Heck Coupling Reaction of Iodobenzene and Styrene Using Supercritical Water in the Absence of a Catalyst

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Abstract: Heck coupling reaction of iodobenzene and styrene proceeds rapidly and selectively in supercritical water even without any catalyst in the presence of base. Both the choice of base and the reaction conditions had a significant effect on the conversion and the selectivity of the coupling products. The addition of a relatively mild base such as potassium acetate facilitated the cross-coupling reaction, while the hydrolysis of phenyl halide was favored in the presence of a strong base. The conversion and the yields of coupling products increased with increasing temperature, reaching a maximum at 650 K near the critical temperature of water, and then decreased as the temperature was further increased. Water density had a significant influence on the reaction rate, showing nearly 30% augmentation with a slight increase in density from 0.45 to 0.56 $g\,cm^{-3}$, but had less effect on the product selectivity. Two possibilities of the role of water responsible for the noncatalytic Heck coupling reaction in supercritical water, that is, ion and water-catalyzed mechanisms have been considered.

Keywords: green chemistry · Heck reaction · supercritical fluids

Introduction

Among the various ways known to synthesize arylated olefins, the Heck coupling reaction is one of the most useful methods owing to its tolerance of a wide variety of functional groups.[1] This powerful carbon–carbon bond forming process has been practiced on an industrial scale for the production of compounds such as the anti-inflammatory drug Neproxen and the most common UV-B sunscreen agent octyl methoxycinnamate.[2] Heck reactions are most frequently performed in polar aprotic σ-donor-type solvents such as acetonitrile, dimethyl sulphoxide, or dimethylacetamide in the presence of homogenous or heterogeneous catalysts. Although soluble palladium complexes can promote this reaction in high reactivity and high selectivity, homogeneous catalysts generally present problems in the separation, recovery and regeneration of the catalysts. The problems could, in principal, be minimized by using heterogeneous catalysts. However, such heterogeneous systems show quite slight activities compared with homogeneous catalysts owing to the paucity of activated sites resulting from the presence of a phase boundary. Much effort has so far been put into the development of new, more active, and more stable catalysts.[3–5] In addition, the use of halogenated aromatic compounds requires the use of stoichiometric amounts of base, which leads to the formation of large quantities of halide salt by-products, especially in large-scale processes. To circumvent these problems, aromatic carboxylic acid anhydrides and esters have been used by de Vries and co-workers[6] and Goossen et al.[7] respectively. Considering the environment, safety and economics, efforts are being directed toward decreasing the usage of organic solvents in chemical laboratories and industrial processes.[8] Recently, environmentally benign approaches to the Heck reaction have been developed, such as the application of water,[9–11] as well as supercritical CO_2[12, 13] and ionic liquids as solvent media.[14]

From the viewpoint of sustainable development, supercritical water (scH_2O) should be a more useful replacement for organic solvents for the following reasons. First, water is a cheap, safe, and environmentally benign solvent compared with organic solvents. A new application of water as the reaction medium will not only reduce the use of harmful organic solvents, but will also be regarded as an important re-

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search topic in green chemistry.[15] Second, water has unique physical and chemical properties, and its physicochemical properties can be influenced greatly with pressure and temperature. For example, the static dielectric constant of water is 78.5 at 298 K, and dramatically decreases to about 6.0 at the critical point (647.1 K and 22.1 MPa).[16] As a result, nonpolar organic compounds are very soluble or miscible in scH_2O. By utilizing these properties it would be possible to realize reactivities that cannot be attained in organic solvents. This nature along with high diffusivity and low viscosity is expected to function as an ideal alternative for apolar organic solvents.[16,17] Experimental results of Diels–Alder reactions, hydrolysis of ester and nitriles in scH_2O have been reported.[18] More recently, Sasaki et al.[19] discovered that intramolecular dehydration between 1-hexyl alcohol and acetamide occur in scH_2O without catalyst. scH_2O is thus expected to play an important role according to each reaction, and could provide new reaction pathway.

