechanism of styrene hydrocarboxylation, which includes three key intermediates HPdClL$_{2-n}$(CO)$_n$ (n = 0–2). A change in the solvation properties of the reaction medium due to the replacement of water by butanol affects the kinetic scheme of the process.

INTRODUCTION

The study of the mechanism and nature of the regioselectivity of catalytic carbonylation reactions of vinylarenes similar to reaction (I) is of interest in searching for new approaches to syntheses of pharmaceuticals based on 2-arylpropionic acids [1–3]. As shown previously, the kinetics of styrene hydrocarboxylation (R = H) catalyzed by the PdCl$_2$L$_2$ complex (L = Ph$_3$P) corresponds to the multiroute scheme of a hydride mechanism involving the catalytically active intermediates HPdClL$_{2-n}$(CO)$_n$ (n = 0–2), whose regioselectivity with respect to "linear" product I decreases as n increases [4, 5]. In this work, we studied the kinetics of reaction (I) for R = n-C$_4$H$_9$ (Bu) to reveal to what extent these concepts on the mechanism of the process can be applied to a similar reaction of styrene (R = Alk) hydroalkoxycarbonylation.

$$\text{PhCH=CH}_2 + \text{CO} + \text{ROH}$$

$$\xrightarrow{\text{PdCl}_2\text{L}_2/\text{L}} \text{Ph(CH}_2)_2\text{COOR} + \text{Ph(CH}_3)\text{CHCOOR} \quad (I)$$
$$\qquad\qquad\quad \textbf{I} \qquad\qquad\qquad\qquad \textbf{II}$$

R = H, Bu; L = Ph$_3$P; [L]/[PdCl$_2$L$_2$] = 2–14.

EXPERIMENTAL

Styrene hydrobutoxycarbonylation was carried out in an autoclave [4, 5] in a dioxane medium at 383 K in the CO pressure range 0.5–3 MPa. The components were analyzed by a procedure similar to that in [4, 6]. The reactant and catalyst concentrations are presented in Table 1. The conditions of entry 4 at [BuOH] = 1.6 mol/l

were accepted as standard. The rates of accumulation of regioisomeric esters **I** and **II** (w_I and w_II, respectively) were found from the slopes of linear portions of the kinetic curves in the styrene conversion region to 20–30% styrene. To avoid possible distortions of the kinetic data by a prolonged (~2 h) induction period, we formed catalytically active species in the absence of a carbonylated substrate. An insignificant amount of water (0.05–0.1 mol/l) was added to a mixture of the reactants containing no styrene, and the mixture was allowed to stand for 1 h at the temperature and pressure of the reaction. Thereafter, styrene was added, and the reaction time was measured from this point on. This procedure, to within the experimental error, did not affect the w_I and w_II values.

Preparation of the acyl complex (PhC$_2$H$_4$CO)PdClL$_2$. A mixture of PdCl$_2$L$_2$ (0.1 g), Ph$_3$P (0.11 g), butanol (5 ml), and water (0.02 ml) in dioxane (5.1 ml) was heated for 1 h at 383 K and P_CO = 2 MPa. Then styrene (0.74 g) was introduced, and the mixture was stirred for 30 min at the specified temperature and pressure. The solution was diluted with pentane (20–30 ml) at room temperature, and the precipitate formed after the 1-h exposure at 6–8°C was filtered off. The residue was concentrated to 1.5–2.0 ml in a vacuum. Next, pentane (30 ml) was added, and the mixture was stored for 3 days in the freezing chamber of a refrigerator. The white crystals formed were separated, washed with a pentane–ether (2 : 1) mixture, and dried in a vacuum. The complex was obtained in a 45% yield (0.05 g). IR (cm^{-1}): 1680 s (C=O), 330 m (Pd–Cl); other bands: 1480 m, 1435 w, 1090, 745, 695 m. When

Table 1. Initial rates of accumulation of butyl esters of 3- and 2-phenylpropionic acids (w_I and w_{II}, respectively) in styrene carboxylation and the regioselectivity (S^*) of reaction (I) at [BuOH] = (A) 1.6 and (B) 5.0 mol/l; 383 K

