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Kinetics and Mechanism of a Reaction of Phenylacetylene with Carbon Monoxide and Butanol in Toluene Catalyzed by a Palladium(0) Complex in the Presence of Trifluoroacetic Acid and Triphenylphosphine[1]

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Abstract—The reaction of phenylacetylene with CO and *n*-butanol in toluene (363 K) catalyzed by the $Pd(dba)_2/m(CF_3COOH)/n(Ph_3P)$ system (dba is dibenzylideneacetone; $2 \le m \le 8$; $10 \le n \le 30$) is studied. The initial rate of the main product (butyl 2-phenylpropenoate) buildup is found to depend on the pressure of CO and the concentrations of reactants and system components. The state of the catalyst under reaction conditions is studied *in situ* by IR spectroscopy. A kinetic model is developed based on the experimental results. This model corresponds to the mechanism that resembles the hydride mechanism in the type of main intermediates in the catalytic cycle.

INTRODUCTION

Recently, there has been a trend in the catalytic carbonylation of unsaturated hydrocarbons toward a change from complexes like $PdCl_2L_2$ (henceforth, L denotes triphenylphosphine) to more sophisticated metal–complex systems including strong acids, which are sources of bulky and low-basicity acid ligands [1–7]. It is believed that the high activity of these catalysts results from the weak coordination of acid ligands to a central atom, which is favorable for the formation of ionic intermediate species in a catalytic cycle [1–3]. However, the questions of the reaction mechanisms and the chemical nature of intermediates remain open. Thus, Drent *et al.* [1] considered the alkoxycarbonyl complex of Pd(II) as a key intermediate. However, arguments in favor of a hydride complex were given in more recent publications [3, 4, 7], and other types of mechanisms were hypothesized [6]. At the same time, the kinetic analysis of test reactions was little used to discriminate mechanistic schemes. In this work, we examined the kinetics of phenylacetylene hydrobutoxycarbonylation

$$\begin{gathered}\mathrm{PhC{\equiv}CH + CO + BuOH} \\ \xrightarrow{\mathrm{Cat}} \mathrm{CH_2{=}C(Ph)COOBu + PhCH{=}CHCOOBu}.\end{gathered} \tag{I}$$

On this basis, we can suggest that the process occurs via a hydride-like mechanism.

EXPERIMENTAL

Chemically pure phenylacetylene, *n*-butanol, toluene, and trifluoroacetic acid were additionally purified by distillation. Triphenylphosphine was recrystallized from hexane; it was separated from impurities on a column with SiO_2. The $Pd(dba)_2$ complex (dba is dibenzylideneacetone) was synthesized according to the procedure described in [8].

The reaction was catalyzed by the $Pd(dba)_2/mCF_3COOH/nL$ (Cat) system ($2 \le m \le 8$; $10 \le n \le 30$), which exhibited high activity in reaction (I) [9], in a toluene medium (363 K). The components of the reaction mixture, except for phenylacetylene, were placed in an autoclave equipped with a stirrer and a sampler. The required CO pressure and temperature were set; then, the substrate was added, and the reaction time was measured from this point on. The GLC monitoring was performed as described in [9]. The branched-chain isomer (butyl 2-phenylpropenoate) was the main product (95–97%). The initial rate of buildup (*w*) of this product was determined from the slope of the linear portion of the kinetic curve at substrate conversions up to 30%. The rate of buildup of butyl 3-phenylpropenoate was not measured because of a considerable error (50% or higher) in the determination of its concentration. Experiments with a less active catalyst ($PdCl_2L_2$) were performed at 383 K with the addition of 0.013 ml of water to the reaction mixture to shorten the time needed for the accumulation of catalytically active species [10]. The technique of *in situ* IR spectroscopy was described previously [11]. The pressure of CO, the concentrations of reactants and catalyst components (the total volume of the reaction mixture

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was 7 ml), and the found values of *w* are specified in the tables and figure captions.

