

# Synthesis, structural characterization and catalytic carbonylation of nitrobenzene to phenylurethane using palladium (II) 1,10-phenanthroline diacetato complex<sup>1</sup>

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## Abstract

Four coordinate complexes of Pd(II) of the type [PdLX<sub>2</sub>] where L = 1,10-phenanthroline and X = acetato group were synthesized and characterized by microanalysis, IR, UV/visible spectrometry, <sup>1</sup>H and <sup>13</sup>C [<sup>1</sup>H] NMR. Structural determinations were carried out by single crystal X-ray diffraction method. The complex was found to be nearly square planar by geometry, the coordination valencies being provided by oxygens (one from each acetato group) and two nitrogens of the 1,10-phenanthroline moiety. Cyclic voltammetric studies exhibit an irreversible one electron oxidation with  $E_{pa} = +0.96$  V versus Ag/AgCl. Complex **1** along with a cocatalyst CuCl<sub>2</sub> catalyzed the reductive carbonylation of nitrobenzene in methanol solvent at 200°C and 30 atm CO to give phenylurethane with a turnover (TOF) frequency of 4.5 mol of product per mol catalyst per h. Formation of palladium nitroso intermediate complex through deoxygenation of the -NO<sub>2</sub> group via CO<sub>2</sub> is proposed to be the rate determining step in the carbonylation of nitrobenzene. Based on the rate dependence studies rate law has been derived and thermodynamic activation parameters are calculated from the Arrhenius plot. © 1997 Elsevier Science B.V.

**Keywords:** Palladium; Carbonylation; Monoclinic; 1,10-phenanthroline; phenylurethane

## 1. Introduction

Transition metal complexes containing nitrogen and oxygen donor ligands were found to be active and stereoselective catalysts for oxidation [1,2], reduction [3], hydrolysis and other organic transformations [4–6]. Bidentate nitrogen containing ligands are expected to exhibit unique

catalytic behavior. Although, there are a large number of square planar complexes containing bidentate ligands, the availability of *trans*-chelating ligands are rare in literature [10]. Therefore, *cis*-chelated complexes having these ligands have been used as catalysts [7–9] for many transformations.

Synthesis of isocyanates via the carbonylation route has received considerable attention during the last two decades and this has been made possible through transition metal com-

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<sup>†</sup> In memory of the crystallographer.

plexes catalyzed carbonylation of aromatic nitro compounds [11–15]. The isocyanate (-NCO) group, being very reactive, undergoes side reactions such as dimerization and trimerization resulting in lower yields and hence extensive studies on reductive carbonylation of aromatic nitro compounds have been carried out using alcoholic solvents to get higher selectivities for corresponding urethanes [16,17]. Isocyanates in good yields can be recovered by thermal decomposition of the corresponding urethanes. In continuation of our earlier work [8], we report in this paper, the kinetic study of the catalytic activity of complex **1** in the carbonylation of nitrobenzene to phenylurethane which is an industrially important reaction.

## 2. Experimental

$\text{Pd}(\text{CH}_3\text{COO})_2$  was prepared by the known method [18]. 1,10-phenanthroline (procured from M/s National Chemicals) and dry benzene were used as such. Nitrobenzene (double distilled) and methanol (AR grade) were used in our study.

### 2.1. Catalyst preparation: *cis*-diacetato 1,10-phenanthroline palladium (II) monohydrate **1**

A solution of (0.01 mmol) of  $\text{Pd}(\text{CH}_3\text{COO})_2$  in dry benzene was stirred with (0.01 mmol) of 1,10-phenanthroline for 4 h to give a pale yellow compound. It was filtered, washed with petroleum ether and recrystallized as a yellow micro-crystalline material in  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  which gave 52% yield. Found C, 47.39%, H, 3.45%, N, 6.89%. Calc. for  $\text{PdC}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ : C, 47.48%, H, 3.48% and N, 6.92%. IR spectral data (KBr/Nujol mull,  $\text{cm}^{-1}$ ): 3400(m), 3150(m), 1570(s), 1430(s), 1415(s), 1350(s), 1015(s), 850(s), 715(s) and 580(m). UV/Vis (MeOH):  $\lambda_{\text{max}}(\epsilon)$ : 297(2498), 347(1194), 337 sh (1343).  $^1\text{H}$  NMR (ppm) (MeOD). 7.92, -8.74, 2.13 and  $^1\text{H}$  NMR(MeOH) (ppm) 126.2, 150.2, 185.41, 22.82.