Entry	P_{CO}, MPa	[L] × 10³, mol/l	[Pd] × 10³, mol/l	[St], mol/l	$\dfrac{w_I \times 10^4}{mol\ l^{-1}\ min^{-1}}$		$\dfrac{w_{II} \times 10^4}{mol\ l^{-1}\ min^{-1}}$		S^*, %	
					A	B	A	B	A	B
1	0.5	39	6.5	0.65	1.7	7.6	2.0	3.3	46	70
2	1.0	39	6.5	0.65	2.8	13.8	6.8	10.1	29	58
3	1.5	39	6.5	0.65	3.7	15.2	15.2	17.0	20	47
4	2.0	39	6.5	0.65	3.4	16.0	19.4	27.1	15	37
5	2.5	39	6.5	0.65	3.5	16.5	27.2	34.7	11	32
6	3.0	39	6.5	0.65	3.7	18.1	33.6	44.2	9	29
7	2.0	39	6.5	0.21	2.8	9.81	11.8	14.4	19	41
8	2.0	39	6.5	0.33	2.9	10.2	14.2	17.5	17	37
9	2.0	39	6.5	1.03	5.4	16.2	28.7	24.4	16	40
10	2.0	39	6.5	1.30	6.1	19.0	35.9	26.1	15	42
11	2.0	13	6.5	0.65	5.0	15.6	35.5	37.0	13	30
12	2.0	104	6.5	0.65	3.7	12.8	17.6	14.5	18	47
13	2.0	104	3.25	0.65	1.9	6.8	11.7	8.8	14	44
14	2.0	104	13	0.65	6.9	23.2	29.7	26.7	19	47

$* S = w_I/(w_I + w_{II}) \times 100\%$.

a mixture of the complex (20 mg) with butanol (1 ml) and diphenyl (4 mg, GLC standard) was heated in a sealed tube (383 K, 1 h), the yield of the butanolysis products were 43% for **I** and 4% for **II**.

RESULTS AND DISCUSSION

The data obtained by the single-factor experiment method for the influence of the CO pressure (P_{CO}) and concentrations of styrene ([St]), excessive triphenylphosphine ([L]), and the palladium complex ([Pd]) on the rates w_I and w_{II} and the selectivity for ester **I** (S) are presented in Table 1. Kinetic measurements were performed simultaneously for two butanol concentrations ([BuOH]) of 1.6 and 5 mol/l. Table 2 summarizes

Table 2. Empirical expressions for the initial rates w_I and w_{II} as functions of P_{CO}, [L], [St], and [Pd] in reaction (I)

No.	[BuOH], mol/l	$\dfrac{w_I \times 10^4}{mol\ l^{-1}\ min^{-1}}$	$\dfrac{w_{II} \times 10^4}{mol\ l^{-1}\ min^{-1}}$
1	1.6	$2.4 P_{CO}^{0.42}$	$5.3 P_{CO}^{1.58}$
2	5.0	$11.1 P_{CO}^{0.44}$	$8.0 P_{CO}^{1.42}$
3	1.6	$4.8/(1 + 3.9[L])$	$44/(1 + 20[L])$
4	5.0	$17/(1 + 3.6[L])$	$47/(1 + 20[L])$
5	1.6	$5.3[St]^{0.65}$	$29[St]^{0.65}$
6	5.0	$17[St]^{0.32}$	$25[St]^{0.32}$
7*	1.6	$511[Pd]$	$611[Pd]^{0.70}$
8*	5.0	$1830[Pd]$	$979[Pd]^{0.83}$

* [L] = 0.104 mol/l.

the rates w_I and w_{II} as empirical functions of P_{CO}, [L], [St], and [Pd] for these two [BuOH] values.

