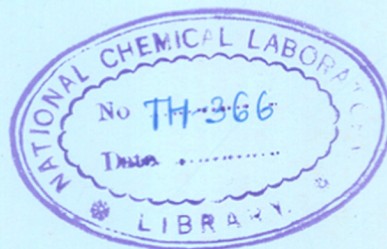


STUDIES IN HOMOGENEOUS CATALYSIS :
CARBONYLATION OF NITROBENZENE
TO PHENYLISOCYANATE

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY



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JUNE 1982

COMPUTERISED

Dedicated to

My parents

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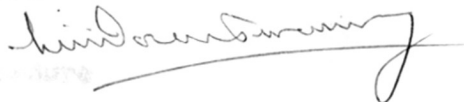
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CERTIFIED that the work incorporated in
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CARBONYLATION OF NITROBENZENE TO
PHENYLISOCYANATE

submitted by Shri S. B. Halligudi was carried out
by the candidate under my supervision. Such
material as has been obtained from other sources
has been duly acknowledged in the thesis.



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SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Organic isocyanates are important raw materials in the manufacture of fibers, polyurethane foams, elastomers and adhesives, etc. Conventionally, the commercial production of isocyanates is based on raw materials such as nitro compounds and phosgene. The existing plants are based on the conversion of nitro compounds to amines and subsequent phosgenation to isocyanates. However, this route has serious problems of corrosion due to the by-product hydrochloric acid. In recent years, considerable effort has been made in developing an alternative route for isocyanates - via direct carbonylation of nitro compounds using homogeneous metal complex catalysts. This route appears to be highly promising, because it involves a single step and also does not have the corrosion problems associated with the phosgenation route.

In the published literature, though the feasibility of the carbonylation route has been established, very few systematic studies on screening of catalysts and the role of various parameters affecting the activity and selectivity of the catalysts have been reported. Considering the potential importance of the carbonylation route in isocyanates synthesis, it was considered desirable to investigate various aspects of this reaction in detail.

The present work was therefore undertaken with the

following objectives:

- (1) Selection of a suitable catalyst system for carbonylation of nitrobenzene to phenylisocyanate.
- (2) Postulation of a plausible mechanism of carbonylation.
- (3) Experimental study of the kinetics of the carbonylation reaction.
- (4) Theoretical analysis of multiplicity and stability in CSTR systems for homogeneously catalysed reactions.

(1) SELECTION OF A SUITABLE CATALYST SYSTEM

Several experiments were carried out to study the activity of palladium complexes as catalysts for the carbonylation of nitrobenzene to phenylisocyanate. The complexes used as catalysts were: (a) $\text{Pd}(\text{Py})_2\text{Cl}_2$, (b) $\text{Pd}(\text{Isoq})_2\text{Cl}_2$, (c) $\text{Pd}(\text{C}_7\text{H}_5\text{N})_2\text{Cl}_2$, (d) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and (e) $\text{Pd}(\text{CO})_2\text{Cl}_2$. The activity of the above complexes was tested at 190°C and 80 atm pressure of CO using a high pressure reactor. It was found that complexes (a) and (b) were significantly active as catalysts, while others were inactive. Therefore, it was concluded that N-containing heterocyclic compounds are the preferred suitable ligands (for example, pyridine, isoquinoline, etc.).

The effect of oxide promoters such as V_2O_5 , Fe_2O_3 , FeBO_3 , Cr_2O_3 and MoO_3 on the activity of catalysts (a) and (b) was studied under identical conditions. Fe_2O_3 , FeBO_3

and V_2O_5 were found to increase the conversion of nitrobenzene marginally, while other oxides had no significant influence on the conversion of nitrobenzene. However, it was interesting to note that the selectivity patterns were considerably improved in the presence of promoters.

The effect of solvent on the activity of catalyst (a) was studied under identical conditions. Highest rate of reaction was achieved with o-dichlorobenzene (ODCB) as solvent. The solvent effect on the conversion of nitrobenzene was found to be in the following order:

o-dichlorobenzene > chlorobenzene > toluene > xylene

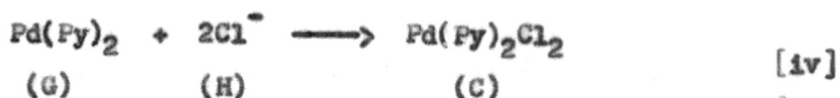
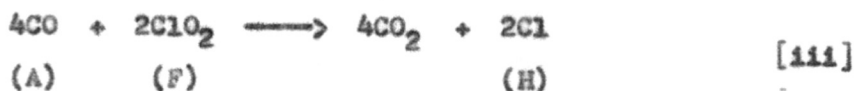
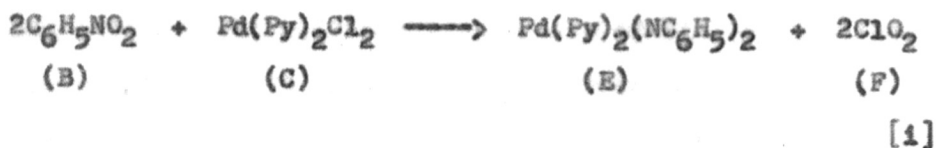
If the selectivity at 25% conversion was compared, xylene appeared to be the best solvent, and the solvent effect on the selectivity for phenylisocyanate was in the following order:

xylene > chlorobenzene > o-dichlorobenzene > toluene

The effect of process variables such as CO pressure, catalyst concentration, nitrobenzene concentration, V_2O_5 concentration and temperature was studied on the rate of carbonylation of nitrobenzene. In general, at higher CO pressures and catalyst concentrations, higher conversion and selectivity were obtained.

