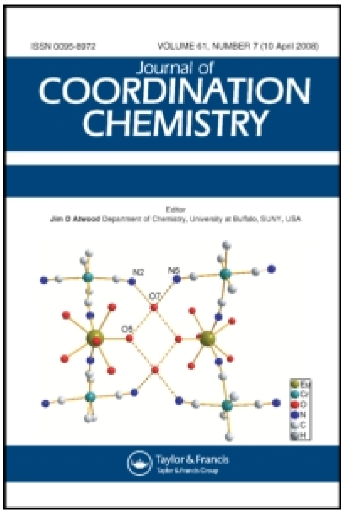

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Reduction of nitrobenzene catalyzed by immobilized copper catalyst under carbon monoxide and water

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Catalytic activity for reduction of nitrobenzene to aniline (98%) and azobenzene (2%) using a poly(4-vinylpyridine)-immobilized Cu catalyst [Cu(II)/P(4-VP)] under a CO atmosphere in aqueous 2-ethoxyethanol was studied as a function of the various reaction parameters ([Cu], P(CO), T, and nitrobenzene/Cu molar ratio). Reaction rates were first-order in $[Cu]_{tot}$ over 1.0–12.0 wt.% range and in P(CO) over the 6.8–27.2 atm range. The catalytic activity proved to be non-linear in nitrobenzene/Cu ratio over 41–500 molar ratio range. These results suggest that the rate-limiting step is preceded by reversible coordination of nitrobenzene to a carbonyl–Cu(I) immobilized species. A catalytic mechanism consistent with the data is proposed.

Keywords: Nitrobenzene reduction; Copper; Poly(4-vinylpyridine); Carbon monoxide; Aniline

1. Introduction

The catalytic reduction of nitrobenzene to aniline under CO/H_2O (equation (1)), promoted by ruthenium [1, 2], rhodium [3–5] and copper complexes [6], has been the topic of several recent investigations. Likewise, the selenium-catalyzed reduction of aromatic nitro compounds with CO/H_2O has been reported [7].

$$C_6H_5NO_2 + 3CO + H_2O \longrightarrow C_6H_5NH_2 + 3CO_2 \qquad (1)$$

The nature of the metal-containing active species formed during reduction of such aromatic nitro compounds by CO and H_2O was partially dealt within a review by Nomura [8].

The promoting effect of water in this reduction process has been related to the formation of an active metal-hydride species [9], an important step in the catalytic cycle,

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via a reaction closely related to the water gas shift reaction (WGSR) [10]. However, little is known about the kinetics of the reduction of nitrobenzene under CO/H_2O by copper complexes; in particular those bearing nitrogen donor ligands.

As a result, the following account presents the outcome of a quantitative study of the effect of variations of reaction parameters in the reduction of nitrobenzene to aniline by poly(4-vinylpyridine)-immobilized copper complexes under water gas shift reaction conditions. These data are also discussed in terms of a possible reaction mechanism.

2. Experimental

2.1. *Materials and instrumentation*

2-Ethoxyethanol (Aldrich) was distilled from anhydrous stannous chloride. Water was doubly distilled. Poly(4-vinylpyridine)/divinylbenzene(2%) (P(4-VP)), was used as provided by Reilly Industries. Nitrobenzene was distilled in H_2SO_4 (1 M) and redistilled in $CaCl_2$ before use. All gas mixtures He/H_2 (91.4%/8.6%, v/v), CO/CH_4 (95.8%/4.2%, v/v) and CO/CH_4/CO_2/H_2 (84.8%/5.1%/5.3%/4.8%, v/v) were purchased from BOC Gases and used as received. Copper(II) chloride (Merck) was used as received. The poly(4-vinylpyridine)-immobilized complex was prepared as reported previously [6] and will be referred to herein as Cu(II)/P(4-VP).

UV-Visible spectra of the solutions (1 cm quartz cell) were recorded on a Perkin-Elmer Lambda 10 spectrophotometer.