The Heck arylation of alkenes has been carried out in hot compressed water (533 K) and also in scH_2O (673 K) in the presence of Pd catalysts.[20–23] In the case of the Pd-catalyzed reaction of iodobenzene and styrene, the yield of coupling products was less than 25% and the catalysts were deactivated rapidly. Further, the influence of water on the selectivity and the reaction mechanism has scarcely been elucidated. We have demonstrated a remarkable stimulation of rearrangement or disproportionation using scH_2O even in the absence of any acid or base catalysts.[24,25] The structural and electronic properties of water close to above the critical point have been analyzed by first principles molecular dynamics,[26] in situ IR[25] and Raman[27] spectroscopic measurements. Close at the critical point, where the density is very low, small clusters, mainly monomer, dimers and trimers, are predominant, but the clusters exhibit no hydrogen-bonding network. The significant reduction of the strength of hydrogen bonding in H_2O peculiar near the critical point would lead to the activation of protons or H_3O^+ or OH^- ions. This might be responsible for the acid and base difunctionality of scH_2O. Hence, we attempted to conduct a noncatalytic arylation of styrene using scH_2O, in which the effects of base, temperature, water density, and reactor material on the conversion and product selectivity were investigated in detail.

in which several alkylarenes, such as stilbene **1** and 1,1-diphenylethylene **2** were formed as shown in Scheme 1, besides hydrogen iodide. In addition to the expected coupling reaction, we observed the hydrogenation of **1**→bibenzyl **4** and **2**→1,1-diphenylethane **5**, and also the hydrogenation of styrene to ethyl benzene. We observed a high conversion of styrene, but ethyl benzene and a tarry polymeric material (styrene oligomers) were the main products.
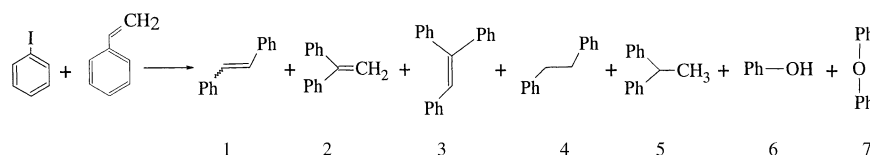
Scheme 1. Heck reaction of styrene and iodobenzene.

In this system, the presence of base, which is necessary to bind the hydrogen halide formed during C–C bond coupling, and the choice of base can have a crucial effect on the rate and the product distribution of the Heck reaction.[3] Thus, the effect of base on the Heck reaction in scH_2O was investigated. Experiments were carried out in the presence of $N(Et)_3$, NaOAc, KOAc, K_3PO_4, K_2CO_3, Na_2CO_3, $NaHCO_3$, or NaOH base. The results are shown in Table 1. The kind of base has a strong influence on both the conversion and the selectivity in scH_2O. That is, KOAc base was the most effective for synthesizing coupling compounds such as stilbene **1**. The conversion of iodobenzene and styrene reached over 70%. High regioselectivity (>95:5) towards the internal olefin **1** was observed with only a small amount of terminal olefin **2**, and the yield of double arylated Heck coupling compound, 1,1,2-triphenylethylene **3** was less than 3%. The yield of stilbene was 55.6% and the ratio of *trans*- to *cis*-stilbene (*E:Z* in Table 1) was approximately 81:19. In addition, white crystals of *trans*-stilbene can be easily separated from the reaction system.

