

Kinetics of vinylation of 4'-bromoacetophenone with *n*-butyl acrylate using palladacycle catalyst

Abhishek Sud, Raj M. Deshpande, Raghunath V. Chaudhari*

Homogeneous Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

Received 5 September 2006; received in revised form 16 January 2007; accepted 21 January 2007

Available online 24 January 2007

Abstract

The kinetics of vinylation of 4'-bromoacetophenone (4'-BAP) with *n*-butyl acrylate (*n*-BA) has been studied using palladacycle catalyst precursor **1**, in the presence of sodium acetate (NaOAc) as a base and tetrabutylammonium bromide (TBAB) as a promoter in *N*-methyl-2-pyrrolidinone (NMP) solvent. The rate was found to be first order with respect to 4'-BAP, fractional order with the catalyst, and first order tending to zero order with NaOAc concentration. The rates passed through a maximum with variation of TBAB and *n*-butyl acrylate concentrations. The rate data have been analyzed to propose an empirical model, which is in good agreement with the mechanism already established for Heck reactions using palladacycle catalysts.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Kinetics; Heck reaction; Palladacycle

1. Introduction

The Mizoroki–Heck [1,2] reaction of aryl halides with olefins has become an important tool in synthetic chemistry for C–C bond formation with the olefinic structure retained. This reaction has also gained importance due to its ability to tolerate a variety of functional groups, thus avoiding the need for protection and deprotection of functional groups during the synthesis. Numerous reports have been published on this reaction detailing the use of improved catalysts in order to achieve higher turnover numbers (TON) and the influence of various operating variables such as reactants [3], promoters [4], and catalysts [5,6] on the reaction rates and selectivity towards the desired products. Since the industrially important aryl chlorides react very slowly with the presently available catalysts, most of the present research is aimed at synthesis of better catalysts for higher activity, stability, and substrate tolerance. Palladacycles have turned out to be the best catalysts employed for these reactions in terms of TON and turnover frequency (TOF), although these require higher temperatures in order to be active [6]. The mechanism of this reaction has also been established but doubts remain regarding

the actual catalytic species involved [7]. The reactions involving the use of acrylate as an olefin source 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. In spite of extensive studies on Heck chemistry, not much work has been published on the detailed kinetics of these reactions [8]. Zhao et al. [8e] have studied the kinetics of the Heck reaction of iodobenzene with methyl acrylate with Pd(OAc)₂/PPh₃ as the catalyst precursor system. The authors have reported a fractional order dependence on the Pd(OAc)₂ concentration, first order dependence on iodobenzene concentration, and a first order tending to zero order with methyl acrylate concentration. With respect to base (triethylamine) concentration they have observed that the rates pass through a maximum with increasing base concentration. Blackmond and co-workers [8c] have studied the kinetics of the Heck reaction of *p*-bromobenzaldehyde with *n*-butyl acrylate with N–C palladacycle. They have reported a fractional order dependence of the rate on the catalyst concentration, first order on olefin concentration and zero order on the halide concentration. Dupont and co-workers [8d] have studied the kinetics of the Heck reaction of iodobenzene and *n*-butyl acrylate in the presence of N–C palladacycle, wherein a first order dependence of the rate with catalyst concentration, and saturation kinetics in PhI and *n*-BA is reported. However, this study is restricted only

* Corresponding author. Tel.: +91 20 25902620; fax: +91 20 25902621.
E-mail address: rv.chaudhari@ncl.res.in (R.V. Chaudhari).

to a temperature of 80 °C. In homogeneous catalytic systems, the reactions are extremely sensitive to the temperature and hence detailed kinetic studies at different temperatures are necessary. Therefore, the effect of concentration variation of catalyst, aryl halide, olefin, base, and tetraalkyl ammonium salt was studied on the vinylation of 4'-bromoacetophenone using palladacycle catalyst **1** in a temperature range of 403–433 K. This study would be useful in understanding of the rate behaviour as well as the mechanism of the reaction.

2. Experimental

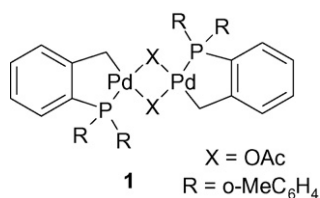
2.1. Chemicals and apparatus

Palladium acetate and tri (*o*-tolyl) phosphine were purchased from Aldrich Chemical Co. 4'-Bromoacetophenone, sodium acetate, *n*-butyl acrylate, tetrabutylammonium bromide, and *N*-methyl-2-pyrrolidinone (NMP) were purchased from commercial sources and used as received. The reactions were carried out in a 50 ml two-necked stirred glass reactor fitted with a condenser immersed in an oil bath held at a desired temperature. The stirring was by means of a magnetic stirrer. The analysis of the contents of the reaction mixture was done using an Agilent 6850A gas chromatograph, with an HP-I capillary column of 30 m length (methyl siloxane as stationary phase) and a flame ionization detector. The analysis was carried out using a temperature programme between 80 and 250 °C.

2.2. Experimental procedure

In a typical experiment, 10 mmol of 4'-bromoacetophenone, 15 mmol *n*-butyl acrylate, 15 mmol sodium acetate, 2 mmol tetrabutylammonium bromide, and 2 μmol palladacycle [6a] catalyst **1**, shown in Scheme 1, were taken in NMP solvent in 50 ml two-necked stirred glass reactor under nitrogen atmosphere. This was then immersed in an oil bath pre-heated to a required temperature. The reaction was then started by switching the stirrer on. Samples were withdrawn at regular intervals, filtered and analyzed for conversion of 4'-bromoacetophenone and cinnamate formation. Some reactions were carried out to complete conversion, following which the reaction mixture was washed with 5% HCl (three washes with 25 ml each) extracted with CH₂Cl₂ (50 ml) and dried over MgSO₄. The solvent was removed under vacuum and then the mixture was separated by column chromatography to isolate the products.