Gas sample analyses from catalytic runs were performed as described in detail previously [11] on a Hewlett-Packard 5890 Series II programmable (ChemStation) gas chromatograph fitted with a thermal conductivity detector. The column used was a Carbosieve-B (80–100) mesh obtained from Hewlett-Packard using a He/H_2 mixture as the carrier gas. Analyses of the liquid phases were done on a Chrompack CD9001 programmable gas chromatograph fitted with a methyl silicone, (30 m × 0.323 mm × 0.17 μm) capillary column and flame ionization detector using He as the carrier gas. A Varian Chrompack 3800 programmable gas chromatograph fitted with a CP-Sil-8-CB (phenyldimethylpolysiloxane) (30 m × 0.250 mm) column and a Varian Chrompack Saturn 2000 mass selective detector was used to confirm the identity of the organic reaction products at the end of each run. Organic products were also separated by column chromatography and analyzed by ^{13}C and ^{1}H-NMR in a Jeol Eclipse 270 NMR spectrometer.

2.2. *Catalysis runs*

Catalytic runs of nitrobenzene reduction were conducted in a 150 mL mechanically stirred stainless steel Parr reactor. In a typical run, 0.5 g of catalyst (typically, [Cu] = 2.5 wt.%), 10 mL of 80% aqueous 2-ethoxyethanol and 1.2 mL nitrobenzene (8.13×10^{-3} mol, S/C = 41) were added to the reaction vessel. The reactor was then charged with a CO/CH_4 (95.8%/4.2%, v/v) gas mixture at the desired pressure and placed in a preheated stirred thermostatic silicone oil bath at a given temperature for 4 h (the content of the reactor typically achieves the working temperature in less than five minutes). The reaction was then stopped, the reactor cooled to room temperature, and, before venting the excess pressure, gas samples were taken and analyzed by GC. Liquid samples were taken after venting the excess pressure and analyzed by GC and GC-MS techniques. A response factor method for the GC analyses of the aniline was employed [12]. The GC-MS spectra of the aniline (molecular ion peak at $m/e = 93$ and base peak at $m/e = 66$) and azobenzene (molecular ion peak at $m/e = 182$ and base peak at $m/e = 77$) products are similar to those obtained from pure samples of aniline and azobenzene, respectively. Methane was used as an internal standard, to allow calculation of absolute quantities of CO consumed and CO_2 produced, during a time interval with calibration curves being prepared periodically for CO, CH_4 and CO_2.

3. Results and discussion

3.1. *General aspects*

The Cu(II)/P(4-VP) catalyst was previously investigated by our group as precursor for the water gas shift reaction and the reduction of nitrobenzene to aniline (98%) and azobenzene (2%) in contact with aqueous 2-ethoxyethanol under CO (27.2 atm) at 150°C. Turnover values for aniline formation varied from 5.6 to 9.8 ($24\,h^{-1}$) as a function of the reaction time in the 4–72 h range. This variation was associated with changes in the pH of the reaction medium, from 7.23 to 7.49, as a consequence of the increment of aniline (Brønsted base) content with time [6]. Furthermore, both aniline formation (detected by analyzing the liquid phase in a GC fitted with an FID detector) and CO_2 formation (the only gas product detected by analyzing the gas phase with a GC fitted with a TCD detector) were equal stoichiometrically (1/3 aniline/CO_2 molar ratio (±5%)) as required by equation (1) with a confidence level of 95% [13].

Additionally, control experiments showed a lack of catalytic activity toward nitrobenzene reduction when a 0.5 g sample of P(4-VP) in contact with 10 mL of 80% aqueous 2-ethoxyethanol solution under P(CO) = 27.2 atm at 150°C for 4 h was tested in the absence of copper. Moreover, the supernatant solution left over from the previous reactions after separation of the Cu/P(4-VP) solid exhibited no activity towards either WGSR or nitrobenzene reduction. This supernatant was tested in the absence of the immobilized copper catalytic precursor in the presence of nitrobenzene under conditions similar to those described in table 1.

