Insight into PdCl₂(bipy) Complex as an Efficient Catalyst for Heck Reaction and Kinetic Investigations in Homogeneous Medium¹

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Abstract—PdCl₂(bipy) complex (bipy = 2,2'-bipyrydine) efficiently catalyzes the vinylation of aryl halides. The activity of this catalyst for the Heck reactionwas demonstrated for a variety of aryl halides and olefins in the presence of different organic and inorganic bases. The catalyst is stable under the reaction conditions and no degradation was observed. The kinetics of the Heck coupling of styrene with iodobenzene using the PdCl₂(bipy) complex with potassium acetate as a base was studied over a temperature range of 393-413 K in 2-nitro-2-methyl-1-propanol medium. An empirical rate model has been proposed to fit the observed data and is found to be in good agreement with experimental results. The activation energy of the reactionwas found to be 98.70 kJ/mol.

DOI: 10.1134/S0023158413030051

The Heck reaction [1, 2]

 $\begin{array}{c} \text{Ar} & \begin{array}{c} CH_{2} \\ CH \\ Olefin \end{array} + \begin{array}{c} Ar - X \end{array} \xrightarrow{PdCl_{2}(bipy)} Mr \\ Aryl halide \end{array} \xrightarrow{IS0^{\circ}C} CH \\ Base \\ Product \end{array} + \begin{array}{c} \oplus \\ BHX \\ BHX \\ BhX \\ BhX \\ Product \\ (bipy = 2,2'-bipyrydine, \\ NMP = 2-nitro-2-methyl-1-propanol) \end{array}$

bipy = 2,2'-bipyrydine, NMP = 2-nitro-2-methyl-1propanol) is an important class of C-C coupling reactions [3, 4], as it is tolerant to many functional groups [5]. The use of Pd-phosphine complexes for the Heck reaction has been reported in a number of studies [6]. These catalysts are known to suffer decomposition in the course of the reaction involving the palladacycle catalysts, which are reportedly more stable than the monodentate phosphine complexes [7]. Hence, the development of stable phosphine-free catalysts resistent to the reaction temperatures encountered in the Heck reaction would be an important achievement. Compared to the phosphine modified Pd catalysts, the Pd complexes incorporating nitrogen-containing ligands although equally active have received less attention [8-11]. There are still few reports on the kinetics of Heck reactions using Pd complexes with nitrogen containing ligands [12, 13].

Cabri et al. [8] have reported that Pd complexes of bidentate nitrogen ligand such as 1,10-phenanthroline derivatives are active for Heck reactions in N,N-dim-

ethylformamide (DMF) to give a 94% yield of product.Surprisingly, the same authors report very little or no activity for Heck reaction using the Pd complexes of 2,2'-bioxazoline or of 2,2'-bipyridine ligands. Tsai et al. [14] have used heterogenized palladium bipyridyl complex anchored on MCM-41 as an efficient and recyclable heterogeneous catalyst for Heck reactions with a Turn Over Number (TON) up to 10^6 . *n*-Butyl acrylate on reaction with *p*-bromoacetophenone was reported to give a 98% conversion in 16 h, but for iodobenzene 96 hare needed to achieve the same conversion level. There is however no study on the Heck reaction in a homogeneous medium using this Pd complex catalyst. The Heck reaction using iminophosphinepalladium (0) complexes in NMP [15], has been reported by Scrivanti et al. This catalyst is active only in an inert atmosphere and is easily poisoned in the presence of oxygen.

The kinetics of Heck reaction using Pd complexes has been reported in a few studies [16–21]. In general it has been observed that the catalyst activity has a positive dependence on olefin, aryl halide and the base. All these studies have been conducted with PdCl₂ or Pd-phosphine complexes. For the phosphine-free complexes only few studies on the kinetics exist. Rosner et al. [12] have investigated the kinetics of olefination of *p*-bromobenzaldehyde with butyl acrylate using a dimeric CN-palladacycle complex underthe dry conditions. They observed a firstorder dependence on olefin concentration and a zero order dependence on aryl halide (*p*-bromobenzaldehyde) concentration.