For kinetic analysis the reactions were carried out for short durations such that the conversion of the 4'-bromoacetophenone was less than 20% to ensure differential conditions. The bulk



Scheme 1.

catalyst solution was prepared in the solvent used, prior to the reaction. From this catalyst solution, the required quantity was added to the reaction mixture. It was observed that, when the catalyst was added from the previously prepared solution (after warming the solution to 50 °C), no induction period was observed. The induction period is due to the time required for the formation of the active catalytic species from the catalyst precursor. In the case of pretreated catalyst, the active catalytic species is already formed and hence the induction period is no longer observed. The initial rates of the reaction were calculated from the plots of formation of butyl-3-(4-acetylphenyl)acrylate products as a function of time, in a region where the conversion of 4'-bromoacetophenone was less than 20%.

3. Results and discussion

A few preliminary experiments were carried out on vinylation of 4'-bromoacetophenone with *n*-butyl acrylate, using palladacycle **1** as the catalyst in the presence of TBAB promoter, to ensure material balance of reactants/products and to select a suitable solvent and a base for the kinetic study. A typical concentration–time profile for the reaction is presented in Fig. 1. The consumption of 4'-BAP and *n*-butyl acrylate, and the formation of butyl-3-(4-acetylphenyl)acrylate was monitored by GC. The consumption of 4'-BAP and *n*-butyl acrylate was found to be stoichiometrically consistent with the formation of butyl-3-(4-acetylphenyl)acrylate according to Scheme 2 in all the experiments.

3.1. Effect of solvent on the reaction rates

In order to carry out the study on the effect of various parameters on the reaction rates, the reaction was carried out in various solvents so as to ascertain the best solvent for investigation of the kinetics. The results of this study are presented in Fig. 2. For the preliminary screening of the solvents, 4'-bromoacetophenone

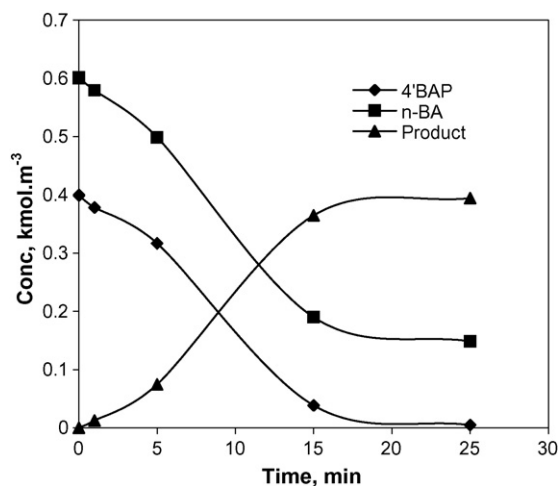
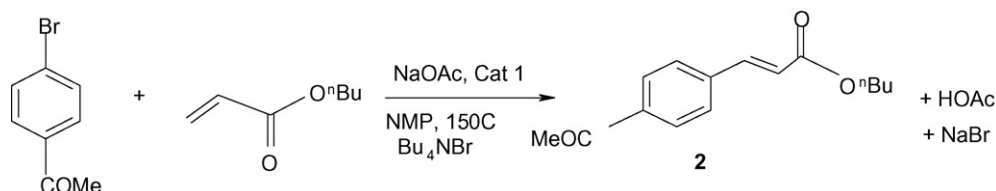


Fig. 1. Concentration–time profile for the standard reaction. Reaction conditions: 4'-BAP, 0.399 kmol/m³; *n*-BA, 0.602 kmol/m³; NaOAc, 0.6 kmol/m³; TBAB, 0.074 kmol/m³; catalyst **1**, 8.51 × 10⁻⁵ kmol/m³; solvent, NMP; total volume, 25 ml; temperature, 150 °C.



Scheme 2.

(as halide), *n*-butyl acrylate (as olefin), sodium acetate (as base), and tetrabutylammonium bromide (as promoter) were taken as the standard reaction system components. Both polar solvents such as *N*-methylpyrrolidinone, *N,N*-dimethylformamide, and ethylene glycol, and non-polar solvents *viz* diethylene glycol dibutyl ether, quinoline, and *n*-decane were screened for their activity and selectivity in the Heck reactions.

The rates of reaction are faster in polar solvents than in non-polar solvents. In the case of NMP, the reaction was complete in 20 min. With DMF, it took 30 min to achieve the maximum conversion. In non-polar solvent decane, the reaction rate was very slow and the reaction was not complete even after 2 h of reaction due to the insolubility of NaOAc base in the solvent. In the case of ethylene glycol, the substrates and products were only partially soluble in the solvent. Hence, each sample was extracted with toluene and then analyzed by GC. There was an induction period observed with all the solvents screened as the catalyst precursor was added to the reaction mixture without any pretreatment. This induction period can be attributed to the formation of active catalytic species from the palladacycle catalyst precursor. The dimeric palladacycle forms a catalytically active monomeric species in the reaction mixture [7d].

No product formation was observed when quinoline was used as a solvent. Quinoline can act as a ligand to form a stable complex with palladium, thus making it unavailable for the catalytic reaction.

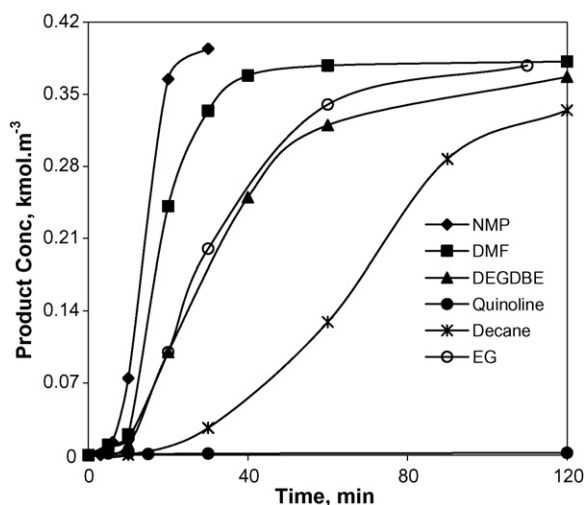


Fig. 2. Effect of solvents on the rate of the reaction. Reaction conditions: 4'-BAP, 0.399 kmol/m^3 ; *n*-BA, 0.602 kmol/m^3 ; NaOAc, 0.6 kmol/m^3 ; TBAB, 0.074 kmol/m^3 ; catalyst **1**, $8.51 \times 10^{-5} \text{ kmol/m}^3$; total volume, 25 ml; temperature, 150°C . DMF, *N,N*-dimethylformamide; DEGDBE, diethyleneglycol dibutyl ether.

