

Soluble and Polymer-Anchored Rhodium Catalyst for Carbonylation Reaction: Kinetics and Mechanism of Diphenylurea Formation

D. K. Mukherjee^{†,1} and C. R. Saha*

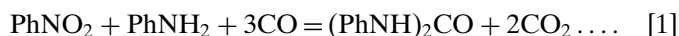
*Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India; and [†]Department of Chemistry, Ramsaday College, Amta, Howrah-711 401, West-Bengal, India

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The high catalytic activity of rhodium(I) complexes toward the reductive carbonylation of nitroaromatics under high carbon monoxide pressure prompted investigation of the polymer-bound complex of rhodium(I). The polymer-supported complex [RhA(Ph₂P-CH₂-polystyrene)CO] having the same coordination environment as [RhA(CO)PPh₃] (HA; 2-aminobenzoic acid) was prepared and the catalytic behavior studied under various reaction conditions and methanol concentrations. The carbonylation of nitrobenzene at low temperature and atmospheric or elevated pressure using both soluble and polymer-supported rhodium species is reported. *N,N'*-Diphenylurea is the main product under moderate carbon monoxide pressure while methyl-*N*-phenyl carbamate is formed predominantly as *P*_{CO} and methanol concentration is increased. Spectroscopic and kinetic studies showed that the reaction proceeds through the species [Rh(A)(PPh₃)(COOCH₃)(μ-OCH₃)₂] and the isocyanate formed at an intermediate stage is immediately scavenged by excess amine to form *N,N'*-diphenylurea. A tentative reaction mechanism based on the identification of reactive intermediates has been proposed for the carbonylation process.

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and water or aniline using a new catalytic system have also been reported (19). The stoichiometry of this synthesis is expressed by



Generally *d*⁸ metal complexes with π-acid ligands are active for the carbonylation of nitroaromatics, although detailed reaction mechanisms have been reported only in few cases (20–24). Compared to other *d*⁸ metal complexes, rhodium(I) compounds have been much less studied for the carbonylation reaction. The high catalytic activity of [RhA(CO)Py] (HA; anthranilic acid) toward reductive carbonylation of nitroaromatics under moderate carbon monoxide pressure (25) prompted examination of polymer-bound rhodium(I) complexes of a similar nature. The present paper reports the catalytic conversion of PhNO₂ to PhNHCONHPh by soluble and polymer-supported rhodium catalysts in mild coordinating solvents containing methanol and the relationship this has to the mechanism of the catalytic carbonylation process.

INTRODUCTION

The search for environmentally friendly processes to replace the use of phosgene for the production of isocyanates has focused attention on the homogeneous catalytic carbonylation of nitroarenes (1). Many industrially important compounds, such as carbamates, ureas, azo and azoxyarenes, oximes, and several heterocycles, can be selectively obtained in one step by either reductive carbonylation of nitroaromatics (2–6) or oxidative carboxylation of anilines (7–10). The nature and distribution of products depend on the reaction parameters and the catalyst system. *N,N'*-Diphenylurea and methyl-*N*-phenyl carbamate are of growing interest in the field of chemical technology, as is evident from numerous patents and papers in the literature (11–18). Details of the synthesis of DPU from PhNO₂, CO,

EXPERIMENTAL

Instrument and Chemicals

Analytical-grade reagents and freshly distilled solvents were used throughout the investigation. DMF was purified by drying over CaH₂ under N₂ for 24 h followed by distillation under reduced pressure. PhNH₂ was purified by vacuum distillation in an inert atmosphere prior to use. CO (99.5%) purchased from IOL, Mumbai, and RhCl₃ · 3H₂O from Arora Matthey Ltd., India, were used as received. Macroporous polystyrene beads crosslinked with 5% DVB were supplied as hard insoluble 20- to 50-mesh spheres of average pore diameter 800 Å by Aldrich Chemical Company, USA.

The polymer-supported complex [Rh(A)CO(Ph₂P-CH₂-(P))], where (P) is the polystyrene moiety having the same coordination environment as the soluble rhodium complex [Rh(A)CO(PPh₃)], was prepared and characterized as described below. Vibrational, electronic, and

¹To whom correspondence should be addressed. E-mail: debkumarmukherjee@rediffmail.com.

PMR spectra were taken with Perkin–Elmer 883, Shimadzu MPC-3700, and Bruker 200-MHz instruments, respectively. XPS studies and thermal analyses were made with VG-scientific ESCA lab mark (E) and Shimadzu DT-400 instruments, respectively. Gas chromatographic analysis was performed with a Chrompack CP-9000 with a 15% FFAP ss column and flame ionization detector, with temperature programming from 110 to 240°C at a rate of 10°C/min. The progress of the reaction was monitored by periodic analysis of the reaction mixture by GC. Diphenylurea was identified and estimated by HPLC using a Bondapack column with mobile phase as 62% methanol in aqueous sodium acetate solution.

