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Effect of water on the palladium-catalyzed reaction of styrene with iodobenzene

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The effect of the amount of water in the solvent (DMF) on the rate of the reaction of styrene with iodobenzene in the presence of various palladium compounds has been studied. Addition of water to reaction mixture promotes the reaction. The effect of the addition water depends on the nature of the palladium complexes and temperature.

Key words: Heck reaction, catalysis, palladium, water, iodobenzene, styrene.

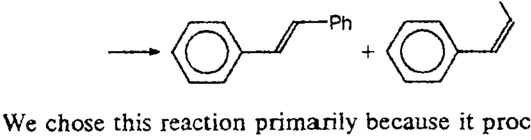
The reaction of organic halides with olefins catalyzed by palladium compounds (Heck reaction) is a widely used method for the formation of a carbon-carbon bond.[1–4] This reaction attracts great interest, because it makes it possible to perform highly regio- and stereoselective syntheses of unsaturated compounds of various types containing almost all functional groups. This reaction is conventionally carried out in an anhydrous organic solvent in the presence of a base. Recently several new modifications of the Heck reaction have been developed that make it possible to carry out the process either in a water-containing organic solvent or in water with both water-soluble and water-insoluble reactants in the presence of conventional palladium catalysts [PdX_2, $PdX_2(PPh_3)_2$, and $PdX_2(P(o\text{-}Tol)_3)_2$].[5–11] Palladium complexes with hydrophilic phosphine ligands, $PPh_2(m\text{-}C_6H_4SO_3Na)$[12–13] and $P(m\text{-}C_6H_4SO_3Na)_3$,[14] have been used as the catalysts to carry out the reactions in water-organic solvent media ($MeCN-H_2O$, $EtOH-H_2O$). Additives of water to the catalytic systems DMF/K_2CO_3 and $EtOH/Bu_4NCl/Et_3N/NaHCO_3$ are of crucial importance in these reactions.[5,11]

In this work we have studied the influence of the addition of water on the rate of the Heck reaction in the presence of various palladium compounds. We succeded in finding new effective reaction conditions ($DMF/H_2O/Et_3N$/"Pd") that allow us to decrease the reaction temperature.

Results and Discussion

As a model, we chose the reaction of styrene with iodobenzene in DMF in the presence of various palladium compounds and triethylamine (as a base). The reaction (Scheme 1) was carried out at 60 °C, and the reaction mixture was analyzed after 1.5 h.

Scheme 1



We chose this reaction primarily because it proceeds without the formation of any by-products to give *trans*-

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and *cis*-stilbenes ($E/Z \approx 13$) in quantitative yield based on the amount of PhI consumed. The amounts and ratios of the *E*- and *Z*-isomers of stilbene and the starting iodobenzene and styrene were easily monitored by GLC. Concurrently, the concentration of *trans*-stilbene was determined by TLC and UV-spectroscopy.[15] When water was added, the reaction mixture was a homogeneous solution until the DMF/H_2O ratio reached at least 6 : 1.

The results presented in Table 1 indicate that the addition of water to the reaction system DMF/Et_3N/"Pd" promotes the reaction. The value of this effect depends on the palladium compound used. For example, the maximum acceleration of the reaction with water is observed in the presence of $PdCl_2(PPh_3)_2$: in anhydrous DMF, there is no reaction at all, whereas in a mixture of water and DMF (DMF : H_2O = 6 : 1), at 60 °C the yield of *trans*-stilbene reaches 70% after 1.5 h (entries 1 and 2).

When $Pd(OAc)_2$ is used as the catalyst, the yield is 32% in anhydrous DMF, and in a mixture of water and DMF it increases to 70% (entries 7 and 9). The minimum effect of the addition of water to the reaction mixture is observed in the case of $PdCl_2[P(o\text{-Tol})_3]_2$: the reaction carried out in DMF alone gives *trans*-stilbene in 47% yield, and in the presence of water the yield increases to 75% (under the same conditions) (entries 4 and 5)

It is important that in the presence of water, the reaction occurs at almost the same rate regardless of the nature of the palladium catalyst used (entries 2, 5, 6, and 9). The water-soluble palladium complex with the sulfonated phosphine ligand gives almost the same result as $PdCl_2(PPh_3)_2$, $PdCl_2(P(o\text{-Tol})_3)_2$, and $Pd(OAc)_2$. Apparently, the optimum DMF: H_2O ratio is 12:1 to 6:1. When the water content increases to (DMF:H_2O = 2.5:1) the stilbene yield significantly decreases probably because the homogeneity of the reaction medium is disturbed (entries 7—11).

