

Reductive carbonylation of nitroaromatics using $\text{RhA}(\text{CO})_2$

S.M. Islam, D. Mal, B.K. Palit, C.R. Saha *

Department of Chemistry, Indian Institute of Technology, Kharagpur, 721302, W.B., India

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Abstract

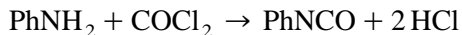
The investigation of the catalytic activity of $\text{RhA}(\text{CO})_2$ (HA = anthranilic acid) towards the reductive carbonylation of nitroaromatics in DMF medium under high P_{CO} ($8.0 \times 10^3 \text{ kNm}^{-2}$) at 140°C without cocatalyst showed moderate conversion of the substrates to the corresponding diphenylureas and anilines as major and minor products respectively. The presence of acidic cocatalysts increased the yield of diphenylurea while in the presence of basic cocatalysts and alcohols, corresponding carbamates were the main products. The maximum yield and selectivity of the carbamate were achieved using NaOMe and MeOH as cocatalyst and cosolvent respectively under optimum reaction conditions. A tentative reaction mechanism based on the identification of reactive intermediates was proposed for this carbonylation process. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carbonylation; Nitroaromatic compounds; $\text{RhA}(\text{CO})_2$

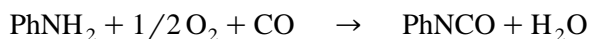
1. Introduction

The catalytic carbonylation of aromatic nitrocompounds is an area of current interest from both academic and industrial viewpoint [1–9]. Many industrially important compounds such as isocyanates, carbamates, ureas, azo and azoxyarenes, amines, amides, oximes and several heterocycles can be selectively obtained in one step by either reductive carbonylation of nitroaromatics [1–8,10–15] or oxidative carbonylation of anilines [1–8,16–25]. Importance of the catalytic formation of these products is evident from the numerous patents and papers in the literature [26–33]. Isocyanates, carbamates and ureas are the raw materials for the synthesis of pesticides, polyurethanes, fertilisers, synthetic leather adhesives, coating, etc. [1–8,34–41].

Conventional process for the production of isocyanates according to the reaction



is hazardous because of the use of poisonous COCl_2 and production of corrosive HCl. Hence the development of alternative phosgene free route for isocyanate synthesis as per the following reactions

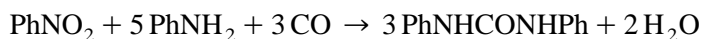
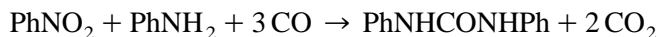


* Tel.: +91-3222-55221; Fax: +91-3222-55303

in the presence of suitable catalysts has become a field of high interest due to the simplicity and cleanliness of the process. Isocyanates, due to their high reactivities with moisture and other components in the reaction mixture form undesirable products and hence in many cases, they are converted to the corresponding stable carbamates [15]. Thermal decomposition of carbamates can regenerate isocyanates as per the following reaction



Diphenylurea may be formed by the following reactions



Generally d^8 metal complexes of Ru(0) [42–45], Fe(0) [46–48], Pd(II) [49–56], Pt(II) [57–59] and Rh(I) [60,61] with Π -acid ligands are active for the carbonylation of nitroaromatics to phenylisocyanates, diphenylureas, carbamates, formanilides, anilines, etc., and the nature and distribution of products depend on the reaction parameters and the catalyst system. The platinum(II) complexes are generally effective for the carbonylation of dinitroaromatics [58,59]. Reaction mechanisms have been studied only in few cases and [62–66] detail mechanisms have been reported with the complexes of ruthenium [67] and palladium(II) [68–70].

Compared to the other d^8 metal complexes, rhodium(I) compounds have been much less studied for the carbonylation reaction [71]. High catalytic activity of $\text{RhA}(\text{CO})_2$ (HA = anthranilic acid) for the reduction of unsaturated substrates [72] prompted us to investigate its catalytic activity towards the carbonylation of nitroaromatics under different experimental conditions and the results are presented in this paper.

2. Experimental

Analytical grade reagents and freshly distilled solvents were used throughout the investigation. DMF was purified by drying over CaH_2 under N_2 for 24 h followed by distillation under reduced pressure. Carbon monoxide (99.9%) purchased from IOL Bombay and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ from Arora Matthey, India were used as received.

The complex $\text{RhA}(\text{CO})_2$ was prepared and purified according to the literature method [73]. Vibrational, electronic and PMR spectra were taken with Perkin-Elmer 883, Shimadzu MPC-3100 and Bruker 200 MHz instruments respectively. Gas Chromatographic analysis was carried out with Crompack CP-9000 instrument using SE-30, 15% FFAP capillary column with temperature programming from 110°C to 240°C at the rate of 10°C/min. The progress of the reaction was monitored by the periodical analysis of the reaction mixture by GC immediately. Diphenylurea was identified and estimated by HPLC using a ν -Bondopack column with mobile phase as 62%, methanol in aqueous sodium acetate solution.