Analysis of the obtained results, compared to the data [4, 5], reveals some similarity in the kinetics of the formation of acids **I** and **II** and their butyl esters by reaction (I). In the presence of butanol, as well as in the reaction with water, the rate w_I plotted versus [ROH] exhibits a Michaelis shape (with saturation), and the corresponding curve for w_{II} exhibits a maximum with a linear portion at low (<2.5 mol/l) ROH concentrations (Fig. 1). The above difference is responsible for the inversion of the reaction regioselectivity observed in the hydrocarboxylation under changes in the medium composition: at [BuOH] < 2.5 mol/l (<20 vol % alcohol), $S = 17$–19%, whereas $S = 65\%$ at [BuOH] = 8 mol/l (~70 vol % alcohol) (S reaches 75% in 100% butanol [6]). As usual, the formal order with respect to P_{CO} slightly differs from zero for w_I and is noticeably higher than the first order for w_{II} (Table 2, entries 1 and 2). The inhibition effect of triphenylphosphine toward w_{II} is much more pronounced than that toward w_I (entries 3 and 4). The carbonylation rate obeys the first order (for w_I) or is close to the first order (for w_{II}) with respect to the catalyst (entries 7 and 8).

At the same time, the kinetics of both reactions exhibit several distinctions. Thus, the orders of w_I and w_{II} with respect to P_{CO} are virtually independent of [BuOH], whereas the reaction order noticeably decreases with increasing [H₂O] [4], and the inhibition effect of L is not enhanced with increasing [BuOH] (cf. entries 3 and 4 in Table 2). The nature of the coreactant ROH also affects w_I and w_{II} as functions of [St]: at a water concentration of 1.6 mol/l, the formal order of w_I with respect to [St] equals zero and that of w_{II} equals

0.33 [5], whereas at the same concentration of butanol, the orders of both reactions are much higher than zero and equal to each other (Table 2, entry 5). When [BuOH] increases to 5 mol/l, both of the reaction orders remain higher than zero, although they decrease (entry 6), whereas both rates are independent of [St] at $[H_2O]$ = 5 mol/l [5].

As in the reaction with water [7], when the $PdCl_2L_2$ catalyst is promoted with an equivalent amount of $SnCl_2$, isomer II becomes the main hydrobutoxycarbonylation product: under standard conditions, S increases from 23 to 72% (in the reaction with water, from 15 to 73%). An increase in the regioselectivity is achieved due to an increase in w_I and a decrease in w_{II}. However, in this case, the overall rate of hydrocarboxylation decreases somewhat, whereas the rate of styrene conversion increases by a factor of 1.5 in the reaction with butanol.

The replacement of water by butanol in reaction (I) results in substantial changes in the kinetics of the process. Thus, a prolonged induction period appears: the reaction starts only 2 h after the $PdCl_2L_2$ complex is introduced into the reaction mixture (Fig. 2, curve 1). If the catalyst is exposed within this time to a solution at the CO pressure and temperature of the reaction, the carbonylation products begin to form immediately after the addition of styrene. Evidently, catalytically active palladium intermediates are formed with the participation of butanol much more slowly than with the participation of water. The introduction of minor water additives has virtually no effect on the reaction rate (the slope of the kinetic curve remains almost unchanged), but substantially shortens the induction period (curve 2). This indicates the hydride nature of the above intermediates, which are known to be easily formed from Pd complexes under the action of CO and H_2O [8], for example, according to the scheme