¹ The article is published in the original.

They also proposed an empirical rate model to predict the rate observed for the dimeric palladacycle complex with chelating nitrogen ligands [18]. Consorti and coworkers [13] reported a first order dependence with respect to Pd catalyst and a fractional order with respect to iodobenzene and methyl acrylate for the coupling of aryl halides with butyl acrylate and methyl acrylate using the CN-palladacycle. Van Strijdonck et al. [22] reported a first order kinetics on styrene and a zero order on iodobenzene concentration for Pd(dba) catalyst (dba = dibenzylideneacetone). An empirical rate equation was derived to fit the experimental data.

We report here the results of our investigation into the Heck reaction catalyzed by the PdCl₂(bipy) complex. Contrary to the reports mentioned earlier, the PdCl₂(bipy) complex as catalyst was very efficient for Heck reaction in polar solvents. This catalyst is stable and does not degrade to metallic Pd as most of the other catalysts reportedly do, permitting the reactions to occurat higher temperatures. This catalyst was applied for the coupling of a variety of aryl halides and olefins in the presence of different organic and inorganic bases in different solvents. Further, in order to understand the kinetics and mechanism of this reaction, the effect of the process parameters on the catalytic activity of the PdCl₂(bipy) complex was also investigated for the Heck coupling of styrene with iodobenzene in a temperature range of 393-413 K. An empirical rate model has been proposed which was found to fit the experimental data.

EXPERIMENTAL

PdCl₂, 2,2'-bipyridine, the olefins and aryl halides used were procured from "Aldrich" (USA) and used without any further treatment. The solvents were obtained from "Ms SDs Chemicals" (India). Bases and tetrabutyl ammonium bromide (**TBAB**) used were of analytical grade, purchased from "Loba Chemicals" (India).

A portion of the reaction mixture was periodically taken out from the round bottom flask and was analyzed for its contents by using a capillary gas chromatograph Agilent 6850 series (India) with flame ionization detector, on HP1 column with film thickness $0.25 \,\mu\text{m}$ (initial temperature 80°C, final temperature 250°C). Formation of stilbene was confirmed on GC by comparison with authentic standards. The identification of products of screening reaction was done using a GC-MS Agilent 6890N series equipped with 5973N mass selective detector. Besides the confirmation from GC-MS the identification was also confirmed with authentic samples of the products—*cis*and trans-stilbenes. No other products except these two were observed in the GC analysis. 1,1-Diphenyl ethylene can form as an additional product in the reaction, however it was not observed in this case because its concentration was very low (below the detectable limit).

The conversion of the aryl halide (Ar-X) and TON were calculated by using the following relations:

$$Conversion = \frac{\text{Initial amount of ArX(mole)-Final amount of Ar-X(mole)}}{\text{Initial amount of Ar-X(mole)}} \times 100,$$
 (1)

$$TON = \frac{Amount of product(mole)}{Amount of catalyst(mole)}.$$
 (2)

Procedure for Preparation of Catalyst

In a typical preparation, 0.234 g (1.33 mmol) 2,2'bipyridine was added into a 50 ml round bottom flask containing 10 ml methanol, 0.266 g (1.33 mmol) PdCl₂. The mixture was stirred at room temperature for 6 h. An orange yellow colored PdCl₂(bipy) complex precipitated, which was filtered and washed with methanol and then dried under vacuum. Practical yield of the complex was 0.440 g (88%). Characterization of the PdCl₂(bipy) complex was carried out by IR, NMR and the elemental analysis and was found to match with the reported values [23].

General Procedure for Screening Experiments

In a 25 mL two necked round bottom flask 2.2 mmol of olefin, 2 mmol of aryl halide, 2.0 mmol of base, and 0.002 mmol of $PdCl_2(bipy)$ catalyst were

added. TBAB (1% of base) was added as a phase transfer agent every time in case of inorganic bases. Then N-methyl-2-pyrrolidinone was added to make the volume to 10 mL. The reaction was carried out for 1 h at 150° C.