Furthermore, the Cu/P(4-VP) catalytic system exhibits no WGSR, (equation (2)) activity (i.e. no molecular hydrogen is formed) in the presence of nitrobenzene and CO/H_2O under similar reaction conditions.

$$CO + H_2 \rightleftharpoons CO_2 + H_2 \qquad (2)$$

For this active Cu(II)/P(4-VP) system the effects of varying the copper concentration, carbon monoxide pressure, temperature, and nitrobenzene/Cu molar ratio on the nitrobenzene reduction were explored. Due to the low conversion of nitrobenzene to azobenzene (less than 2%), the following discussion will be concerned only with aniline formation. In addition, the results reported in tables 1–4 represent the average of duplicate runs performed under identical experimental conditions after the reaction solutions reached the working temperature. The calculated kinetic activity defined as TF(aniline) = ([(mol of aniline)/((mol of Cu) × (rt))] × 24 h) (rt = reaction

Table 1. The effects of copper content variation on nitrobenzene reduction under WGSR conditions catalyzed by poly(4-vinylpyridine)-immobilized Cu complexes.[a]

[Cu] (Wt.%)	Nitrobenzene (mL)	$[CO_2]^b$ mol × 10^{-4}	$TF(CO_2)^c$	$[Aniline]^d$ mol × 10^{-4} (Yield %)	$TF(Aniline)^c$
1.0	0.4	3.4	9.9	1.1 (1.3)	3.2
2.5	1.2	5.6	17.1	1.8 (2.2)	5.5
6.0	2.4	9.9	29.5	3.2 (3.9)	9.5
9.1	3.5	15.9	45.9	4.9 (6.1)	14.8
12.0	5.0	21.1	62.9	6.8 (8.3)	20.3

[a] 0.5 g P(4-VP), P(CO) = 27.2 atm at 150°C for 4 h; 10 mL of 80% aqueous 2-ethoxyethanol; nitrobenzene/Cu molar ratio = 41.
[b] Based on GC data from gas phase.
[c] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.
[d] Based on GC data from liquid phase. Selectivity 98%.

Table 2. The effects of carbon monoxide pressure on nitrobenzene reduction under WGSR conditions catalyzed by poly(4-vinylpyridine)-immobilized Cu complexes.[a]

P(CO) (atm)	$[CO_2]^b$ mol × 10^{-4}	$TF(CO_2)^c$ Total	$[Aniline]^d$ mol × 10^{-4} (Yield %)	$TF(Aniline)^c$
6.8	1.92	5.8	0.62 (0.8)	1.9
10.2	2.59	7.8	0.83 (1.0)	2.5
13.6	3.17	9.5	1.02 (1.3)	3.1
17.0	3.84	11.5	1.24 (1.5)	3.7
20.4	4.71	14.1	1.52 (1.9)	4.6
23.8	5.00	15.0	1.61 (2.0)	4.8
27.2	5.67	17.0	1.83 (2.2)	5.5

[a] [Cu] = 2.5 wt.%, 0.5 g P(4-VP), $T = 150$°C for 4 h, 10 mL of 80% aqueous 2-ethoxyethanol, 1.2 mL of nitrobenzene (8.13×10^{-3} mol), nitrobenzene/Cu molar ratio = 41.
[b] Based on GC data from gas phase.
[c] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.
[d] Based on GC data from liquid phase. Selectivity 98%.

Table 3. The effects of temperature on nitrobenzene reduction under WGSR conditions catalyzed by poly(4-vinylpyridine)-immobilized Cu complexes.[a]

Temperature (°C)	$[CO_2]^b$ mol × 10^{-4}	$TF(CO_2)^c$	$[Aniline]^d$ mol × 10^{-4} (Yield %)	$TF(Aniline)^c$
100	1.7	5.2	0.6 (0.7)	1.7
110	2.3	6.9	0.7 (0.9)	2.2
120	2.9	8.6	0.9 (1.1)	2.8
130	3.5	10.4	1.1 (1.4)	3.4
140	4.0	12.1	1.3 (1.6)	3.9
150	5.6	16.7	1.8 (2.2)	5.4

[a] [Cu] = 2.5 wt.%, 0.5 g P(4-VP), P(CO) = 27.2 atm for 4 h; 10 mL of 80% aqueous 2-ethoxyethanol, 1.2 mL of nitrobenzene (8.13×10^{-3} mol), nitrobenzene/Cu molar ratio = 41.
[b] Based on GC data from liquid phase. Selectivity 98%.
[c] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.
[d] Based on GC data from liquid phase.