Carbonylation Procedure

In a typical experiment, a DMF solution (10 ml) of the catalyst (10^{-4} M) and the substrate (1.0 M) was taken in a 50-ml glass-lined stainless-steel autoclave provided with an inlet and outlet and equipped with a magnetic element. The reactor was first evacuated and flushed with nitrogen. After nitrogen was pumped out, it was immersed in a thermostated silicone oil bath preheated to the desired reaction temperature. The whole arrangement was then placed on a magnetic stirrer and the reaction mixture was subjected to the required pressure of pure carbon monoxide, which was maintained constant throughout the run. At the end, the autoclave was rapidly cooled in an ice salt bath and blown off. The products were identified and analyzed after subsequent workup by GC and HPLC using authentic samples for comparison.

Preparation and Isolation of the Complexes

[RhA(CO)PPh₃]... (1). The rhodium(I) complex was prepared according to the literature (26). A deoxygenated solution of RhCl₃·3H₂O in DMF was treated with a twofold excess of anthranilic acid and the mixture was heated under reflux for 2 h. The solution was cooled to about 20°C and diluted with a double volume of water when a yellow precipitate separated out. The solution with its precipitate was cooled to 5°C for 1 h and then filtered off, washed with H₂O and Me₂CO, and dried in a vacuum. The yellow complex formed was [RhA(CO)₂] and was highly soluble in DMF. A solution of [RhA(CO)₂] (1.02 mmol, 0.3 g) in DMF (10 ml) was treated with excess triphenyl phosphine (1.5 mmol, 0.4 g) and the mixture was heated under reflux for 2 h. The solution changed from yellow to brown within 15 min. The solution was cooled to 20°C and diluted with a double volume of water (20 ml). During dilution of the reaction mixture a light brown precipitate formed. The solution with the precipitate was further cooled to 5°C for 1 h and filtered and the residue washed with H₂O and MeOH and dried in a vacuum. The brown amorphous compound was very much soluble in DMF and C₆H₆.

[Rh A(CO) (Ph₂P–CH₂–polystyrene)]... (2). Polystyrene beads with 5% crosslinking of divinylbenzene were chloromethylated by the procedure adopted by Pepper *et al.* (27). The chloromethylated polymer was treated with a 1 M tetrahydrofuran solution of lithiodiphenyl phosphine for 24 h to replace 80% of the chlorines with diphenyl phosphine groups (28). These beads were then equilibrated with a twofold excess of dicarbonylanthranilato rhodium(I) for 2 weeks. At the conclusion of the equilibration period the brown beads were washed with fresh oxygen-free benzene several times and dried in a vacuum.

[RhA(PPh₃)(COOCH₃)(μ-OCH₃)₂]... (3). A 50-ml stainless-steel autoclave containing [Rh(A)CO(PPh₃)] (1.2 mmol) was purged several times with CO. A solution of *o*-nitrotoluene (1.5 mmol) in 15 ml of toluene was injected into the autoclave via an exhaust valve. After 5 min, 3 ml of methanol was injected in the same manner and the system was pressurized with CO (60 atm) and heated to 80°C. After 24 h, the reactor was cooled, the pressure was released, and the solution was transferred to a two-necked 100-ml rb flask. Solvent was removed under vacuum and the resulting brown oil was stirred and washed three times with 20-ml portions of diethyl ether until a light brown solid was obtained. This was filtered and dissolved in a minimum quantity of pure benzene, and the process of stirring and washing with ether was continued until the brown compound separated out. The compound thus isolated was subjected to ¹H NMR and IR studies for characterization: ¹H NMR (ppm, C₆D₆) 3.03 (s, OCH₃), 3.77 (s, OCH₃), 6.17 (m, Ar H), 7.41 (m, Ar H), 8.02 (m, Ar H), IR(KBr, cm⁻¹) 1628, 1616; Anal. (found: C, 56.38; N, 2.28; H, 4.42%; calcd: C, 57.04; N, 2.37; H, 4.58%).

Characterization

The compounds [RhA(CO)PPh₃] (1), [RhA(CO)Ph₂P–CH₂–polystyrene] (2), and [RhA(PPh₃)(COOCH₃)(μ-OCH₃)₂] (3) were characterized on the basis of their analytical and vibrational spectral data (Table 1) and electronic, ¹H NMR, and XPS data (Table 2).

Due to the insolubility of the polymer catalyst in organic and inorganic solvents, its characterization was limited to chemical analysis, IR spectra, and XPS and DTA studies. The IR peaks at 1580 cm⁻¹ (ν_{COO}, as) and 1360 cm⁻¹ (ν_{COO}, s) and in the region 3000–3200 cm⁻¹ (ν_{NH₂}) are present in the spectra of all the complexes, indicating the presence of coordinated anthranilate in all of them. Weak asymmetric NH₂ bending in the region 1660–1610 and symmetric bending at 1510–1490 cm⁻¹ are also observed for the complexes. The peaks of 1616 (w) and 1628 in complex 3 in the ν_{CO} region are characteristic of a methoxy carbonyl ligand (29). The peak at 1088 cm⁻¹ in complex 3 is common to both δPPh₃ and ν(O–CH₃) of the bridging ligand.