RESULTS AND DISCUSSION

Solvent effects. A study of the effect of butanol concentration on the rate of butyl 2-phenylpropenoate formation (Table 1) demonstrated that the activity of the catalytic system (catalyst turnover frequency (TOF)) increased from 125 to 180 h^{-1} as [BuOH] increased from 0.8 (20% excess with respect to substrate) to 2 mol/l. A further increase in [BuOH] resulted in a decrease in the catalyst activity, and the TOF was as low as 35 h^{-1} in neat butanol (in the absence of toluene). It is likely that a positive effect of the alcohol at [BuOH] < 2 mol/l (at such concentrations, the formal order of reaction with respect to this reactant is 0.4) was caused by the contribution from a step of its interaction with a catalytically active palladium complex to the kinetics of reaction (I). The low order of reaction can be explained by the formation of alcohol associates (at least dimers) in the given hydrocarbon medium, whereas a monomeric form is probably required for the above step. It is conceivable that butanol also takes part as a σ-donor ligand in other steps to decrease the activity of catalytic intermediates. This can be one of the reasons (if not the main reason) for reaction deceleration at [BuOH] > 2 mol/l. This hypothesis was supported by the fact that the replacement of toluene with dioxane, which is as nonpolar as toluene but more basic [12] and can serve as a σ-donor, resulted in a considerable decrease in the catalytic activity of the system (20 h^{-1} at [BuOH] = 1.6 mol/l, cf. data in Table 1). In a dioxane–butanol mixture, the catalyst was even less active than in butanol.

It should also be borne in mind that the dilution of toluene with an alcohol enhances the capacity of the medium for the specific solvation of the acid HX, which is of primary importance in the formation of catalytically active species, the X^- anion, and the substrate prone to form hydrogen bonds with bases [13]. In other words, the multiple role of an alcohol in this complex reaction mixture makes it almost impossible to quantitatively consider its effect on the kinetics of reaction (I). Because of this, we shall restrict our consideration to analysing kinetic data relevant to the constant concentration of butanol (Table 2).

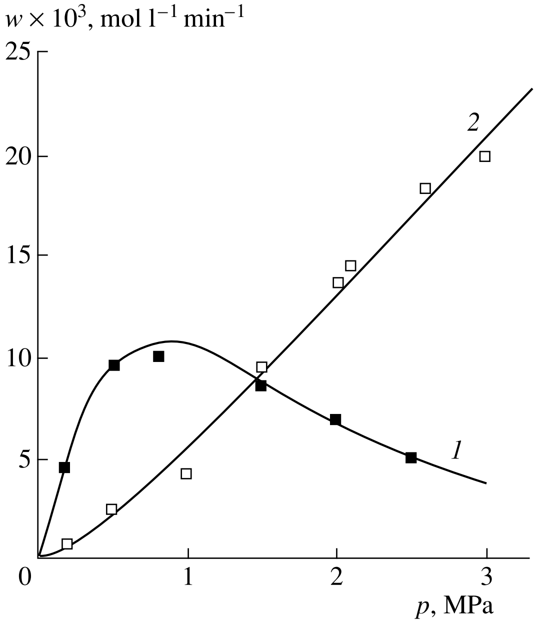


Fig. 1. Rates of buildup (*w*) of the products of phenylacetylene hydrobutoxycarbonylation in reaction (I) as functions of CO pressure: (*1*) butyl 2-phenylpropenoate (Cat = $Pd(dba)_2/2CF_3COOH/10Ph_3P$; 363 K) and (*2*) butyl 2-phenylpropenoate and butyl 3-phenylpropenoate (Cat = $PdCl_2(Ph_3P)_2/8Ph_3P$; 383 K).