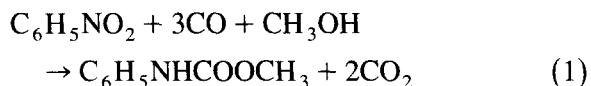
### 2.2. Instrumentation and techniques

Microanalysis of the complexes was performed on a Carlo-Erba analyzer Model 1106. Molar conductance values were obtained at room temperature on a Digisun Electronic Conductivity bridge DI-909. IR spectra was recorded on Carl-Zeiss-Specord M-80 spectrophotometer in Nujol mull/KBr. Electronic spectra was recorded on a Shimadzu UV/Vis recording spectrophotometer model 160.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained on a Jeol FX-100 NMR spectrometer in deuterated and methanol using  $[\text{Si}(\text{CH}_3)_4]$  as an internal standard and operating at 99.55 and 24.99 MHz, respectively. Cyclic voltammograms and differential pulse voltammograms were recorded with a Princeton Applied Research (PAR) instrument using tetrabutyl ammonium tetrafluoroborate as supporting electrolyte in dichloromethane.

### 2.3. Catalytic experiments

Carbonylation experiments were conducted in a 300 ml pressure reactor (M/S Parr Instrument Co., USA) using carbon monoxide gas (purity > 99.9%) procured from M/S B.O.C, UK. In a typical run, a reaction mixture consisting of known amounts of nitrobenzene, complex **1** and cocatalyst  $\text{CuCl}_2$  in methanol (total volume = 100 ml) solvent was placed in the reactor. The vessel was pressurized with the required CO pressure at 200°C. The reaction continued for 10 h and was then cooled to room temperature and the reaction mixture analyzed by gas chromatograph (Shimadzu G.C 9A, Japan) with a SE-30 column and FID detector. TOF was calculated based on the amount of product formed. For kinetic investigations, the progress of the reaction was monitored by recording the fall of pressure with time. Rates of carbonylation of nitrobenzene (expressed in moles of nitrobenzene reacted) were calculated taking the stoichiometry of the reaction (shown in Eq. (1)) into consideration and the depen-

dence of initial rates were expressed graphically.



#### 2.4. X-ray crystallography studies

Suitable crystals for X-ray studies were grown by a slow evaporation technique from H<sub>2</sub>O–MeOH solvent mixture. Yellow plate like crystals of approximate dimensions 0.16 × 0.20 × 0.23 mm were selected for X-ray studies. Intensity data were collected at 295 K on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Accurate cell dimensions were determined from the least-squares refinement of 25 arbitrarily chosen high-angle reflections within the  $2\theta$  range 25–30°.

Crystal decay and orientation during the entire period of data collection was monitored periodically by measuring two sets of three

control reflections. Intensities were corrected for Lorentz and polarization factors. Empirical absorption correction [19] was applied to the data using five strong reflections near  $\chi = 90^\circ$  by the Psi scan method. Crystal data for **1** is given in Table 1. The structure was solved by the heavy atom method; full-matrix least-squares refinement for the isotropic and the anisotropic using a weighting scheme ( $W = F/\text{Pivot}$ , where  $\text{Pivot} = \frac{1}{3}F_{\text{max}}$ , CUTOFF2 value = 0.1) as in the SDP package [20] was carried out until convergence was reached. Hydrogen atoms were generated using the known stereochemical constraints or located in the difference map and were given temperature factors based on the atom to which they were attached. Final cycles of full-matrix least square refinement with all non-H atoms (anisotropic) and H atoms (isotropic, kept fixed) with the same weighting scheme applied converged to the final  $R$  value of 0.054 ( $R_w = 0.048$ ) using 1572 observed reflections. All the computations were carried out using the SDP software [20] available in the

Table 1  
Crystal data of complex **1**

Formula	Pd(C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> )
Mol wt.	360.43
System	Monoclinic
Space group	C2/c
$a$ (Å)	18.915(3)
$b$ (Å)	16.837(3)
$c$ (Å)	7.452(2)
$\alpha$ (°)	90.00
$\beta$ (°)	109.93
$\gamma$ (°)	90.00
$V$ (Å <sup>3</sup> )	2231.00(5)
$Z$	4
No. of reflections and range for unit cell parameters	25, 25–30°
Radiation used	Graphite monochromatized Cu K $\alpha$ (1.5418 Å)
Absorption coef. ( $\mu\text{cm}^{-1}$ )	70.57
Temp. (K)	295
Scan method	$\omega/2\theta$
Measured reflections	1847
Observed reflections $I > 3\sigma(I)$	1572
No. of intensity control reflections, frequency and variations	3, every 1 h, nil
No. of orientation controlled reflections, frequency and variations	3, every 200 reflections, nil
Refinement on	$ F $
Final $R$	0.054
Weighted $R$	0.048

PDP-11/73 system. The scattering factors were taken from Ref. [21]. A full list of H atom positions, anisotropic thermal parameters and list of observed and calculated structural factors are available upon request.

