

Heck Reactions with Ultralow Concentration of Transition Metals under Microwave Irradiation

Hongjun Wang^{1,2}, Haiyang Cheng^{1,2*}, Fengyu Zhao^{1,2*}

¹State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China

²Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China

Email: *hycyl@ciac.ac.cn, *zhaofy@ciac.ac.cn

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ABSTRACT

The Heck coupling reactions of aryl halides and olefins were performed under the microwave assistance. Interestingly, the ultralow concentration of transition metals (in ppb) coming from the reactants could catalyze the Heck coupling reactions under microwave irradiation, without addition of any catalysts, ligands and phase-transfer agents. The influences of bases, solvents and temperature were discussed, and the reaction rate was enhanced largely in the mixed solvents of NMP and water due to the solubility of base in water.

KEYWORDS

Heck Reaction; Microwave Irradiation; Ultralow Concentration; Transition Metal Catalysts; Water

1. Introduction

Heck reaction of aryl halide and olefin is still attracting much attention, for it is one of the important methods to build up new carbon-carbon bond [1]. Heck reactions are most frequently performed in polar solvents such as acetonitrile, dimethyl sulphoxide, or dimethylacetamide and N-methylpyrrolidone (NMP) in the presence of palladium catalysts. It was reported that the addition of water could markedly accelerate the Heck reactions in the presence of Pd(OAc)₂ or Pd/C catalysts, but colloidal palladium particles were formed in these cases [2-5]. Reetz *et al.* [3] and de Vries *et al.* [4] had reported that the Heck reactions could be run in the mixed solvent of NMP and water in the presence of quantities of Pd(OAc)₂, and they suggested that the reaction be proceeded via the formation of palladium colloids. Recently, the real active species has been well discussed for the Heck reactions catalyzed with heterogeneous catalyst of supported palladium since the Heck reactions were reported to be catalyzed homogeneously by the dissolved palladium in the solution [6,7]. It was reported that the ligand-free

palladium catalyst of Pd(OAc)₂ could be recycled successfully by adding the supports like active carbon or silica into the reaction solution [8]. Water is the most abundant, cheap, safe, and environmentally benign solvent in nature and the study of organic reaction in/on water is an important theme of current research from the point of green chemistry [9]. The Heck coupling of iodobenzene with styrene could be performed in supercritical water in the absence of any transition metal catalysts [10]. Microwave heating has been shown to dramatically reduce reaction times, increase product yields, and enhance product purities compared to conventional synthetic methods in organic synthesis [9], and Suzuki and Heck reactions were reported to proceed successfully under microwave irradiation with or without the addition of catalyst [11-29]. Leadbeater and coworkers reported that Suzuki coupling reactions could carry out in water in the presence of tetrabutylammonium bromide (TBAB) as a phase-transfer agent by microwave irradiation in the absence of transition metal catalysts [14,15], while subsequently they found that the transition metals contaminated to a level of 50 and 500 ppb (contained in bases) should be possible for Suzuki and Heck coupling reactions

*Corresponding authors.

respectively rather than their previous suggested non-transition metal-mediated pathway [16,17]. However, the presence of phase-transfer agent makes it difficult to separate the product and the solvent.

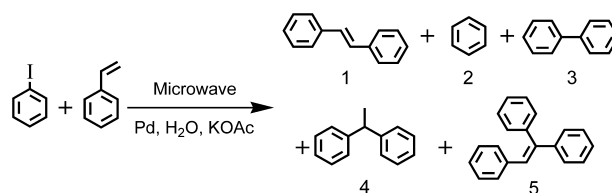
In the present work, microwave irradiation can promote the Heck coupling reactions of aryl halides and olefins in the presence of ultralow transition metals in various solvents and in the absence of ligands and phase-transfer agents, and a high conversion and selectivity were obtained. The influences of several parameters such as solvent, base and reaction temperature have been discussed, and the existence of transition metals in the reaction solution as well as the reactions in the presence of ultralow concentration of palladium compound has been examined.

2. Results and Discussion

The coupling reactions of styrene and aryl halides of iodobenzene, bromobenzene and chlorobenzene could be promoted by microwave irradiation in the presence of ultralow transition metals, in which several products have been detected except for the main coupling product of stilbene (**1**) as shown in the [Scheme 1](#).