$$PdCl_2L_2 + CO + H_2O$$

$$\xrightarrow[-CO_2, -2HCl]{L} PdL_3 \xrightarrow[-L]{HCl} HPdClL_2. \qquad (II)$$
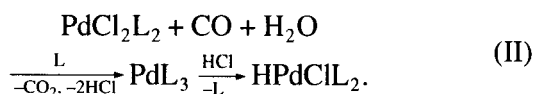
The isolation of the acyl complex $(PhC_2H_4CO)PdClL_2$ from the reaction mixture also indicates that the hydrobutoxycarbonylation of styrene proceeds by the hydride mechanism (see Experimental). On the other hand, reaction (III), which results in the formation of the palladium butoxycarbonyl complex, the intermediate of an alternative "alcoholate" mechanism [9], was not observed in the reaction system. In the case of R = Bu, all attempts to perform this transformation at either 383 K or room temperature did not give the desired result, even in the presence of trioctylamine as a scavenger of HCl (Table 3, entries 1–3). When a stronger base (sodium butylate) is used, the initial material is reduced to Pd(0) complexes (entry 4). The corresponding alkoxycarbonyl complex is easily formed in methanol (entry 5). However, as found previously [11], it does not catalyze olefin carbonylation. Note that a lower Broensted activity (pK_a 19) of butanol
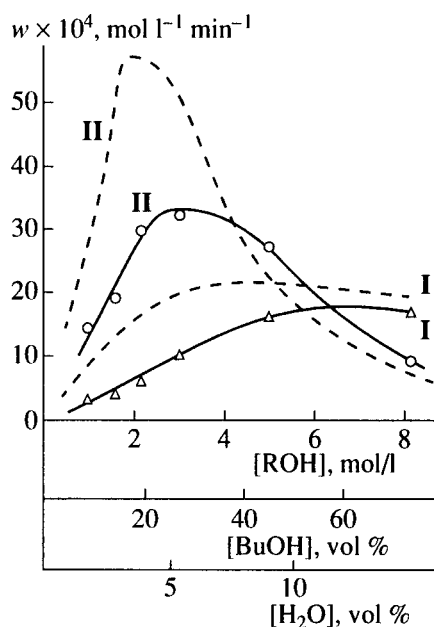
Fig. 1. Initial rates of accumulation of products I and II in reaction (I) as functions of concentration of the coreactant ROH. Dotted lines indicate H_2O [4], and solid lines, BuOH. $[Ph_3P]$ = 39 × 10^{-3} mol/l, [Pd] = 6.5 × 10^{-3} mol/l, [St] = 0.65 mol/l, P_{CO} = 2 MPa.
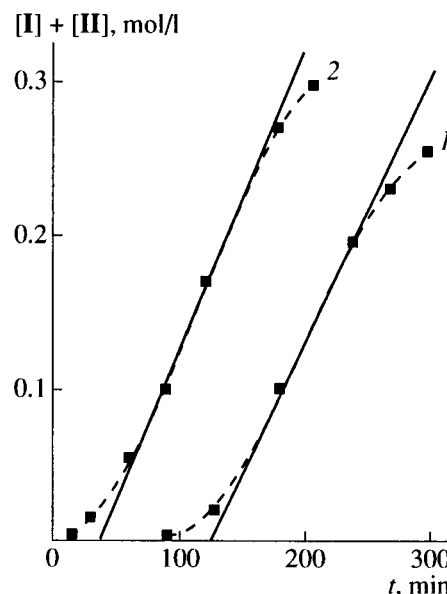

Fig. 2. Kinetic curves of accumulation of esters I and II in reaction (I) with the participation of BuOH (1) in the absence of H_2O and (2) with an additive of H_2O (0.1 mol/l). The zero point in time corresponds to the introduction of $PdCl_2(Ph_3P)_2$ into the reaction mixture at 383 K and P_{CO} = 2 MPa, $[Rh_3P]$ = 39 × 10^{-3} mol/l, [Pd] = 6.5 × 10^{-3} mol/l, [St] = 0.65 mol/l, [BuOH] = 1.6 mol/l.

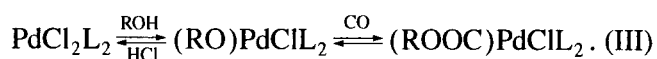than that of methanol (pK_a 16 [12]) can be responsible for the inertness of butanol in the reaction

$$PdCl_2L_2 \xrightarrow[HCl]{ROH} (RO)PdClL_2 \xrightarrow{CO} (ROOC)PdClL_2. \qquad (III)$$