Table 4. The effect of nitrobenzene/Cu (S/C) molar ratio on nitrobenzene reduction under WGSR conditions catalyzed by poly(4-vinylpyridine)-immobilized Cu complexes.[a]

S/C (molar ratio)	Nitrobenzene (mmol)	$[CO_2]^b$ mol × 10^{-4}	$TF(CO_2)^c$	$[\text{Aniline}]^{c,d}$ mol × 10^{-4} (Yield %)	TF $(\text{Aniline})^c$
44	8.8	5.6	16.7	1.8 (2.2)	5.4
100	20.0	6.8	20.8	2.2 (1.1)	6.7
200	40.0	8.0	23.3	2.6 (0.6)	7.5
300	60.0	8.9	25.7	2.9 (0.5)	8.3
400	80.0	10.2	30.7	3.3 (0.4)	9.9
500	100.0	10.2	30.7	3.3 (0.3)	9.9
600	120.0	10.2	30.7	3.3 (0.2)	9.9

[a] [Cu] = 2.5 wt.%, 0.5 g P(4-VP), Cu/P(4-VP), P(CO) = 27.2 atm at 150°C for 4 h; 10 mL of 80% aqueous 2-ethoxyethanol.
[b] Based on GC data from gas phase. Selectivity 98%.
[c] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.
[d] Based on GC data from liquid phase.

time in h; TF = turnover frequency) was reproducible to within less than 10% for a given series of experimental runs. It is important to stress that TF(aniline) for the kinetics runs were determined for short periods of time (4 h) where the pH, P(CO), $[H_2O]$ and [nitrobenzene] were essentially constant, diminishing by less than 20% overall. Furthermore, CO, H_2O and nitrobenzene are present in vast excess and their concentrations should be considered as constant. This consistency of P(CO), $[H_2O]$ and [nitrobenzene] results in minimal shifts in P(CO)–, $[H_2O]$– and [nitrobenzene]-dependent equilibria among the catalyst component during a run.

3.2. *Effect of the copper content*

The effect of changing Cu content in the range 1.0–12.0 wt.% on the TF(aniline)/24 h value was investigated by carrying out the reaction at a fixed temperature (150°C) and carbon monoxide pressure (27.2 atm). However, the amount of nitrobenzene was varied from 0.4 mL at [Cu] = 1.0 wt.% to 5.0 mL at [Cu] = 12.0 wt.% in order to keep the ratio of nitrobenzene/Cu = 41 in all runs (table 1).

The reaction rate defined as TF(aniline) as a function of [Cu] is plotted in figure 1, showing an increase in [Cu] from 1.0 to 12.0 wt.% enhanced the TF(aniline) values. These results indicate that reaction rate is first order in copper content in the [Cu] range 1.0–12.0 wt.%. Cu(II) complexes of the type $[P(4\text{-VP})_x\text{–Cu(OH)(Cl)}]$ ($x = 2$ and 3) were proposed to form by the reaction of $CuCl_2$ with P(4-VP) in contact with 80% aqueous 2-ethoxyethanol in air [6]. Furthermore, reduction of transition metal salts [14] as well as the reduction of soluble Cu(II) complexes to Cu(I) by the CO/H_2O mixture is well known (equation (3)) [15]. In similar manner, reduction of the Cu(II) catalyst precursor, $[P(4\text{-VP})_x\text{–Cu(OH)(Cl)}]$, by the CO/aq. 2-ethoxyethanol mixture leads to formation of immobilized carbonyl-Cu(I), $[P(4\text{-VP})_x\text{–Cu(OH)(CO)}]$ complexes (equation (4)). The nature of these complexes was confirmed by FT-IR, EPR and XPS studies [6]. Accordingly, we suggested the formation of a similar immobilized carbonyl–Cu(I)