2.1. Reaction procedure

In a typical experiment, DMF solution (5 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 inlet and outlet and equipped with a magnetic element. The reactor was first evacuated and then flushed thrice with nitrogen. After

pumping out nitrogen, it was immersed in a thermostatted 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. The extent of reaction occurring during the attainment of desired pressure and temperature was found to be negligible. Reaction time was measured from the moment the reaction mixture attained the desired pressure and temperature. At the end, the autoclave was cooled in an ice salt bath and blown off. The components in the product mixture were identified and estimated by GC and HPLC analysis using authentic samples as standards. In certain cases, the products were identified by IR and PMR spectra whenever possible.

2.1.1. Preparation and isolation of the complexes

2.1.1.1. $RhA(CO)_2$ (I). The Rh(I) complex was prepared according to literature method [73]. The deep red solution mixture of $RhCl_3 \cdot 3H_2O$ (0.26 g, 0.98 mmol) and anthranilic acid (0.2 g, 1.46 mmol) in dry, deoxygenated DMF was refluxed for 2 h. The cold solution diluted with 20 ml of distilled water produced yellow precipitate on keeping at 5°C for 1 h. The precipitate after successive washing with water and acetone was dried under high vacuum. The purity of the compound was checked by tlc, m.pt, chemical analysis, IR and UV–VIS spectral studies.

2.1.1.2. $[RhA(CO)(\mu-CO)]_2$ (II). The yellow solution of $RhA(CO)_2$ (0.300 gm, 1.02 mmol) in dry, deoxygenated DMF (10 ml) changed to deep green on stirring for 24 h under nitrogen. The solution was reduced to 1 ml by vacuum evaporation at 60°C, mixed with dry chloroform (5.0 ml) and kept at 0°C for 24 h when the green crystalline precipitate separated out. This was washed with dry chloroform and dried under vacuum.

2.1.1.3. $[RhA(\mu-CO)(PhNO_2)]_2$ (III). Dry $PhNO_2$ (0.5 ml) was added to the deep green solution obtained by stirring the DMF solution (10 ml) of $RhA(CO)_2$ (0.30 g, 1.02 mmol) for 24 h under nitrogen. The stirring under nitrogen was continued for 12 h more, chloroform (5 ml) was added and the mixture was kept at 0°C for 48 h when the deep green precipitate separated out. This was washed with dry chloroform and finally dried under vacuum. The compound can also be prepared by direct addition of $PhNO_2$ (0.5 ml) to the deep green DMF solution (10 ml) of $[RhA(CO)(\mu-CO)]_2$ (0.30 g) and following the above procedure.

2.1.1.4. $Na[RhA(PhNO_2)(COOCH_3)]$ (IV). The green DMF solution (10 ml) of $[RhA(CO)(\mu-CO)]_2$ (0.6 g, ~ 1 mmol) was mixed with NaOMe (0.50 g, ~ 10 mmol) and $PhNO_2$ (0.06 g, ~ 5 mmol) and the mixture was stirred for 24 h under N_2 at 25°C when the solution colour changed to brownish green. The filtered solution was concentrated to 2 ml under reduced pressure at 60°C and mixed with chloroform (5 ml). The mixture on keeping at 0°C for 24 h produced yellowish green precipitate which was washed successively with dry methanol and chloroform and finally dried under vacuum.

2.1.2. Characterization

The compounds $[RhA(CO)_2]$ (I), $[RhA(CO)(\mu-CO)]_2$ (II), $[RhA(\mu-CO)PhNO_2]_2$ (III) and $Na[RhA(PhNO_2)(COOCH_3)]$ (IV) were characterized on the basis of their analytical and vibrational spectral data (Table 1), electronic, PMR spectral and XPS data (Table 2). Compared to the IR spectra

Table 1
Analytical and vibrational data of the compounds

Compounds	$\nu\text{CO cm}^{-1}$	$\nu\text{-NH}_2 \text{ cm}^{-1}$	$\nu\text{OCO cm}^{-1}$	$\nu\text{-COOCH}_3 \text{ cm}^{-1}$	$\nu\text{-NO}_2 \text{ cm}^{-1}$	Analytical data found (calculated)		
						C	H	N
I. RhA(CO) ₂	2085 (s) 2008 (s)	3170 (ν_{as})(m) 3070 (ν_{s})(m)	1585 (as) (s) 1360 (s) (s)			36.01 (36.20)	2.0 (2.1)	4.5 (4.55)
II. [RhA-(μ -CO)- (CO)] ₂	2005 (s) 1810 (s)	3175 (ν_{as})(m) 3075 (ν_{s})(m)	1580 (as) (s) 1360 (s) (s)			36.40 (36.60)	2.01 (2.05)	4.71 (4.75)
III. [RhA-(μ -CO)- (PhNO ₂)] ₂	1810 (s)	0.3173 (ν_{as})(m) 3072 (ν_{s})(m)	0.1582 (as) (s) 1360 (s) (s)		1520 (m) 1345 (m)	40.80 (40.95)	3.81 (3.88)	6.32 (6.35)
IV. Na[RhA-(PhNO ₂)- (COOCH ₃)]		3172 (ν_{as})(m) 3072 (ν_{s})(m)	1585 (as) (s) 1362 (s) (s)	1620 (m)	1520 (m) 1345 (m)	42.50 (42.75)	3.01 (3.12)	6.54 (6.56)