Reaction kinetics. It can be seen from Table 2 that, as the pressure of CO (*p*) was increased from 0.2 to 0.8 MPa, the rate of phenylacetylene carbonylation increased. However, a further increase in *p* was accompanied by a decrease in *w* (experiments 1, 2, and 4–7; Fig. 1, curve *1*), and the value of *w* at 2.5 MPa was lower than that at 0.5 MPa (cf. also experiments 9 and 16; 11 and 17; and 22 and 23). As the pressure of CO in the course of an experiment was reduced from 2.5 to 0.5 MPa, the rate increased (Fig. 2). This fact indicates that processes responsible for a negative effect of CO pressure are reversible. Unlike the test system, in catalysis by the $PdCl_2L_2$ complex (Fig. 1, curve *2*), reaction (I) is of an order higher than first with respect to *p* (1.2), which is often observed in olefin carbonylation [14, 15]. In this case, a fraction of butyl 2-phenylpropenoate in a regioisomer mixture was 62–64% regardless of *p*. Note that this fraction increased to 72% after adding $SnCl_2$ to the palladium complex in an equivalent amount. This addi-

Table 1. Initial rates (*w*) of butyl 2-phenylpropenoate buildup and activities (TOF) of a $Pd(dba)_2/2CF_3COOH/10Ph_3P$ catalyst at different butanol concentrations ([BuOH]); the CO pressure is *p* = 0.5 MPa; $[Pd(dba)_2]$ = 0.004 mol/l; the phenylacetylene concentration is 0.64 mol/l; 363 K

[BuOH], mol/l	0.8	1.2	1.6	2.0	2.5	3.2	10.1*
$w \times 10^3$, mol l^{-1} min^{-1}	8.4	9.1	9.8	12.5	11.0	9.7	2.3
TOF, h^{-1}	126	137	147	182	165	146	35

* In the absence of toluene.

tion resulted in the formation of the acid ligand $SnCl_3^-$, which is more labile than Cl^- [16].

The substrate and triphenylphosphine effects in reaction (I) are analogous to effects usually observed in olefin carbonylation catalyzed by palladium complexes. Thus, an increase in *w* with an increase in the phenylacetylene concentration is described by the Michaelis equation; that is, the formal reaction order with respect to this reactant is lower than first, namely 0.45 (experiments 2, 8–10; cf. experiments 7 and 16; 19 and 20). At a low triphenylphosphine content ($n \leq 6$) or in the absence of triphenylphosphine, the catalyst was rapidly deactivated (palladium black was precipitated), whereas an excess of triphenylphosphine inhibited the reaction (experiments 2, 11, and 12; 7 and 17; 20–22). Note that the replacement of this ligand with 2-pyridyldiphenylphosphine insignificantly increased the catalyst activity in the test reaction (experiments 2 and 3); however, in this case, 100% regioselectivity for a branched isomer was attained.

The presence of an acid in the system is required for the formation of catalytically active species from the parent Pd(0) complex [3, 4]. However, our results suggest that the role of this system component in the reaction kinetics is insignificant at a low CO pressure. Thus, an increase in the concentration of CF_3COOH by a factor of four at $p = 0.5$ MPa resulted in an increase in *w*

Table 2. Initial rates (*w*, mol l^{-1} min^{-1}) of butyl 2-phenylpropenoate buildup as functions of CO pressure (*p*, MPa) and concentrations (mol/l) of phenylacetylene ([PhCCH]), Ph_3P ([L]), CF_3COOH ([HX]), and the $Pd(dba)_2$ complex ([Pd]); [BuOH] = 1.6 mol/l, 363 K

No.	*p*	[PhCCH]	$[L] \times 10^3$	$[HX] \times 10^3$	$[Pd] \times 10^3$	$w \times 10^3$	
						experimental	calculated*
1	0.2	0.64	40	8	4	4.6	4.98
2	0.5	0.64	40	8	4	9.8	9.46
3	0.5	0.64	40	8	4	11.5**	–
4	0.8	0.64	40	8	4	10.1	10.80
5	1.5	0.64	40	8	4	8.6	8.84
6	2.0	0.64	40	8	4	7.0	6.80
7	2.5	0.64	40	8	4	5.1	5.18
8	0.5	0.35	40	8	4	7.5	7.37
9	0.5	0.45	40	8	4	7.8	8.24
10	0.5	0.90	40	8	4	11.2	10.4
11	0.5	0.64	80	8	4	7.9	7.40
12	0.5	0.64	120	8	4	6.8	6.08
13	0.5	0.64	80	16	4	8.5	7.88
14	0.5	0.64	40	32	4	11.2	10.5
15	2.0	0.64	40	16	4	11.2	10.8
16	2.5	0.45	40	8	4	3.8	3.70
17	2.5	0.64	80	8	4	4.1	4.33
18	0.5	0.64	80	16	6	12.8	12.0
19	0.5	0.45	60	12	6	10.7	11.3
20	0.5	0.64	60	12	6	12.0	13.2
21	0.5	0.64	80	12	6	11.1	11.7
22	0.5	0.64	120	12	6	9.6	9.53
23	2.5	0.64	120	12	6	7.3	7.06
24	0.5	0.64	120	16	8	12.9	13.1