These results are in conformity with the earlier reports on Heck reactions, where it was observed that the reaction proceeds faster in polar solvents than in non-polar solvents [10]. This is attributed to the stabilization of the polar catalytic species formed by the addition of the olefin to the palladium centre when a chelating ligand is present [9]. Apart from this, the solubility of sodium acetate is higher in polar solvents than in non-polar solvents. As the liquid phase concentration of the base is higher in polar solvents, the removal of H–X in catalytic cycle and conversion of Pd(II) to active Pd(0) species is facilitated, resulting in enhanced activity.

Out of all the solvents screened, NMP was the best solvent in terms of the rate activity. Hence, for the further studies on the kinetics of Heck reactions, NMP was the solvent of choice {NMP, DMF, and DMA (*N,N*-dimethylacetamide) are the most commonly used solvents for Heck reactions reported [6,8]}. The Heck reaction is generally favoured in polar non-protic solvents.

3.2. Effect of base on the reaction rates

Various organic and inorganic bases were screened in NMP solvent for their activity and selectivity for the Heck reaction of 4'-BAP and *n*-BA to give butyl-3-(4-acetylphenyl)acrylate. For this purpose, sodium acetate, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium acetate, potassium hydroxide, potassium carbonate, and *n*-tributyl amine were screened. The results are shown in Table 1. The use of strong bases like sodium hydroxide and potassium hydroxide gave <3% product formation. Both these bases led to the decomposition of the halide and the olefin. Acetophenone was formed as the decomposition product of the 4'BAP. Acrylic acid and 1-butanol were the decomposition products of the butyl acrylate. Sodium bicarbonate turned out to be a better base than sodium carbon-

Table 1
Effect of different bases on the rate of the reaction

Serial number	Base	Time (min)	Conversion (4'-BAP) (%)	Selectivity (%)
1	NaOAc	20	98.9	99.8
2	KOAc	20	99.5	99.1
3	KOH	200	75.4	2.5
4	NaOH	180	81.0	0.4
5	K ₂ CO ₃	20	97.2	99.1
6	Na ₂ CO ₃	50	92.0	98.9
7	<i>n</i> Bu ₃ N	30	91.8	99.4
8	NaHCO ₃	30	97.1	99.6

Reaction conditions: 4'-BAP, 0.399 kmol/m^3 ; *n*-BA, 0.602 kmol/m^3 ; base, 0.6 kmol/m^3 ; TBAB, 0.74 kmol/m^3 ; catalyst **1**, $8.51 \times 10^{-5} \text{ kmol/m}^3$; solvent, NMP; total volume, 25 ml; temperature, 423 K.

Table 2

Range of conditions investigated for kinetic study

Concentration of catalyst (kmol m^{-3})	4.26×10^{-5} to 2.55×10^{-4}
Concentration of 4'-bromoacetophenone (kmol m^{-3})	0.1–0.75
Concentration of <i>n</i> -butyl acrylate (kmol m^{-3})	0.25–1.1
Concentration of base (kmol m^{-3})	0.1–1.1
Concentration of TBAB (kmol m^{-3})	0.03–0.2
Temperature (K)	403–433

ate, leading to 97% conversion of 4'-BAP in 30 min as compared to 92% conversion with sodium carbonate in 50 min. Sodium acetate was a better base than sodium bicarbonate, giving a 98.9% conversion in 20 min. Potassium bases gave better activity compared to their respective sodium counterparts. Potassium acetate gave the best conversion amongst all the bases screened. This may be attributed to better ionization of the potassium bases in the organic solvents as compared to sodium bases, thus leading to better solubility of these bases in the solvent. Organic base (*n*-tributylamine) gave inferior conversions than acetate and bicarbonate bases.

Sodium and potassium acetate remain the most commonly used bases for the Heck reactions [6,8]. It may be noted that in our study, though potassium acetate gave the highest conversion of 4'-BAP, it was not considered for the further kinetic studies due to its hygroscopic nature. Keeping all the factors in mind, sodium acetate was used as the base in further studies.

3.3. Kinetic analysis

The kinetics of vinylation of 4'-bromoacetophenone with *n*-butyl acrylate with the palladacycle **1** as the catalyst precursor in the presence of sodium acetate base and tetrabutylammonium bromide promoter was studied. For this study, several experiments were carried out in the range of conditions shown in Table 2. The initial rates were calculated from the observed data on the consumption of 4'-bromoacetophenone as a function of time. The rate of reaction was calculated from the slope of product formed *versus* time plot. A typical concentration *versus* time plot for different initial concentrations of palladacycle catalyst **1** at 150 °C is shown in Fig. 3. The dependence of the rate on the various parameters was investigated at four different temperatures. The results showing the dependence of the rates on different parameters and kinetic modelling are discussed below.

3.3.1. Effect of catalyst concentration on the rate of reaction

The effect of the concentration of the catalyst precursor (palladacycle **1**) on the rate was studied at constant 4'-BAP, *n*-BA, NaOAc, and TBAB concentrations of 0.399, 0.602, 0.6, and 0.074 kmol/m^3 , respectively, in a temperature range of 403–433 K. It was observed that the rate increased with an increase in the catalyst concentration, in the range under investigation. The rate showed a fractional order dependence on the concentration of the catalyst as shown in Fig. 4. This is in agreement with the earlier reports on Pd catalyzed Heck reactions

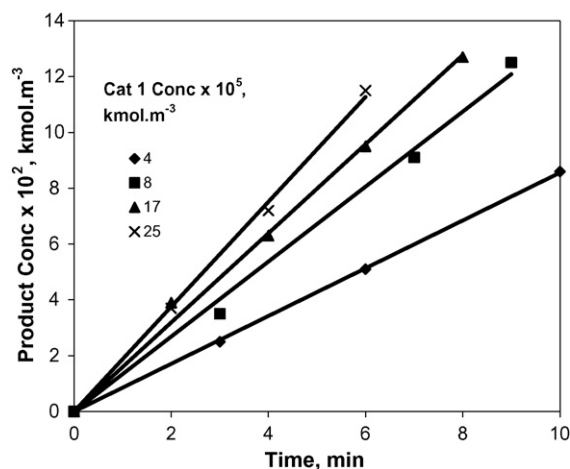


Fig. 3. Initial rate slopes for different initial concentrations of palladacycle catalyst **1**. Reaction conditions: 4'-BAP, 0.399 kmol/m^3 ; *n*-BA, 0.602 kmol/m^3 ; NaOAc, 0.6 kmol/m^3 ; TBAB, 0.074 kmol/m^3 ; catalyst, **1**; solvent, NMP; total volume, 25 ml; temperature, 150 °C.