Table 3. Characterization of products of the reaction of the $PdCl_2(Ph_3P)_2$ complex (100 mg, 0.14 mmol) with CO in the presence of alcohols

| Entry	Reaction medium	T, °C	P_{CO}, MPa	Time, h	IR spectrum of products in the region 1600–2150 cm^{-1}, color	Assignment	Yield*, %
1	BuOH (5 ml)	110	1.7	3	No absorption, dark-green	Decomposition products with Pd metal traces	–
2	BuOH (5 ml) Oct$_3$N (5 ml)	50	0.6	25	No absorption, brown	$PdCl_2L_2$, L = Ph$_3$P, Oct$_3$N	–
3	BuOH (5 ml) Oct$_3$N (5 ml)	25	0.6	30	No absorption, yellow	Initial complex	–
4	BuOH (5 ml) BuONa (0.16 mmol)	25	0.6	50	1860 cm^{-1}, v_{CO}, beige	$Pd_3(CO)_3L_3$**, L = Ph$_3$P	56
5	MeOH (5 ml) Oct$_3$N (5 ml)	25	0.6	5	1655 cm^{-1}, v_{CO} 1065 cm^{-1}, v_{COC}, white	(MeOCO)PdClL$_2$** L = Ph$_3$P	80

* Calculated in terms of the isolated product.
** Assigned using the data [10].

It is likely that replacing the coreactant ROH (water by butanol) does not result in principal changes in the multiroute scheme of the hydride mechanism of reaction (I), which is presented below in a simplified form.

$$L = Ph_3P; \quad St = PhCH=CH_2; \quad R' = PhCH_2CH_2-; \quad R'' = Ph(CH_3)CH-$$

(IV)
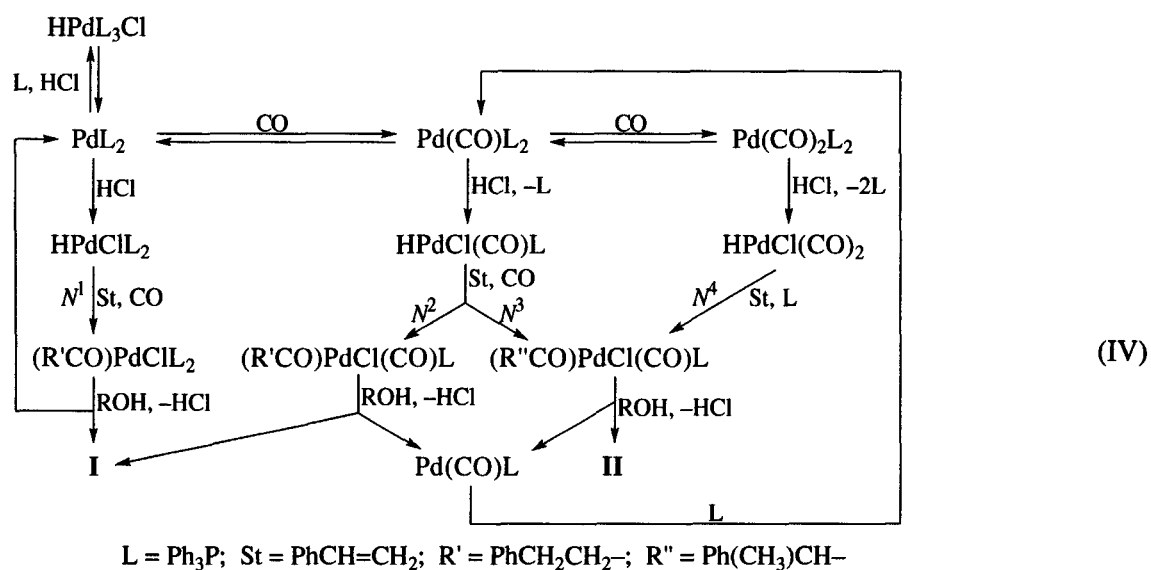
A similarity in the kinetic curves describing the effects of [CO] and [L] to those observed in [4, 5] indicates that not only the bisphosphine intermediate, but also the mono- and dicarbonyl hydride intermediates participate in styrene conversion at R = Bu. The isolation of the acyl complex (PhC$_2$H$_4$CO)PdClL$_2$ indicates that its transformation into product I with the participation of butanol by route N^1 remains the slowest step of the process. The processing of the data (Table 1) that characterize w_I and w_{II} as functions of P_{CO}, [L], and [Pd] at [BuOH] = 1.6 mol/l by the mathematical model [5] indicated that the rate constant of the final step of route N^1 at R = Bu (0.013 l mol^{-1} min^{-1}) is much lower than that at R = H (0.061 l mol^{-1} min^{-1}). This is consistent with that in reaction (I) with water, where the palladium acyl complex cannot be isolated from the reac-