The rhodium content in each complex was determined by refluxing them with concentrated HCl for 24 h and then

TABLE 1

Analytical and Vibrational Data of the Compounds^a

Compounds	ν_{CO}	ν_{NH_2}	ν_{OCO}	$\nu_{\text{C(O)OCH}_3}$	δPPh_3	C (%)	H (%)	N (%)	Rh (%)
[RhA(CO)PPh ₃] (1)	1960	3175 (as) 3075 (s)	1575 (as) 1350 (s)		1085	59.40	4.40	2.21	20.7
[RhA(CO)Ph ₂ P-CH ₂ -(P)] (2)	1955	3175 (as) 3070 (s)	1575 (as) 1340 (s)		1085				1.38
[RhA(PPh ₃)(COOCH ₃)(μ -OCH ₃) ₂] (3)		3172 (as) 3072 (s)	1585 (as) 1362 (s)	1628 1616	1088	56.38	4.42	2.28	17.2

^a All ν values are given in cm^{-1} . (P) = Polystyrene.

estimating the metal concentration in the solution by atomic absorption spectrometry at a wavelength of 255.6 nm using an air-acetylene flame. Analysis of complex **2** after five catalytic runs indicated the Rh content (1.19%) was reduced by 13% compared to that of the original catalyst (1.38%). This modest loss does not appear to be metal elution, as the complex showed similar catalytic activity and the beads showed no visible color change. The metal loss may be a consequence of changes in the bead structures, as is evident from a slight shift in the ν_{CO} absorption peaks (Fig. 1).

The electronic spectra of complex **1** in DMF medium show three absorption bands, at 280 (sh), 363, and 380 nm. The former was assigned to an intramolecular charge transfer of a coordinated anthranilate anion (26), while that of 363 nm may be due to π - π transition of the ligand. The weak band at 380 nm has been attributed to d - d transition of the rhodium(I) complex. For complex **3**, in addition to the bands at 280 and 363 nm, the third band, at 398 nm (w, sh), is due to the d - d transition of the rhodium(III) octahedral complex. The ¹H NMR spectra (ppm, C₆D₆) of complexes **1** and **3** exhibit multiple signals in the region 6.7–8.0 (phenyl protons) and a broad signal at 7.38 (NH₂) (Table 2). New PMR signals at 3.03 and 3.77 ppm of complex **3** are attributed to CH₃ protons of C(O)OCH₃ groups and to the O-CH₃ protons of the bridging ligands, respectively (30, 31). ¹H NMR signals in the methoxide and aromatic methyl regions of complex **3** are masked at higher concentrations of aromatic amine and CH₃OH.

XPS study of the compounds were carried out in the range 290–320 eV using Al $K\alpha$ (1486.3 eV) as target material in order to determine the oxidation state of rhodium in them. The 3d_{5/2} and 3d_{3/2} levels of the metal in complexes **1**

and **2** have binding energies of \sim 308 and \sim 312 eV, respectively. The energies are comparable with the +1 oxidation state of rhodium (32). The binding energy for the isolated complex **3** was found to be 310.2 (3d_{5/2}) and 314.2 eV (3d_{3/2}), which suggests the presence of Rh(III) in the species (Fig. 2). To avoid possible X-ray-induced metal reduction in the polymer host, measurements were made with the power of the X-ray source reduced to 10 kV, 10 mA. Survey spectra were recorded for all samples in the binding energy range 0–1400 eV at steps of 0.5 eV.

RESULTS AND DISCUSSION

The catalyst [RhA(CO)₂] (HA; 2-amino benzoic acid) was found to be highly efficient for the reductive *N*-carbonylation of nitroaromatics in mild coordinating solvents at high temperature (140°C) and high P_{CO} (80 atm) in the presence of cocatalyst and cosolvent (33). With the idea that polymer-based catalysts can withstand more drastic conditions and can influence product distribution due to their steric factors, two groups of catalysts (**1** and **2**) were prepared and their catalytic properties examined. The soluble catalyst [RhA(CO)PPh₃] and its polymer analogue were used for the reductive carbonylation of nitroaromatics in DMF medium under a wide range of carbon monoxide pressures and reaction temperatures. In the absence of methanol, low conversion of nitrobenzene (20%) to aniline and diphenylurea was achieved with the soluble rhodium catalyst but the polymer-supported complex showed no conversion of the nitroaromatics. Reaction at room temperature and low P_{CO} (20 atm), in the presence of methanol, did not give satisfactory results.

TABLE 2

XPS and PMR Data of the Complexes^a

No.	Compounds	ESCA Data (eV)		PMR spectral data (ppm, C ₆ D ₆)		
		3d _{5/2}	3d _{3/2}	Aromatic-H	-NH ₂	-COOCH ₃
1	[RhA(CO)PPh ₃]	308	312	6.7–7.8 (m)	7.38 (s)	
2	[RhA(CO)Ph ₂ P-CH ₂ -(P)]	308.6	312.8			
3	[Rh(A)PPh ₃ (COOCH ₃)(μ -OCH ₃) ₂]	310.2	314.2	6.9–8.02 (m)	7.36 (s)	3.03 (s)/3.77 (s)

^a (P) = Polystyrene.