* Data calculated using the mathematical model.

** L = 2-pyridyldiphenylphosphine.

by only 14% (experiments 2 and 14). The effect of the acid was much greater at higher CO pressures: an increase in the rate was 60% when the concentration of CF_3COOH was doubled (p = 2 MPa; experiments 6 and 15). The value of w is a linear function of the concentration of the $Pd(dba)_2/2CF_3COOH$ binary system at a constant high concentration of triphenylphosphine (experiments 12, 22, and 24; average TOF of 98 ± 3 h^{-1}). This suggests the first-order reaction with respect to the catalyst.

***In situ* IR-spectroscopic data.** The *in situ* IR spectra in the region 1600–2200 cm^{-1} were measured for the test system at p = 0.2–4 MPa and 363 K. The IR spectrum of the catalyst (m = 2; n = 10) in a toluene–butanol mixture ([BuOH] = 1.6 mol/l) exhibited absorption bands of the C=O and C=C bonds of uncoordinated dibenzylideneacetone (1650 and 1625 cm^{-1}), which can easily be replaced by triphenylphosphine and CO from the starting $Pd(dba)_2$ complex. It is well known that, in a tenfold excess of phosphine, the replacement of dba was almost complete even in the absence of CO [17]. The absorption bands of dissolved CO (2135 cm^{-1}) and C=O vibrations in Pd(0) complexes $Pd(CO)L_2$ (1980 cm^{-1}) and $Pd(CO)_2L_2$ (1980 and 2020 cm^{-1}) were also present. The same bands were observed previously in the IR spectra of reaction systems in the carbonylation of styrene catalyzed by the $PdCl_2L_2$ complex in dioxane–butanol [10] and dioxane–water [11] mixtures. However, our system differs from these in that the equilibrium

$$Pd(CO)L_2 + CO \rightleftharpoons Pd(CO)_2L_2 \qquad \text{(II)}$$

between Pd(0) carbonyls is shifted toward a dicarbonyl species. The equilibrium constant of reaction (II), which was found from the intensities of absorption bands for these complexes as functions of CO pressure, is equal to 6.1 MPa^{-1} at 363 K.

The absorption band of νC=O stretching in the AlkO–C(O)– group (a fragment of the Pd(II) alkoxycarbonyl complexes) at 1600–1700 cm^{-1} [18] was not detected. This may be explained by the fact that these species with weakly bound acid ligands are easily converted into Pd(0) complexes on exposure to CO and an alcohol [19]. Upon the addition of phenylacetylene to a catalyst solution, the spectrum acquired an absorption band assignable to hydrobutoxycarbonylation products (νC=O 1720 cm^{-1}). The intensity of this band increased in the course of the reaction. However, in contrast to the IR spectra of catalytic systems with a strongly coordinated halide anion [10, 11], the νC=O band of Pd(II) acyl was not detected in this case. This is likely due to the fact that its quasi-steady-state concentration is lower than the detection limit.

Mechanistic scheme and the mathematical model of kinetics. Based on the *in situ* IR-spectroscopic data, we conclude that in the absence of a substrate, as well as in the case of $PdCl_2L_2$, the test catalyst consists of various Pd(0) complexes, which are in equilibrium with each other. In particular, it is likely that the PdL_x (x = 2, 3) complexes, which are not detected in the IR spectrum, and products of their protonation (hydride complexes) [20] are present. We did not observe the νH–Pd absorption band of hydride complexes in the IR spectrum, probably because of its low intensity. Moreover, because the position of this band varied over a wide range depending on the ligand environment of the palladium atom (for example, 2050 cm^{-1} in $HPdCl(Ph_3P)_2$ [21] and 2140 cm^{-1} in $HPd(OCOCF_3)(Ph(\textit{tert}\text{-}Bu)_2P)_2$ [22]), this band may fall into the region of strong absorption of dissolved CO (2135 cm^{-1}).