General Procedure for Kinetic Studies

In a 25 mL two necked round bottom flask styrene, iodobenzene, potassium acetate, TBAB (1% of base), and catalyst PdCl₂ (bipy) were added as per the requisite concentration. N-methyl-2-pyrrolidinone was then added to make volume to 10 mL. The reaction was carried out for 2 h at desired temperature in the range $120-140^{\circ}C$ (393–413K).

The kinetic experiments were carried out for a short duration, such that the conversion of liquid phase reactant was less than 20-25% to ensure differential conditions. It was generally observed that in this low conversion range, the rates of Heck reaction were constant. The experiments were found to be reproducible within an error of 2-4%. In each reaction, initial, intermediate and final samples were analyzed in order

Entry	Olefin	Ar–X	Base	Conversion, %	TON	Trans-/cis-stilbenes
1	Styrene	Iodobenzene	TBA + TBAI	68	552	87/13
2	»	»	Et ₃ N	66	543	87/13
3	»	»	KOAc + TBAB	59	482	88/12
4	»	»	TBA	56	455	84/16
5	»	»	NaOAc + TBAB	33	268	88/12
6	»	»	Piperidine	27	224	90/10
7	»	»	NaHCO ₃ + TBAB	23	190	89/11
8	»	*	Morpholine	20	161	86/14
9	»	*	MgOAc + TBAB	13	98	88/12
10	»	4-Bromo-acetophenone	KOAc + TBAB	89	733	95/5
11	»	4-Bromo-1-iodobenzene	*	70	573	88/12
12	»	4-Iodoanisole	*	58	477	86/14
13	»	4-Bromotoluene	*	54	445	92/8
14	»	2-Bromotoluene	*	45	370	80/20
15	Methylacrylate	Iodobenzene	*	100	887	100/0
16	Allyl alcohol	*	*	92	754	100/0
17	<i>n</i> -Butylacrylate	»	*	84	706	100/0
18	4-Vinylanisole	»	*	75	594	87/13
19	4-Methylstyrene	*	*	72	508	88/12
20	4-Chlorostyrene	»	*	48	401	92/8
21	3-Nitrostyrene	»	*	40	333	87/13

Table 1. Effect of various bases, olefins and aryl halides on activity of $PdCl_2$ (bipy) catalyst in Heck reaction in homogeneous medium

Note: Reaction conditions: olefin (2.2 mmol) + Ar–X (2.0 mmol) + catalyst (0.002 mmol) and base (2.0 mmol) along with TBAB (0.02 mmol) (if inorganic bases used) in NMP (10 mL). Temperature 150°C, time 1 h, selectivity to stilbene 96–100%.

to check the material balance. Following this procedure, the effect of catalyst, styrene, iodobenzene and KOAc concentrations on the rate of Heck reaction was studied at 393–413 K.

RESULT AND DISCUSSION

Screening Studies

Preliminary reactions and solvents screening studies. Since solvents are known to play a very important role in the activity and selectivity of homogeneous catalysts, the activity of PdCl₂(bipy) catalyst for Heck coupling of styrene and iodobenzene was investigated in different solvents, in the presence of PdCl₂(bipy) catalyst with KOAc base and TBAB promoter (1% of KOAc) at 150°C and a reaction time of 1 h. The solvents screened were polar solvents having a boiling point of above 120°C as it is well known that certain Pd complexes require minimum temperatures for reaction to proceed [15, 24, 25]. The highest activity was observed in NMP solvent with a TON of 482. The reaction was also facilitated in other polar solvents like N,N-dimethylformamide (DMF) and N,N-dimethylsulfoxide (DMSO) where TON's of 369 and 290 respectively were obtained at a given reaction temperatures. Since NMP was found to be the best solvent for the reaction, all further studies were conducted in this solvent.