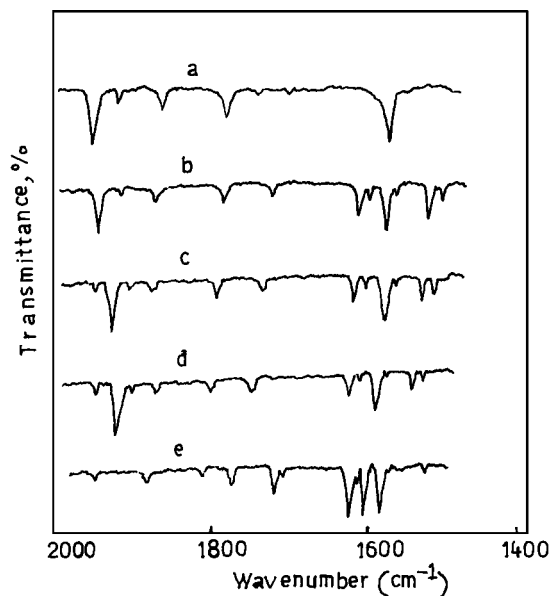


FIG. 1. IR spectra showing ν_{CO} peaks of (a) complex **1**, (b) complex **2**, (c) used catalyst **2** after 3 runs, (d) used catalyst **2** after 5 runs, and (e) complex **3**.

Effect of temperature and P_{CO} on the carbonylation of nitrobenzene in the presence of an optimum concentration of methanol was therefore studied. The highest conversion of PhNO_2 (100%) to diphenylurea (DPU) was achieved at $P_{\text{CO}} = 60$ atm and temperature = 80°C and at a methanol concentration of 6 M. A higher methanol concentration increased the yield of aniline at the cost of DPU. Comparable results were obtained with both the soluble and polymer-anchored rhodium complex (Table 3).

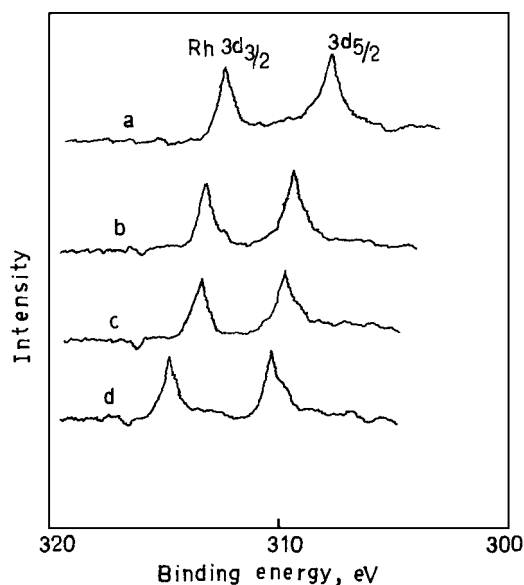


FIG. 2. XPS spectra of $3d_{5/2}$ and $3d_{3/2}$ levels of Rh in the catalysts: (a) complex **1**, (b) complex **2**, (c) used catalyst **2** after 5 runs, and (d) complex **3**.

TABLE 3

Influence of $\text{PhNO}_2 : \text{PhNH}_2$ Molar Ratio on the Reductive Carbonylation of PhNO_2^a in the Presence of Methanol

Run	Molar ratio $\text{PhNO}_2 : \text{PhNH}_2$	Conversion ^b (%)	Selectivity (%)			
			DPU ^c	MPC ^d	PhNH_2	NPF ^e
1	1:0	100	59 (53)	16 (20)	9 (13)	10 (10)
2	0:1	40	74 (66)	4 (16)	—	17 (15)
3	1:0.5	100	69 (60)	9 (15)	7 (10)	12 (10)
4	1:1	100	70 (62)	9 (14)	8 (10)	13 (10)
5	1:2	100	71 (62)	13 (15)	— (08)	14 (12)
6	1:4	100	70 (60)	13 (16)	— (08)	14 (12)

Note. Values in parentheses are those for the soluble rhodium catalyst.

^a Conditions: $\text{PhNO}_2 + \text{PhNH}_2 = 0.5$ mol, $\text{CH}_3\text{OH} = 2$ ml, catalyst = Rh, content = 2×10^{-4} mol, medium = DMF, $T = 80^\circ\text{C}$, $t = 4$ h, $P_{\text{CO}} = 60$ atm.

^b Calculated to the conversion of PhNO_2 (runs 1, 3–6) and PhNH_2 (run 2).

^c *N,N'*-Diphenylurea.

^d Methyl-*N*-phenyl carbamate.

^e *N*-Phenylformamide.

At temperatures lower than 20°C , the rate of conversion was very low even after 24 h of a catalytic run (Fig. 3). A high reaction temperature ($T > 140^\circ\text{C}$), however, produced some unidentified brown resinous product ($\sim 5\%$) but no phenyl isocyanate was detected at the end. PhNCO was expected to be formed by the thermal decomposition of the carbamate at such high temperatures. Complexes **1** and **2** were stable and showed no signs of decomposition even under such severe conditions (Fig. 4). TGA curve for the soluble and the polymer-supported complex show 22 and

