



Kinetics of arylation of 3-bromo-benzophenone with *n*-butylacrylate using NC palladacycle catalyst

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ABSTRACT

The kinetics of arylation of *n*-butylacrylate (*n*-BA) with 3-bromo-benzophenone (BBP) using a monomeric palladacycle complex [Pd(ppy)(PPh₃)(OTs)] (ppy = 2-phenylpyridine) catalyst has been studied. The effect of concentration of the substrate, base (NaOAc), and catalyst was studied at three different temperatures (413–433 K). The rate was found to be first order with respect to catalyst, first order tending to zero order with respect to *n*-butylacrylate and NaOAc concentrations. The rate passed through a maximum with variation of BBP concentration. The observed results have been explained on the basis of formation of Pd species (PdX₂, PdX₃⁻, PdX₄²⁻, and Pd₂X₆²⁻) which are inactive for the Heck reaction. Various empirical rate equations were considered to fit the rate data and the best fitting model has been selected. The rates predicted by model were found to be in good agreement with the observed experimental data.

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1. Introduction

The reactions involving the use of acrylate as an olefin source in Heck coupling reactions are very important, as the products are industrially useful cinnamates. The cinnamates obtained are used as UV absorbers, antioxidants, and as intermediates in perfumery, pharmaceutical, and dye industry. For example octyl *p*-methoxy-cinnamate is a sunscreen agent obtained by the reaction of *p*-bromoanisole with 2-ethylhexylacrylate [1]. The coupling of olefin with aryl halide can be accomplished by a plethora of palladium catalyst precursors, among these catalytic processes, palladacycles including CP, CN, CS, PCP, SCS, NCN, are some of the most investigated catalyst precursors [2,3]. The mechanism of this reaction using palladacycle catalysts is often discussed. Two mechanisms have been reported for the Heck reaction one following Pd(II)/Pd(IV) mechanism and the other with Pd(0)/Pd(II) mechanism [4,5]. It is now accepted (based on inhibition tests using Hg, Dibenzo[a,e] cyclooctatetraene, PVPy) [6,7] that in most of the cases, the catalytically active species involved in these reactions are based on Pd(0) and that the reaction proceeds through

a Pd(0)/Pd(II) catalytic cycle, whatever the nature of the catalyst precursor. Significant progress has been made in the development of catalytic systems for Heck catalysis over the last 30 years; it is surprising that detailed kinetic studies have been rarely carried out for these important reactions. Zhao et al. [8] have studied the kinetics of the Heck reaction of iodobenzene with methylacrylate using Pd(OAc)₂/PPh₃ as the catalyst and found that the rate of the reaction has a fractional order dependence with respect to the Pd(OAc)₂ concentration, first order with respect to iodobenzene concentration, and a first order tending to zero with respect to methylacrylate concentration. With respect to triethylamine concentration they have observed that the rate passes through a maximum with increasing triethylamine concentration. van Leeuwen and co-workers [9] have reported kinetics of iodobenzene and styrene using bulky monodentate phosphorus ligands, which showed the reaction to be first order with respect to styrene, zero order with respect to iodobenzene concentration, and half-order with respect to catalyst concentration. Blackmond and co-workers [10] have studied the kinetics of Heck reaction of *p*-bromobenzaldehyde and *n*-butylacrylate using dimeric NC palladacycle complex [$\{Pd(C_6H_4CH=NC_6H_5)(O_2CMe)\}_2$] as the catalyst precursor. Authors have reported a fractional order dependence of the rate on the catalyst concentration, first-order dependence on the concentration of olefin, and zero order on halide concentration. Dupont and co-workers [7] have reported the kinetics of iodobenzene and *n*-butylacrylate using NC palladacycle complex [Pd{N=C(C₆H₅)C(Cl)CH₂NMe₂(μ-Cl)}₂] as a catalyst precursor. They found first-order dependence of reaction

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rate with respect to palladacycle concentration and a zero-order dependence on NaOAc and Bu₄NBr concentrations. Chaudhari and co-workers [11] have described the kinetics of vinylation of 4-bromoacetophenone with *n*-butylacrylate using Herrmann palladacycle catalyst. The rate was found to be first order with respect to 4-bromoacetophenone, fractional order with the catalyst concentration, and first order tending to zero order with NaOAc concentration. The rate passed through a maximum with variation of TBAB and *n*-butylacrylate concentrations. As evident from the literature, the majority of the kinetic studies have been done using the dimeric palladacycles as catalysts. In many cases, the kinetics was investigated at only one temperature [7,9,10]. There are no reports on the kinetics using the monomeric palladacycle as the catalyst precursor. In homogeneous catalytic systems, the reactions are extremely sensitive to the temperature and hence detailed kinetic studies at different temperatures are necessary to understand the rate behavior as well as the mechanism of the reaction.