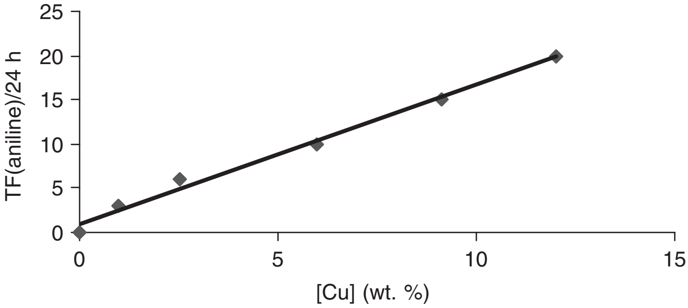


Figure 1. A plot of TF(aniline)/24 h *vs*. copper content on nitrobenzene reduction. The reaction conditions are given in table 1.

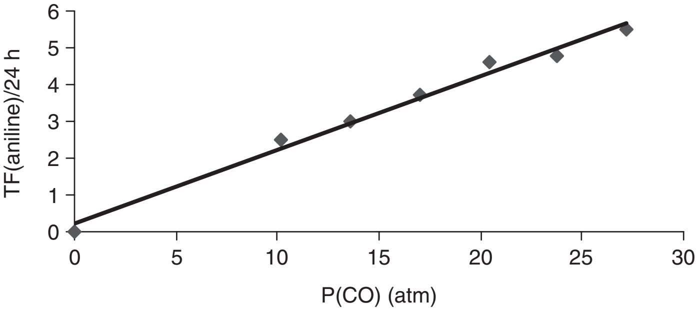


Figure 2. A plot of TF(aniline)/24 h *vs*. P(CO). The reaction conditions are given in table 2.

species during the reduction of nitrobenzene under CO/H_2O conditions.

$$2Cu^{2+} + H_2O + CO \longrightarrow 2Cu^{+} + CO_2 + 2H^{+} \tag{3}$$

$$\begin{aligned} &2[P(4\text{-}VP)_x\text{–}Cu(OH)(Cl)] + H_2O + 3CO \\ &\quad \rightarrow 2[P(4\text{-}VP)_x\text{–}Cu(OH)(CO)] + CO_2 + 2HCl \end{aligned} \tag{4}$$

3.3. *Effect of carbon monoxide pressure*

Figure 2 is a plot of TF(aniline) *versus* P(CO) for [Cu] = 2.5 wt.%, at 150°C (table 2). A linear dependence of TF(aniline) on P(CO) variation in the studied range was noted, indicating that the reaction is first order in [CO]. This was confirmed by plotting Ln TF(aniline) *versus* Ln P(CO) in which a slope with a value of ca 1 was observed, clearly establishing a first-order dependence in P(CO) in the range 0–27.2 atm. Similar first-order [CO] behavior was reported in the catalytic reduction of nitrobenzene to aniline by [Rh(cod)(4-picoline)]/P(4-VP) (cod = 1,5-cyclooctadiene) under CO/H_2O [16].

3.4. *Effect of temperature*

TF(aniline) values for this Cu/P(4-VP) system were measured at various temperatures (table 3) in the 100–150°C range. The TF(aniline) values increase from 1.7 ($24\,h^{-1}$)

at 100°C to 5.4 at 150°C. The resulting Arrhenius plot is linear over the 100–150°C range and an activation energy ($E_a = 64.7\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$) was calculated over this relatively narrow range of temperature.