### 3. Results and discussion

The stoichiometric composition of complex **1** is consistent with the microanalysis of the complexes. Millimolar solutions of the complex in methanol show the nonelectrolytic in nature. IR spectral data of complex **1** show characteristic bands at 1570, 1415, 1430, 1350, 1015, 850 and 715  $\text{cm}^{-1}$  due to coordination of 1,10-phenanthroline to the metal ion. The band observed around 585  $\text{cm}^{-1}$  is due to  $\nu(\text{M}-\text{N})$ .

The UV/Vis spectra of the complex **1** exhibit strong charge transfer bands in the UV range near 337–297 nm of the aromatic nitrogen containing ligand, while the metal ligand charge transfer band lies at 347 nm.

The cyclic voltamogram of the complex in dichloromethane show an irreversible oxidation behavior ( $50 \text{ mV s}^{-1}$ ) with  $\Delta E_p = +0.96 \text{ V}$  versus  $\text{Ag}/\text{AgCl}$  in tetrabutyl ammonium tetrafluoroborate in dichloromethane. No reduction wave up to 1.2 V as already reported earlier [19] was seen in complex **1**. A positive shift in the oxidation potential may be due to the  $\pi$ -acidic nature of 1,10-phenanthroline.

The  $^1\text{H}$  NMR spectrum of complex **1** recorded in deuterated methanol show signals in the range 7.92 to 8.74 ppm due to the ring proton of the coordinated 1,10-phenanthroline group. While the signal at 2.13 ppm is due to methyl protons of an acetato group. The  $^{13}\text{C}[^1\text{H}]$  NMR spectra of complex **1** in methanol lie in the range 126.2–150.52 ppm due to the carbon atom directly attached to the coordinated nitrogen of 1,10-phenanthroline moiety. The signal at 185.91 ppm is due to the carbon atom of carboxylate group while the up field signal at 22.82 ppm is due to the carbon atom of methyl group.

An ORTEP [22] view of complex **1** along with the atom numbering scheme is shown in Fig. 1. The molecule possesses a two-fold axis passing through the palladium atom and the mid points of C7–C7' and C8–C8' bonds. The complex has a slightly distorted square planar geometry. The average Pd–O and Pd–N distances being 2.028 (5) Å and 2.031(5) Å, respectively, are well within the range reported earlier [23–29]. The average *trans* angles O–Pd–N =  $175(7)^\circ$  deviated by  $4.3^\circ$  and *cis* angles O–Pd–N =  $94.7(2)^\circ$  and N–Pd–N =  $82.4(2)^\circ$  deviated  $4.7$  and  $7.6^\circ$ , respectively, from the ideal square planar values. The lower value of the *cis* N–Pd–N angle compared to that of the O–Pd–O could be attributed to the chelate formation of the rigid 1,10-phenanthroline group. The acetate moiety retains its non-resonating form since C=O and C–O could be distinguished from the geometry of the carboxyl group ( $\text{O}_1\text{C}_1 = 1.255(8) \text{ Å}$ ,  $\text{C}_1\text{C}_2 = 1.51(2) \text{ Å}$ ,  $\text{C}_1\text{O}_2 = 1.235(8) \text{ Å}$ . Angles  $\text{O}_1\text{C}_1\text{C}_2 = 115.9(6)^\circ$ ,  $\text{O}_2\text{C}_1\text{C}_2 = 119.3(4)^\circ$  and  $\text{O}_1\text{C}_1\text{O}_2 = 124.4(3)^\circ$ ). On the basis of atomic radii, M–N bonds are expected to be around 0.05 Å longer than that of M–O bonds. In the present case, an average difference between the Pd–N and Pd–O distances are almost equivalent (Table 2), which