of (I), the spectra of (II) show the appearance of a new peak at 1810 cm^{-1} (νCO , bridged) at the cost of one νCO (terminal) peak at 2085 cm^{-1} . The other νCO (terminal) peak at 2005 cm^{-1} remains unchanged. Most probably, RhA(CO)₂ in DMF solution dimerises through CO bridging to form a pentacoordinated rhodium(I) complex containing both linear and bridged CO groups. The spectra of (III) exhibits two new peaks at 1520 and 1345 cm^{-1} due to coordinated PhNO₂ [8,77] and only the bridged νCO peak at 1810 cm^{-1} . In case of (IV), all peaks in the νCO region disappear but the presence of peaks at 1620 cm^{-1} (νCOOCH_3) [62–64], 1520 and 1340 cm^{-1} (νNO_2) suggests the coordination of these species to the metal atom in (IV). The peaks at $\sim 1580 \text{ cm}^{-1}$ (νCOO , as), 1360 cm^{-1} (νCOO , s) and in the region 3200–3400 cm^{-1} (νNH_2) are present in the spectra of all the complexes indicating the presence of coordinated anthranilate in all of them.

The electronic spectra of all the complexes in DMF medium show two common absorption bands at $\sim 280 \text{ nm}$ (sh) and $\sim 336 \text{ nm}$. The former was assigned to intramolecular charge transfer of coordinated anthranilate anion [73] while the latter may be due to $\pi\text{-}\pi^*$ transition of the ligand. Both the compounds (I) and (IV) exhibit peaks at $\sim 380 \text{ nm}$ indicating them to be square planer in nature [73]. The low intensity peak at 620 and 500 nm observed in the spectra of (II) and (III) may be due to the d–d transition in these five coordinated Rh(I) complexes.

The PMR spectra of compound (I) in $d_6\text{-DMSO}$ exhibit multiple signals in the region 7.8–6.4 δ (phenyl protons) and a broad signal at 7.38 δ (NH₂) (Table 2). For compound (II), the position of phenyl proton signals remain almost unaltered while the NH₂ proton signals show upfield shift at 6.58 δ . The same upfield shift of NH₂ protons was observed in case of complex (III) and (IV). The

Table 2
UV–VIS, XPS and PMR data of the compounds

Compounds	ESCA data (eV)		UV–VIS	PMR spectral data (in δ)		
	3d _{5/2}	3d _{3/2}	λ_{max} (nm)	Aromatic H	–NH ₂	–COOCH ₃
I. RhA(CO) ₂ d.t. 185°C	308.0	312.0	280, 336, 380	6.4–7.8 (m)	7.38 (s)	
II. [RhA(μ -CO)(CO)] ₂ d.t. 200°C	307.8	311.9	280, 280, 336, 600	6.7–8.0 (m)	6.58 (s)	
III. [RhA(μ -CO)(PhNO ₂)] ₂ d.t. 180°C	307.9	311.9	280, 280, 336, 510, 500	6.50–8.20 (m)	6.24	
IV. Na[RhA(PhNO ₂)(COOCH ₃)] d.t. 190°C	307.8	312.0	280, 336, 380, 490	7.24–8.34 (m)	6.85 (s)	3.75 (s)

d.t. = Decomposition temperature.

Melt with decomposition.

upfield shift may be due to increased electron density at the NH_2 group caused by the lowered number of terminal CO groups in the molecule or due to influence of metal d-orbitals in the changed coordination environment of the metal. Compound (IV) exhibits a new PMR signals at 3.75 δ due to CH_3 protons of $-\text{COOCH}_3$ group [74].

XPS studies of the compounds were carried out in the range of 290–320 eV using Al-K_α 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 these complexes have binding energies of ~ 308 and ~ 312 eV respectively (Table 2). The energies are comparable with +1 oxidation state of rhodium [75]. The very small difference of XPS values of $3d_{5/2}$ and $3d_{3/2}$ levels among these species (I, II, III, IV) may be due to different coordination environment around the metal atom in them.

3. Results and discussion

The catalyst, $\text{RhA}(\text{CO})_2$ was found to be highly efficient for the carbonylation of nitroaromatics in mild coordinating solvents at high temperature and high P_{CO} in the presence of cocatalyst and cosolvent only. At high temperature ($T > 140^\circ\text{C}$) and high P_{CO} ($8.0 \times 10^3 \text{ kNm}^{-2}$) moderate conversion of nitroaromatics (40%) to the corresponding amine (10%) and diphenylurea (30%) as minor and major products respectively occurred in absence of cocatalyst and cosolvent (Table 3). The presence of moisture is probably responsible for this conversion as the experiment performed under strictly dry

Table 3
Carbonylation of nitrobenzene in the presence of different cocatalyst and cosolvent