If the temperature is increased to 75 °C the reaction is complete after 1 h to form 93% *trans*- and 7% *cis*-stilbenes. When the reaction is carried out at this temperature in anhydrous DMF for 1 h, the yield of *trans*-stilbene is 60% (entries 12 and 13). It should be noted that the reaction carried out in Bu_3N (100 °C, 2 h) gives *trans*-stilbene in 75% yield.

The use of K_2CO_3 or K_2CO_3/Bu_4NBr instead of triethylamine at 60 °C proved to be ineffective (entries 17 and 18). The addition of K_2CO_3 and Bu_4NBr to the initial reaction mixture also sharply decreased the yield (entry 19). The low effectiveness of these systems at 60 °C may be attributed to the heterogeneity of the reaction medium.

The reaction can be carried out in water alone (without additives of DMF), however, in this case the

Table 1. Reaction of PhI with $CH_2{=}CHPh$ (1.5 equiv.) ("Pd" 1 mol %, argon). Effect of reaction conditions on the yield of (*E*)-PhCH=CHPh,

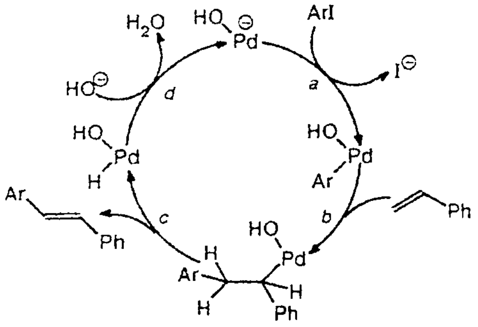
Entry	Solvent (vol. ratio)	«Pd»	Base (mol. equiv)	Time /h	*T* /°C	Yield of (*E*)-PhCH=CHPh [a] (%)	Conversion PhI [b] (%)
1	DMF	$PdCl_2(PPh_3)_2$	Et_3N (2)	1.5	60	Traces	1
2	DMF : H_2O (6 : 1)	$PdCl_2(PPh_3)_2$	Et_3N (2)	1.5	60	70	76
3	DMF : H_2O (1 : 1)	$PdCl_2(PPh_3)_2$	Et_3N (2)	1.5	60	26	29
4	DMF	$PdCl_2(P(o\text{-Tol})_3)_2$	Et_3N (2)	1.5	60	47	51
5	DMF : H_2O (6 : 1)	$PdCl_2(P(o\text{-Tol})_3)_2$	Et_3N (2)	1.5	60	75	80
6	DMF : H_2O (6 : 1)	$PdCl_2(PPh_2(m\text{-}C_6H_4SO_3Na))$	Et_3N (2)	1.5	60	76	82
7	DMF	$Pd(OAc)_2$	Et_3N (2)	1.5	60	32	34
8	DMF : H_2O (12 : 1)	$Pd(OAc)_2$	Et_3N (2)	1.5	60	69	75
9	DMF : H_2O (6 : 1)	$Pd(OAc)_2$	Et_3N (2)	1.5	60	70	75
10	DMF : H_2O (2.5 : 1)	$Pd(OAc)_2$	Et_3N (2)	1.5	60	9	10
11	DMF : H_2O (1 : 1)	$Pd(OAc)_2$	Et_3N (2)	1.5	60	Traces	1
12	DMF	$Pd(OAc)_2$	Et_3N (2)	1	75	60	65
13	DMF : H_2O (6 : 1)	$Pd(OAc)_2$	Et_3N (2)	1	75	93	100
14	DMF : H_2O (6 : 1)	$Pd(OAc)_2$	Et_3N (2)	16	18	8	10
15	Et_3N : H_2O (12 : 1)	$PdCl_2(PPh_3)_2$	Et_3N (56)	1.5	60	0	0
16	Et_3N : H_2O (1 : 5.4)	$PhPdBr(PPh_3)_2$	Et_3N (2)	3	100	85	100
17	DMF : H_2O (6 : 1)	$Pd(OAc)_2$	K_2CO_3 (1)	1.5	60	4	5
18	DMF : H_2O (6 : 1)	$Pd(OAc)_2$	K_2CO_3 (1) + + Bu_4NBr (0.1)	1.5	60	7	8
19	DMF : H_2O (6 : 1)	$Pd(OAc)_2$	K_2CO_3 (1) + + Bu_4NBr (0.1) + + Et_3N (2)	1.5	60	12	13