3.5. *Effect of the nitrobenzene/Cu molar ratio*

The effect of variations in the nitrobenzene/Cu molar ratio was studied to complete determination of the optimal experimental conditions in the reduction of nitrobenzene under CO/H_2O using this catalyst. Blank experiments revealed that only WGSR occurred in the absence of nitrobenzene [6]. As seen in table 4, TF(aniline) values increase from 5.4 ($24\,h^{-1}$) at [nitrobenzene] = 8.8 mmol, to a maximum of 9.9 ($24\,h^{-1}$) at [nitrobenzene] = 80, 100 and 120 mmol. This non-linear response shown in figure 4, indicates reversible addition of nitrobenzene to the Cu center before the rate-determining step on the nitrobenzene/Cu (0–600) molar ratio range. The coordination of nitrobenzene to carbonyl metal complexes is well known [17, 18].

Based on the observed behavior in [Cu], P(CO) and [nitrobenzene] a mechanism in which reversible coordination of nitrobenzene (RNO_2) to the immobilized Cu(I) carbonyl complex (K_1) preceding the rate-limiting step (k_1) is proposed (equation (5)), e.g.

$$[\mathrm{Cu{-}CO}]^+ + \mathrm{RNO_2} \overset{\mathrm{K_1}}{\rightleftharpoons} [\mathrm{RNO_2{-}Cu{-}CO}]^+ \xrightarrow{k_2,\mathrm{H_2O}} [\mathrm{Cu}]^+ + \text{products} \tag{5}$$

The rate of production of aniline (r_{aniline}) for equation (5) would be:

$$r_{\text{aniline}} = (k_2\mathrm{K_1P(CO)[RNO_2][Cu]_{tot}})(1 + \mathrm{K_1[RNO_2]})^{-1} \tag{6}$$

where $[\mathrm{Cu}]_{tot} = [\mathrm{Cu{-}CO}]^+ + [\mathrm{RNO_2{-}Cu{-}CO}]^+$. The above expression (equation (6)) can be reduced to equation (7) (Note that TF(aniline) would be the rate of aniline formation divided by $[\mathrm{Cu}]_{tot}$):

$$\text{TF(aniline)} = (k_2\mathrm{K_1P(CO)[RNO_2]})(1 + \mathrm{K_{eq}[RNO_2]})^{-1} \tag{7}$$

At high [nitrobenzene], $\mathrm{K_1[RNO_2]} \gg 1$, equation (7) can be reduced to equation (8):

$$\text{TF(aniline)} = k_2\mathrm{P(CO)} \tag{8}$$

Furthermore, under the condition of high [nitrobenzene], TF(aniline) levels off at its maximum value when $\mathrm{K_1[RNO_2]} \gg 1$. As can be seen from figure 3, TF(aniline) values start to be independent of [nitrobenzene] at high [nitrobenzene] (80.0–120.0 mmol) as predicted by equation (8).

On the other hand, at low nitrobenzene concentrations, $\mathrm{K_1[RNO_2]} \ll 1$, equation (7) is reduced to equation (9):

$$\text{TF(aniline)} = k_2\mathrm{K_1P(CO)[RNO_2]} \tag{9}$$

For this kinetics model, a plot of TF(aniline)/day *versus* $[\mathrm{RNO_2}]$ at low nitrobenzene concentration (8.8–60.0 mmol) should be linear with a slope of $k_2\mathrm{K_1P(CO)}$. Indeed, the experimental plot (figure 3) is linear in the 44–200 molar range as predicted by equation (9).

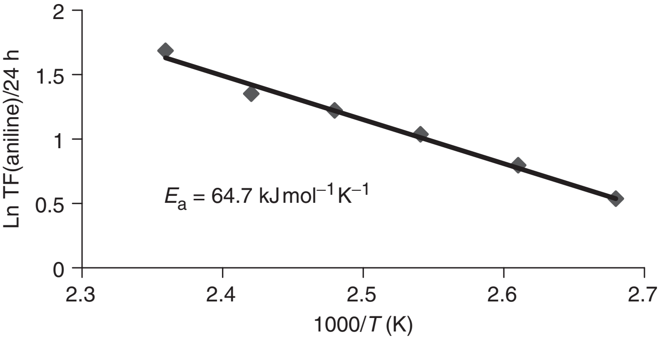


Figure 3. The Arrhenius plot for nitrobenzene reduction. The reaction conditions are given in table 3.