Similarly to the case without base addition, in the presence of $N(Et)_3$ base, high conversion of styrene was obtained; however, the yield of stilbene **1** was low and ethyl benzene and the hydrogenated products (**4** and **5**) were obtained in about 10.5 and 6.8% yields, respectively. When a strong base such as NaOH was used, the conversion of iodo-

Results and Discussion

Effect of base: We found for the first time that the coupling of styrene and iodobenzene can be promoted even in the absence of any catalysts in scH_2O,

Table 1. Effect of base on reaction of styrene and iodobenzene.[a]

Base	Conversion [%]		Yield [%]					E:Z
	styrene	iodobenzene	**1**	**2**	**3**	**6**	**7**	
_[b]	100.0	39.7	5.0	0	0			
			(3.3)	(1.3)[d]	(1.8)	0	0	–
N(Et)₃[c]	94.1	45.1	13.9 (5.0)	0 (1.8)	0	0	0	–
KOAc	72.5	77.5	55.6	2.3	3.0	0	0	81:19
NaOAC	65.4	65.6	43.8	1.9	2.0	6.3	0	81:19
K₃PO₄	60.4	77.2	42.2	1.8	1.4	25.7	1.9	81:19
Na₂CO₃	64.6	100.0	27.8	1.2	0.5	44.3	5.2	83:17
K₂CO₃	39.0	93.1	10.7	0.5	0.1	58.2	7.7	81:19
NaHCO₃	55.2	95.0	10.2	0.4	0.1	52.8	4.1	83:17
NaOH	41.4	100.0	7.7	0.3	0	59.4	11.5	80:20

[a] 650 K and water density 0.51 g cm^{-3}. [b] Ethylbenzene 10.2%. [c] Ethylbenzene 10.5%. [d] The numbers in the parentheses are yields of corresponding hydrogenated products.

benzene was high and phenol was the main product. Other bases, such as K_3PO_4, K_2CO_3, Na_2CO_3, and $NaHCO_3$, gave results in-between potassium acetate and sodium hydroxide. Unlike the Heck reactions in organic solvent with catalysts,[3] the nature of base had no influence on the regioselectivity of the double bond, but there was a slight different in the E:Z selectivity. Moreover, homocoupling of iodobenzene to biphenyl has not been observed in scH_2O regardless of the base used.

It is noteworthy that in the absence of base or presence of the $N(Et)_3$ base, the hydrogenation of styrene and the coupling products took place to a large extent. It would be predicted that the hydrogenation would be caused by the resulting hydrogen iodide, because the hydrogenation of styrene to ethyl benzene in scH_2O was shown to proceed only when hydrogen iodide is present. On the other hand, in the absence of hydrogen iodide the formation of a small amount of 1-phenylethyl alcohol from styrene in scH_2O was confirmed, and so that the hydrogen for the hydrogenation can only be donated from scH_2O itself.

Effect of temperature and water density: Figure 1 shows the temperature dependence of the conversion and the yield of stilbene in the presence of KOAc. One can see an interesting temperature dependence in which both the conversion and the yield increased, reaching a maximum conversion and yield at 650 K near the critical temperature of water, and then decreased as the temperature further increased. It was found that higher temperatures favored the formation of gaseous products, resulting in the low yield of stilbene. Furthermore, the E:Z ratio was approximately 81:19 regardless of the temperature.
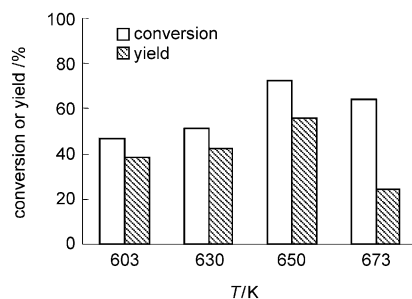

Figure 1. Influence of temperature on the conversion and the yield of stilbene at 25 MPa in the presence of KOAc conversion yield.

The effect of water density on the conversion of styrene is shown in Figure 2. The reaction seems to be significantly accelerated by water density, especially showing nearly 30% augmentation with a slight increase in density from 0.45 to 0.56 g cm^{-3}. The E:Z ratio remained almost unaltered, ranging from 80:20 to 82:18. The yield of the terminal olefin **2** decreased slightly with increasing density, while that of double arylated product **3** increased with pressure (see Figure 3).