2.1. The Heck Reaction in the Presence of Ultralow of Pd(OAc)₂

The Heck reactions of iodobenzene with styrene have been performed in the presence of Pd(OAc)₂ with low Pd concentrations of 0.5 - 2 ppm without using any ligands and phase transfer reagents in water, and the results are shown in [Table 1](#). Under the microwave irradiation at 200°C, when the reaction was carried out in the presence of 0.5 ppm Pd in H₂O, the conversion of iodobenzene achieved 26% and the selectivity to stilbene reached 85%, while the conversion and selectivity were increased to 62% and 97% respectively when the Pd concentration was enhanced to 2 ppm ([Table 1](#), Entries 1 and 2). In the mixed solvent of THF and water, the conversion increased also with the concentration of Pd, and the selectivity decreased slightly ([Table 1](#), Entries 3 and 4), but the selectivity was still higher than the results obtained in the mixed solvents of NMP and water, in which even though the higher conversion could be obtained ([Table 1](#), Entries 4 and 5). When enhanced the temperature to 245°C, the conversion of iodobenzene achieved 100% at reaction for 30 min, and the yield to stilbene reached 73% ([Table 1](#), Entry 6). However, when the blank reaction was carried out without addition of Pd(OAc)₂, surprisingly, a very high conversion of 88% was obtained and the selectivity to stilbene reached 60% ([Table 1](#), Entry 7). We have repeated the reaction several times to check the reproducibility of the reaction data, including with new reaction tube to decrease the possible influences, but the



Scheme 1. Heck reaction of iodobenzene with styrene under the microwave irradiation.

similar results have been obtained. It was been reported that the Heck reaction could occur in supercritical water in the absence of catalysts [10]. For the present work, the reactions were carried out in a closed vessel, thus reactions were carried out under a pressure higher than the atmosphere, but the system was far from the conditions of supercritical water for that the pressure in the reaction system was lower than 2 MPa. The coupling reactions could be promoted by microwave irradiation in the transition metal-free conditions [14,15], while subsequently it was found that the ultralow transition metal concentrations should be possible for catalyzing the reactions [16,17]. For confirming the present reaction is real transition metal-free or not, the ICP-MS was used to examine transition metals like Pd, Ru, Pt and Rh in the reaction solution, all these metals are active for the Heck coupling reactions. These transition metals were detected in the reaction solution in a concentration of 3.418 ppb Pd, 1.162 ppb Rh, 1.048 ppb Ru and 0.750 ppb Pt, and the transition metals mainly come from the mixture of reactants rather than base like KOAc in the present work. Although the concentration of the transition metals is quite lower than that reported in literature (500 ppb) [17], such low concentration of transition metal is still effective for the Heck reaction under microwave irradiation. Then, the influence of several reaction parameters were examined and discussed on the Heck reactions without addition of any ligands, phase transfer reagents and metal catalysts.

2.2. The Influence of Solvent and Temperature

[Table 2](#) shows the reaction of iodobenzene with styrene in several solvent systems at different temperatures. Under the reaction conditions used, the solvent presents a significant effect on the conversion and selectivity in the presence of a base of KOAc. Comparing all the solvents used, DMF and NMP are more effective ([Table 2](#), Entries 1 and 2), but water and THF are less effective ([Table 2](#), Entries 3 and 4). When ethanol was used, no product could be detected at 180°C ([Table 2](#), Entry 5). It is obviously that the total conversion and product yield could be improved largely by adding a co-solvent of water to mix with the organic solvents even at low reaction temperature ([Table 2](#), Entries 6 and 7). It was considered that the presence of water could increase the solubility of

Table 1. Results for Heck coupling reactions in the presence of Pd(OAc)₂.

Entry	Pd ²⁺ (ppm)	Catalyst loading (mol %)	Solvent	T (°C)	Conversion (%)	Selectivity to stilbene (%)	Yield to stilbene (%)
1	0.5	0.67 × 10 ⁻³	H ₂ O	200	26	85	22
2	2	2.67 × 10 ⁻³	H ₂ O	200	62	97	60
3	0.5	0.67 × 10 ⁻³	THF + H ₂ O	180	6	94	6
4	2	2.67 × 10 ⁻³	THF + H ₂ O	180	23	89	20
5	2	2.67 × 10 ⁻³	NMP + H ₂ O	180	64	67	43
6	2	2.67 × 10 ⁻³	NMP + H ₂ O	245	100	73	73
7	-	-	NMP + H ₂ O	245	88	60	53

Reaction conditions: 5 mmol iodobenzene, 5 mmol styrene, 5 mmol KOAc, 6 ml solvent, in mixed solvent H₂O/organic solvent: 1/5, 30 min.