tion mixture, and this intermediate was detected only *in situ* [13]. Note that, according to the composition of the stoichiometric butanolysis products (see Experimental), the isolated sample of the acyl complex contains more than 90% linear hydrocarbon fragments, whereas the fraction of ester I in the products of the catalytic reaction when this intermediate was produced did not exceed 30%. In the framework of a multiroute mechanism (IV), this distinction can be explained by the occurrence, under carbonylation conditions, of high-lability carbonyl-containing acyl complexes, which mainly contribute to the formation of product II (routes N^3 and N^4), whereas the isolated stable bisphosphine intermediate appears predominantly in the route of formation of I (N^1). According to the estimate in [5], the steady-state concentrations of the (PhCH$_2$CH$_2$CO)PdCl(CO)L and

(Ph(CH₃)CHCO)PdCl(CO)L complexes are negligible as compared to that of the (PhCH₂CH₂CO)PdClL₂ complex.

At the same time, the above distinctions in the reaction kinetics at R = H and R = Bu suggest that the mechanisms of both reactions differ in some features. A reasonable explanation could be that, at equal molar concentrations, the volume concentration of butanol in the reaction mixture is much higher than that of water. Thus, at a standard concentration of 1.6 mol/l, the volume fraction of butanol (in a mixture with dioxane and styrene) is 15%, which would correspond to [H₂O] = 8.3 mol/l at the same volume content of water, and at a concentration of 5 mol/l, the volume fraction of butanol in the reaction medium approaches 50% (Fig. 1). Evidently, such a strong dilution of dioxane with the alcohol is accompanied by a substantial change in the polarity and proton- and electron-donating properties of the medium. The resulting changes in the conditions of solvation of the intermediates of the liquid-phase catalytic process will certainly affect their reactivity and, hence, the kinetic scheme of the reaction.

In particular, it cannot be ruled out that replacing water by butanol results in a decrease in the rate of the reaction of the HPdCl(CO)L complex with styrene due to the changed conditions of its specific solvation. In this case, the irreversible step of HCl addition to Pd(CO)L₂ (scheme (IV), routes N^2 and N^3) can become quasi-equilibrium or reversible, in which case the styrene concentration should be taken into account in the expression for the reaction rate in these two routes. If this step is accompanied by the dissociation of the phosphine ligand, the rate of route N^2 and, hence, the rate of accumulation of isomer w_1 should decrease noticeably with an increase in [L]. However, w_1 only slightly depends on [L] (Table 2, entries 2 and 4). The obtained data agree better with the hypothesis that the pentacoordination complex HPdCl(CO)L₂ participates in routes N^2 and N^3. This complex irreversibly reacts with styrene and simultaneously loses a phosphine ligand. The corresponding mechanism is shown in scheme (V) with the numeration of steps accepted in [4, 5], but quasi-equilibrium step 5 is supplemented by irreversible step 5'. Unlike the scheme of the hydrocarboxylation mechanism [4, 5], the hydrated forms of the HPdClL₃ complex and a "parasitic" route of water gas shift reaction with the participation of HPdCl(CO)₂ are absent.