[8a,c,e]. This trend can be attributed to the formation of an inactive dimeric species, C3 (step 7), shown in Scheme 3. As the catalyst concentration is increased more of the dimeric species is likely to form. Hence, the enhancement in the concentration of the active catalyst species available for the reaction is not proportional to the increase in the concentration of the catalyst precursor. Thus the increase in the observed reaction rates is not first order as normally observed, but instead shows a half order dependence on the catalyst concentration as would be expected from the equilibrium deactivation as shown in the mechanism (Scheme 3). It should also be noted that the catalyst precursor is a dimer, which will dissociate to a monomeric species in equilibrium (step 1, Scheme 3). This may also contribute to the fractional order observed with respect to the catalyst concentration.

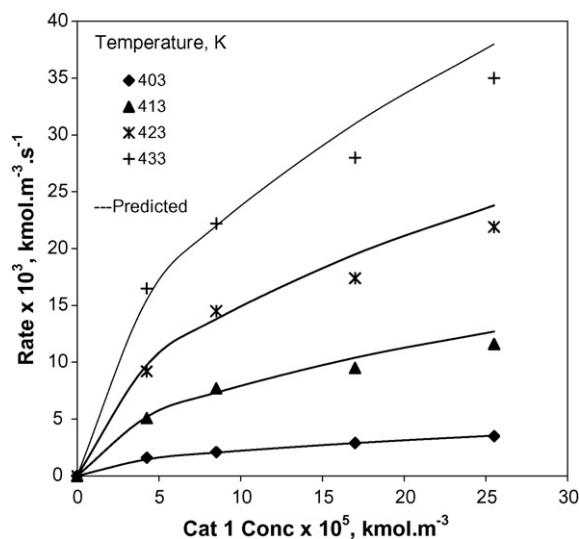
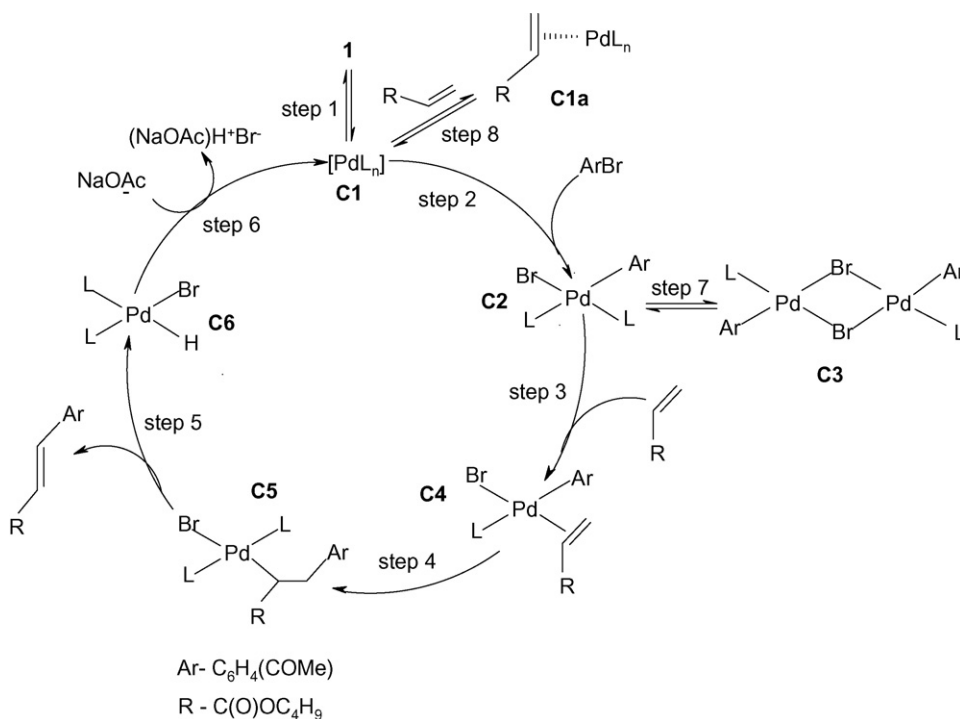


Fig. 4. Effect of catalyst concentration on the reaction rates. Reaction conditions: 4'-BAP, 0.399 kmol/m^3 ; *n*-BA, 0.602 kmol/m^3 ; NaOAc, 0.6 kmol/m^3 ; TBAB, 0.074 kmol/m^3 ; catalyst, **1**; solvent, NMP; total volume, 25 ml.



Scheme 3.

3.3.2. Effect of *p*-bromoacetophenone concentration on the rate of reaction

The effect of 4'-bromoacetophenone concentration variation on the activity was studied at constant *n*-BA, palladacycle **1**, NaOAc, and TBAB concentrations of 0.602, 8.511×10^{-5} , 0.6, and 0.074 kmol/m³, respectively, in a temperature range of 403–433 K. The results are shown in Fig. 5. The rate was found to increase with increase in the concentration of 4'-BAP. This is to be expected as the ArX moiety oxidatively adds to the catalytic species in step 2 of the catalytic cycle as shown in Scheme 3. This step is usually considered to be the rate-determining step in the catalytic cycle [7e], and hence, any increase in the con-

centration of the 4'-BAP leads to enhancement in the rate of the reaction. This observation is similar to the earlier report by Zhao et al. [8e] for the kinetics of Heck reaction of iodobenzene with methyl acrylate with Pd(OAc)₂/PPh₃ as the catalyst precursor. Dupont and co-workers [8d] report a saturation kinetics (first order at lower concentration and zero order at higher concentration) for PhI concentration for the reaction of iodobenzene with *n*-BA. Blackmond and co-workers [8c] report a zero order dependence on the halide concentration for the reaction of *p*-bromobenzaldehyde with *n*-BA: however, as is expected, any zero order reaction essentially will be first order in the lower concentration range.