A significant part of the effect of pressure on the reaction rate in scH_2O could be assignable to the thermodynamic pressure effect. For a simple bimolecular reaction, the ther-
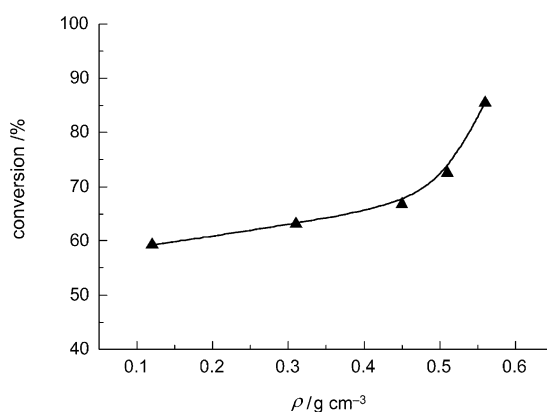

Figure 2. Effect of water density on the conversion of styrene at 650 K in the presence of KOAc conversion.
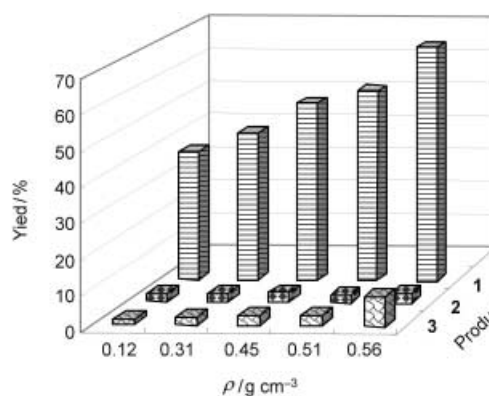

Figure 3. Yields of coupling products under different water densities at 650 K in the presence of KOAc; product **1**: stilbene, product **2**: 1,1-diphenylethylene, product **3**: 1,1,2-triphenylethylene.

modynamic pressure effect on the rate constant at a given temperature can be obtained as:[16]

$$(\partial \ln k/\partial P)_T = -V^{\pm}/RT$$

where k is the bimolecular rate constant, $V^{\pm}$ is the reaction activation volume, R is the gas constant, and P and T are the pressure and the temperature, respectively. Processes accompanied by a decrease in partial molar volume such as a C–C bond formation, in which the distance between two carbon atoms decreases from the van der Waals distance to the bonding distance, are known to be accelerated by pressure and the equilibrium should be shifted toward the side of products. In most liquid solutions, the values of activation volume are typically in the range of −30 to 30 cm^{3}mol^{-1}.[28] Thus, pressure changes in the kilobar range are required to achieve large variations in rate constant. For example, the coupling of iodobenzene with ethyl acrylate hardly occurred at 298 K and atmospheric pressure, but the conversion reached nearly 100% at 1 GPa.[29] Moreover, for the palladium catalyzed cross-coupling of iodobenzene with 2,3-dihydrofuran, very high pressures amounting to 8 kbar has been reported to increase the turnover number in organic solvent

systems, owing to an improved lifetime of the catalysts.[30,31] Unlike the Heck reaction in normal organic solutions, small pressure changes can make substantial variations in the rate constant in supercritical fluids because the absolute value of activation volume is in the orders of liters per mol.[16] As a result, for the Heck coupling reaction in scH$_2$O, increasing the pressure from 20.3 to 32.1 MPa would elicit 40% augmentation in the conversion.

The $E:Z$ ratio was independent of the density, which suggests that there is no large difference in partial molar volume between the two transition states. The slight decrease in the selectivity to terminal olefin might be due to that the transition state of internal olefin having a relatively larger dipole moment than that of terminal olefin. Therefore, the internal olefin transition state would interact more strongly with the solvent and be favored as the solvent density increased.