$$PdL_3 \xrightleftharpoons[21]{HCl} HPdClL_3$$

L ↕ 20

L = Ph₃P; St = PhCH=CH₂; R' = PhCH₂CH₂–; R" = Ph(CH₃)CH–

(V)
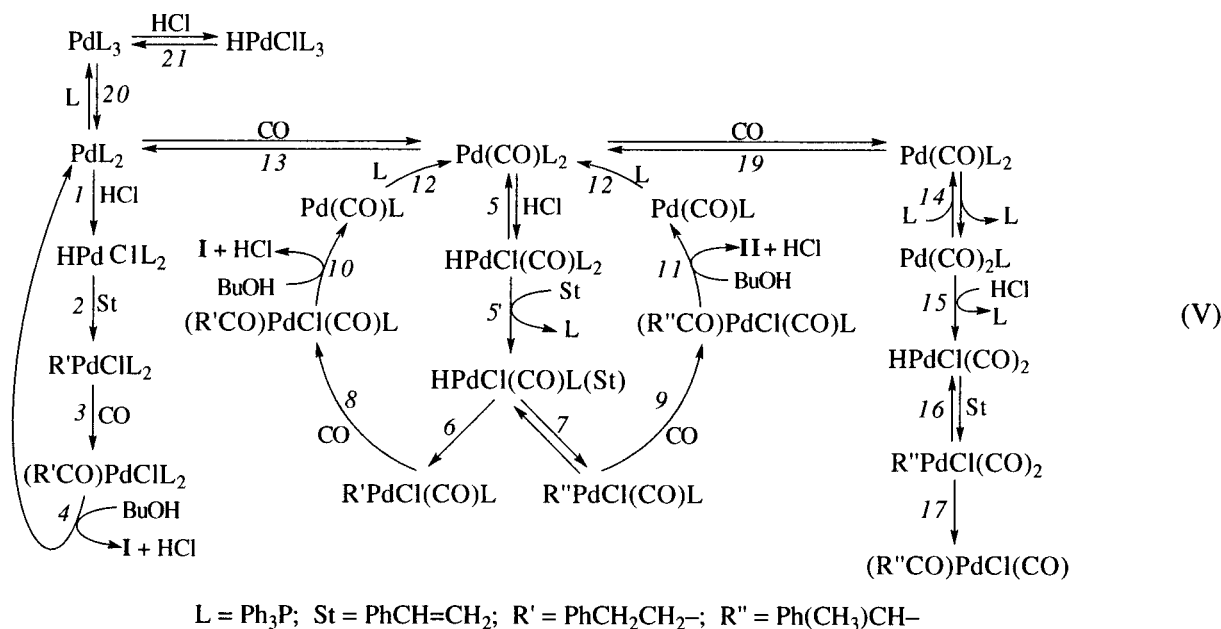
Steps 5, 7, 13, 16, 19–21 are equilibrium, step 14 is reversible, and the other steps are irreversible.

According to mechanism (V), in deriving equations (1) and (2) of the kinetic model, the acyl intermediate (PhCH₂CH₂CO)PdClL₂ and the Pd(CO)L₂ and HPdClL₃ complexes were included into the material balance on the catalyst, as in [4], and the steady-state concentrations of the other intermediates were neglected. The concentration of free hydrogen chloride formed in the reduction of PdCl₂L₂ (scheme (II)) was considered to be approximately equal to [Pd]. Other assumptions are discussed in detail in [4, 5] and are not considered in the present work.

$$w_1 = \frac{[BuOH][Pd]}{1 + A_1 P_{co}[BuOH]/[HCl] + A_2[L][BuOH]} \times \left(A_3 + \frac{A_4 P_{co}[St]}{1 + A_5 P_{co}}\right);$$
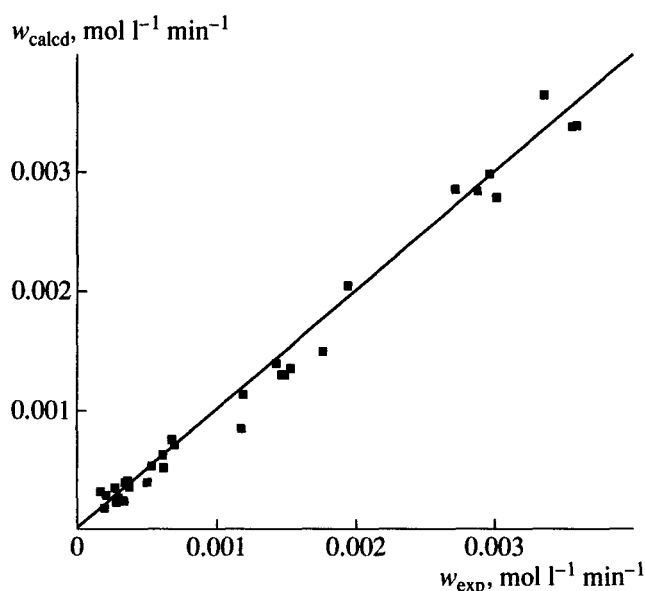
(1)

w_{calcd}, mol l^{-1} min^{-1}

Fig. 3. Comparison between the experimental rate constants w_I and w_{II} (w_{exp}, Table 1, [BuOH] = 1.6 mol/l) and the rate constants calculated (w_{calcd}) by equations (1) and (2). The slope of the straight line is equal to unity.