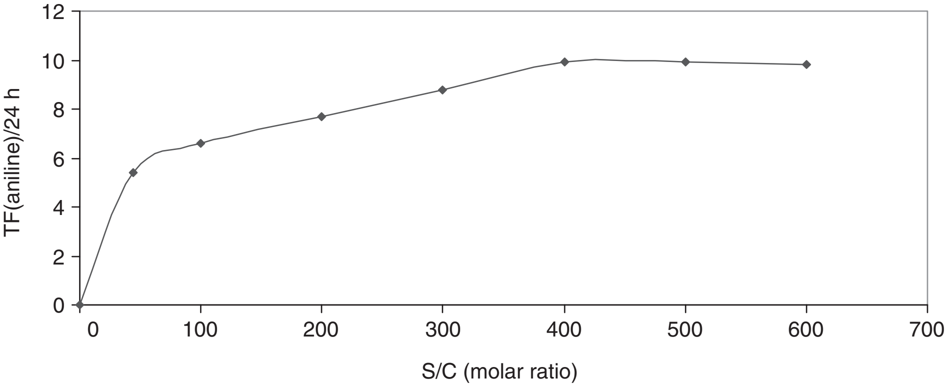
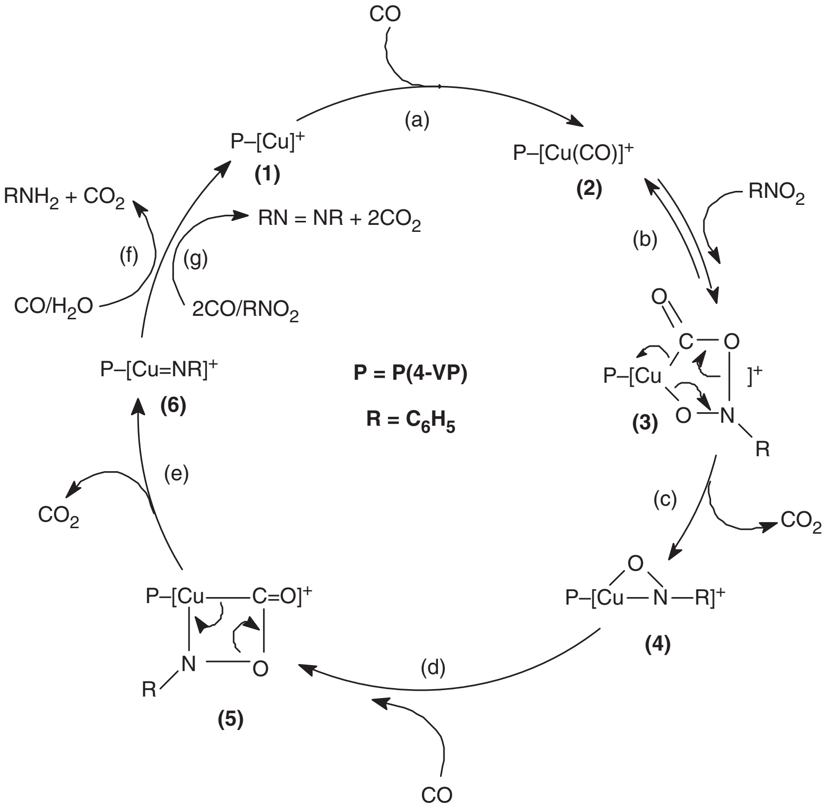


Figure 4. A plot of TF(aniline)/24 h *vs.* nitrobenzene/Cu molar ratio. The reaction conditions are given in table 4.

Further, the highest value (TF(aniline)/24 = 20) was achieved under optimal conditions e.g., [Cu] = 12.0 wt.%, P(CO) = 27.2 atm at 150°C for 4 h (8.3% nitrobenzene conversion).