Effect of reactor material: We had conducted the scH$_2$O reaction under certain conditions using iron-base stainless steel (SUS 316) and nickel-base alloy (Inconel 625) reactors with the same volume. The conversion and the yields of coupling products are shown in Table 2. For both reactors, the conversion of styrene reached 70%, while the yield of stilbene was 49.3 and 55.6%, respectively. Moreover, there was no discernible difference between the two reactors with respect to the selectivity to the coupling products. High regioselectivity towards the internal olefins **1** was observed and the ratio of *trans*- to *cis*-stilbene was approximately 81:19. Thus, the effect of the reactor wall is considered to be negligible. Furthermore, after extracting the products, both organic and water phases were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The concentrations of nickel, iron, chromium, and molybdenum in both phases were lower than the identification limitation. Hence, the possibility of catalytic effect of metal content of the reaction solution was also excluded.

Table 2. Results of Heck coupling reaction using different reactors.[a]

Reactor	Conversion [%]		Yield [%]			$E:Z$
	styrene	iodobenzene	**1**	**2**	**3**	
SUS 316	71.3	67.8	49.3	2.1	2.5	81:19
Inconel 625	72.5	77.5	55.6	2.3	3.0	81:19

[a] 650 K, 25 MPa, in the presence of KOAc.

The role of water: Two possibilities for the role of water responsible for the noncatalytic Heck coupling in scH$_2$O, that is, ion and water-catalyzed mechanisms have been considered. First the supposition implicit in this ion mechanism is that ionic species such as proton, H$_3$O$^+$, and hydroxide ion originated from water molecules can be activated under supercritical state and promote the coupling reaction. Our IR[25] and Raman[27] measurements of the hydrogen bonding of sub- and supercritical water suggest that the tetrahedral configurations disappear near the critical point, where the monomer or dimer or trimer structures are predominant. This result was further supported by a recent first-principle molecular dynamics study.[26] The ion product (K_w) monot-

onically decreases with increasing temperature above 573 K at 25 MPa,[32] and so the proton or hydroxide ion (OH$^-$) concentration anticipated from the K_w concept is not so high near the critical temperature at 25 MPa. However, in scH$_2$O the OH$^-$ or proton adjacent to substrate molecules cannot migrate throughout the hydrogen-bond network near the critical point. At least ten water molecules are considered to be required for appreciable interaction between the hydrogen-bonding network and proton.[33] Moreover, the local proton and OH$^-$ concentrations would be high when the transferring ions cannot escape. An increase in local proton or hydroxide ion concentration around substrate molecules might induce the enhancement in the rate of reaction. Hence the OH$^-$ or proton species could react spontaneously with substrate molecules to form a transient intermediate owing to the lower activation energies for bond cleavage and formation. For the coupling reaction between styrene and phenyl halide in scH$_2$O, it was proposed that the OH$^-$ removes the β-H of styrene, giving a carbanion. Then the nucleophilic carbanion attacks iodobenzene at the electrophilic carbon, resulting in the formation of coupling products.

The second possibility is the direct participation of water molecules through a transition state involving one or two water molecules as shown in Scheme 2.
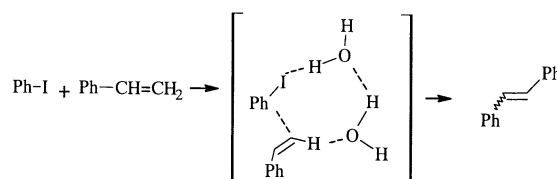
Scheme 2. Formation of stilbene via a transition state involving two water molecules.