[a] Yield of (*E*)-PhCH=CHPh was determined by TLC and UV-spectroscopy. (*Z*)-PhCH=CHPh is also formed. The ratio of (*E*)- and (*Z*)-isomers remained almost unchanged under the studied conditions (*E*/*Z* 13). [b] Conversion was determined by GLC from the amount of PhI, which did not react.

hydrophobic palladium complexes with phosphine ligands must be used as the catalysts (entry 16), and the interaction proceeds at a higher temperature (100 °C).

The observed acceleration of the reaction of styrene with iodobenzene resulting from the addition of water to an organic solvent may be caused by several things. First, oxygen-containing palladium complexes (for example, $[Pd^0L_nOH]^-$) are formed in the presence of water and a base; these complexes are more active in the steps of the catalytic cycle than the corresponding halogen-containing analogs. Scheme 2 presents the well known steps of the catalytic cycle: (*a*) oxidative addition of ArI to Pd^0, (*b*) coordination and insertion of olefin into the Ar—Pd bond, (*c*) β-elimination and dissociation of the palladium hydride complex giving the substituted olefin, and (*d*) regeneration of Pd^0 under the action of a base (the other ligands that are not involved in the catalytic cycle are not presented in the scheme).

Scheme 2

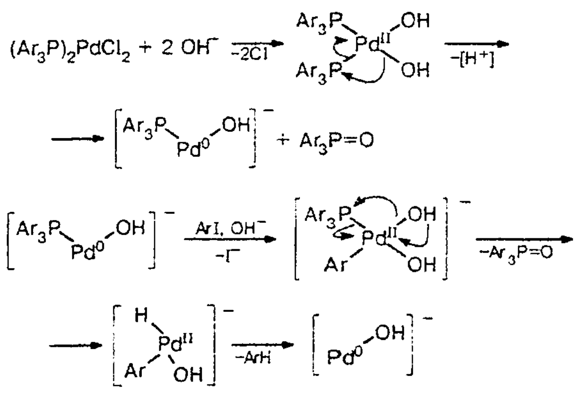


In our opinion, all steps of the catalytic cycle may involve highly active hydroxy complexes of palladium. Many researches have established that ligand exchange on palladium complexes occurs to form the Pd—O bond. For example, the authors of Ref. 17 comprehensively studied replacement of the halogen in $ArPdXL_2$ (X = Cl, Br, I) and of triphenylphosphine in $Pd(PPh_3)_4$ with an acetate ion, which results in $ArPdOAcL_2$ and highly active anionic Pd(0) complexes. Oxidative addition of ArI to Pd^0L_n in the benzene/KOH/H_2O system gives binuclear palladium complexes $[L_2Ar_2Pd(\mu\text{-}OH)_2]$.[18] Oxypalladium complexes were isolated and characterized in Ref. 19.

Secondly, oxidation of phosphine ligands Ar_3P to the corresponding phosphine oxides $Ar_3P{=}O$ may occur in the coordination sphere of the palladium complex in the presence of water and a base (Scheme 3).