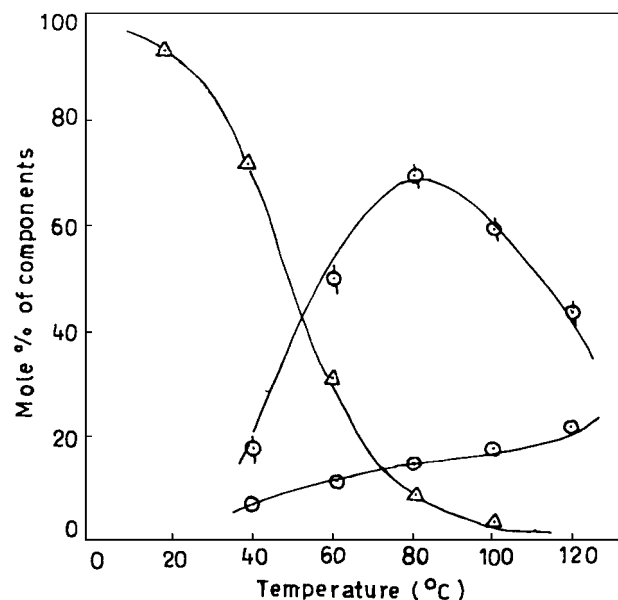


FIG. 3. Effect of temperature on reductive carbonylation of PhNO_2 using **1** as catalyst. $P_{\text{CO}} = 60$ atm, solvent = DMF, time = 4 h, $\odot = \text{PhNH}_2$, $\diamond = \text{DPU}$, and $\triangle = \text{PhNO}_2$.

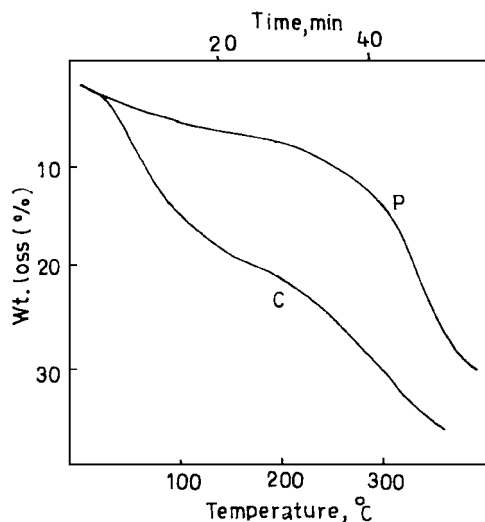


FIG. 4. TGA curve for the soluble (C) and the polymer-supported (P) catalysts.

9% weight loss, respectively, at 200°C. The corresponding weight loss at 300°C is 30 and 15%.

At a carbon monoxide pressure of 20 atm or below, no carbonylation reaction takes place, as nitrobenzene concentration remained unchanged and no reaction products were observed even after 16 h of a catalytic run (Fig. 5). As the pressure of carbon monoxide was slowly raised from as low as 20 to 100 atm, the percentage of diphenylurea increased gradually and reached the optimum value of 70% at $P_{\text{CO}} = 60$ atm.

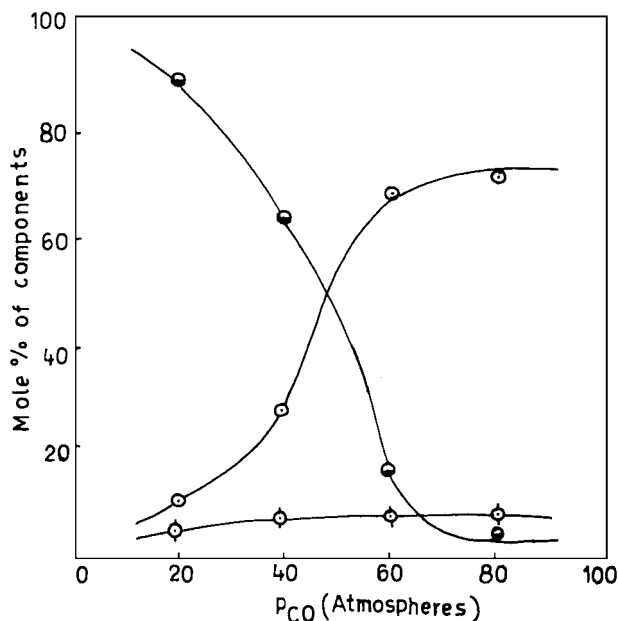
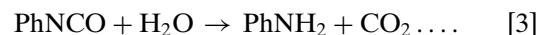
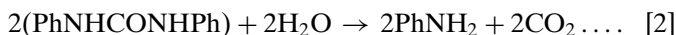
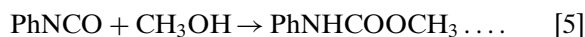
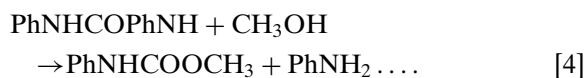


FIG. 5. Effect of P_{CO} on reductive carbonylation of PhNO_2 . Temperature = 80°C, solvent = DMF, time = 4 h, \circ = PhNH_2 , \bullet = DPU, and \odot = PhNO_2 .