Run no.	Cocatalyst	Cosolvent	PhNH ₂	Carbamate PhNHCOOR (R = Me/Et/Ph)	D.P.U. PhNHCONHPh	PhNO ₂
1	–	–	10	–	30	60
2	–	H ₂ O	99	–	–	–
3	–	CH ₃ OH	10	40	–	50
4	–	C ₂ H ₅ OH	15	35	–	50
5	–	MeOH (15M)	35	10	–	–
6	FeCl ₃	–	10	–	85	–
7	SnCl ₄	–	15	–	80	–
8	PTS	–	20	–	75	–
9	FeCl ₃	MeOH	95	5	–	–
10	SnCl ₄	MeOH	90	10	–	–
11	PTS	MeOH	92	8	–	–
12	Py	–	10	–	20	70
13	Et ₃ N	–	15	–	15	65
14	2-Picoline	–	20	–	15	65
15	Py	MeOH	30	70	–	–
16	Et ₃ N	MeOH	20	80	–	–
17	2-Picoline	MeOH	40	60	–	–
18	NaOMe	MeOH	7	90	–	–
19	NaOEt	EtOH	10	85	–	–
20	NaOPh	PhOH	25	75	–	–

PTS = *p*-toluenesulphonic acid.

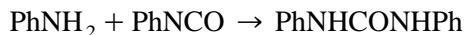
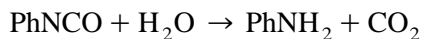
Reaction condition: $[\text{PhNO}_2] = 1.0 \text{ M}$. $[\text{Cat}] = 10.0 \text{ mM}$.

Yield refers to GC and HPLC analysis.

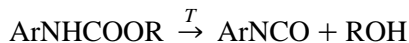
Medium = DMF, $[\text{Cosolvent}] = 8.0 \text{ M}$, $P_{\text{CO}} = 8.0 \times 10^3 \text{ kNm}^{-2}$, $T = 140^\circ\text{C}$, $t = 5.5 \text{ h}$.

$[\text{Cocatalyst}] = 0.40 \text{ M}$. total volume = 10 ml.

conditions produced only a trace amount of phenylisocyanate ($\sim 2\%$) and diphenylurea ($\sim 8\%$). Probably phenylisocyanate formed in small amount react with the available moisture present in DMF to produce aniline in the first step which further reacts with PhNCO to produce diphenylurea in the second step as



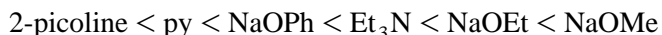
Due to high reactivity and extreme sensitivity of phenylisocyanate to moisture, attempts were made to produce the more stable carbamate which on thermal cracking at suitable temperature may lead to isocyanate as



Accordingly the nitrobenzene carbonylation was conducted in DMF containing CH_3OH in order to convert any phenylisocyanate, if formed during reaction to the corresponding carbamate. Reaction at room temperature under high P_{CO} ($20.0 \times 10^3 \text{ kNm}^{-2}$) in presence of CH_3OH did not give any satisfactory result. Under high P_{CO} ($8.0 \times 10^3 \text{ kNm}^{-2}$) at high temperature, nitrobenzene carbonylation occurred but the nature and yields of products depend on the amount of alcohol present. Up to 1 M concentration of CH_3OH , low conversion of nitrobenzene to aniline diphenylurea and carbamate occurred. Highest conversion of nitrobenzene (50%) to aniline (10%) and carbamate (40%) was observed at a methanol concentration of 8 M above which the yield of aniline increased at the cost of carbamate (Table 3). Comparable results are obtained using ethanol. Water is a serious problem in the catalytic reaction and its presence in sufficient amount led to the formation of only aniline in presence or absence of alcohol.

The use of acidic or basic cocatalysts are known to influence the nature and distribution of carbonylated products to a great extent [1–8,10–25]. Carbonylation of nitrobenzene was conducted in presence of both acidic and basic cocatalysts with and without alcohol and the results are presented in Table 3. In presence of acidic cocatalysts such as FeCl_3 , SnCl_4 and *p*-toluenesulphonic acid (PTS), almost complete conversion of PhNO_2 to diphenylurea (75–85%) and aniline (10–20%) occurred in absence of alcohol. The selectivities of the cocatalysts for the conversion of PhNO_2 to diphenylurea are comparable though highest yield of diphenylurea was obtained using FeCl_3 . In presence of methanol and acidic cocatalysts, PhNO_2 is completely converted to only aniline (90–95%) and carbamate (5–10%). Reactions using basic cocatalysts such as py, 2-picoline, Et_3N but without alcohol resulted in abnormally low conversion of PhNO_2 to aniline and diphenylurea. Phenylisocyanate could not be detected in the product mixture.

The nature and distribution of products changed abruptly using basic cocatalysts and alcohol (Table 3). Carbonylation of PhNO_2 under optimum conditions of P_{CO} , temperature and alcohol concentration but without basic cocatalysts gave low conversion of the substrate to carbamate (major) and aniline (minor) but in presence of basic cocatalysts and alcohol, the conversion of PhNO_2 was nearly complete but the selectivity of the corresponding carbamate formation varied widely depending on the nature of cocatalysts. The activity of basic cocatalysts with respect to carbamate selectivity may be arranged in the order



The activity order was found parallel to their basicities. Alkoxides corresponding to alcohols were always used in all these catalytic runs. The results presented in Table 3 shows NaOMe–MeOH to be