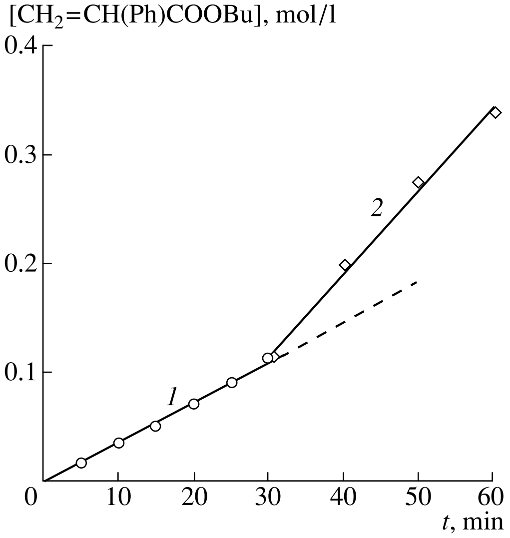
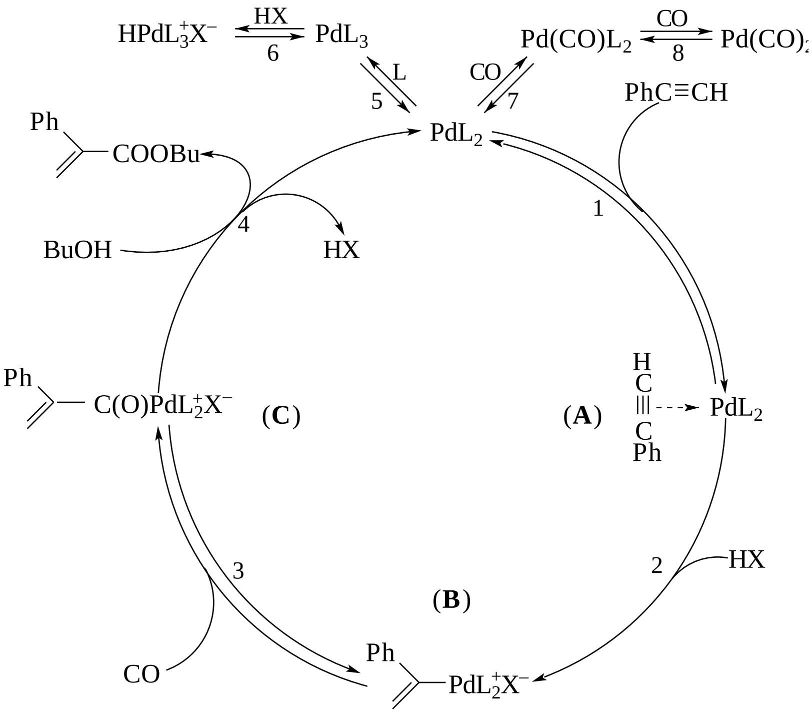


Fig. 2. Buildup of butyl 2-phenylpropenoate with a decrease in the pressure of CO in the course of reaction (I) from (*1*) 2.5 to (*2*) 0.5 MPa; Cat = $Pd(dba)_2/2CF_3COOH/10Ph_3P$.