Both catalysts **1** and **2** exhibited similar behavior, though with slightly different rates. It is therefore likely that the soluble and polymer-anchored rhodium complexes pass through the common intermediate stages of the carbonylation process. With regard to the formation of aniline as the by-product during reductive carbonylation of nitrobenzene in the presence of methanol to carbamate (run 1, Table 3), the influence of PhNO_2 to PhNH_2 molar ratio in the reductive carbonylation process was also the subject of study. It is clear from the results that though the molar ratio ($\text{PhNO}_2 : \text{PhNH}_2$) decreased, the percentage conversion to DPU and MPC remained almost unaltered. When no aniline was added to the system, conversion of PhNO_2 to DPU and PhNH_2 (~15%) suggested the role of methanol as hydrogen provider (the system was degassed to free it from air and moisture). With PhNH_2 as substrate, the product distribution changed substantially, with the highest recorded yield of DPU (70%). The presence of moisture in the system greatly hinders the catalytic conversion of PhNO_2 to DPU and almost 90% aniline was recorded. High aniline formation may be due to hydrolysis of any DPU formed (reaction 2)



A high methanol content in the system greatly reduced the extent of DPU formation while simultaneously increasing the percentage of MPC and PhNH_2 . Reactions 4 and 5 seem to be the most probable reason for low conversion to DPU:



Formation of NPF in the system (detected in all six runs; Table 3) is believed to be due to direct interaction of CO and PhNH_2 :



An increase in aniline concentration however resulted in no significant change in NPF formation (runs 3–6).

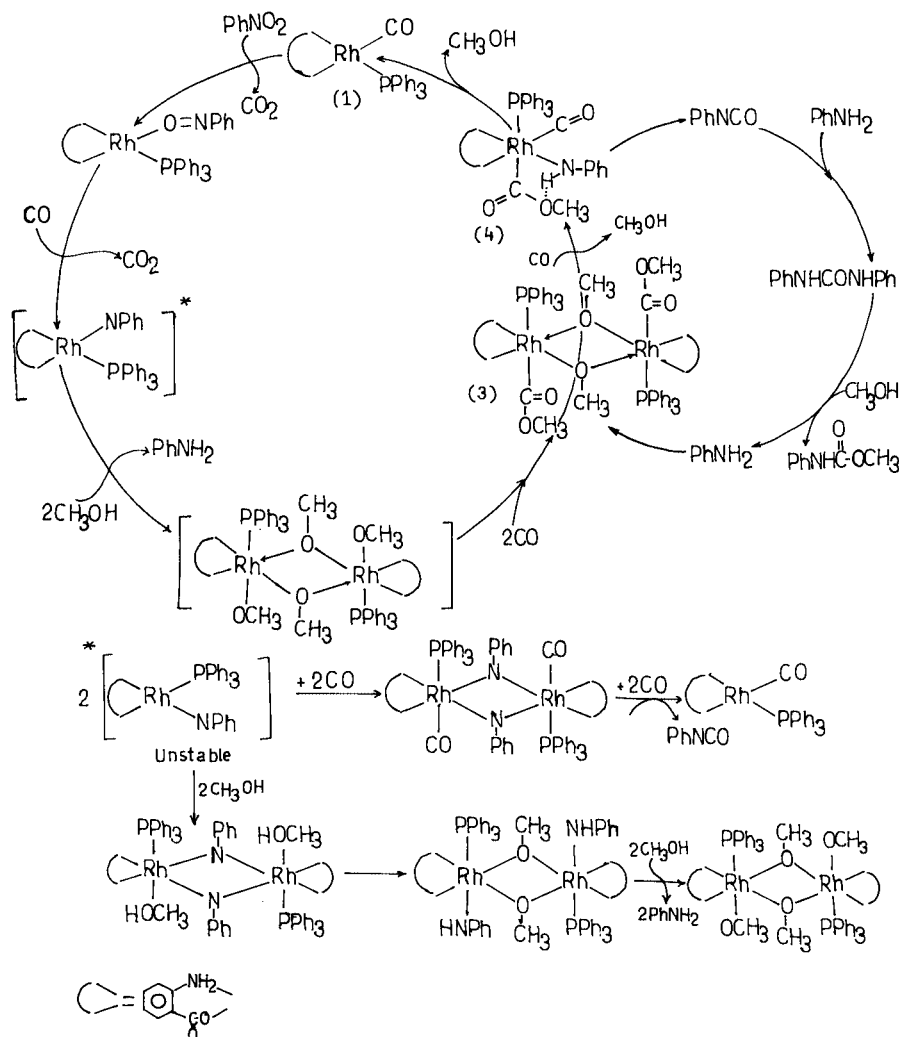
Several runs were conducted in a completely dry alcohol-free medium with and without aniline to study the nature of product distribution and to monitor how much PhNCO , if any, was formed at the intermediate stage. PhNCO could not however be detected at any intermediate stage of these catalytic runs. Monitoring the IR and ^1H NMR spectra of the solutions during a catalytic run did not show the formation of intermediate metal hydride species. Carbonylation of nitrobenzene was conducted in DMF containing either 1-hexene or phenylacetylene under optimum reaction conditions. The alkene and the alkyne remained unchanged during the entire carbonylation process. Formation of metal

hydride species has therefore been ruled out, as its formation should reduce alkene or alkyne to the corresponding saturated products.