In this work, experimental results on kinetics of arylation of *n*-butylacrylate (BA) with 3-bromo-benzophenone (BBP) using a monomeric palladacycle complex Pd(ppy)(PPh₃)(OTs) (ppy = 2-phenylpyridine) catalyst have been presented. The effects of concentrations of the substrate, base, and catalyst on the initial rate of the reaction have been studied at three different temperatures (413–433 K). Based on the kinetics data obtained rate equations have been proposed and possible reaction pathway discussed.

2. Experimental

2.1. Chemicals and apparatus

Bases potassium acetate (KOAc), sodium acetate (NaOAc), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃) and the solvents *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) were procured from SRL. 2-Phenylpyridine, palladium acetate [Pd(OAc)₂], triphenyl phosphine, *p*-toluene-sulphonic acid were procured from Sigma–Aldrich. BBP was synthesized according to the literature procedure [12]. Palladium complex [Pd(ppy)(PPh₃)(OTs)] was prepared as per the literature reports [13].

2.2. Experimental procedure

Heck coupling reactions were carried out in a 50 ml two necked stirred glass reactor equipped with a condenser and a magnetic stirrer. In a typical experiment 3.43 mmol of BBP, 5.1 mmol of butylacrylate, 5.1 mmol of sodium acetate were taken in NMP to make total volume 25 ml in a 50 ml stirred glass reactor. The glass reactor was immersed in an oil bath preheated and controlled at a pre-decided temperature and switched the stirrer on. Stock solution of the catalyst in NMP (1.732 μmol of palladacycle) was added to the reactor with a syringe after the desired temperature was attained and the reaction was initiated. Samples were taken at the regular intervals of time to monitor the progress of the reaction. The reactions were carried out for a fixed time duration by varying initial sets of conditions.

3. Results and discussions

A few preliminary experiments were carried out on the arylation of BBP with butylacrylate using palladacycle catalyst to find a suitable solvent and base for the reaction system and to ensure material balance of the reaction. This is important to ensure reliable data for interpretation of the reaction kinetics.

Table 1
Effect of solvent on the reaction of BBP and *n*-BA.

Entry	Solvent	Time (h)	Conv. (%)	TOF (h ⁻¹)
1	DMF	2.5	85	850
2	DMAc	2	90	1125
3	NMP	2	98	1225

Reaction conditions: BBP, 3.43 mmol; BA, 5.1 mmol; NaOAc, 5.1 mmol; Pd(ppy)(PPh₃)(OTs), 0.04 mol%; solvent, total volume, 25 ml; T, 423 K.

3.1. Effect of solvents on the arylation of *n*-BA with BBP

Solvents play a critical role in making the reaction homogeneous and allowing the molecular interactions to be more efficient. Since Heck reaction mainly involves ionic components, and involves the exclusion of acid (the role of the base is to regenerate the active palladium complex by capturing the acid HBr and to complete the catalytic cycle), polar aprotic solvents are usually the candidates of choice [4]. From the literature reports it was observed that the non-polar solvents give poor activity with inorganic bases [11]. Hence, the effect of different polar solvents viz., DMF, NMP and DMAc on the reaction rate was studied and the results are summarized in Table 1. The activity expressed as TOF was found to be higher using NMP as a solvent. Best results were obtained using NMP as a solvent and hence further experiments were carried out using NMP as a solvent.

3.2. Effect of different bases

The choice of a base can have a crucial effect on the rate and product distribution of Heck reactions [11,14]. Beller and Riermeier have reported the enhancement in the Heck product for coupling of 4-bromofluorobenzene with butylmethylacrylate by changing base sodium acetate with tributylamine [14]. Strong bases such as NaOH and KOH decompose *n*-butylacrylate to give *n*-butanol and acrylic acid [11] and hence were not used in this work. The results of the reactions carried out with inorganic bases are shown in Table 2. Sodium acetate (TOF: 1225) and potassium acetate (TOF: 1250) showed highest activity among the bases evaluated (the TOF has been calculated for the overall reaction time). However, because of hygroscopic nature of potassium acetate, further work was carried out using sodium acetate as a base. A typical concentration–time profiles for the reaction of BBP and *n*-BA (Scheme 1) using NMP as the solvent and NaOAc as the base is presented in Fig. 1, which clearly shows a very good mass balance between the amount of reactant BBP consumed and the product cinnamate formed.