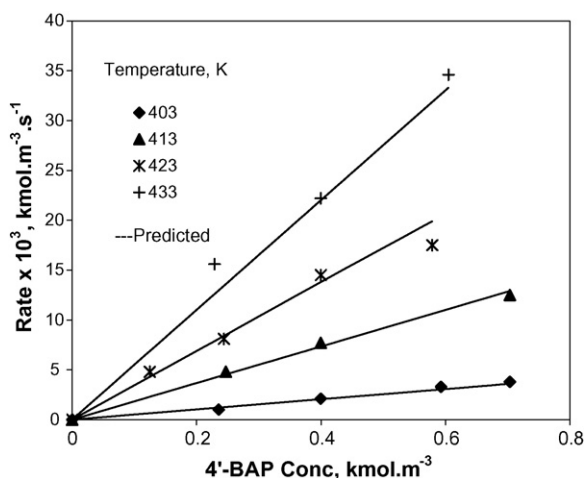


Fig. 5. Effect of 4'-bromoacetophenone (4'-BAP) concentration on the reaction rates. Reaction conditions: *n*-BA, 0.602 kmol/m³; NaOAc, 0.6 kmol/m³; TBAB, 0.074 kmol/m³; catalyst **1**, 8.51×10^{-5} kmol/m³; solvent, NMP; total volume, 25 ml.

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

The effect of *n*-butyl acrylate concentration was studied at constant 4'-BAP, catalyst **1**, NaOAc, and TBAB concentrations of 0.399, 8.511×10^{-5} , 0.6, and 0.074 kmol/m³, respectively, in the temperature range of 403–433 K. The rate of the reaction showed a complex dependence and passed through a maximum. Initially a first order dependence with the acrylate concentration was observed in the lower concentration range (0.6 kmol/m³) and then, after attaining a maximum, the rates decreased marginally with increasing concentration of the olefin. This is the first time a negative order dependence of the rate on concentrations of *n*-BA is observed. In earlier studies Dupont and co-workers [8d] report a saturation kinetics with respect to *n*-BA concentration for the reaction of iodobenzene with *n*-BA, whereas Blackmond and co-workers [8c] report a first order dependence on the olefin concentration for the reaction of *p*-bromobenzaldehyde with *n*-BA using a N-C palladacycle catalyst. The olefin concentration range used in the present

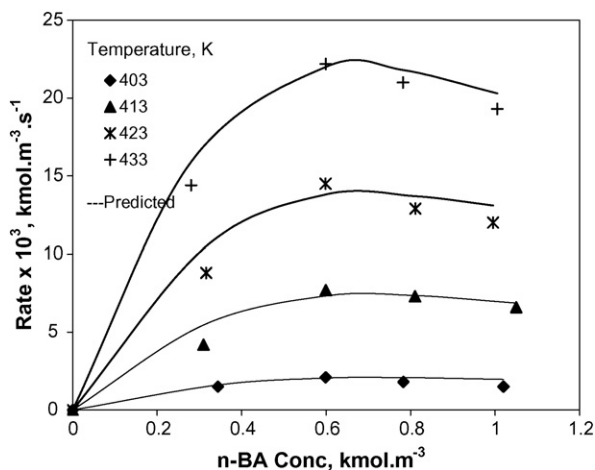


Fig. 6. Effect of *n*-butyl acrylate (*n*-BA) concentration on the reaction rates. Reaction conditions: 4'-BAP, 0.399 kmol/m³; NaOAc, 0.6 kmol/m³; TBAB, 0.074 kmol/m³; catalyst **1**, 8.51×10^{-5} kmol/m³; solvent, NMP; total volume, 25 ml.

study is higher than that used in the earlier studies. This might be one of the reasons why the decrease in the reaction rate with increase in olefin concentrations has not been observed in these studies. Zhao et al. [8e] report a first order tending to zero order dependence of rates on the olefin (methyl acrylate) concentration.

The olefin addition to the catalyst complex leads to the formation of a π complex C4 (step 3, Scheme 3) in an equilibrium reaction which then leads to the formation of σ complex. It has been reported that the presence of high concentrations of olefins leads to the formation of species C1a (step 8, Scheme 3), which is inactive for the reaction [11]. This leads to a decrease in the active catalyst available for the reaction and hence a drop in the rate at higher *n*-butyl acrylate concentration is observed as shown in Fig. 6.

3.3.4. Effect of NaOAc concentration on the rate of reaction

The effect of base concentration on the vinylation of 4'-BAP with *n*-BA was studied at constant 4'-BAP, *n*-BA, catalyst **1**, and TBAB concentrations of 0.399, 0.602, 8.511×10^{-5} , and 0.074 kmol/m³, respectively, in a temperature range of 403–433 K. The rate shows a linear dependence on NaOAc concentration in the lower concentration range (<0.8 kmol/m³). With further increase in NaOAc concentrations the rate increases marginally. The results are presented in Fig. 7. Earlier report by Dupont and co-workers [8d] shows a zero order dependence on the base concentration but the concentration ranges used were significantly lower. Zhao et al. [8e] report the rates passing through a maximum as the concentration of the base (triethylamine) is increased.