Several authors resorted to nitrene mechanism in rationalizing the products, e.g., isocyanates, carbamates, and urea, formed during reductive carbonylation of nitrobenzene (33, 34). Attempts were therefore made to trap any phenylnitrene formed at the intermediate stage using diphenylacetylene in the reaction medium. The phenylnitrene derivatives could not be detected under the optimum reaction conditions using either the soluble or the polymer-supported complex. PhN coordinated to Rh(I)/Rh(III) may not allow its reaction with diphenylacetylene and the unstable species in solution may quickly be transformed into the dimer-bridged complex (Scheme 1). Spectroscopic studies however showed that the reaction proceeds through species $[\text{RhA}(\text{PPh}_3)(\text{COOCH}_3)(\mu\text{-OCH}_3)]_2 \dots$ (3) and the isocyanate formed at an intermediate stage is immediately scavenged by excess amine to *N,N'*-diphenylurea (30). For-

mation of intermediate compound **3** requires CO insertion in one of the stages, which explains the requirement of moderate carbon monoxide pressure for the carbonylation process. Low P_{CO} (<20 atm) prevents the formation and isolation of the intermediate and therefore no carbonylation products were observed under such conditions even at high methanol concentration. The monomer species at initial stages of the reaction is readily transformed during isolation into the dimer and this isolated complex **3** was subjected to carbonylation reaction under reaction conditions (Table 3) identical to that maintained for the starting catalyst, **1**. GC analysis showed >50% DPU formation within 1 h of the catalytic run. Several runs were conducted in DMF using PhNO as substrate and the similar product distribution suggests that PhNO₂ was deoxygenated to PhNO at some earlier stage of the catalytic cycle (Scheme 1).

¹H NMR spectra of a CH₃OH/C₆D₆ solution of **3** and *p*-toluidine were monitored for a period of 24 h. After 12 h, the spectrum collected revealed resonances from **3**, CH₃OH,



p-toluidine, and three new signals. There was a singlet at 10.72 ppm, similar in chemical shift to the hydrogen-bonded amide proton (35), a singlet at 2.55 ppm, characteristic of a methoxy carbonyl proton (30), and a singlet at 2.04 ppm, a shift similar to methyl resonance from the *p*-tolyl moiety. The integration of these three signals was 1:3:3, respectively. ¹H NMR signals are masked at higher concentration of aromatic amine and methanol. The result describes the formation of the methoxy carbonyl-carbamoyl species **4** in the reaction medium although all attempts to isolate the solid sample were unsuccessful. During the experiments described above, the concentration of **4** increased to a constant ratio with **3**, suggesting that an equilibrium was achieved. The reaction quotient [4]/[3] decreased in a linear fashion as CH₃OH concentration was increased from 1.0 to 8.0 M at a constant concentration of *p*-toluidine. Formation of the intermediate species **4** by the reaction of *p*-toluidine with **3** and simultaneous liberation of one equivalent of methyl alcohol, as predicted in the catalytic cycle, is more probable.

An effort was also made to identify the reaction pathway by treating a solution of *p*-toluidine and methanol in a septum-sealed vial with *p*-tolylisocyanate. Visible amounts of *N,N'*-ditolylurea were noticed within 5 min at ambient temperature. After 30 min the solution in the vial was analyzed by gas chromatography. The belief that the isocyanate formed at an intermediate stage is immediately taken up by the amine resulting in the formation of urea is therefore substantial and no trace of carbamate could be detected at any stage of the reaction. That reaction (4) led to the formation of carbamate seemed unlikely due to CH₃OH having a basicity lower than PhNH₂.

Kinetic Analysis of the Reaction of [RhA(PPh₃)(COOCH₃)(μ-OCH₃)₂] with *p*-Toluidine at 80°C

These reactions were carried out in a high-pressure cell designed for spectroscopic studies under high gas pressure (36) in order to simulate the conditions of the actual catalytic process. Various volumes of the isolated complex **3** and *p*-toluidine in toluene-*d*₈ and CD₃OD were taken in a 5-mm NMR tube to give a total volume of 0.5 mL. The initial concentrations of **3** and *p*-toluidine in these solutions are listed in Table 4. The valve of the high-pressure tube was connected to the pressure line and the cell was pressurized with carbon monoxide (60 atm). The solution in the cell was shaken to insure that a reasonable amount of CO dissolved in solution. The pressure was released and the tube was placed in an NMR spectrometer with the probe warmed to the desired temperature. The organic product observed from the reaction of **3** and *p*-toluidine under all conditions was *N,N'*-di-*p*-tolylurea:

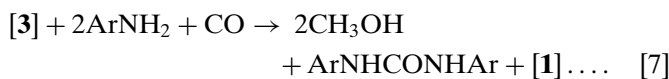
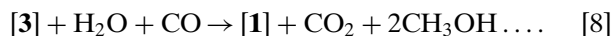


TABLE 4
Rate Constant for the Reaction of **3** with *p*-Toluidine

Temp (°C)	[ArNH ₂] (M)	[Rh] (mM)	<i>k</i> (M ⁻¹ min ⁻¹)
80	0.20	30.2	0.24
80	0.44	30.2	0.21
80	0.56	30.2	0.23
80	0.15	30.2	0.23
80	0.15	14.4	0.20
80	0.15	44.2	0.21