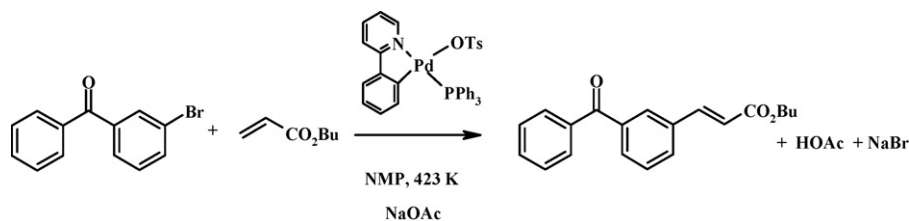
3.3. Kinetic analysis

The kinetics of arylation of *n*-BA with 3-bromo-benzophenone with NC palladacycle Pd(ppy)(PPh₃)(OTs) as the catalyst precursor was investigated in the presence of NaOAc as a base using NMP as a solvent. For this purpose, several experiments were carried out in the range of conditions shown in Table 3. The progress of

Table 2
Effect of inorganic bases on the reaction of BBP and *n*-BA.

Entry	Base	Time (h)	Conv. (%)	TOF (h ⁻¹)
1	NaOAc	2	98	1225
2	KOAc	2	100	1250
3	Na ₂ CO ₃	2	60	750
4	K ₂ CO ₃	2	80	1000

Reaction conditions: BBP, 3.43 mmol; BA, 5.1 mmol; base, 5.1 mmol; Pd(ppy)(PPh₃)(OTs), 0.04 mol%; solvent (NMP), total volume, 25 ml; T, 423 K.



Scheme 1. Heck reaction of BBP and *n*-BA catalyzed by Pd(ppy)(PPh₃)(OTs).

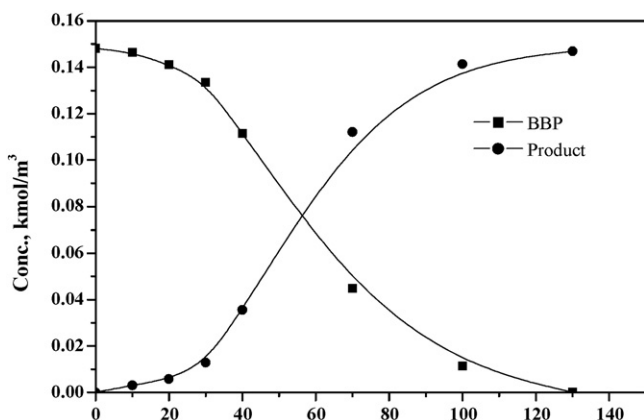


Fig. 1. A typical concentration–time profiles in arylation of BA with BBP. Reaction conditions: BBP, 3.43 mmol; BA, 5.1 mmol; NaOAc, 5.1 mmol; Pd(ppy)(PPh₃)(OTs), 0.04 mol%; solvent (NMP), total volume, 25 ml; T, 423 K; time, 2.1 h.

the reaction was monitored by analysis of concentrations of reactants/products as a function of time. The results revealed that the reaction exhibits active catalyst formation period (the conversion of BBP was ~5% during the first 10–12 min, after this period there is rapid increase in the conversion of BBP). It is likely that during this time the actual catalytic species are generated from NC palladacycle precursor [Pd(ppy)(PPh₃)(OTs)]. Hence, the catalytically active species is formed during the initial period of the reaction and afterwards consistent activity was observed. It may be noted that previous reports using dimeric palladacycle complexes displayed induction period [10]. As per these reports the dimer is converted to Pd(0) species and hence induction period is observed. In the case of Pd(ppy)(PPh₃)(OTs) the complex is present in Pd(II) state and needs to be converted to Pd(0) complex. This will involve the removal of PPh₃ and OTs ligands to form active species, thus leading to the active catalyst formation period observed. The exact mechanism of the formation of active catalytic species is not known. The reduction of Pd(II) to Pd(0) can be accomplished by either acetate ions (NaOAc) or olefin (*n*-butylacrylate) under reaction conditions [7]. The initial rates were calculated from the observed data on the consumption of 3-bromo-benzophenone as a function of time after the active catalyst formation period.

The dependence of the initial rate on various parameters was investigated at three different temperatures and the results are presented below.