The base is required for the regeneration of the active catalytic species by abstraction of HBr from the species C6 (step 6) as shown in Scheme 3. As the concentration of the base increases, a faster regeneration of active catalytic species takes place leading to an increase in the rate as observed. Further increase in the base concentration above a certain value does not lead to any additional enhancements in the rate. This could

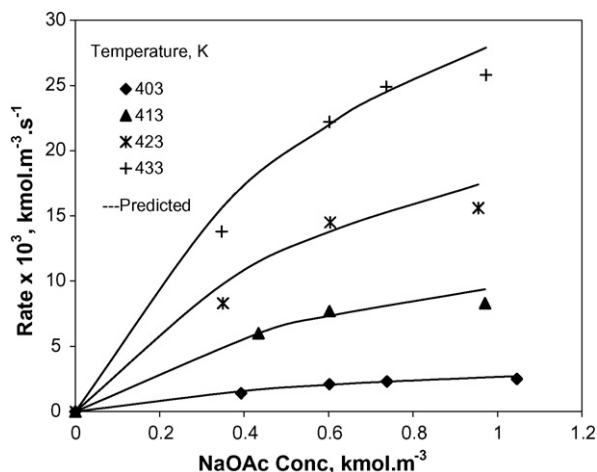


Fig. 7. Effect of NaOAc concentration variation on the reaction rates. Reaction conditions: 4'-BAP, 0.399 kmol/m³; *n*-BA, 0.602 kmol/m³; TBAB, 0.074 kmol/m³; catalyst **1**, 8.51×10^{-5} kmol/m³; solvent, NMP; total volume, 25 ml.

be due to the solubility limitation of NaOAc in NMP at higher concentrations.

3.3.5. Effect of TBAB concentration on the rate of reaction

The effect of tetrabutylammonium bromide concentration on the rate of the reaction was studied at constant 4'-BAP, *n*-BA, catalyst **1**, and NaOAc concentrations of 0.399, 0.602, 8.511×10^{-5} , and 0.6 kmol/m³, respectively, in a temperature range of 403–433 K. The rates passed through a maximum as the concentration of tetrabutylammonium bromide was increased. The results are presented in Fig. 8. The TBAB is known to play diverse roles in the reaction mechanism. It acts as a phase transfer agent in order to increase the solubility of NaOAc in NMP. At higher concentrations of TBAB this can lead to more solubility of NaOAc in NMP, thus making it viscous (experimentally observed), thereby reducing the rates. It can also act as a promoter to increase the rate of oxidative addition step by increasing

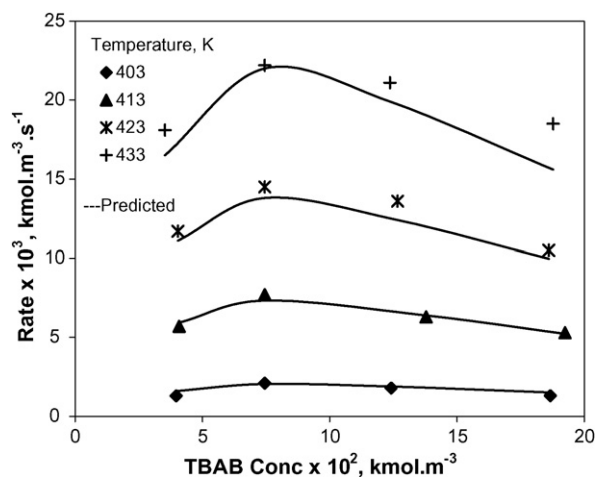


Fig. 8. Effect of TBAB concentration variation on reaction rates. Reaction conditions: 4'-BAP, 0.399 kmol/m³; *n*-BA, 0.602 kmol/m³; NaOAc, 0.6 kmol/m³; catalyst **1**, 8.51×10^{-5} kmol/m³; solvent, NMP; total volume, 25 ml.

the electron density on the palladium atom due to the formation of more electron-rich anionic Pd(0) species [9]. It can also act as a stabilizing additive to increase the lifetime of underligated Pd(0) species. The bromide of the TBAB can enter the coordination sphere of the palladium and form a stable complex that can prevent collisions between the Pd(0) species and thus formation of metal clusters [9]. However, at higher TBAB concentrations this may reduce the reaction rates as vacant metal sites may not be available for the oxidative addition step. The exact nature of the influence of TBAB on the reaction rate cannot be restricted to a single effect but rather is a superposition of all the effects mentioned earlier.

3.3.6. Rate model

The kinetic data was used to develop a rate equation for the Heck reaction of 4'-bromoacetophenone and *n*-butyl acrylate. 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:

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

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

3.3.7. Estimation of kinetic parameters and model discrimination

The rate parameters k , K_B , K_C , and K_D were evaluated at 403, 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 [12]. The values of the rate parameters at different temperatures are presented in Table 3.

The values of Φ_{\min} suggest the extent of fit of the kinetic models used (least value of the Φ_{\min} shows the best fit):

$$R = \frac{k[A][B][C][D][Q]}{(1 + K_B[B]^2)(1 + K_C[C])(1 + K_D[D]^2)} \quad (\text{I})$$

$$R = \frac{k[A][B][C][D][Q]^{0.5}}{(1 + K_B[B]^2)(1 + K_C[C])(1 + K_D[D]^2)} \quad (\text{II})$$

$$R = \frac{k[A][B][C][D][Q]^{0.5}}{(1 + K_B[B])(1 + K_C[C])(1 + K_D[D])} \quad (\text{III})$$

$$R = \frac{k[A][B][C][D][Q]^{0.5}}{(1 + K_B[B]^2)(1 + K_C[C])(1 + K_D[D])} \quad (\text{IV})$$

$$R = \frac{k[A][B][C][D][Q]^{0.5}}{(1 + K_B[B]^2)(1 + K_D[D]^2)} \quad (\text{V})$$

Model (I) was rejected as it gave negative values for the equilibrium constants. Model (V) gave very high value for Φ_{\min}