Table 2. Influence of solvent and temperature on the reactions of iodobenzene with styrene.

Entry	Solvent	Temperature (°C)	Conversion (%)	Selectivity of stilbene (%)	Yield of stilbene (%) ^a	E:Z
1	DMF	245	37	46	17	90:10
2	NMP	210	33	55	18	85:15
3	H ₂ O	210	5	58	3	100
4	THF	210	14	7	1	100
5	Ethanol	180	Nd	-	-	-
6 ^b	DMF + H ₂ O	210	42	82	34	80:20
7 ^b	NMP + H ₂ O	180	44	10	4	100
8 ^b	NMP + H ₂ O	245	88	60	53	65:35
9 ^{b,c}	NMP + H ₂ O	245	76	66	50	77:23

Reaction conditions: 5 mmol iodobenzene, 5 mmol styrene, 5 mmol KOAc, 6 ml solvent, 30 min. ^aYield of stilbene was calculated based on the total conversion of iodobenzene; ^bin mixed solvent H₂O/organic solvent: 1/5; ^cThe reaction was carried out by conventional heating in a 50 ml autoclave with a Teflon tube for 8 h. Nd: not detected.

inorganic bases in the solution and then enhance the reaction conversion. High total conversion (88%) of iodobenzene and yield (53%) of coupling product, stilbene, have been obtained in the mixed solvents of NMP and water (Table 2, Entry 7). In the present work, the Heck coupling product contains two isomers of trans- and cis-stilbene, and the ratio of trans- to cis- (E:Z) decreases with the total conversion. Which is contrast to the results reported for the Heck reactions in the supercritical water [10]. Furthermore, the reaction temperature presented a significant effect on the total conversion and product yield, the higher conversion and yield were obtained at the higher reaction temperature (Table 2, Entries 7 and 8). Moreover, when the reaction was carried out with the conventional heating method in an autoclave fitted with a teflon cell, the Heck coupling product could also be produced, but the total conversion of reaction for 8 h is lower than that obtained under the microwave irradiation for a short time of 0.5 h (Table 2, Entries 8 and 9).

2.3. The Influence of Base

The presence of base is necessary to bind the hydrogen halide formed during the catalytic Heck coupling reactions [1], the effect of base in the present work has also

been investigated. Experiments were carried out in the presence of Na₃PO₄, Na₂CO₃, K₂CO₃, Cs₂CO₃, Et₃N, NaOAc and KOAc, when Na₃PO₄ and Na₂CO₃ were used, product could not be detected. While, the other bases are effective under the reaction conditions used as shown in Table 3. The bases exhibited a strong influence on both the total conversion and product yield, and KOAc is the most effective for forming coupling product of stilbene (Table 3, Entry 2), it shows that higher ratio of E:Z could be obtained with acetates compared to that of carbonates (Table 3, Entries 1, 3, 4 and 5). In our present work, the Heck reaction could occur with all the bases and it is irrespective to the base used like Na₂CO₃, Et₃N, K₂CO₃ and KOAc, but depended significantly on the temperature and solvents used.

2.4. The Heck Reactions with Different Substrates

It is well known that the C-C coupling reactions with chlorobenzene and bromobenzene are quite difficult even in the presence of the active catalysts. Choudary *et al.* have obtained high turnover numbers in Heck couplings with aryl chlorides by using supported nano Pd catalysts. They suggested that the reaction proceeded on the surface of the nanoparticles [30]. In the present work, the

Heck coupling reactions of chlorobenzene and bromobenzene with styrene have been also checked without addition of catalysts, the results are shown in **Table 4**. It indicated that a certain conversion could be obtained for coupling reactions of chlorobenzene and bromobenzene with styrene under microwave irradiation. However, several by-products such as benzene and biaryl were formed. For the reaction of bromobenzene with styrene, a 28% yield of coupling product was obtained (**Table 4**, Entry 2), while the yield was less than 2% for the reaction of chlorobenzene and styrene (**Table 4**, Entry 1). In the literature, PdCl₂ catalyzed Heck reactions in ionic liquids was reported to be an effective system for reactions of iodobenzene or bromobenzene with styrene, but only 10% yield of stilbene was obtained from chlorobenzene and styrene in the presence of 0.16 mol % PdCl₂ [31]. When methyl acrylate and butyl acrylate were used as olefin to couple with iodobenzene, lower conversions and selectivities have been obtained compared with that of styrene (**Table 4**, Entries 3 - 5).