Table 3
Range of parameters for kinetic studies.

Parameters	Units	Range
Catalyst	kmol m ⁻³	4.32 × 10 ⁻⁵ to 1.74 × 10 ⁻⁴
3-Bromo-benzophenone	kmol m ⁻³	0.07–0.3
<i>n</i> -Butylacrylate	kmol m ⁻³	0.11–0.45
NaOAc	kmol m ⁻³	0.11–0.45
Temperature	K	413–433
Volume of liquid phase, NMP	m ³	2.5 × 10 ⁻⁵

3.3.1. Effect of catalyst concentration on the rate of reaction

Effect of catalyst concentration was studied at three different temperatures in the range of 413–433 K and the results are presented in Fig. 2. A first-order dependence on catalyst concentration was observed. The increase in rate can be attributed to the increased concentration of catalytically active species. This is in agreement with the earlier report on Pd catalyzed Heck reaction [7]. However kinetics with dimeric palladacycle as catalyst precursors [7,9–11] exhibit a fractional order dependence on catalyst concentration. The observed results have been explained based on the formation of inactive dimeric species, and hence the active catalytic species is not proportional to the increase in the concentration of the catalyst precursor. In the present study first-order dependence on catalyst concentration has been observed using Pd(ppy)(PPh₃)(OTs) as the catalyst precursor, indicating that there is no formation of such dimeric species in the concentration range studied. Also the first-order dependence on catalyst concentration indicates that with increase in the catalyst concentration there is no agglomeration of Pd(0) species [15] or the formation of palladium black.

3.3.2. Effect of BBP concentration on the rate of the reaction

The effect of BBP concentration on the rate of reaction was studied at constant *n*-BA, NC palladacycle, NaOAc concentrations of 0.203, 5.76 × 10⁻⁵, 0.203 kmol/m³, respectively, in a temperature range of 413–433 K. The results are shown in Fig. 3. It was observed that with increase in the BBP concentration the rate passes through a maximum showing a substrate inhibition at higher BBP concentrations. It may be noted that similar behavior has also been observed for the Heck reaction of iodobenzene and styrene. However, with bromobenzene (PhBr) as a substrate the inhibition is not so prominent at 413 K [16]. In the case of iodobenzene (PhI) and styrene, decrease in reaction rate is explained because of the for-

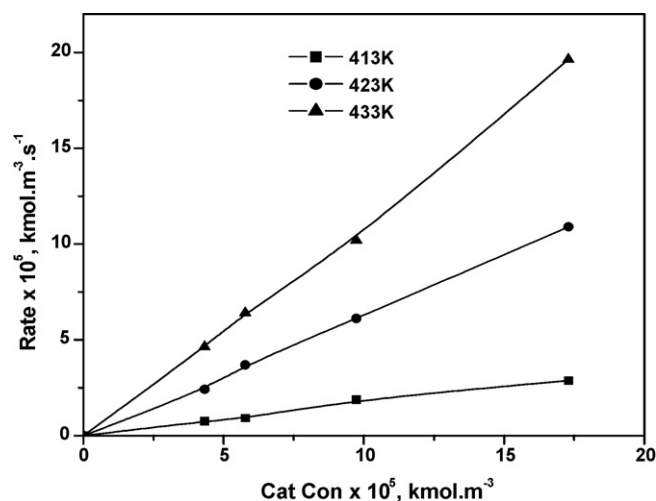


Fig. 2. Effect of catalyst concentration on the rate of reaction. Reaction conditions: BBP, 0.137 kmol/m³; BA, 0.203 kmol/m³; NaOAc, 0.203 kmol/m³; Pd(ppy)(PPh₃)(OTs); solvent (NMP), total volume, 25 ml.

