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Hydrocarbobutoxylation of Phenylacetylene on Palladium Complexes: A Solvent Effect

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Abstract—Data on changes in the activity of the $Pd(dba)_2/2TsOH/10Ph_3P$ (dba is dibenzylideneacetone) and $PdCl_2(Ph_3P)_2/8Ph_3P$ catalytic systems in the reaction of phenylacetylene with CO and *n*-butanol under the action of a solvent (aromatic hydrocarbons, chloroalkanes, ethers, esters, ketones, and dipolar aprotic media) are presented. The differences found in the response of either of the systems to changes in the properties of the medium are discussed in terms of a scheme of the catalytic cycle of reaction. It is noted that activity does not correlate with the physicochemical characteristics (polarity, basicity, and electron-acceptor ability) of solvents.

INTRODUCTION

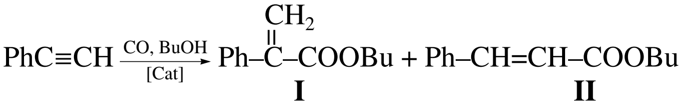
Palladium complexes containing weakly coordinated anionic ligands, particularly sulfonic acid anions, are successfully used in the catalysis of liquid-phase carbonylation reactions of unsaturated hydrocarbons with carbon monoxide [1–8]. The effects of anionic and neutral ligands on the catalytic properties of the above complexes have been adequately studied. The effect of a medium, whose properties may affect not only the rate [4] but also the direction of a process [5, 6], has received very little attention. We evaluated the effects of solvents different in chemical nature on the catalytic properties of the $Pd(dba)_2$–TsOH–Ph_3P (dba is dibenzylideneacetone, and TsOH is *para*-toluenesulfonic acid) system in the hydrocarbobutoxylation reaction of phenylacetylene, which was studied previously [9]. For comparison, data on the effects of a number of solvents on the course of the above reaction in the presence of the $PdCl_2(Ph_3P)_2$ complex, which is a commonly used carbonylation catalyst [10, 11], were obtained.

EXPERIMENTAL

A glass reactor containing a catalyst, a solvent (6 ml), and *n*-butanol (1.1 ml) was placed in a 100-ml steel autoclave, which was equipped with a sampler, a thermocouple, and a magnetic stirrer. The catalyst composition was as follows: (system **A**) 13.1 mg of the $Pd(dba)_2$ complex, 59.7 mg of Ph_3P, and 8.7 mg of TsOH or (system **B**) 16 mg of the $PdCl_2(Ph_3P)_2$ complex and 47.8 mg of Ph_3P. The catalyst and butanol concentrations were 0.003 and 1.6 mol/l, respectively. The autoclave was blown with carbon monoxide at room temperature; a required pressure of CO was adjusted, and the contents were heated to the temperature of the experiment ((**A**) 1 MPa, 363 K or (**B**) 2 MPa, 383 K); thereafter, phenylacetylene (465 mg, substrate/palladium ratio of 200) was added to the reaction mixture. The accumulation of reaction products was monitored by GLC (a Tsvet-110 chromatograph) on a column (3 × 2000 mm) packed with 3% SE-30 on Chromaton N-Super; nitrogen was a carrier gas; fluorene was used as an internal standard. All the solvents, phenylacetylene, and *para*-toluenesulfonic acid (chemically pure reagents) were dried and purified by distillation; triphenylphosphine was recrystallized from hexane and separated from impurities on a column with SiO_2. The $Pd(dba)_2$ and $PdCl_2(Ph_3P)_2$ complexes were synthesized in accordance with published procedures [9, 11].

RESULTS AND DISCUSSION

The catalytic carbonylation of phenylacetylene (reaction (1)) leads to two isomeric products: butyl 2-phenylpropenoate (**I**) and butyl 3-phenylpropenoate (**II**).



$$PhC\equiv CH \xrightarrow[\text{[Cat]}]{\text{CO, BuOH}} \underset{\textbf{I}}{Ph\text{–}\overset{CH_2}{\overset{\|}{C}}\text{–}COOBu} + \underset{\textbf{II}}{Ph\text{–}CH{=}CH\text{–}COOBu} \qquad (1)$$

Cat: (**A**) $Pd(dba)_2/2\,(TsOH)/10(Ph_3P)$ or (**B**) $PdCl_2(Ph_3P)_2/8(Ph_3P)$.