As a result, palladium complexes that do not contain inactive phosphine ligands and are more active at all steps of the catalytic cycle are formed. A similar oxidation process of one phosphine ligand in the Pd coordination sphere has been observed by several authors.[17,18] The occurrence of oxidation of two phosphine ligands L (L = Ar_3P) in an aqueous DMF solution is confirmed indirectly by the almost equal yields of products and the reaction rates in the presence of water (DMFA : H_2O = 6 : 1), when either $Pd(OAc)_2$ or phosphine Pd complexes, L_2PdCl_2, were used as catalysts (see Table 1, entries 2, 5, 6, and 9)

Scheme 3



Thus, we may suggest that the reactions actually proceed on non-phosphine palladium complexes, and the starting phosphine complex is a precursor of the catalyst, and enables a "soft" transformation (without formation of Pd-black) of $(Ar_3P)_2PdCl_2$ to the highly reactive palladium species.

Experimental

UV spectra were recorded on a Hitachi-124 spectrophotometer. GLC analysis was carried out on an LKhM-8MD chromatograph (flame-ionization detector, 1000×3 mm column packed with 3% SP-2100 on Chromaton N-super). DMF was successively distilled over P_2O_5 and K_2CO_3, stirred with anhydrous $CuSO_4$, and distilled, b.p. 48 °C (10 Torr). Styrene was distilled before use. $Pd(OAc)_2$,[20] $PdCl_2(PPh_3)_2$,[21] and $PPh_2(m\text{-}C_6H_4SO_3Na)$[22] were obtained using well known procedures, that were slightly modified.

$PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2 \cdot 3H_2O$ complex. A solution of $PPh_2(m\text{-}C_6H_4SO_3Na)$ (1.284 g, 3.54 mmol) in a mixture of water and ethanol (20 mL of EtOH and 0.5 mL of H_2O) was added to a solution of $PdCl_2$ (0.298 g, 1.68 mmol) in acetonitrile (30 mL) at 60—70 °C. The resulting mixture was refluxed with stirring for 1 h. After cooling, the precipitate was filtered off and dried *in vacuo* to afford $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2 \cdot 3H_2O$ (1.53 g, 95%).[21]

Reaction of styrene with iodobenzene in the presence of $PdCl_2(PPh_3)_2$ (general procedure). Iodobenzene (0.204 g, 1 mmol), DMF (3.8 mL), triethylamine (0.202 g, 2 mmol), styrene (0.156 g, 1.5 mmol), and water (0.63 mL) were added to $PdCl_2(PPh_3)_2$ (0.0070 g, 0.01 mmol) under argon with stirring. The reaction mixture was vigorously stirred in an argon flow at ~20 °C for 15 min and at 60 °C for 1.5 h. After cooling, the reaction mixture was diluted with water and extracted with diethyl ether (4×25 mL). The yield of *trans*-stilbene (70%) was determined by TLC and UV spectroscopy.[15] The starting iodobenzene (24%) and *cis*-stilbene (6%) were determined in the ether solution by GLC.

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Interaction of rhenium hydride $(\eta^5\text{-}C_5Me_5)ReH(CO)(NO)$ with fluorinated alcohols

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The interaction between the fluorinated alcohols R^FOH ($R^F = (CF_3)_2CH$ and $(CF_3)_3C$) and rhenium hydride $(\eta^5\text{-}C_5Me_5)ReH(CO)(NO)$ in hexane and liquid freon was studied in a wide temperature range by IR and ^1H NMR methods, respectively. The formation of hydrogen-bonded complexes of two types, $ReH...HOR^F$ and $NO...HOR^F$, was established. The hydride signal in the ^1H NMR spectra at 96 K splits into two signals (at $\delta = -7.54$ and -8.87) corresponding to the free ReH and the ReH...HO complex, respectively.

Key words: hydrogen bond, hydrides of transition metals, molecular spectroscopy.

It has been shown that an unusual type of intermolecular hydrogen bond $MH^{\delta-}...H^{\delta+}X$ exists in the interaction of proton donors with tungsten hydrides $WH(CO)_2(NO)L_2$ in solution[1a] and in the interaction of rhenium polyhydride $ReH_5(PR_3)_3$ with indole in the crystal.[1b] In this work, the first results of IR and

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