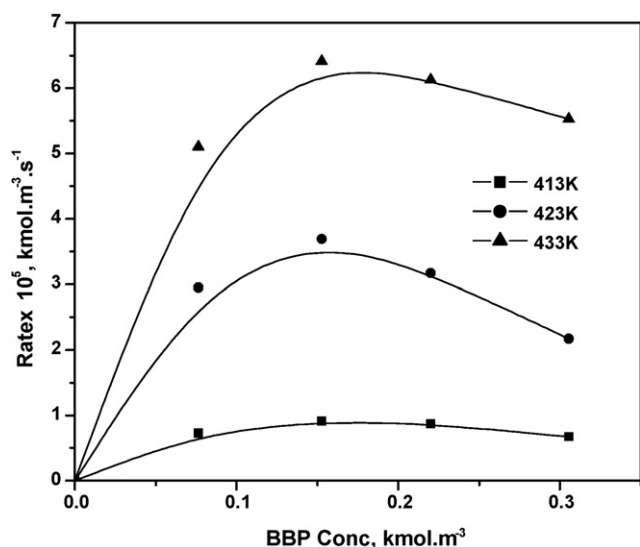


Fig. 3. Effect of BBP concentration on the rate of reaction. Reaction conditions: *n*-BA, 0.203 kmol/m³; NaOAc, 0.203 kmol/m³; Pd(ppy)(PPh₃)(OTs), 5.76 × 10⁻⁵ kmol/m³; solvent (NMP), total volume, 25 ml.

mation of inactive species (PdI₄)²⁻ together with biphenyl as the product. The authors have explained the biphenyl formation in the case of PhI due to the increased oxidative addition of PhI to the palladium to form ArPdI. The thus formed ArPdI favors the biphenyl formation. The decrease in reaction is also explained because of the slowdown of catalyst regeneration which favors the conversion of palladium into its inactive species (PdI₄)²⁻.

Sud et al. [11] and Zhao et al. [8] have observed first-order dependence on the concentration of aryl halide in their work. Blackmond and co-workers [10] described the zero-order dependence on halide (4-bromo-benzaldehyde) concentration. Dupont and co-workers [7] also have reported saturation kinetics in iodobenzene.

In the present case the rate increases at lower concentration of BBP, but as the substrate concentration is further increased the rate decreases. As per the accepted mechanism (Fig. 4) the first step of the catalytic cycle is the oxidative addition of aryl halide to the palladium (0) complex. At high BBP concentration, the concentration of RPdX increases. Also, as per the literature reports [7] the association equilibrium involving olefin coordination to palladium is a highly unfavorable step and hence a slow reaction. It is quite likely that at higher concentration of RPdX (Fig. 5), part of the RPdX undergoes dehalogenation to give Pd (PdX₂, PdX₃⁻, PdX₄²⁻, and Pd₂X₆²⁻) [15,7] species which are inactive for the Heck reaction. These species are slowly converted back to catalytically active species. It may be noted that the formation of benzophenone (0.5–1% dehalogenated product) was observed at higher concentration of BBP. Thus the observed drop in initial rate of reaction at higher BBP concentration can be explained on the basis of the conversion of RPdX species to inactive species (Fig. 5). The possible deactivation steps as proposed by Schmidt et al. [17] and Dupont and co-workers [7] are presented in Fig. 5.

3.3.3. Effect of *n*-butylacrylate concentration on the rate of the reaction

Effect of *n*-butylacrylate concentration on the rate of reaction was investigated in a temperature range of 413–433 K. The reaction showed a first order tending to zero-order dependence of rate on the olefin concentration (Fig. 6). It has been reported [7] that the coordination of olefin to the palladium is a highly unfavorable step and there is equilibrium involving olefin coordination to palladium as shown in Fig. 4. A first-order dependence with the butylacrylate concentration was observed in the lower concentration range,

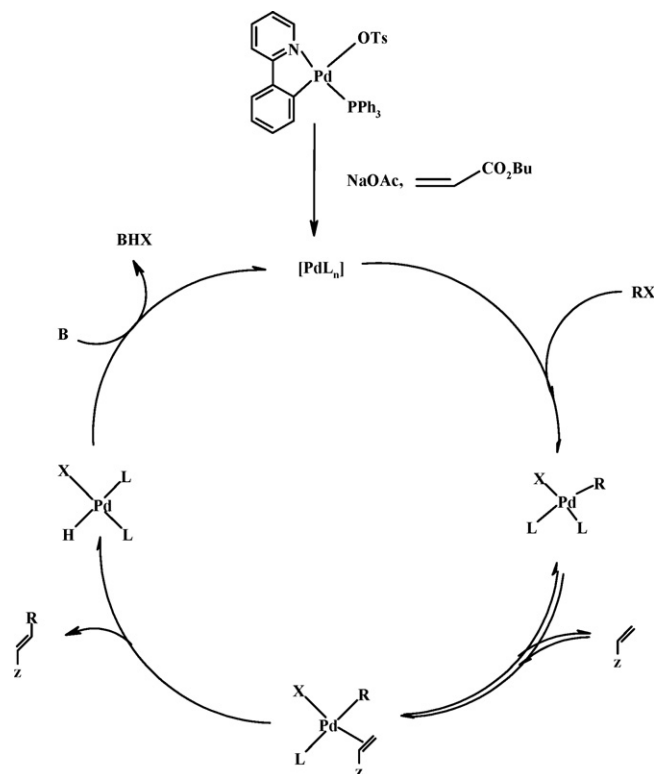


Fig. 4. Heck catalytic cycle.