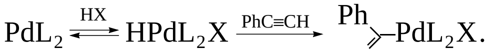
The presence of the Pd(II) alkoxycarbonyl complex, which is a key intermediate in the alcoholate mechanism, is improbable. Therefore, we believe that reaction (I) occurs via the hydride mechanism or similar with mostly the same intermediates in a catalytic cycle. Recall that carbonylation catalyzed by the $PdCl_2L_2$ complex occurs with the participation of three types of hydride intermediates formed by the interaction of HCl with the coordinatively unsaturated complexes PdL_2, $Pd(CO)L_2$, and $Pd(CO)_2L$ [14, 15]. The contribution from $Pd(CO)L_2$ and $Pd(CO)_2L$ to the reaction kinetics is responsible for the higher-than-first order of reaction with respect to CO pressure. This is also the case with phenylacetylene carbonylation catalyzed by the $PdCl_2L_2$ complex. Curve *1* with an extremum in the w–p coordinates in Fig. 1 found for the catalytic test system suggests that the above Pd(0) carbonyls take no part in catalysis, and the conversion of phenylacetylene takes place only through the Pd(0) phosphine complexes. In this case, a mechanistic scheme for the formation of the main product of reaction (I) can be represented as catalytic cycle (III). This cycle includes the following stages: the two-step formation of σ-vinyl (2-styryl) intermediate **B** (steps 1 and 2); the addition of

CO to this intermediate followed by the insertion into the C–Pd bond (step 3); and the reaction of butanol with the acyl complex **C** (step 4) to form the product and regenerate the coordinatively unsaturated PdL_2 complex and acid HX. Palladium complexes that constitute a ballast fraction of the catalyst are in equilibrium with PdL_2 (steps 5–8). The relatively weak coordination of the acid ligand X^- to the Pd atom in the given catalytic system is reflected in the schematic diagram as the ionic structure of intermediates **B** and **C**.



(III)

A similar mechanistic scheme was suggested previously [3] for phenylacetylene carbonylation in the presence of methanol and $Pd(OAc)_2/MeSO_3H/2\text{-}PyPPh_2$ in dichloromethane. Both of the schemes differ from the universally accepted hydride mechanism in the first stage. According to the hydride mechanism, the intermediate $HPdL_2X$ is initially formed by the addition of the HX acid to the PdL_2 complex (or by the elimination of ligand L from the complex $HPdL_3^+X^-$) followed by the insertion of a substrate into the H–Pd bond:



$$PdL_2 \xrightleftharpoons{HX} HPdL_2X \xrightarrow{PhC{\equiv}CH} \overset{Ph}{\rangle}\!\!\text{–}PdL_2X. \qquad \text{(IV)}$$

The routes of the formation of intermediate **B** represented in schemes (III) and (IV) are difficult to distinguish, particularly if their first steps are quasi-equilibrium and the second steps are irreversible. In our opinion, the problem of deciding on the route under discussion is of little importance. However, following Scrivanti *et al.* [3], we note that data on the ability of alkynes to form π-complexes like **A** with the derivatives of zero-valence Group VIII metals, the protonation of which leads to σ-vinyl intermediates [23, 24], count in favor of scheme (III). At the same time, there is indirect evidence against route (IV). For example, with the hydride mechanism of this reaction, it is improbable that the catalyst in which Ph_3P is replaced with bis(diphenylphosphino)ethane (dppe) [9] will exhibit a high activity because the *cis*-hydride complex with a bidentate ligand is unstable. On the other hand, it might be expected that the resulting unsaturated ester undergoes carbonylation at the C=C bond in the presence of the active hydride complexes of palladium. However, even traces of products of this reaction were not detected in our experiments or in [3, 4]. It is also unlikely that the reaction proceeds via the interaction of the substrate with the complex $HPdL_3^+X^-$ shown in scheme (III) because, in this case, the reaction rate should increase or at least remain constant with an increase in the triphenylphosphine concentration, however this is inconsistent with experimental data (see Table 2).

In principle, step 1 in scheme (III) can be reversible; however, for simplicity (in order to use minimum parameters for constructing a kinetic model), we considered it as quasi-equilibrium. Step 2 can be considered irreversible because complexes like **B** are resistant to the β-elimination of hydrogen. Data on a high quasi-steady-state concentration of the vinyl intermediate under the conditions of an autocatalytic process [3], as well as an increase in *w* with increasing *p* over the range 0.2–0.8 MPa, suggest that the insertion of CO into the C–Pd bond of complex **B** is a rate-limiting step of catalytic cycle (III). At the same time, based on data in Table 1 for [BuOH] ≤ 2 mol/l, the effect of the butanolysis of the acyl complex on the reaction kinetics cannot be ignored. Therefore, we believe that steps 3 and 4 are quasi-equilibrium and irreversible, respectively. Note that the interaction of intermediate **A** with HX (step 2) yields branched complex **B** and its linear analog, which leads to the formation of butyl 3-phenylpropenoate. However, we neglected the route of its formation because the regioselectivity to this product is lower than 5%.