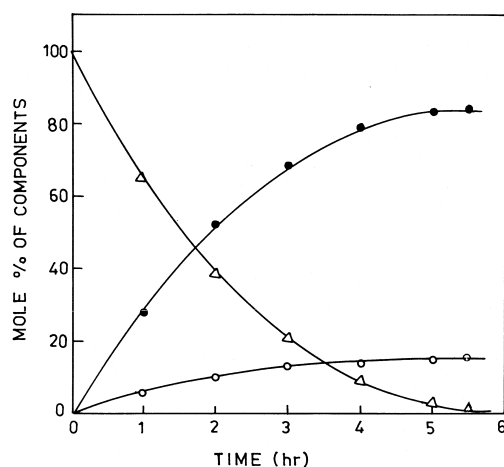


Fig. 1. Carbonylation of nitrobenzene under optimum reaction condition. Cat = $[\text{RhA}(\text{CO})_2] = 10.0 \text{ mM}$. $[\text{PhNO}_2] = 1.0 \text{ M}$. $[\text{NaOMe}] = 0.4 \text{ M}$. $T = 140^\circ\text{C}$. $P_{\text{CO}} = 8.0 \times 10^3 \text{ kNm}^{-2}$, $t = 5.5 \text{ h}$. Cosolvent = $[\text{MeOH}] = 8.0 \text{ M}$. Solvent = DMF. Total volume = 10 ml. $\Delta = \text{PhNO}_2$. $\circ = \text{PhNH}_2$. $\bullet = \text{PhNHCOOMe}$.

the best combination while NaOPh–PhOH being the worst. The conversion of PhNO_2 to aniline and carbamate increased almost monotonically with time under optimum reaction conditions and its complete conversion to aniline ($\sim 7\%$) and carbamate (90%) was achieved at $t = 5.5 \text{ h}$ (Fig. 1).

The effect of temperature and P_{CO} on the carbonylation of nitrobenzene was studied in presence of optimum concentration of methanol and NaOMe. At P_{CO} of $8.0 \times 10^3 \text{ kNm}^{-2}$ there was hardly any reaction below 70°C and the reaction rate increased slowly up to 140°C at which the extent of reaction and the selectivity of carbamate formation became maximum. In between 140°C to 160°C there is no noticeable change of reaction products above 170°C , the yield of carbamate decreased sharply with increased formation of aniline and unidentified resinous products (Fig. 2).

The effect of P_{CO} on the carbonylation of nitrobenzene and selectivity of carbamate formation was studied at 140°C . The conversion of nitrobenzene and the selectivity of the carbamate formation increased steadily up to $8.0 \times 10^3 \text{ kNm}^{-2}$ above which there is no appreciable effect (Fig. 3).

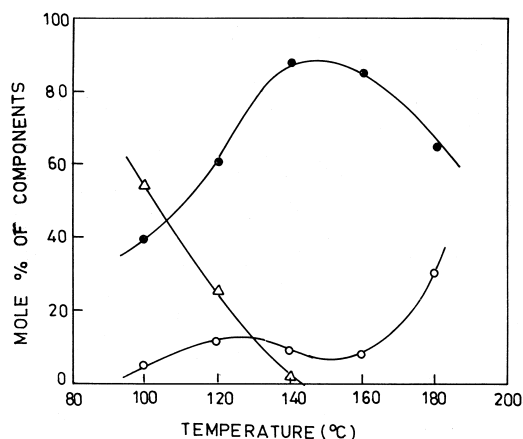


Fig. 2. Effect of temperature on reductive carbonylation of nitrobenzene. Cat = $[\text{RhA}(\text{CO})_2] = 10.0 \text{ mM}$. $[\text{PhNO}_2] = 1.0 \text{ M}$. $[\text{NaOMe}] = 0.4 \text{ M}$. Cosolvent = $[\text{MeOH}] = 8.0 \text{ M}$, Solvent = DMF. Total volume = 10 ml. $P_{\text{CO}} = 8.0 \times 10^3 \text{ kNm}^{-2}$, $T = 140^\circ\text{C}$, $t = 5.5 \text{ h}$. $\Delta = \text{PhNO}_2$. $\circ = \text{PhNH}_2$. $\bullet = \text{PhNHCOOMe}$.

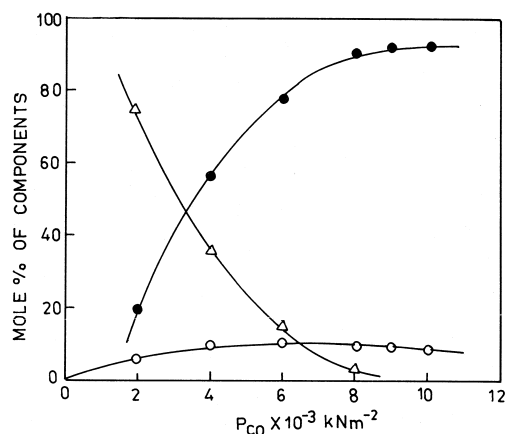


Fig. 3. Effect of carbon monoxide pressure on carbonylation of nitrobenzene under optimum condition. Cat = $[\text{RhA}(\text{CO})_2] = 10.0 \text{ mM}$, $[\text{PhNO}_2] = 1.0 \text{ M}$, $[\text{NaOMe}] = 0.4 \text{ M}$, $[\text{MeOH}] = 8.0 \text{ M}$, Solvent = DMF. Total volume = 10 ml, $T = 140^\circ\text{C}$, $t = 5.5 \text{ h}$. $\Delta = \text{PhNO}_2$. $\circ = \text{PhNH}_2$. $\bullet = \text{PhNHCOOMe}$.