further increase of the butylacrylate concentration does not lead to increase in the rate of the reaction. Since the addition of olefin to catalyst complex to form π complex is an equilibrium reaction, at higher olefin concentration the rate of reverse reaction is likely to be less dominant leading to marginal rate dependence. Amatore et al. [18] have shown the formation of inactive palladium complexes arising between palladium (0) species and the alkene, and described the decelerating effect of alkenes in the oxidative addition of phenyl iodide to palladium (0) complexes in Heck reactions. Sud et al. [11] have similarly observed a negative order dependence of the rate on the concentration of *n*-BA and have explained their results as described by Amatore et al. However, no such decrease in rate of the reaction was observed in the present study for the concentration range of alkene between 0.11 and 0.45 kmol/m³. Our results are in close agreement with the results obtained by Zhao and Dupont. Dupont and co-workers [7] report saturation kinetics (first order at lower concentration and zero order at higher concentration) with respect to *n*-BA concentration for the reaction of *n*-BA

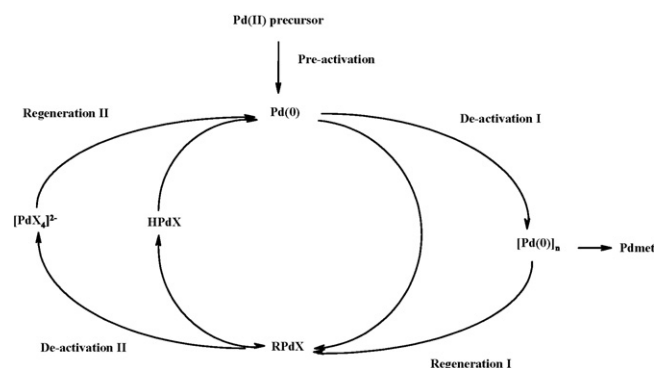


Fig. 5. Possible deactivation/regeneration of the Pd species involved in the Heck catalytic process.

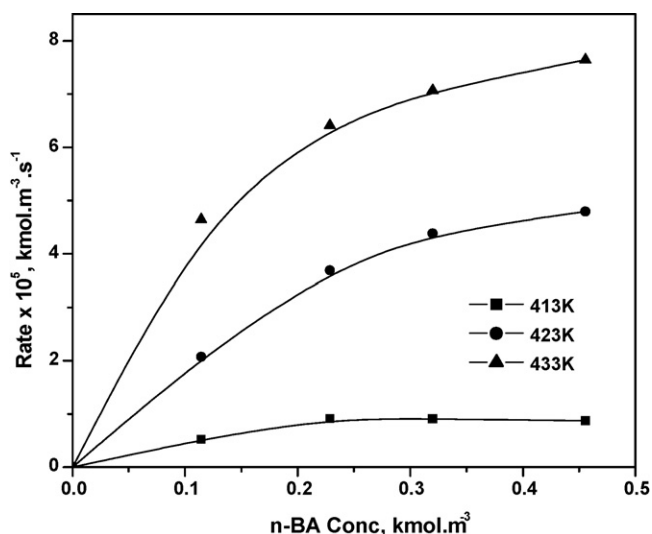


Fig. 6. Effect of *n*-BA concentration on the rate of reaction. Reaction conditions: BBP, 0.137 kmol/m³; NaOAc, 0.203 kmol/m³; Pd(ppp)(PPh₃)(OTs), 5.76 × 10⁻⁵ kmol/m³; solvent (NMP), total volume, 25 ml.

with iodobenzene. Zhao et al. [8] have reported a first order tending to zero-order dependence of rates on the olefin concentration.

3.3.4. Effect of sodium acetate concentration on the rate of the reaction

The effect of sodium acetate concentration on the arylation of BA with BBP was studied at constant BBP, BA, NC palladacycle concentrations of 0.137, 0.203, 5.76 × 10⁻⁵ kmol/m³, respectively, in a temperature range of 413–433 K. The rate was found to increase with increasing the concentration of NaOAc up to 0.229 kmol/m³. Above this concentration the rate was found to be independent of base concentration (Fig. 7). It is likely that there is solubility limitation of base at higher concentrations hence the increase in the rate is not observed. The role of the base is to neutralize the acid HBr liberated in the reaction to complete the catalytic cycle and regenerating the catalytically active Pd(0) complex. Dupont and co-workers [7] also have observed zero-order dependence on base concentration. Zhao et al. [8] have reported the rate passing through a maximum as the concentration of the base (triethylamine) is increased.