3.6. *Mechanistic consideration*

The evaluation of the mechanism for nitrobenzene, azobenzene, and CO_2 formation catalyzed by Cu/P(4-VP) in contact with 80% aqueous 2-ethoxyetanol and nitrobenzene under CO shows several key features: first, FT-IR and XPS spectroscopy studies of the used catalysts point to the presence of Cu(I)–CO species. Second, the kinetics studies indicate that the reaction is first order in [Cu] and P(CO). Third, S/C studies suggest a mechanism in which the rate-limiting step is preceded by reversible coordination of nitrobenzene to active Cu(I) immobilized species. Fourth, catalytic schemes for the reduction of nitrobenzene to aniline have been proposed in which nitrobenzene cycloaddition to a metal carbonyl complex is an important first step [8]. And finally fifth, a similar mechanism for the reduction of nitrobenzene



Scheme 1. Proposed mechanism.

to aniline catalyzed by soluble Rh complexes has been proposed [4]. Given the above, the catalytic reaction mechanism depicted in scheme 1 is proposed for the reduction of nitrobenzene to aniline and azobenzene by the Cu(I)–CO immobilized species.

In scheme 1, the auxillary ligands are omitted for clarity. Coordination of CO (step a) to the P–$[Cu]^+$ complex (**1**), where $P = P(4\text{-VP})_x$, would give P–$[Cu(CO)]^+$ (**2**). The reversible cycloaddition of nitrobenzene (RNO_2, $R = C_6H_5$) to the Cu-CO bond (step b) followed by elimination of CO_2 (step c) leads to formation of copper nitrosobenzene P–$[Cu(\eta^2\text{–ONR})]^+$ complex (**4**) through a deoxygenating process of the copper nitrobenzene P–$[Cu(\eta^2\text{–O(CO)RNO})]^+$ species (**3**). There is precedence for the structures proposed; Skoog *et al.* isolated and characterized by X-ray crystallography the $[Ru(\eta^2\text{-ONR})]$ intermediate [17, 18]. Formation of a P–$[Cu(\eta^2\text{–O(CO)RNO})]^+$ species (**3**) as the rate-limiting step would rationalize first-order dependence of TF(aniline) on P(CO) (step b) and the reversible addition of nitrobenzene. Insertion of one CO molecule to the Cu–O bond of the nitrosobenzene complex **4** forms P–$[Cu(\eta^2\text{–O(CO)NR})]^+$ complex (**5**) (step d).

Decarboxylation of P–$[Cu(\eta^2\text{–O(CO)NR})]^+$ (**5**) generates a copper–nitrene complex P–$[Cu(NR)]^+$ (**6**) and CO_2 (step e). Hydrogenation of this copper–nitrene, likely by P–[Cu–H] species formed under conditions similarly to the WGSR, affords aniline, CO_2 and the P–$[Cu]^+$ complex closing the aniline-catalytic cycle (step f) [19].

Alternatively, the copper–nitrene species (**6**) can allow coordination of CO and cycloaddition of a second molecule of nitrobenzene to give the P–[Cu(η^2–CO)(O)N(O)RNR]$^+$ complex. Deoxygenating the latter with two CO molecules affords, azobenzene (R–N = N–R), two CO_2 molecules and the P–[Cu]$^+$ complex to get the azobenzene-catalytic cycle closed (step g) [20].

In summary, it was found that $CuCl_2 \cdot 2H_2O$ immobilized on P(4-VP) in contact with aqueous 2-ethoxyethanol under CO formed a slightly-active catalyst system for the reduction of nitrobenzene to aniline and azobenzene. The kinetics studies of the Cu/P(4-VP) system suggest the presence of copper species having the same nuclearity as reaction intermediates. The Cu/P(4-VP) system shows a first order dependence of the rate on P(CO) indicating coordination of CO to catalytic species precedes the rate-limiting step. Also, the catalytic activity proved to be non-linear in nitrobenzene content suggesting its reversible coordination to Cu immobilized species before the rate-limiting step.

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