Screening of base. A detailed study on the influence of bases on the activity of PdCl₂(bipy) catalyst for the vinvlation of iodobenzene with styrene was conducted using NMP solvent. The bases studied included aliphatic organic bases and monovalent or divalent inorganic bases. TBAB was added as a phase transfer agent (1% of base) in case of inorganic bases. The results are shown in Table 1 (Entries 1-9). Organic bases were found to give better activity, since they are soluble in the organic solvent. Inorganic bases gave relatively lower activity [26, 27], which increases only in the presence of a phase transfer agent like TBAB [28]. Aliphatic bases like triethylamine (Et₃N) and tributylamine (TBA) were found to be more active than piperidine and morpholine, suggesting that tertiary amines are more reactive than secondary amines. Between Et₃N and TBA, the former is more active probably because it is sterically less hindered compared to TBA. Potassium acetate was found to have better activity compared to other inorganic bases. The role of TBA salt is not restricted to a phase transfer catalyst [28] as addition of a quaternary ammonium salt enhances the activity even for organic bases, which are miscible with the reaction solvents (Table 1, Entry 1). The Jeffrey

			Reaction					
Catalyst	Styrene	Iodobenzene	Base	TBAB (1% of base)	<i>T</i> , K (°C)	Solvent	volume, cm ³	Time, min
$(1.0-5.0) \times 10^{-4}$	0.11-0.44	0.10-0.40	0.10-0.40	$(1.0-4.0) \times 10^{-3}$	393–413 (120–140)	NMP	10	120

Table 2. Range of conditions studied for the kinetics of Heck reaction in NMP medium

effect reported earlier shows that in the presence of TBAB the rates are enhanced [28]. The stereoselectivity of the product for all the bases—organic and inorganic and regardless of their strength and size—was found to be more or less the same for the iodobenzene and styrene system. For styrene and iodobenzene system 86–90% *trans*-stilbene was formed with the rest being *cis*-stilbene, unlike that reported by Beller and Riermeier for other Heck reactions using palladacycle complexes [29]. In their study it was observed that the amine changes the stereoselectivity of coupling reaction of aryl bromides with butyl methacrylate at 135–140°C catalyzed by cyclometallated palladium complexes, *via* coordination to palladium during the catalytic cycle.

Screening of aryl halides. The activity of PdCl₂ (bipy) was assessed for the coupling of styrene with different aryl halides. The results are presented in Table 1 (Entries 3, 10-14). Halides with strong electron withdrawing substituents showed a high activity, whereas those with electron donating substituents were poor catalysts for this reaction. This observation is in accordance with general trends observed for Pd complex catalyzed Heck reactions [30]. For the reaction of 4-bromoiodobenzene only the iodosubstituent underwent reaction to produce 4-bromostilbene. Since iodoarenes are reportedly more active than the bromoderivatives, this behavior is expected. Also, no further reaction of the 4-bromostilbene was observed within the reaction period. This was confirmed by GC-MS, wherein no double Heck reaction product was observed.

Screening of olefins. The results presented in Table 1 (Entries 3, 15-21) show the activity of PdCl₂ (bipy) catalyst for the vinylation of iodobenzene with different olefins. The olefins with strong electron withdrawing substituents gave poor activity whereas those with electron donating substituents were more active. This trend is opposite to that observed for the aryl halides. In the reported Heck reaction mechanism, addition of the olefin to the Pd(II) species occurs to form a π -complex. Electron rich olefins are expected to react faster than those with electron withdrawing substituents for this step, thereby enhancing rates. It can also be seen from Table 1 (Entries 15-17) that the stereoselectivity of the aliphatic olefins shows 100% trans-product, whereas the styrene derivatives show some *cis*-product formation (8-12%). The results obtained in the screening studies show that the presence of electron withdrawing group attached to the aryl halide and an electron donating substituent on the olefin result in higher activity.

Kinetic Study

The kinetics of the Heck reaction of styrene with iodobenzene in the presence of $PdCl_2(bipy)$ was investigated. Such a study has not been reported so far and would help elucidate the mechanism and the similarities with Pd-phosphine catalyzed system, for which kinetics studies have been reported.