Table 3
Values of kinetic parameters at different temperatures

Model	Temperature (K)	k (m ³ /kmol) ⁵	K_B (m ³ /kmol) ²	K_C (m ³ /kmol)	K_D (m ³ /kmol) ²	Φ_{\min} ($\times 10^4$)
(I)	403	9.36×10^3	3.03	0.60	117.98	0.169
	413	1.26×10^3	0.04	-0.47	-113.37	24.647
	423	5.17×10^4	1.86	0.91	91.81	10.087
	433	9.91×10^4	2.31	0.76	126.08	21.509
Model	Temperature (K)	k (m ³ /kmol) ^{4.5}	K_B (m ³ /kmol) ²	K_C (m ³ /kmol)	K_D (m ³ /kmol) ²	Φ_{\min} ($\times 10^4$)
(II)	403	1.09×10^2	1.90	1.18	148.76	0.017
	413	4.11×10^2	2.01	1.23	154.69	0.198
	423	8.06×10^2	2.08	1.29	158.25	1.234
	433	1.37×10^3	2.28	1.31	163.37	2.074
Model	Temperature (K)	k (m ³ /kmol) ^{4.5}	K_B (m ³ /kmol)	K_C (m ³ /kmol)	K_D (m ³ /kmol)	Φ_{\min} ($\times 10^4$)
(III)	403	5.14×10^2	3.13	1.05	59.19	0.059
	413	2.41×10^3	3.33	1.35	75.63	0.561
	423	5.77×10^3	3.89	1.22	86.71	2.421
	433	1.47×10^4	4.35	1.31	128.26	2.336
Model	Temperature (K)	k (m ³ /kmol) ^{4.5}	K_B (m ³ /kmol) ²	K_C (m ³ /kmol)	K_D (m ³ /kmol)	Φ_{\min} ($\times 10^4$)
(IV)	403	2.77×10^2	1.49	1.07	59.45	0.052
	413	1.27×10^3	1.66	1.12	75.03	0.460
	423	3.09×10^3	2.04	1.22	88.98	2.065
	433	7.59×10^3	2.29	1.29	131.02	2.447
Model	Temperature (K)	k (m ³ /kmol) ^{4.5}	K_B (m ³ /kmol) ²	K_C (m ³ /kmol)	K_D (m ³ /kmol) ²	Φ_{\min} ($\times 10^4$)
(V)	403	25.56	1.17		148.32	0.330
	413	97.55	1.37		154.57	4.693
	423	187.69	1.73		163.33	18.008
	433	358.79	2.34		173.66	31.084

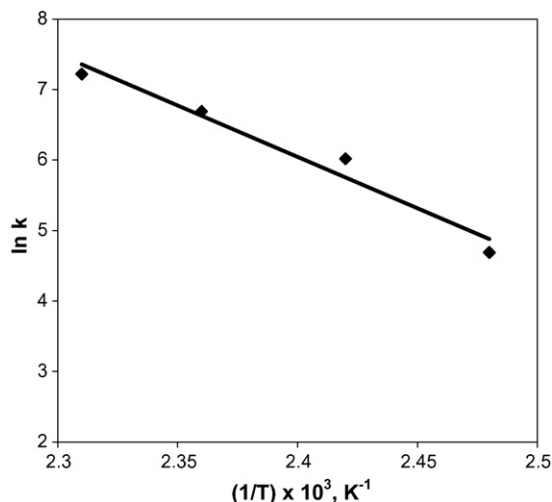


Fig. 9. Temperature dependence of rate constant (k) (Arrhenius plot).

and hence was rejected. Models (III) and (IV) gave the Φ_{\min} value higher than model (II). In addition, on comparison of the predicted values of the rates using these three models, it was observed that overall prediction using model (II) was closest to the experimental values. Model (II) gave overall lowest values for Φ_{\min} . This model thus turned out to be superior amongst all the models considered. Activation energies were calculated using Arrhenius plots (Table 3 and Fig. 9).

The following model was found to best fit the data at all the temperatures studied:

$$R = \frac{k[A][B][C][D][Q]^{0.5}}{(1 + K_B[B]^2)(1 + K_C[C])(1 + K_D[D]^2)}$$

where R is the rate of reaction, expressed in $\text{kmol}/(\text{m}^3 \text{ s})$, $[A]$ the concentration of *p*-bromoacetophenone (kmol/m^3), $[B]$ the concentration of *n*-butyl acrylate (kmol/m^3), $[C]$ the concentration of NaOAc (kmol/m^3), $[D]$ the concentration of TBAB (kmol/m^3), and $[Q]$ is the concentration of the palladacycle catalyst precursor **1** (kmol/m^3). k is the rate constant, and K_B , K_C and K_D are equilibrium constants.

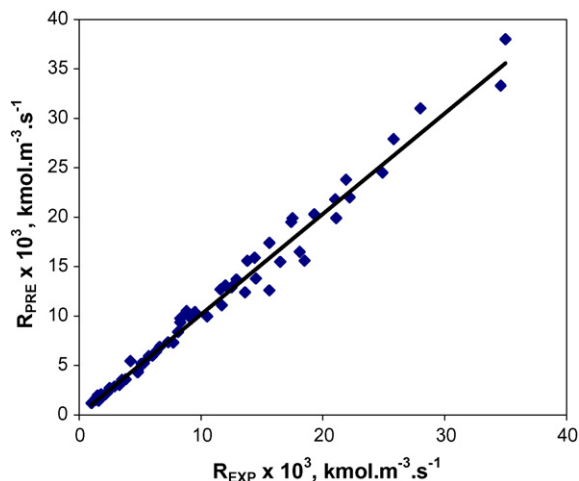


Fig. 10. Comparison of experimental rates and rates predicted using model (II).

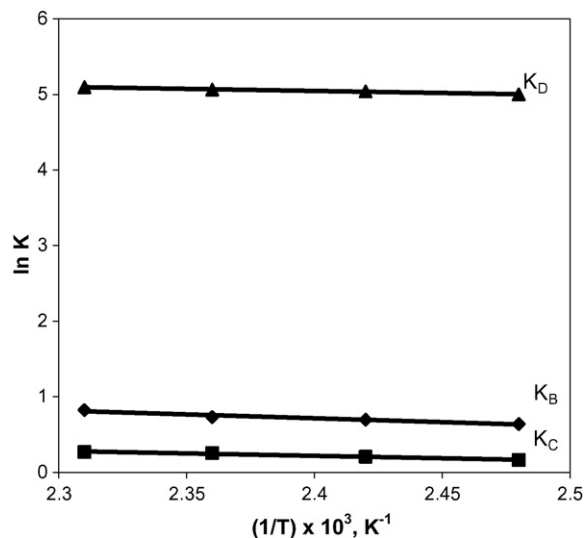


Fig. 11. Temperature dependence of equilibrium constants K_B , K_C , and K_D .