Under optimum reaction conditions the conversion of nitrobenzene and the formation of carbamate increased with increasing methanol concentration up to 8.0 M above which the yield of carbamate decreased significantly though the conversion of nitrobenzene remained constant. However, lower concentration of methanol gave better selectivity for carbamate formation (Fig. 4). The carbamate selectivity for methanol is greater than that of ethanol (Table 4).

The catalyst is insoluble in water, acetone, benzene, toluene, xylene, etc. and among the few catalyst-soluble solvents such as DMF, DMSO and THF used for this carbonylation reaction, DMF was found to be best followed by DMSO. Very low conversion of the substrates occurred in THF where the solubility of the catalyst is very poor. Probably a moderately strong coordinating solvent capable of stabilizing the intermediate solvent adduct is necessary for the progress of the reaction.

Almost complete conversion of nitrobenzene and its *ortho*- and *para*-substituted derivatives to the corresponding carbamates and aniline as major and minor products respectively was achieved under

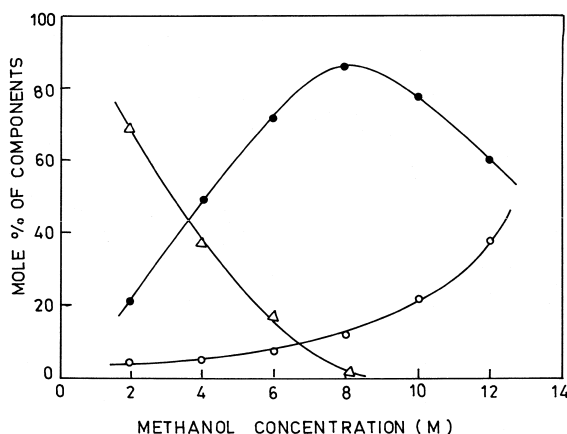


Fig. 4. Effect of methanol concentration on reductive carbonylation of nitrobenzene. Cat = $[\text{RhA}(\text{CO})_2] = 10.0 \text{ mM}$, $[\text{PhNO}_2] = 1.0 \text{ M}$, Solvent = DMF, $[\text{NaOMe}] = 0.4 \text{ M}$, $P_{CO} = 8.0 \times 10^3 \text{ kNm}^{-2}$, $T = 140^\circ\text{C}$. Cosolvent = MeOH, Total volume = 10 ml. $\Delta = \text{PhNO}_2$. $\circ = \text{PhNH}_2$. $\bullet = \text{PhNHCOOMe}$.

Table 4
Reductive *N*-carbonylation of various nitro aromatics catalyzed by RhA(CO)₂

Run No.	Substrate	Cosolvent/ Cocatalyst	Yield%		Cosolvent/ Cocatalyst	Yield%	
			monourethane/ diurethane*	amine		monourethane / diurethane*	amine
1.	Nitrobenzene	MeOH/NaOMe	85	15	EtOH/NaOEt	80	20
2.	<i>p</i> -chloronitrobenzene	„	72	26	„	67	30
3.	<i>p</i> -nitrotoluine	„	80	20	„	75	25
4.	<i>p</i> -methoxynitrobenzene	„	74	23	„	70	25
5.	<i>o</i> -chloronitrobenzene	„	66	34	„	60	38
6.	<i>o</i> -nitrotoluine	„	72	28	„	65	32
7.	<i>o</i> -methoxynitrobenzene	„	69	30	„	64	35
8.	<i>m</i> -dinitrobenzene*	„	15/50*	30	„	20/40*	35
9.	<i>p</i> -dinitrobenzene*	„	20/55*	20	„	25/50*	20
10.	Methyl 4,5 dimethoxy 2 nitrobenzoate	„	70	30	„	65	35

Reaction condition: [Cat] = [RhA(CO)₂] = 10.0 mM, [nitroarene] = 1.0 M. $P_{CO} = 8.0 \times 10^3 \text{ kNm}^{-2}$, $T = 140^\circ\text{C}$, $t = 5.5 \text{ h}$.

* $P_{CO} = 12.0 \times 10^3 \text{ kNm}^{-2}$, $T = 160^\circ\text{C}$, $t = 9 \text{ h}$.

Medium = DMF, [Cosolvent] = 8.0 M, [Cocatalyst] = 0.40 M. Total volume = 10 ml.

Yield refers to GC analysis.

optimum reaction conditions. Nitrobenzene has the highest selectivity for carbamate formation followed by *para*- and *ortho*-substituted derivatives (Table 4). The lower selectivity for orthosubstituted derivatives is probably due to steric in origin. In case of any substituted nitrobenzene, the carbamate selectivity follow the order:

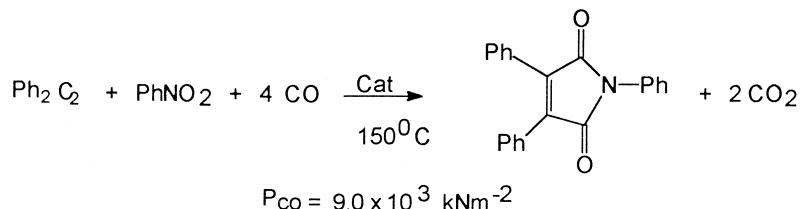


The selectivity follows the order of increasing electron density at the $-\text{NO}_2$ group.