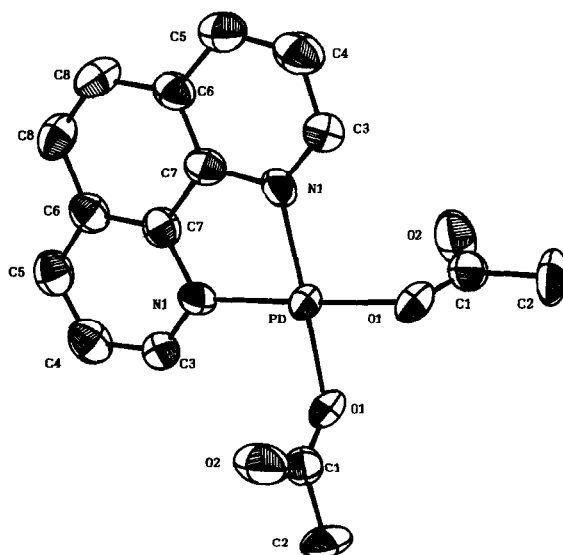


Fig. 1. An ORTEP view of the complex.

Table 2  
Bond distances (Å) and angles (°) for complex 1

PD–O1	2.022 (5)	N1–C3	1.294 (8)	C5–C6	1.40 (1)
PD–O1*	2.033(5)	N1–C7	1.374 (8)	C6–C7	1.397 (9)
PD–N1	2.037 (5)	C1–C2	1.51 (2)	C6–C8	1.441 (9)
PD–N1*	2.025 (5)	C3–C4	1.38 (2)	C7–C7*	1.439 (9)
O1–C1	1.255 (8)	C4–C5	1.37 (2)	C8–C8*	1.38 (1)
O2–C1	1.235 (6)	C1–C2*	1.517 (2)	O2–C1*	1.235 (8)
O1–PD–O1*	88.4 (2)	PD–N1–C3	129.7 (4)	C5–C6–C7	117.3 (6)
O1–PD–N1	94.6(2)	PD–N1–C7	112.2 (4)	C5–C6–C8	125.0 (6)
O1–PD–N1	175.7 (2)	C3–N1–C7	118.1 (6)	C7–C6–C8	117.7 (6)
O1*–PD–N1	175.7 (2)	O1–C1–C2	115.9 (6)	N1–C1–C6*	122.3 (6)
O1*–PD–N1*	94.7 (2)	N1–C3–C4	123.8 (7)	N1–C7–C7*	116.5 (5)
N1–PD–N1*	82.4 (2)	C3–C4–C5	119.5 (7)	C6–C7–C7*	121.3 (6)
PD–O1–C1	117.8 (5)	C4–C5–C6	119.0 (7)	C6–C8–C8*	121.0 (5)
C1–O1–O2	124.43 (5)	C1–O1–C2	116.21 (5)	C1–O2–C2	119.36 (4)

Numbers in parentheses are estimated standard deviations.

indicates that the acetato group are more labile and this lability may be the reason for the catalytic activity of the complex in the reductive carbonylation of nitrobenzene to phenylurethane.

### 3.1. Kinetic study

Reductive carbonylation of nitrobenzene catalyzed by complex 1 with cocatalyst  $\text{CuCl}_2$  at 200°C and 30 atm CO gave phenylurethane selectively with a turnover frequency (TOF) 4.5 mol product per mol catalyst per h. Kinetic investigations of the reductive carbonylation of nitrobenzene catalyzed by complex 1 with cocatalyst  $\text{CuCl}_2$  was carried out by varying the concentrations of the catalyst, nitrobenzene, carbon monoxide pressure and temperature. Initial rates were calculated from the plots of the moles of nitrobenzene reacted versus time. As this is a gas–liquid reaction, it is necessary to ensure that the rates are to be measured in the absence of diffusional resistance and hence the reaction mixture was thoroughly agitated by a stirrer at a speed of 600 rpm in all the experiments. Carbon monoxide solubility data required under the reaction conditions were independently determined and used to interpret kinetic data of this reaction.

#### 3.1.1. Effect of catalyst concentration

The effect of catalyst concentration on the reaction rate was studied at 200°C, 0.097 mol nitrobenzene,  $\text{CuCl}_2$  0.5 g and 30 atm of carbon monoxide. Catalyst concentration was varied in the range 0.2 to 1.0 m mole and the rate of moles of nitrobenzene reacted showed a first dependence with respect to catalyst concentration. This is shown in Fig. 2.