A comparison of the experimental rates with the predicted rates using model (II) is shown in Fig. 10, which indicates a good agreement between experiments and predictions. The average percent error between the experimental and predicted data was 0.95%. The activation energy for this model was estimated at 114.49 kJ/mol based on the Arrhenius plot (Fig. 9). The dependence of K_B , K_C , and K_D on temperature was also studied and is shown in Fig. 11.

4. Conclusions

The kinetics of vinylation of 4'-bromoacetophenone with *n*-butyl acrylate with palladacycle catalyst **1** was studied in NMP as solvent, NaOAc as base, and in the presence of TBAB promoter. The effect of different parameters *viz* concentration of the substrates, catalyst, base, and TBAB on the rate of the reaction was investigated in a temperature range of 403–433 K. The rate data were fitted to various empirical rate models. The following model was found to predict the rates in good agreement with experimental values:

$$R = \frac{k[A][B][C][D][Q]^{0.5}}{(1 + K_B[B]^2)(1 + K_C[C])(1 + K_D[D]^2)}$$

Acknowledgement

A.S. thanks CSIR New Delhi for the award of research fellowship.

References

- [1] T. Mizoroki, K. Mori, A. Ozaki, Bull. Chem. Soc. Jpn. 44 (8) (1971) 581.
- [2] R.F. Heck, J.P. Nolley, J. Org. Chem. 37 (14) (1972) 2320.
- [3] (a) R.F. Heck, J.B. Melpolder, J. Org. Chem. 41 (2) (1976) 265;
(b) M. Santelli, H. Doucet, M. Feuerstein, F. Berthiol, Tetrahedron. Lett. 43 (2002) 5625.
- [4] (a) T. Jeffery, J. Chem. Soc., Chem. Commun. (1984) 1287;
(b) T. Jeffery, Tetrahedron 52 (30) (1996) 10113;

- (c) J.J. Bozell, C.E. Vogt, *J. Am. Chem. Soc.* 110 (1998) 2655.
- [5] (a) R.F. Heck, H.A. Dieck, *J. Am. Chem. Soc.* 96 (4) (1974) 1133;
(b) B.L. Shaw, S.D. Perera, *Chem. Commun.* (1998) 1863;
(c) Y. Wu, J. Hou, H. Yun, X. Cui, R. Yuan, *J. Organomet. Chem.* 637 (2001) 793.
- [6] (a) A.A. Herrmann, C. Brossmer, C. Reisinger, T.H. Riermeier, K. Ofele, M. Beller, *Chem. Eur. J.* 3 (8) (1997) 1357;
(b) I.P. Beletskaya, A.N. Kashin, N.B. Karlstedt, A.V. Mitin, A.V. Cheprakov, G.M. Kazankov, *J. Organomet. Chem.* 622 (2002) 89;
(c) A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, J. Dupont, *Org. Lett.* 2 (9) (2000) 1287;
(d) C.S. Consorti, G. Ebeling, F.R. Flores, F. Rominger, J. Dupont, *Adv. Synth. Catal.* 346 (2004) 617;
(e) K. Takenaka, Y. Uozumi, *Adv. Synth. Catal.* 346 (2004) 1693;
(f) F. Miyazaki, K. Yamaguchi, M. Shibasaki, *Tetrahedron Lett.* 40 (1999) 7379;
(g) I.G. Jung, S.U. Son, K.H. Park, K.C. Chung, J.W. Lee, Y.K. Chung, *Organometallics* 22 (2003) 4715;
(h) M.H. Huang, L.C. Liang, *Organometallics* 23 (2004) 2813.
- [7] (a) A. Jutand, C. Amatore, *Acc. Chem. Res.* 33 (2000) 314;
(b) V.P.W. Bohm, W.A. Herrmann, *Chem. Eur. J.* 2 (19) (2001) 4191;
(c) B.L. Shaw, *New J. Chem.* (1998) 77;
(d) G.T. Crisp, *Chem. Soc. Rev.* 27 (1998) 427;
(e) A. Sundermann, O. Uzan, J.M.L. Martin, *Chem. Eur. J.* 7 (8) (2001) 1703.
- [8] (a) G.P.F. Van Strijdonck, M.D.K. Boele, P.C.J. Kamer, J.G. de Vries, P.W.N.M. van Leeuwen, *Eur. J. Inorg. Chem.* (1999) 1073;
(b) M. Casey, J. Lawless, C. Shirran, *Polyhedron* 19 (2000) 517;
(c) T. Rosner, J.L. Bars, A. Pfaltz, D.G. Blackmond, *J. Am. Chem. Soc.* 123 (2001) 1848;
(d) C.S. Consorti, F.R. Flores, J. Dupont, *J. Am. Chem. Soc.* 127 (2005) 12054;
(e) F.G. Zhao, B.M. Bhanage, M. Shirai, M. Arai, *Stud. Surf. Sci. Catal.* 122 (1999) 427.
- [9] I.P. Beletskaya, A.V. Cheprakov, *Chem. Rev.* 100 (2000) 3009.
- [10] (a) F.G. Zhao, B.M. Bhanage, M. Shirai, M. Arai, *J. Mol. Catal. A: Chem.* 142 (1999) 383;
(b) A. de Meijere, F.E. Meyer, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2379;
(c) W. Cabri, I. Candiani, *Acc. Chem. Res.* 28 (1995) 2;
(d) A.A. Kelkar, T. Hanaoka, Y. Kubota, Y. Sugi, *Catal. Lett.* 29 (1994) 69;
(e) K. Ohrai, K. Kondo, M. Sodeoka, M. Shibasaki, *J. Am. Chem. Soc.* 116 (1994) 11737.
- [11] C. Amatore, E. Carre, A. Jutand, Y. Medjour, *Organometallics* 21 (2002) 4540.
- [12] D.W. Marquardt, *J. Soc. Ind. Appl. Math.* 11 (1963) 431.