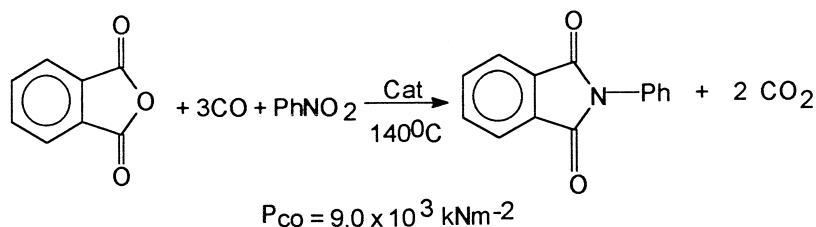
Carbonylation of dinitroaromatics was more difficult as more drastic condition, i.e., higher P_{CO} and higher temperature were required to achieve moderately good conversion. The dicarbamate selectivity was, however, low. The components in product mixture identified by HPLC and NMR and estimated by GC was found to contain dicarbamate, mononitro-carbamate and the unreacted dinitrobenzene and no dianiline. Use of higher temperature in case of dinitroaromatics leads to catalyst decomposition in many cases. A highly substituted mononitrobenzene could be carbonylated to the corresponding carbamate in moderately high carbamate selectivity (Table 4).

Several authors restored to a nitrene mechanism in rationalizing the products such as isocyanate, carbamate, urea, azobenzene, etc. formed during carbonylation of nitrobenzene [9,76]. Attempts were made to trap any phenylnitrene if formed at intermediate stage using diphenylacetylene and phthalic anhydride in the reaction medium. The carbonylation of nitrobenzene was conducted in DMF in

presence of $\text{RhA}(\text{CO})_2$ and diphenylacetylene at 150°C under $P_{\text{CO}} = 9.0 \times 10^3 \text{ kNm}^{-2}$ without any cocatalyst and cosolvent for 10 h. Appreciable amount of *N*-aryl diphenyl maleimide formed during the reaction was identified by NMR after separation of the components by HPLC. The product is suggested to be produced as per the following reaction.



The catalytic deoxygenation of PhNO_2 by CO was also investigated in presence of phthalic anhydride at 140°C and $P_{\text{CO}} = 9.0 \times 10^3 \text{ kNm}^{-2}$ and the desired product formed was isolated by tlc, HPLC and identified by NMR spectral data [9,76].



In both cases about 50–70% of unreacted nitrobenzene was present in the product mixture. The phenylnitrene derivatives could not be obtained in absence of catalyst.

Several runs were taken in DMF using PhNO as substrate and $\text{RhA}(\text{CO})_2$ as catalyst under optimum conditions of carbamate synthesis. PhNO undergoes carbonylation at faster rate than PhNO_2 . The nature and yield of final products in both cases are almost comparable. These suggest that carbonylation of PhNO_2 and PhNO follows the same route and PhNO_2 is deoxygenated to PhNO at the first step which is probably the rate determining.

The carbonylation reaction of PhNO_2 was conducted in presence of cyclohexene, benzonitrile, benzophenone in the reaction medium under optimum reaction condition for carbamate synthesis. The unsaturated substrate remained unchanged in the final product mixture though nitrobenzene underwent carbonylation at a slower rate to produce carbamate and aniline. These unsaturated substrates were hydrogenated when the catalytic run were carried out under normal pressure of hydrogen [75]. It appears that during the catalytic carbonylation of nitrobenzene, no metal-hydride species were formed as its formation should hydrogenate the unsaturated substrates.

It was not possible to isolate and identify the final catalytic species left at the end of the run. The catalytic activity of the final solution was almost comparable to the original solution. The catalytic run with the final solution was repeated with further addition of PhNO_2 or PhNO and cosolvent in appropriate amount under optimum reaction conditions and the nature and yield of the final products were comparable to that of the original one. The catalytic solution left at the end could be used several times without any appreciable loss of activity.

4. Mechanism

In order to find out any transformation of $[\text{RhA}(\text{PhNO}_2)(\mu\text{-CO})_2]$ that may undergo in solution at higher temperature, IR spectra of the DMF solution of the compound at 100°C was taken. The spectra