The rate was followed by the study of the 3.03 and 3.77 signals characteristic of CH₃ protons of the C(O)OCH₃ group of **3** and the peak areas were evaluated with the integration for all species normalized to the initial concentration of **3**. The reaction was complete within 90 min at 80°C, and upon standing for an additional 24 h, crystals of *N,N'*-di-*p*-tolylurea were visible in the reaction tube and **1** was the major metal species present in the reaction solution. It was imperative that the kinetic reaction be strictly performed under dry conditions, as the smallest measurable concentration of water caused an erroneous result due to the hydrolysis of complex **3** with liberation of the starting catalyst **1**, CO₂, and two equivalents of CH₃OH:



The kinetics outlined in the paper were conducted in different temperature regimes. Although the final products were identical, the kinetic work in the low-temperature region was complicated by the appearance of peaks

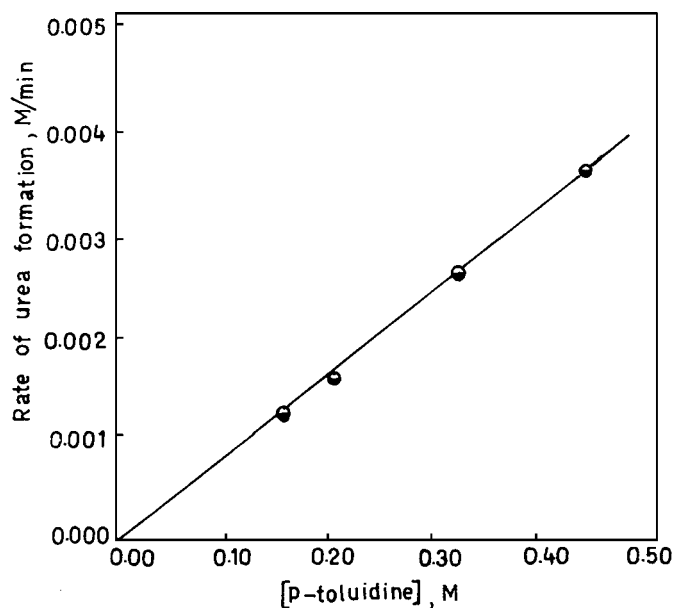


FIG. 6. A first-order rate dependence is shown w.r.t the concentration of *p*-toluidine from the reaction of **3** with *p*-toluidine at 80°C.

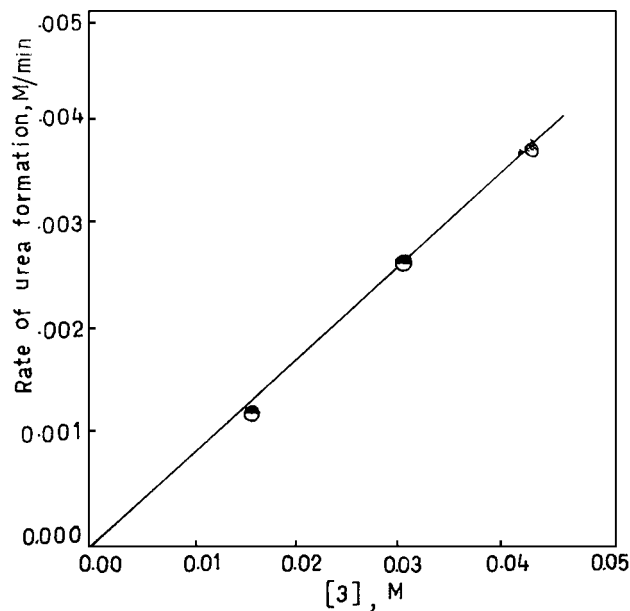


FIG. 7. Initial rate of urea formation from the reaction of **3** with *p*-toluidine at 80°C.

corresponding to intermediate **4**. The effects of the varying concentrations of **3** and *p*-toluidine on the initial rate of urea formation are shown in Figs. 6 and 7, respectively. The observed rate constants shown in Table 4 were determined by the rate law

$$\text{Rate} = k[\text{ArNH}_2][\text{Rh}(\text{A})(\text{PPh}_3)(\text{COOCH}_3)(\mu\text{-OCH}_3)]_2.$$

Based on the above observations and identification of the reactive intermediates, the mechanism shown in Scheme 1 has been proposed for the carbonylation process using both the soluble and the polymer-supported rhodium catalyst. The *in situ* spectroscopic studies of the high-pressure catalysis established that the principal species observed in solution was $[\text{Rh}(\text{A})(\text{PPh}_3)(\text{COOCH}_3)(\mu\text{-OCH}_3)]_2$ and that several intermediate steps were involved in the conversion of nitroarene to useful diarylurea in the presence of alcohol.

CONCLUSION

The reaction conducted under catalytic conditions produced either diarylurea or the carbamate depending upon the conditions. Even in those runs that produced carbamates, urea was still proposed to be the intermediate. Intramolecular elimination of aryl isocyanate is the mechanism which releases the organic product from the catalyst, and in all of the stoichiometric reactions, the isocyanate is immediately trapped by ArNH_2 to form the observed product, diarylurea.

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