Preliminary results. Since the main objective of this work was to investigate the kinetics, it was necessary to first ensure the material balance and reproducibility of experiments. For this purpose, few experiments were carried out in which the amount of substrates consumed and the product formed were compared. A typical concentration time profile for a reaction pertains to the Heck coupling of styrene and iodobenzene in the presence PdCl₂(bipy) catalyst and KOAc as a base at 413 K. It was observed that the material balance of substrates, i.e. styrene and iodobenzene, consumed was consistent with the amount of stilbenes formed. Also, in the range of conditions covered in this work, only *trans*- and *cis*-stilbene was formed which was confirmed by GC–MS.

For the purpose of kinetic study, several experiments were carried out at different styrene, iodobenzene, base and catalyst concentrations, in the temperature range of 393-413 K. In each case the amount of stilbene formed, as a function of time was observed. It was observed that in the initial period of reaction, the rate of reaction was almost constant. From these data the rates of Heck reaction (*r*) were calculated as the slope of plot of concentration of stilbene formed (kmole) in m³ of total volume vs time (s). These were essentially initial rates of reaction, observed under differential conditions for various concentrations of aryl halides at 393 K.

Based on observations of preliminary experiments, the kinetics of Heck reaction was investigated under the range of conditions given in Table 2.

Effect of catalyst concentration on activity. The effect of catalyst concentration on the rate of Heck reaction was investigated at an iodobenzene concentration of 0.20 kmol/m³, styrene concentration of 0.22 kmol/m³ and KOAc concentration of 0.20 kmol/m³ (with TBAB 1% of KOAc) at tempera-



Fig. 1. Experimental and predicted rates for effect of catalyst concentration at temperatures 413 (*1*), 403 (*2*) and 393 K (*3*): points—experimental data, lines—predicted rates. Reaction conditions: concentrations of styrene, iodobenzene and KOAc—0.22, 0.20 and 0.20 kmol/m³, respectively, TBAB—1% of base, NMP—10 mL.

tures of 393–413 K in NMP. The results are presented in Fig. 1.

The rate was found to have a first order dependence on the catalyst concentration. The well-known mechanism [31] of Heck reaction is shown in Fig. 2. With enhancement of catalyst concentration there is a commensurate increase in the active species. In a large number of Pd catalyzed Heck reactions, a first order tending to a zero order is reported. The partial order dependence at higher catalyst concentrations has been attributed to the formation of inactive dimeric species. From the observed data, it appears that the formation of such dimeric species does not occur with PdCl₂ (bipy) catalyst in the range of conditions investigated. This leads to the observed first order dependence.

Effect of iodobenzene concentration on activity. The effect of iodobenzene concentration on activity was investigated at a styrene concentration of 0.22 kmol/m³, KOAc concentration of 0.20 kmol/m³ (with TBAB 1% of KOAc) and catalyst concentration of 2.0×10^{-4} kmol/m³ at temperatures of 393–413 K in NMP. The results are presented in Fig. 3. The rate was found to increase with a first order with respect to iodobenzene concentration at 393 K, but at higher temperatures, a fractional order was observed. A positive order with respect to iodobenzene is expected from the mechanism (Fig. 2, step a). With increasing

iodobenzene concentration the interaction of iodobenzene with catalyst species increases, thereby increasing the rate. This step is reported to be the ratedetermining step in Heck chemistry.

Effect of styrene concentration on activity. The effect of styrene concentration on activity was investigated at iodobenzene concentration of 0.20 kmol/m³, KOAc concentration of 0.20 kmol/m³ (with TBAB 1% of KOAc) and catalyst concentration of 2.0 × 10^{-4} kmol/m³ at temperatures of 393–413K in NMP. The results presented in Fig. 4 show a first order dependence on styrene concentration at all the temperatures studied. Addition of olefin to catalyst complex leads to formation of π -complex (Fig. 2, step b₁) in an equilibrium reaction followed by σ -complex formation (step b₂ in Fig. 2). This being an equilibrium reactional order is observed, particularly at higher temperature.