$$w_{II} = \frac{[BuOH][Pd]P^2_{CO}}{1 + A_1 P_{CO}[BuOH]/[HCl] + A_2[L][BuOH]}$$

$$\times \left(\frac{A_4 A_5 [St]}{1 + A_5 P_{CO}} + \frac{A_6}{[HCl] + A_7[L]} \right), \tag{2}$$

where [HCl] = [Pd], $A_1 = k_4 K_{19}/k_1$, $A_2 = k_4 K_{20} K_{21}/k_1$, $A_3 = k_4$, $A_4 = K_5 k_5 \times k_4 K_{19}/k_1$, $A_5 = K_7 k_9/k_6$, $A_6 = k_4 K_{13} k_{14} K_{19}/k_1$, and $A_7 = k_{-14}/k_{15}$. Here k_i are the rate constants, and K_i are the equilibrium constants in scheme (V).

The mathematical model thus modified [5] adequately describes the majority of the kinetic curves at low BuOH concentrations (1.0–2.2 mol/l). At the optimum parameters $A_1 = 1.96 \times 10^{-6}$ MPa^{-1}, $A_2 = 0.798$ l^2 mol^{-2}, $A_3 = 0.0131$ l mol^{-1} min^{-1}, $A_4 = 0.124$ l^2 mol^{-2} MPa^{-1} min^{-1}, $A_5 = 2.69$ MPa^{-1}, $A_6 = 2.25 \times 10^{-3}$ min^{-2}, and $A_7 = 3.0$, the average relative error of approximation is not higher than 15% and is comparable to the measurement error of w_I and w_{II} (~10%). The quality of the description can be judged from Fig. 3, where the calculation and experimental data are compared. The rate constant of the reaction of the (PhC$_2$H$_4$CO)PdClL$_2$ intermediate with butanol (parameter A_3) still remains much lower than that of the hydrolysis of this complex found in [5]. Also note that equations (1) and (2) provide a lower order with respect to the catalyst for w_{II} than that for w_I (see nos. 7 and 8 in Table 2). This is due to a decrease in the relative contribution of route N^4, which is highly selective with respect to isomer II, and to the styrene conversion due to an increase in the concentration of free hydrogen chloride linearly related to [Pd] (see the denominator of the second term in equation (2)).

At the same time, the model proposed is inappropriate for all obtained data, including the plots of w_I and w_{II} versus [BuOH] in the region >2.2 mol/l. It is remarkable that the linear character of the latter (Fig. 1) is retained in a broader interval of butanol concentrations in the liquid phase (to 20 vol %) than that in the case of water (to 3.5 vol %). The reasons for their deviation from linearity with the further increase in the butanol content are as yet unclear, but they are hardly related to considerable changes in the solubility of CO and in the activity of HCl, as in hydrocarboxylation [4]. It is likely that the solvation effects of the medium with a variable composition interfere in a complicated manner with the kinetics of the test reaction, and they cannot be considered (or are very difficult to be considered) in the framework of a single mathematical model.

Nevertheless, these results clearly show that the multiroute hydride mechanism of PdCl$_2$(Ph$_3$P)$_2$-catalyzed styrene carbonylation, which we proposed for reaction (I) in [4, 5], remains valid when water as a coreactant is replaced by butanol. However, the styrene conversion is substantially inhibited due to a decrease in the rate of the reaction of the acyl complex (PhC$_2$H$_4$CO)PdCl(Ph$_3$P)$_2$ with ROH (the slowest step).

ACKNOWLEDGMENT

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