The number of ligands L in catalytic intermediates remained unchanged in all steps of cycle (III), including step 2 which is responsible for regioselectivity. In this case, if the hypothetical contribution from $HPdL_3^+X^-$ to substrate conversion is insignificant, a change in [L] will have no effect on the regioselectivity of reaction (I) (in the given case, this is very difficult to verify because of a high concentration of one of the regioisomers). However, the regioselectivity of step 2 can depend on the spatial and electronic structure of a neutral ligand. It is likely that this fact can explain 100% selectivity to butyl 2-phenylpropenoate with L = 2-$PyPPh_2$.

The material balance of the catalyst takes into account intermediate **B**, carbonyl-containing Pd(0) complexes, and the protonated form of the PdL_3 complex (as found by a kinetic simulation, the quasi-steady-state concentrations of PdL_3 and PdL_2 can be neglected) as follows:

$$\begin{aligned}[Pd]_0 &= [CH_2{=}C(Ph){-}PdL_2^+X^-] \\ &+ [Pd(CO)L_2] + [Pd(CO)_2L_2] + [HPdL_3^+X^-].\end{aligned} \tag{1}$$

In accordance with scheme (III), the rate w can be expressed as

$$\begin{aligned} w &= K_1k_2[HX][PhCCH][PdL_2] \\ &= K_3k_4p[BuOH][CH_2{=}C(Ph){-}PdL_2^+X^-],\end{aligned} \tag{2}$$

where K_1, K_3, k_2, and k_4 are the equilibrium and rate constants of the corresponding steps in scheme (III), as indicated by subscripts. Thus, expressing the quasi-steady-state concentration of the complex $CH_2{=}C(Ph){-}PdL_2^+X^-$ in terms of the concentration of PdL_2 and considering material balance (1), we obtain the rate law

$$w = A_1p[BuOH]\frac{[Pd]_0[PhCCH][HX]'}{[HX]'([PhCCH] + A_2[L]'p[BuOH]) + A_3p^2(1 + A_4p)[BuOH]}, \tag{3}$$

where [HX]' and [L]' are the quasi-steady-state concentrations of CF_3COOH and Ph_3P, respectively, and the target values A_i are expressed in terms of the equilibrium and rate constants of steps in scheme (III) as follows: $A_1 = K_3k_4$, $A_2 = K_5K_6/K_1k_2$, $A_3 = K_7/K_1k_2$, and $A_4 = K_8$. Taking into account the presence of at least two ligands L in each of the palladium-containing species included in the material balance, we assumed that $[L]' = [L] - 2[Pd]_0$ (the neglect of a contribution from the third ligand in the complex $HPdL_3^+X^-$ left the results of calculations almost unaffected). The acid concentration is corrected for the value of its decrease as a result of the formation of complexes **B** and $HPdL_3^+X^-$ using the equation

$$[HX]' = [HX]_0 - \frac{[Pd]_0[HX]'([PhCCH] + A_2[L]'p[BuOH])}{[HX]'([PhCCH] + A_2[L]'p[BuOH]) + A_3p^2(1 + A_4p)[BuOH]}. \tag{4}$$

In Eqs. (1), (3), and (4), $[Pd]_0$ and $[HX]_0$ are the initial concentrations of the $Pd(dba)_2$ complex and CF_3COOH, respectively, which are specified in Table 2.