#### 3.1.2. Effect of nitrobenzene concentration

The reaction rates were measured at 200°C as a function of nitrobenzene concentration by keeping constant catalyst concentration (1.0 mmol),  $\text{CuCl}_2$  (0.5 g) and 30 atm CO. Fig. 3

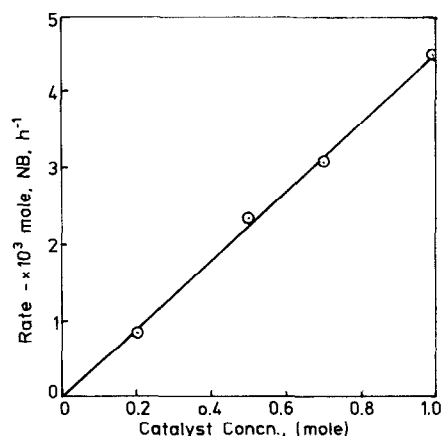


Fig. 2. Effect of catalyst concentration.

shows the plot of rate of mole of nitrobenzene reacted versus initial concentration of nitrobenzene. The reaction exhibits a first order dependence with respect to nitrobenzene concentration.

### 3.1.3. Effect of carbon monoxide pressure

The partial pressure of CO was varied between 5 to 30 atm (initial pressure) keeping other parameters constant as nitrobenzene (0.097 mol), catalyst (1.0 mol),  $\text{CuCl}_2$  (0.5 g) and temperature  $200^\circ\text{C}$ . A plot of the rate of moles of nitrobenzene reacted versus the partial pressure of CO is as shown in Fig. 4, which indicates a first order dependence of the rates with respect to CO pressure.

### 3.1.4. Effect of temperature

The effect of temperature on the rates of moles of nitrobenzene reacted to give phenylurethane was studied in the temperature range 160 to  $200^\circ\text{C}$  at constant conditions of catalyst (1.0 mmol), nitrobenzene (0.097 mol),  $\text{CuCl}_2$  (0.5 g) and 30 atm CO. From the graph of  $-\ln(\text{rate})$  versus  $1/T$  (Fig. 5), the activation energy is evaluated as  $30.0 \text{ kcal mol}^{-1}$ .

### 3.1.5. Mechanism and rate law

Carbonylation of nitrobenzene catalyzed by complex **1** in the presence of a cocatalyst  $\text{CuCl}_2$

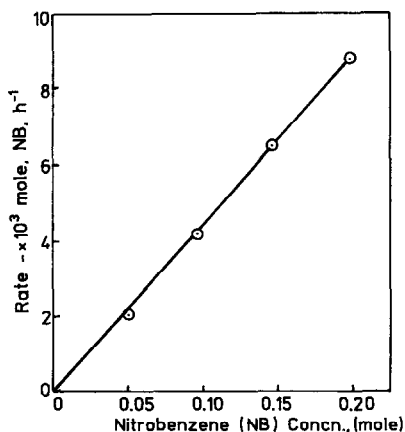


Fig. 3. Effect of nitrobenzene concentration.

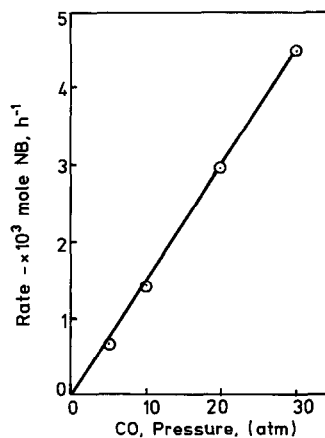


Fig. 4. Effect of partial pressure of CO.

at  $200^\circ\text{C}$  and 30 atm CO gave phenylurethane as the only product. Based on the kinetic investigation, a mechanism proposed is as shown in Scheme 1.

In the proposed mechanism, the active catalytic species is formed by the reaction of complex **1** with CO in a preequilibrium step. In a second pre-equilibrium step, nitrobenzene reacts with complex **2** to give a mixed ligand complex **3**. In a rate determining step, complex **3** reacts with another molecule of CO to give nitroso complex **4** by deoxygenation of  $-\text{NO}_2$  group of nitrobenzene and release of CO. The nitroso complex quickly takes up one more molecule of CO in a fast step to give nitride intermediate species **5** via deoxygenation of nitroso  $-\text{NO}$  group. Migration of CO of the electrophilic nitrogen atom of the  $\text{M}=\text{N}^+-\text{R}$  intermediate