Effect of KOAc (base) concentration on activity. The effect of base concentration on activity was investigated at styrene concentration of 0.22 kmol/m³, iodobenzene concentration of 0.20 kmol/m³ and catalyst concentration of 2.0×10^{-4} kmol/m³ at temperatures of 393-413 K in NMP. The TBAB added was proportional to base concentration (1% w/w concentration with respect to base). The results are presented in Fig. 5. The rate was found to increase with increase in base concentration in the lower range of potassium acetate concentrations. However, on further increase, zero order dependence was observed. This trend is expected, since the solubility of the base in NMP is limited and once saturation is reached, no further rate enhancement is observed. In general, the quaternary ammonium salt added serves as a phase transfer agent to enhance the solubility. Other studies on the kinetics of Heck reactions also show the dependence of rate on base concentration [21, 32].

Kinetic models. From the above study the rate was found to have a first order dependence on catalyst concentration, a first order tending towards a zero order dependence for base concentration and a partial positive order dependence for styrene and iodobenzene concentrations where at high iodobenzene concentration and empirical rate equations at 413 K a zero order was observed. The data were used to develop, based on the observed trends. Four different forms of rate equations were discriminated and the results are presented in Table 3.

The rate parameters k, K_A , K_B and K_D (A, B and D means olefin, Ar–X and base, respectively) were evaluated at 393, 403 and 413 K by fitting the observed experimental rate data to the different models using nonlinear regression analysis and an optimization routine based on Marquardt's method [33]. The values of rate parameters at different temperatures are presented in Table 3. The rate equation best fitting the data was chosen based on the values of Φ_{min} , which is defined as in equation



Fig. 2. Mechanism of Heck reaction.

$$\Phi_{\min} = \sum_{i=1}^{n} (r_{\exp} - r_{pre})^{2}, \qquad (3)$$

where r_{exp} is the rate observed experimentally, r_{pre} is the predicted rate using nonlinear regression analysis and n is number of data points.

Besides Φ_{\min} the thermodynamic considerations regarding equilibrium constants K_A , K_B and K_D also were relied upon to choose the rate model, best representing the observed kinetic data. The analysis of all the models shows absence of negative values for the constants, however in case of model I and model II the values of rate constants k are not consistent with temperature and hence they were not considered. Comparison of the values of Φ_{\min} obtained for models III and IV shows that model IV gives superior fit and hence this model is preferred. The model chosen to best represent the kinetics observed is as follows:

$$r = \frac{k[A][B][C][D]}{(1 - K_{A}[A])(1 + K_{B}[B])(1 + K_{D}[D])}$$
(4)

(here C is catalyst).

This model was found to predict the rate data within an error of $\pm 3\%$ (which is within the range of experimental error). A comparison of the experimental rates with the predicted rates using model IV at three different temperatures, i.e. at 393, 403 and 413 K, is shown in Fig. 6, which also indicates a good agreement between the experimental and predicted

KINETICS AND CATALYSIS Vol. 54 No. 3 2013



Fig. 3. Experimental and predicted rates for effect of iodobenzene concentration at temperatures 413 (*1*), 403 (*2*) and 393 K (*3*): points—experimental data, lines—predicted rates. Reaction conditions: concentrations of styrene and KOAc—0.22 and 0.20 kmol/m³, respectively, TBAB—1% of base, concentration of catalyst—2.0 × 10^{-4} kmol/m³, NMP—10 mL.