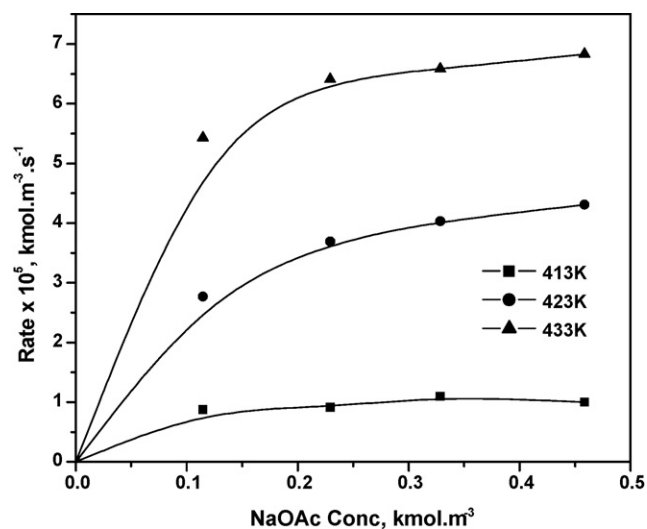


Fig. 7. Effect of NaOAc concentration variation on the rate of reaction. Reaction conditions: BBP, 0.137 kmol/m³; *n*-BA, 0.203 kmol/m³; Pd(ppp)(PPh₃)(OTs), 5.76 × 10⁻⁵ kmol/m³; solvent (NMP), total volume, 25 ml.

Table 4

Values of kinetic parameters at different temperatures.

Rate model	Temp. (K)	k_1	K_2	K_3	K_4	ϕ_{min}
I	413	258.60	26.80	58.50	384.90	7.12E-13
	423	546.80	8.20	45.00	50.10	5.43E-13
	433	792.67	6.68	8.56	19.00	3.10E-13
II	413	2679.53	86.60	3.08	3.18	4.39E-10
	423	22351.97	602.48	1.09	1.84	2.78E-10
	433	10755.19	85.09	1.86	2.88	2.94E-10
III	413	7833.12	94.37	3.08	31.14	4.39E-10
	423	12499.08	240.50	1.07	7.90	2.72E-10
	433	23046.46	77.99	1.83	24.03	2.57E-10
IV	413	1211.80	52.85	-174.47	-78.61	4.60E-10
	423	1852.00	88.91	-246.54	-137.40	9.36E-10
	433	7058.00	54.28	-466.47	-235.45	9.37E-10
V	413	598.92	3.68	1.71	1.66	4.22E-10
	423	1030.22	4.18	0.70	1.07	7.94E-11
	433	2042.99	3.01	1.07	1.51	1.23E-10

3.3.5. Rate model

The kinetic data obtained was used to develop a rate equation for the Heck reaction of 3-bromobenzophenone and *n*-butylacrylate. Based on the observed trends, a variety of empirical models were examined, and the best model was selected based on the criterion of the least average error between predicted and experimental rates (ϕ_{min}) which is defined as

$$\phi_{min} = \sum_{i=1}^n (R_{EXP} - R_{PRE})^2$$

where R_{EXP} is the observed rate of the reaction and R_{PRE} is the rate predicted by the respective models.

3.3.6. Estimation of kinetic parameters and model discrimination

The rate parameters k_1, K_2, K_3, K_4 were evaluated at 413, 423 and 433 K by fitting the experimental rate data with Eqs. (I)–(V) using non-linear regression analysis and an optimization routine based on the Marquardt's method [19]. The values of the rate parameters at different temperatures for various models are presented in Table 4.

$$r = \frac{k_1 ABCD}{(1 + K_2 B)^2 (1 + K_3 C) (1 + K_4 D)} \quad (I)$$

$$r = \frac{k_1 ABCD}{(1 + K_2 B) (1 + K_3 C)^2 (1 + K_4 D)^2} \quad (II)$$

$$r = \frac{k_1 ABCD}{(1 + K_2 B) (1 + K_3 C)^2 (1 + K_4 D)} \quad (III)$$

$$r = \frac{k_1 ABCD}{(1 + K_2 B) (1 + K_3 C) (1 + K_4 D)} \quad (IV)$$

$$r = \frac{k_1 ABCD}{(1 + K_2 B)^3 (1 + K_3 C)^3 (1 + K_4 D)^3} \quad (V)$$

where r = rate of reaction, expressed in kmol/(m³s); A = concentration of NC palladacycle (kmol/m³); B = concentration of *m*-bromobenzophenone (kmol/m³); C = concentration of *n*-butylacrylate (kmol/m³); D = concentration of NaOAc (kmol/m³); k_1 = rate constant K_2, K_3, K_4 are equilibrium constants.