3. Conclusion

Under microwave irradiation, without addition of any catalysts, ligands and phase-transfer agents, Heck coupling reactions of aryl halides and styrene could be smoothly performed in the presence of ultralow transition metals come from the reactants. The microwave irradiation is an effective method for Heck coupling reactions compared with conventional heating method. Moreover, the chlorobenzene and bromobenzene have also showed reactivity under the microwave irradiation with the ultralow concentration of transition metals, therefore the present reaction system is an effective one for the Heck coupling reactions.

4. Experimental Section

The reactants of chlorobenzene (99.5 wt.%), methylacrylate (99.5 wt.%), butylacrylate (98 wt.%) were purchased from Tianjin Chemical Reagent Co. Ltd., and iodobenzene (97 wt.%), bromobenzene (99.5 wt.%), styrene (99.0 wt.%) were purchased from Shanghai Chemical Reagent Co. Ltd. and used as they were received without further purification. Potassium acetate (KOAc, 99 wt.%, Guangdong Xilong Chemical Co. Ltd.) was used as it was received, the bases of triethylamine (Et₃N), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), Cesium carbonate (Cs₂CO₃), sodium acetate (NaOAc·3H₂O), sodium phosphate (Na₃PO₄) and solvents of N-methylpyrrolidone (NMP), Dimethyl formamide (DMF), tetrahydrofuran (THF), Ethanol from Beijing Chemical Co. Ltd. are of analytical grade and used also without further purification. The deionized water was used for all the experiments. The reactions were carried out using a microwave irradiation reactor system (Initiator, Biotage, Sweden). The representative example of a Heck coupling reaction of iodobenzene with styrene was carried out as follows: The reactants of iodobenzene, styrene and base 5 mmol each were added into the 10 ml glass tube reactor, then introduce 6 ml solvent and put a magnetic stirrer bar into the reactor, after the vessel was sealed with a septum, it was placed into the microwave cavity. When the reaction system reached the desired temperature, the reaction was started with continual stirring by a magnetic stirrer (900 rpm) during the reaction. The microwave cavity opened automatically when the reactor was cooled to room temperature. The reaction mixture was extracted by using dichloromethane, then analyzed with gas chromatography (GC-Shimadzu-14C, FID, Capillary column, Rtx-Wax 30 m × 0.53 mm × 0.25 μm) and identified by

Table 3. Influence of base on the reaction of iodobenzene and styrene.

Entry	Base	Conversion (%)	Selectivity to stilbene (%)	Yield to stilbene (%) ^a	E:Z
1	K ₂ CO ₃	26	67	17	49:51
2	Et ₃ N	44	69	30	74:26
3	Cs ₂ CO ₃	49	32	16	37:63
4	NaOAc·3H ₂ O	57	63	36	87:13
5	KOAc	88	60	53	65:35

Reaction conditions: 5 mmol iodobenzene, 5 mmol styrene, 5 mmol base, 5 ml NMP, 1 ml H₂O, 245°C, 30 min. ^aYield of stilbene was calculated based on the total conversion of iodobenzene.

Table 4. Results for Heck coupling reactions promoted by microwave irradiation at 245°C.

Entry	Aryl halides	Olefin	Conversion (%)	Selectivity to coupling product (%)	Yield to coupling product (%)
1	Chlorobenzene	Styrene	27	9	2
2	Bromobenzene	Styrene	88	32	28
3	Iodobenzene	Styrene	88	60	53
4	Iodobenzene	Methylacrylate	18	52	9
5	Iodobenzene	Butylacrylate	27	49	13

Reaction conditions: 5 mmol aryl halide, 5 mmol olefin, 5 mmol KOAc, 5 ml NMP, 1 ml H₂O, 30 min.

gas chromatography/mass spectrometry (GC/MS, Agilent 5890). The product yield was calculated based on the total conversion of iodobenzene. Inductively coupled plasma mass spectrometry (ICP-MS, TJA, POEMS) was used to examine the transition metals in reaction solution.

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