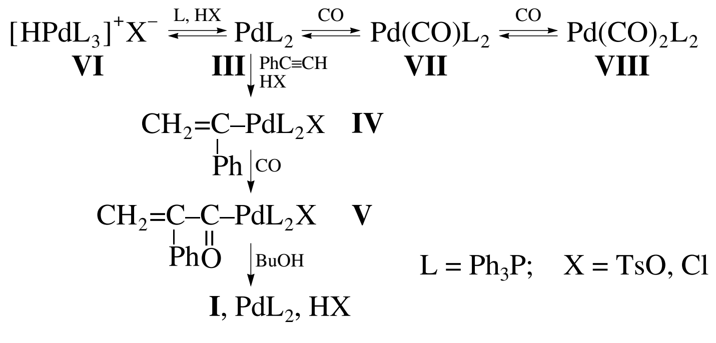
Under the conditions in use, branched regioisomer **I** was the main product; the relative concentrations (*S*) of this product in the product mixtures are summarized in Table 1. Table 1 also specifies the solvents in use, which are arranged in order of decreasing catalytic activity (a, h^{-1}) in system **A**. The values of a were evaluated from the total yield of esters **I** and **II** in the first 15 min of the reaction. The calculations based on product yields after 0.5 and 1 h gave lower values of a because the rate of reaction exhibits a fractional order with respect to substrate (the Michaelis function) [9]. However, in this case, the order of changes in a remained unchanged in the series of the test solvents.

From data given in Table 1, it follows that, in the presence of a palladium complex with a weakly coordinated anionic ligand (**A**), reaction (1) occurred more rapidly in aromatic hydrocarbons (nos. 1, 3, and 6), ethers (nos. 4 and 5), and an ester (no. 2) than in chloroalkanes (nos. 9 and 10), ketones (nos. 11 and 12), highly polar media (nos. 13, 14, and 16), and butanol (no. 15). System **A** exhibited the highest activity in toluene and ethyl acetate and the lowest activity in *N*-methylpyrrolidone and *N,N*-dimethylformamide (the reaction practically did not occur in polar aprotic solvents such as acetonitrile and nitrobenzene). The activity of this catalyst, as well as of the analogous $Pd(dba)_2/2(CF_3COOH)/10(Ph_3P)$ system [9], was very low in butanol. Changes in the nature of the solvent had almost no effect on the regioselectivity of the process: in most cases, the concentration of product **I** was 96–97%, and the value of S was noticeably lower only in chloroalkanes.

The solvent effect manifested itself somewhat differently in reaction (1) performed with the use of a palladium complex with a strongly coordinated Cl^- anion (**B**). This catalyst was also most active in toluene (no. 1); however, its activity in esters and ethers (nos. 2 and 7) was much lower than in a ketone (no. 11) and, particularly, than in butanol (no. 15), which was very similar to toluene in this characteristic. In highly polar media, catalyst **B** also exhibited low activity, as was noted previously for the carbonylation of unsaturated hydrocarbons [12, 13]. In this case, the regioselectivity of reaction (1) was worse than that in catalysis by system **A**; however, the value of S also depended only slightly on the solvent, and it was minimal in dichloroethane (no. 10).

Evidently, the above changes in the catalyst activity were primarily due to a solvent effect on the rate-determining step of the reaction. Because of a considerable difference in the coordination strengths of anionic ligands, the nature of bivalent palladium intermediates in systems **A** and **B** was different: they were mainly represented by cationic [1–4] and neutral species in the former and latter cases, respectively. An important consequence of this difference is a change in the character of the rate-determining step on going from system **A** to system **B** (see [8, 9] for more detail). We explain this with the use of simplified scheme (2) of a catalytic cycle of the buildup of regioisomer **I** (the scheme of the buildup of regioisomer **II**, whose precursor is a β-styryl analog of complex **IV**, has the same form).