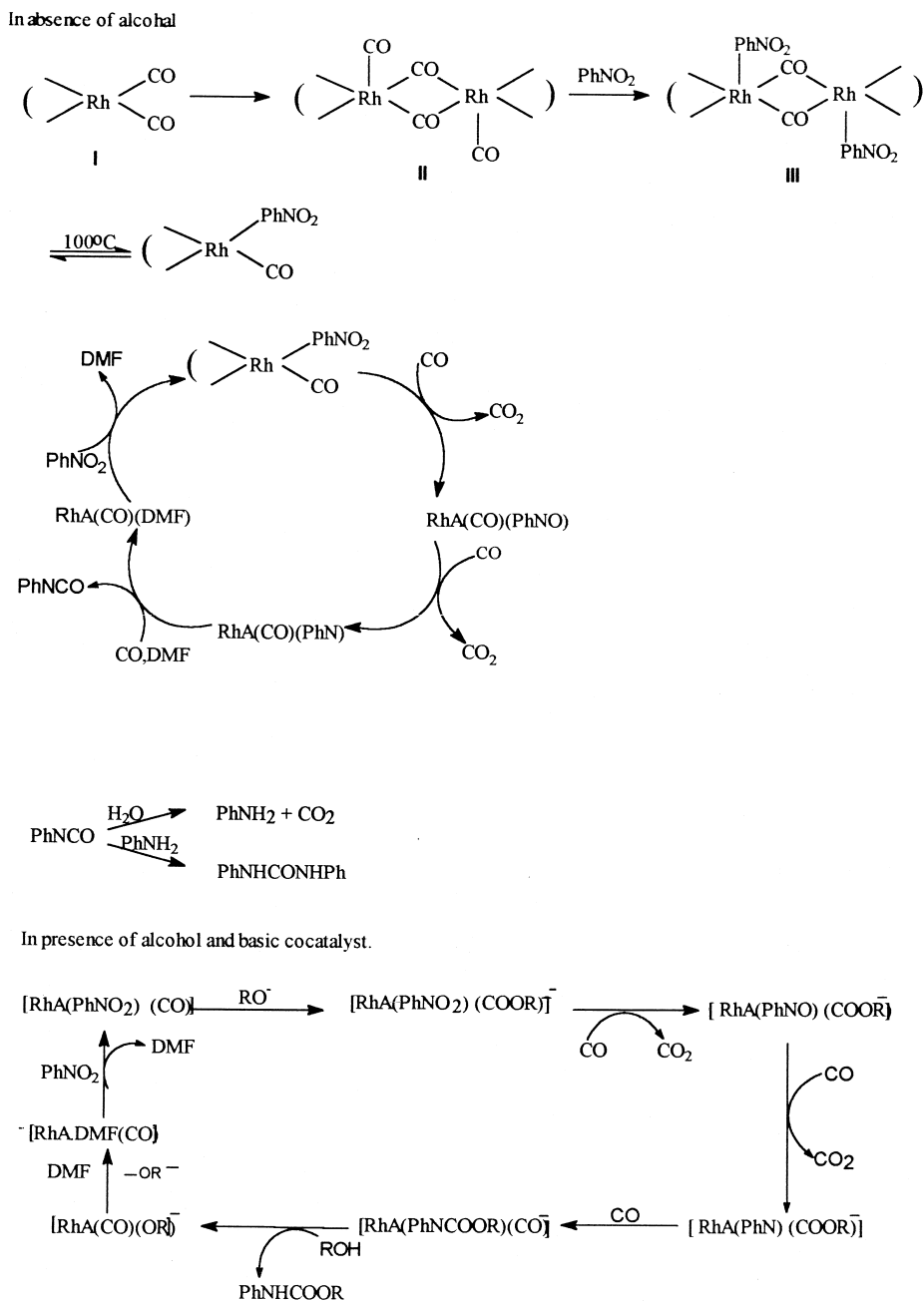
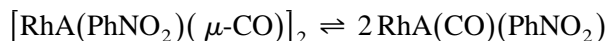


exhibit a new peak at 2008 cm^{-1} (νCO terminal) in addition to the peak at 1810 cm^{-1} suggesting the existence of the following equilibrium in high temperature in DMF solution.



The compounds $[\text{RhA}(\text{CO})(\mu\text{-CO})_2]$ (II), $[\text{RhA}(\text{PhNO}_2)(\mu\text{-CO})_2]$ (III), $\text{Na}[\text{RhA}(\text{PhNO}_2)(\text{COOCH}_3)]$ (IV) and $\text{RhA}(\text{CO})(\text{PhNO}_2)$ may be formed during carbonylation reaction. Under identical experimental conditions, the catalytic activities of (II) and (III) are very much comparable to that of $\text{RhA}(\text{CO})_2$ so far the reaction time and the nature and yields of the products at various stages are concerned. The formation of PhNCO during catalytic carbonylation of PhNO_2 has also been indicated. It appears possible that some or all these species may be involved in the catalytic cycle.

Examination of Table 3 indicates the formation of aniline and diphenylurea in absence of alcohol, and aniline and carbamate in presence of basic cocatalyst and alcohol. Reaction mechanisms in these two cases are supposed to be different. Phenylisocyanate supposed to be formed as an intermediate in the former case can react with aniline to produce diphenylurea. In the later case, absence of any diphenylurea in presence of aniline excludes the formation of intermediate phenylisocyanate and the reaction is supposed to proceed via the formation of carbamoyl complex. The necessary RO^- group for the formation of carbamoyl complex is supplied by ROH alone or more so in presence of basic cocatalyst as $\text{ROH} + \text{B} \rightarrow \text{RO}^- + \text{BH}^+$. On the basis of these experimental facts the following tentative mechanisms have been proposed for these two processes (Scheme 1).

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