Fig. 4. Experimental and predicted rates for effect of styrene concentration at temperatures 413 (*I*), 403 (*2*) and 393 K (*3*): points—experimental data, lines—predicted rates. Reaction conditions: concentrations of iodobenzene and KOAc—0.20 kmol/m³ each, TBAB—1% of base, concentration of catalyst— 2.0×10^{-4} kmol/m³, NMP—10 mL.

rates. Figures 1 and 3–5 also show the comparison of experimental and predicted rates for the varying concentration of catalyst, iodobenzene, styrene and base respectively at temperatures of 393-413 K. The activation energy (E_a) was evaluated from the Arrhenius



Fig. 5. Experimental and predicted rates for effect of base concentration at temperatures 413 (*I*), 403 (*2*) and 393 K (*3*): points—experimental data, lines—predicted rates. Reaction conditions: concentrations of styreneand iodobenzene—0.22 and 0.20 kmol/m³, respectively, TBAB—1% of base, concentration of catalyst 2.0×10^{-4} kmol/m³, NMP—10 mL.

plot and found to be 98.70 kJ/mol. The constants K_A , K_B and K_D were found to be dependent on a temperature. K_D was found to decrease negligibly with a temperature while K_A and K_B showed a strong positive dependence on a temperature.

Model	Rate equation		k, m ³ kmol ⁻³ s ⁻¹	K _A	K _B	K _D	$\Phi_{\min} imes$	R^2
WIOdel				m ³ /kmol			10 ¹²	Λ
Ι	$r = \frac{k[A]^{0.7}[B]^{0.6}[C][D]}{1 + K_{\rm D}[D]}$	393	9.15	_*	_*	89.6	2.83	0.9372
		403	165	_	_	912	2.51	0.9735
		413	9.31	_	_	21.8	7.28	0.9698
II	$r = \frac{k[\mathbf{A}][\mathbf{B}][\mathbf{C}][\mathbf{D}]}{1 + K_{\mathbf{D}}[\mathbf{D}]}$	393	937	_	_	3420	1.41	0.9702
		403	1550	_	_	3120	9.56	0.9117
		413	17.2	_	_	13.5	41.8	0.8606
III	$r = \frac{k[A][B][C][D]}{(1 + K_{B}[B])(1 + K_{D}[D])}$	393	20.5	_	2.62×10^{-4}	70.2	1.38	0.9709
		403	84.2	_	2.34	10.5	5.03	0.9412
		413	47.8		4.51	19.9	1.29	0.9479
IV	$r = \frac{k[A][B][C][D]}{(1 + K_{A}[A])(1 + K_{B}[B])(1 + K_{D}[D])}$	393	20.7	2.63×10^{-3}	1.80×10^{-3}	70.6	1.38	0.9709
		403	42.0	0.636	8.52×10^{-2}	67.7	8.20	0.9226
		413	88.6	1.31	6.11	23.9	3.68	0.9850

Table 3. Comparison of different rate models proposed for Heck reaction in homogeneous medium

* Symbol "—" means that K_A (equilibrium constant of olefins) and/or K_B (equilibrium constant of Ar–X) values are not included in the formula.



Fig. 6. Plot of *r* predicted vs. *r* experimental at 393, 403 and 413 K.

Thus, PdCl₂(bipy) catalyst is found to be an active and stable catalyst for the Heck reaction. This catalyst is stable in polar solvents and does not decompose to metal even at a temperature of 150°C. Detailed investigations on the activity of PdCl₂(bipy) catalyst for Heck reaction in homogeneous medium have been conducted for different solvents, olefins, aryl halides and bases. The results show that electron withdrawing groups attached to the aryl halide and electron donating substituents on olefin enhance the rates. Organic bases were found to be more efficient for the reaction whereas inorganic bases showed poor activity due to solubility limitations. The kinetics of the coupling reaction of styrene and iodobenzene in the presence of KOAc and PdCl₂(bipy) catalyst has been investigated. The rate was found to have a first order dependence on catalyst and a partial positive order dependence on styrene and iodobenzene concentrations. A first order tendency towards a zero order dependence was observed for base concentration. The trends were found to be quite close to those observed for the Pd-phosphine catalyzed reaction except for the dependence on catalyst concentration. An empirical rate model has been proposed to fit the observed data. The activation energy was found to be 98.70 kJ/mol.

ACKNOWLEDGMENTS

S.V. Jagtap thanks University Grant Commission of India for PhD fellowship.

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KINETICS AND CATALYSIS Vol. 54 No. 3 2013

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