In the above water-catalyzed model, water molecules make a hydrogen-bond ring network with the substrate molecules, and then play a role of a catalyst transferring a proton along the locally formed hydrogen-bond network. Stilbene would be formed via a six-membered or eight-membered ring transition state, which greatly lowers the energy for bond cleavage and formation. A similar water-catalyzed mechanism has been proposed for the conversion of 2-nitroaniline to benzofurazan[34] and the decarboxylation of acetic acid derivatives[35] in subcritical water. Moreover, the role of water in the intermolecular hydrogen transfer has been supported by quantum chemistry calculations. In general, water molecules make the geometry of the transition state species less strained, thereby facilitating the formation and cleavage of bonds that lead to the products. Specifically, for the dehydrogenation reaction of ethanol to acetaldehyde, the inclusion of two water molecules in the transition state reduces the activation barrier by ~34 kcal mol^{-1} and increases the rate constant by nine orders of magnitude,[36] compared with those in the absence of water. Water also facilitates the decomposition of formic acid[37,38] and the aldol condensation of an aldehyde (formaldehyde or acetaldehyde) with vinyl alcohol.[39] Thus, it was

postulated that stilbene might be formed through a water-bridged transition state.

It was further confirmed that phenol is obtained over 50% yield by hydrolysis of iodobenzene in scH$_2$O. As for the formation of phenol, hydrolysis of chlorobenzene in NaOH solution under high temperatures (633–663 K) and high pressures (28–30 MPa) has been used commercially for the production of phenol.

From the above results, it may be concluded that four competitive reaction processes take place in scH$_2$O: hydrogenation, polymerization of styrene, coupling reaction of styrene with iodobenzene, and hydrolysis of iodobenzene to phenol. The selectivity would be controlled by the ionic behavior of water. The hydrogen halide formed during the reaction facilitated the polymerization of styrene besides the hydrogenation of both styrene and the coupling products. The presence of a base was a key factor for the unusual selectivity to stilbene in scH$_2$O. The cation of the base might promote the removal of iodine via an intermediate composed of an ion–dipole bond between cation and iodine. The addition of a relatively mild base, such as NaOAc and KOAc, could scavenge the hydrogen halide and promote the cross-coupling reaction. When a strong base is use, the concentration of OH$^-$ was high, thus the hydrolysis of iodobenzene was favored.

Conclusion

The Heck coupling of styrene with iodobenzene occurred in scH$_2$O with high regioselectivity even in the absence of catalyst. Both the choice of base and the reaction conditions had a significant effect on the conversion and the product selectivity. High yields of coupling products were obtained in the presence of mild bases such as KOAc or NaOAc. The conversion and the yields of coupling products increased with increasing temperature, reaching a maximum at 650 K near the critical temperature of water, and then decreased as the temperature was further increased. Water density had a significant influence on the reaction rate, showing nearly 30% augmentation with an increase in density from 0.45 to 0.56 g cm^{-3}, but had minor effect on the products selectivity. Supercritical water might promote the Heck coupling reaction either through an ion reaction process or by taking part in the formation of cyclic transition state involving one or two water molecules.

Experimental Section

All reactants and solvents were obtained from Wako pure or Aldrich and were used as-received without further purification. Triply distilled high-purity water was used for all experiments and deoxygenated by N$_2$ gas prior to use.

The experiments were performed by using an Inconnel 625 batch reactor system with an internal volume of 10.2 cm^3. A predetermined amount of substrates and base (1.0 mmol each) and water were loaded into the reactor under argon atmosphere. The reactor vessel was immersed and vigorously shaken in a molten salt bath. The heat-up time to raise the reactor temperature from 293 K to the reaction temperature was within 30 s and

the temperature was controlled within ±2 K. After the desired reaction time of 10 min had elapsed, the reactor was removed from the molten salt bath and rapidly quenched in an ice/water bath. All of the products were extracted with dichloromethane and identified by GC-MS and pure compounds, and routine quantitative analysis was done using a 30 m DB-WAX capillary column on a HP-6890 gas chromatograph equipped with a FID detector, with response factors determined from the analysis of standard compounds. The product yield was calculated based on styrene. Each data point was measured at least two times and the errors in the conversion and yields were less than 5%. The thermodynamic and transport properties of the system at various conditions were determined using steam table.[40]

Acknowledgement

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