In system **A**, the interaction of cationic α-styryl complex **IV** with CO is a key step [9]. On going from a toluene–butanol mixture to pure butanol, this interaction can be hindered because of cation solvation by polar alcohol molecules. It is likely that the negative role of the specific solvation of the TsOH acid by the alcohol at the step of formation of complex **IV** should not be ignored. In catalysis by system **B**, the rate is determined by the step of butanolysis of acyl complex **V** (X = Cl) [8]; therefore, an increase in the alcohol content of the reaction mixture facilitates an acceleration of the reaction. It is likely that a decrease in the activity of either of the systems in aprotic polar media is due to the blocking of coordination vacancies in Pd(II) intermediates by the highly polar and electron-donating molecules of these solvents.



$$\begin{tikzcd}
\underset{\textbf{VI}}{[HPdL_3]^+X^-} \arrow[r, leftrightarrow, "{L,\ HX}"] & \underset{\textbf{III}}{PdL_2} \arrow[r, leftrightarrow, "CO"] \arrow[d, "{PhC\equiv CH,\ HX}"] & \underset{\textbf{VII}}{Pd(CO)L_2} \arrow[r, leftrightarrow, "CO"] & \underset{\textbf{VIII}}{Pd(CO)_2L_2} \\
 & CH_2{=}\underset{Ph}{C}{-}PdL_2X\ \ \textbf{IV} \arrow[d, "CO"] & & \\
 & CH_2{=}\underset{Ph}{C}{-}\underset{O}{\overset{}{C}}{-}PdL_2X\ \ \textbf{V} \arrow[d, "BuOH"] & & \\
 & \textbf{I},\ PdL_2,\ HX & &
\end{tikzcd} \qquad (2)$$

$L = Ph_3P$; $X = TsO, Cl$

However, in the general case, the rate of this multistep catalytic process depends on the set of solvation interactions with the participation of reactant molecules and palladium-containing species **III**–**VIII**. Therefore, it is difficult to expect a correspondence between the physicochemical parameters of solvents and the activity of catalysts. Indeed, as follows from data given in Table 2, there is no correlation between the activity of a catalyst and the permittivity or the electron-donor and electron-acceptor characteristics of the medium. In this case, even in a series of solvents of the same type—weakly polar aromatic hydrocarbons (Table 1, nos. 1, 3,

Table 1. Solvent effects on the activity (*a*) of catalysts **A** and **B** in reaction (1) and on the concentration of butyl 2-phenylpropenoate (*S*) in the mixture of regioisomeric products **I** and **II**

No.	Solvent	**A** (363 K)		**B** (383 K)	
		a, h^{-1}	S, %	a, h^{-1}	S, %
1	Toluene	336	96	328	61
2	Ethyl acetate	328	94	104	58
3	Benzene	296	96	–	–
4	Tetrahydrofuran	288	96	–	–
5	1,2-Dimethoxyethane	248	96	–	–
6	*ortho*-Xylene	160	97	–	–
7	1,4-Dioxane	152	97	120	54
8	Anisole	128	93	–	–
9	Dichloromethane	128	88	–	–
10	1,2-Dichloroethane	112	84	80	53
11	3-Pentanone	104	96	208	61
12	2-Butanone	96	94	–	–
13	1-Methyl-2-pyrrolidinone	48	100	–	–
14	*N*,*N*-Dimethylformamide	24	97	–	–
15	1-Butanol	32	96	288	63

Table 2. Solvent polarity (ε) and electron-donating (*DN*) and electron-accepting (*AN*) ability and the relative activity (a_{rel}) of catalysts **A** and **B** in reaction (1)

No.	Solvent	ε (25°C) [14]	*DN* [15]	*AN* [15]	a_{rel}	
					A	**B**
1	Toluene	2.38	–	–	1	1
2	Ethyl acetate	6.02	17.1	9.3	0.98	0.32
3	Tetrahydrofuran	7.6	20.0	8.0	0.86	–
4	1,4-Dioxane	2.21	14.8	10.8	0.46	0.37
5	1,2-Dichloroethane	10.4*	0	16.7	0.33	0.24
6	3-Pentanone	17.0**	16.3	–	0.31	0.63
7	1-Butanol	17.1	–	36.8	0.10	0.88
8	*N*,*N*-Dimethylformamide	36.7	26.6	16.0	0.07	–

* 18°C.

** 20°C.

and 6; the ε of benzene and *ortho*-xylene are equal to 2.2 and 2.3, respectively [14])—considerable changes in the activity of catalyst **A** were observed. It is likely that the participation of solvent molecules as labile ligands in the key steps of a catalytic cycle is of importance. To understand the reason for a solvent effect on the activity of a metal complex catalyst and thus to obtain a tool for purposefully affecting a homogeneous catalytic process, the reaction kinetics in various media should be studied in detail. In our opinion, this approach, not yet implemented, to the development of physicochemical fundamentals of metal complex catalysis deserves rapt attention.

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