The discrimination of rate models was done based on the thermodynamic criteria, activation energy and the ϕ_{min} values. The rate models II and III were rejected based on the thermodynamic criteria of inconsistency of temperature dependence of equilibrium constant and range of activation energy values. Model IV had rate parameters less than zero (or -ve) and hence was rejected. In the remaining two models I and V, the model V was discriminated based

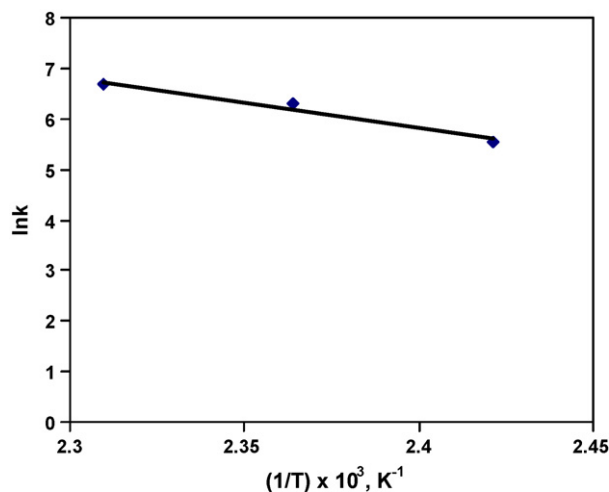


Fig. 8. Temperature dependence of rate constant (k) (Arrhenius plot).

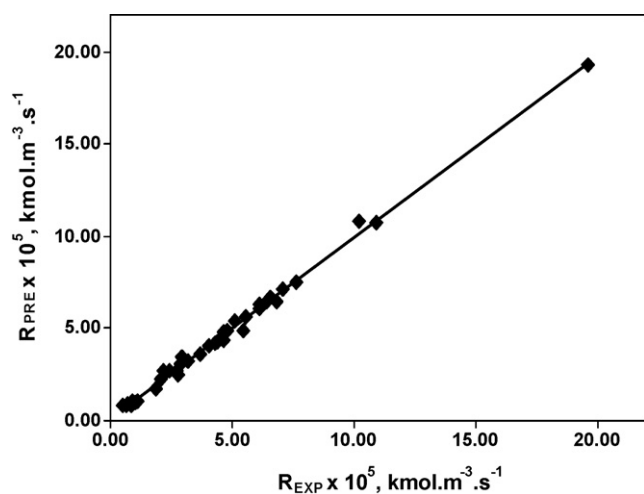


Fig. 9. Comparison of experimental rates and rates predicted using model I.

on the higher ϕ_{min} values than model I. The model I thus turned out to be superior among all the models considered.

Thus, the following rate equation was found to predict the rates in good agreement with experimental values:

$$r = \frac{k_1 ABCD}{(1 + K_2 B)^2 (1 + K_3 C) (1 + K_4 D)}$$

The Arrhenius plot showing the effect of temperature on the rate parameters is shown in Fig. 8 from which the activation energy was evaluated as 84.7 kJ/mol.

A comparison of the experimental rates with the rates predicted by model I are shown in Fig. 9, which shows a reasonably good fit of the experimental data. The average deviation in the predicted and observed rates was found to be in the range of $\pm 2\%$.

4. Conclusions

The detailed kinetics of arylation of *n*-butylacrylate with 3-bromo-benzophenone was studied using monomeric NC palladacycle as catalyst, in NMP as solvent and NaOAc as the base. The effect of different parameters viz., concentrations of the substrates, catalyst and base on the rate of the reaction was investigated in the temperature range of 413–433 K. The rate data were fitted to various empirical rate models. The following rate equation was found to predict the rates in good agreement with experimental values:

$$r = \frac{k_1 ABCD}{(1 + K_2 B)^2 (1 + K_3 C) (1 + K_4 D)}$$

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