Equations (3) and (4) are consistent with the apparent kinetics. At a constant value of [BuOH], they explain the dependence of w on p with an extremum, the Michaelis function of [PhCCH], and a decrease in w with [L]. Moreover, in accordance with Eq. (3), the effect of [HX] on the reaction rate is more pronounced at high values of p. The following values of the parameters A_i were found by the mathematical processing of data in Table 2 (except for experiment 3) using Eqs. (3) and (4): $A_1 = 4.5$ l mol^{-1} MPa^{-1} min^{-1}, $A_2 = 8.5$ l mol^{-1} MPa^{-1}, $A_3 = 3.5 \times 10^{-4}$ mol l^{-1} MPa^{-2}, and $A_4 = 5.6$ MPa^{-1}. The average error of approximation for w was not worse than the average measurement error (8–10%). It was found by calculation that the addition of complexes **A**, **C**, PdL_2, and PdL_3 in various combinations to material balance Eq. (1) for the catalyst did not considerably improve the description, although the number of independent parameters A_i increased. We estimated that the total fraction of the above species accounted for ~5% palladium (p = 2 MPa). Thus, we ignored these catalyst species in constructing a kinetic model to simplify Eq. (3). The quality of simulation can be judged from Fig. 1 (curve *1*) and Table 2, where the calculated and experimental data are compared. Note that the calculated order of reaction with respect to phenylacetylene (0.38) is close to the experimental value (0.45), and the parameter A_4 (K_8) is consistent with the equilibrium constant for the carbonyl complexes of palladium (6.1 MPa^{-1}) calculated from *in situ* IR-spectroscopic data.

Of course, Eqs. (3) and (4) cannot give an exhaustive description of reactions that occur in this complex reaction system. Apart from the above solvent effects, a number of other factors that can affect the course of the reaction are not taken into account, for example, the degradation of the complex $HPdL_2^+X^-$ to form the hydride intermediate $HPdL_2^+X^-$, the reaction between the acid and triphenylphosphine [5], or the dissociation of the vinyl complex into ions. Nevertheless, in general, a satisfactory agreement between this model and the reaction kinetics (at a constant concentration of butanol) suggests that the carbonylation of a substrate proceeds via the sequence of steps presented in scheme (III). The corresponding catalytic cycle can be considered as a modification of the hydride mechanism because of the occurrence of σ-vinyl (alkyl) and acyl complexes, which are typical of this mechanism.

As distinct from catalysis by the $PdCl_2L_2$ complex, where most of the palladium is concentrated in the acyl intermediate [14], the σ-vinyl complex **B** accounts for most the of palladium in catalytic cycle (III). Evidently, this is due to the acceleration of the step of alcoholysis of the acyl intermediate because acid ligand coordination is weakened when Cl^- is replaced by CF_3COO^- resulting in an increase in the catalytic activity. However, as the pressure of CO was increased, a noticeable fraction of palladium transferred into the Pd(0) carbonyl species; that is, the catalyst efficiency decreased. This can be explained by the mathematical model described by Eqs. (3) and (4).

The fractional part of Eq. (3) corresponds to the quasi-steady-state concentration of complex **B** (cf. the right-hand side of Eq. (2)), and the product A_1 p[BuOH], which is equal to the ratio w/[**B**], corresponds to the turnover number (**B** turnover frequency TOF_B) at the corresponding pressure and concentrations of reaction mixture components. It is easy to demonstrate that the catalyst activity almost halved (TOF decreased from 147 to 77 h^{-1}) as p was increased from 0.5 to 2.5 MPa (experiments 2 and 7, Table 2), whereas the value of TOF_B increased by a factor of five (from 216 to 1080 h^{-1}, according to the found value of A_1). However, in this case, [**B**] decreased by an order of magnitude (from 2.7 to 0.28 mmol/l) and the fraction of ballast species increased from 33 to 93%. As follows from the results of other experiments, the fraction of ballast species can be reduced by increasing the acid concentration and minimizing the amount of triphenylphosphine (this minimization provides the stability of Pd(0) complexes).

Thus, a catalytic system can be developed on the basis of $Pd(dba)_2$ and trifluoroacetic acid; this system is efficient at low CO pressures. The carbonylation of acetylene derivatives can be performed under milder conditions and with higher regioselectivity for branched products than that in the catalysis with the $PdCl_2L_2$ complex.

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