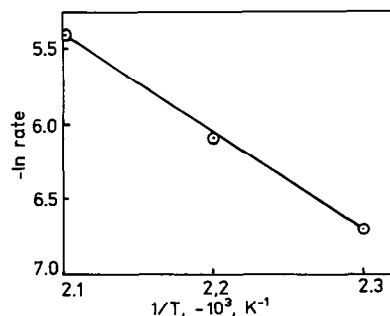
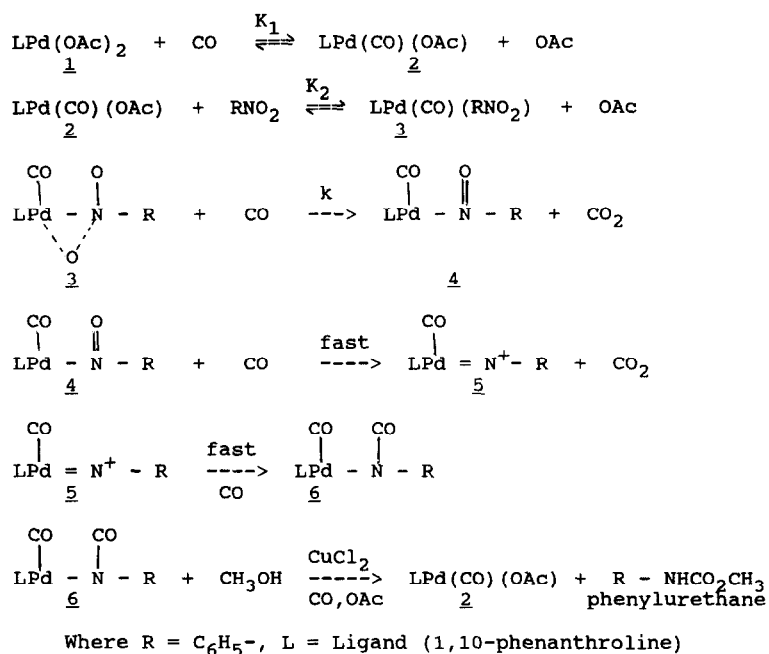


Fig. 5. Arrhenius plot.



Scheme 1.

gives the coordinated phenylisocyanate complex **6**, which reacts with methanol in the presence of CO and CuCl<sub>2</sub> to give phenylurethane, simultaneously regenerating the active catalytic species **2**. In comparison with palladium (II) complexes containing substituted pyridine ligands such as 2,6-lutidine and 3-picoline reported earlier [8], this system is less active in the reductive carbonylation of nitrobenzene to give phenylurethane. The decrease in the catalytic activity of complex **1** is attributed to steric hindrance caused by the bulky 1,10-phenanthroline ligand.

Based on the kinetic observations, the rate law for the reaction can be written as:

$$\text{rate} = \frac{kK_1K_2[\text{CAT}]_T[\text{NB}][\text{CO}]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{NB}]} \quad (2)$$

Where [CAT]<sub>T</sub> = total catalyst concentration, [CO] = dissolved CO concentration, [NB] = nitrobenzene concentration, K<sub>1</sub> and K<sub>2</sub> are preequilibrium constants and k is the rate constant.

For evaluation of the kinetic constants, the above Eq. (2) could be rearranged in the following forms as:

$$\frac{[\text{CAT}]_T}{\text{rate}} = \frac{1}{[\text{NB}]} \left[ \frac{1}{kK_1K_2[\text{CO}]} + \frac{1}{kK_2} \right] + \frac{1}{k} \quad (3)$$

$$\frac{[\text{CAT}]_T}{\text{rate}} = \frac{1}{[\text{CO}]} \left[ \frac{1}{kK_1K_2[\text{NB}]} \right] + \frac{1}{k} \times \left[ 1 + \frac{1}{K_2[\text{NB}]} \right] \quad (4)$$

From Eqs. (3) and (4), the values of k = 66.0 h<sup>-1</sup>, K<sub>1</sub> = 7.6 M<sup>-1</sup> and K<sub>2</sub> = 6.2 M<sup>-1</sup> at 200°C and 30 atm CO were evaluated graphically.

The thermodynamic activation parameters of the reductive carbonylation of nitrobenzene were calculated in the temperature range 160 to 200°C and the average values obtained are E<sub>a</sub> = 30.0 kcal mol<sup>-1</sup>. ΔH<sup>‡</sup> = 29.06 kcal mol<sup>-1</sup>, ΔS<sup>‡</sup> = +112 eu and ΔG<sup>‡</sup> = 16.52 kcal mol<sup>-1</sup>, respectively. These values indicate that the reductive

carbonylation of nitrobenzene is highly endothermic in nature and this is expected because of the bond cleavage in the transition state. A high positive value of entropy reflects the various dissociative steps involved in the formation of active intermediates. The catalytic activity of the complex depends on the presence of labile acetato groups to facilitate such dissociation and the subsequent formation of nitroso complex species.

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