(2) POSTULATION OF A PLAUSIBLE MECHANISM OF CARBONYLATION

In order to study the mechanism of carbonylation, the catalytic complex was isolated from the reaction mixture and characterised by spectroscopic methods. Based on these studies, the following mechanism for the reaction was proposed:



This is the first attempt to propose a mechanism for carbonylation of nitro compounds to isocyanates. While this mechanism is likely, other mechanisms may also be considered.

(3) KINETICS OF CARBONYLATION OF NITROBENZENE TO PHENYL ISOCYANATE

The kinetics of carbonylation of nitrobenzene to phenylisocyanate was studied at 170-230°C and 23-94 atm pressure of CO using a soluble $\text{Pd(Py)}_2\text{Cl}_2$ complex catalyst in a high pressure stirred reactor. This type of reaction can occur in different regimes depending on the relative rates of mass transfer and chemical reaction under the conditions employed. For the purpose of kinetic studies, it is important to ensure that gas-liquid mass transfer resistance is absent. This requires a knowledge of gas-liquid mass transfer coefficient ($K_L a$) and solubility. These data were determined experimentally and used in the interpretation of the kinetic data.

It was found that the rate of carbonylation was kinetically controlled in the range of conditions studied in this work.

The reaction rate was found to be first order with respect to CO partial pressure and catalyst concentration, and zero order in nitrobenzene concentration. The following type of rate model represented the experimental data satisfactorily:

$$R_A = 6 k_2 [A] [C]$$

where

R_A = rate of carbonylation, mol/cm³/sec

k_2 = second order rate constant, cm³/mol/sec

A = concentration of CO, mol/cm³

C = concentration of Pd(Py)₂Cl₂, mol/cm³.

The above rate equation is consistent with the mechanism proposed when the rate determining step is the activation of CO (reaction (ii)).

The activation energy for this reaction was found to be 29.87 kcal/mol.

(4) THEORETICAL ANALYSIS OF MULTIPLICITY AND STABILITY IN CSTR SYSTEMS FOR HOMOGENEOUSLY CATALYSED REACTIONS

The possible occurrence of steady state multiplicity has important implications in the design and control of chemical reactors and it is important to predict a priori when the phenomenon may occur. Unfortunately, no criteria are available for a priori prediction of steady state multiplicity or uniqueness for homogeneously catalysed reactions. Therefore, it was considered desirable to present some exact uniqueness/multiplicity criteria and stability analysis taking the example of rhodium complex catalysed carbonylation of methanol to acetic acid in a CSTR. Necessary and sufficient conditions for multiplicity in a homogeneously catalysed reaction have been obtained analytically. Stability analysis was also carried out to establish the regions of stability of the states.

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CHAPTER -1

INTRODUCTION TO HOMOGENEOUS CATALYSIS AND MANUFACTURE OF ORGANIC ISOCYANATES

CHAPTER-1

1.1 GENERAL INTRODUCTION

Homogeneous catalysts consisting of soluble metal complexes have gained considerable importance in the last decade. This is mainly due to their remarkable activity for a variety of reactions. Particularly, the transition metal complexes have been found to be excellent catalysts for industrially important reactions involving hydrogenation, isomerization, oxidation, polymerization, hydroformylation, carbonylation, etc. Homogeneous catalysts have several advantages over heterogeneous catalysts, such as milder operating conditions, higher selectivity and ease of temperature control. It is the ability of the metal complexes to activate substrates like CO, H₂, O₂ and olefins under moderate conditions that makes them particularly attractive. Already several examples of application of these catalysts in industry exist which include: Wacker process for the manufacture of acetaldehyde [24], Monsanto process for acetic acid via methanol carbonylation [25] and oxo process for the manufacture of alcohols [26]. Reactions involving CO represent the largest use of homogeneous catalysis. Also, this subject is likely to play a major role in the synthesis of chemicals using CO as a raw material since CO can be derived from coal. In general, a large number of carbonylation reactions catalysed by metal

complexes have already shown potential in developing new routes for several products.

The present thesis is concerned with investigation of the carbonylation of nitrobenzene to phenylisocyanate. The subject of carbonylation of nitro compounds to isocyanates is both of practical and theoretical interest. The carbonylation of nitrobenzene to phenylisocyanate is particularly important as it is likely to provide an alternative route for the manufacture of organic isocyanates. The conventional process for isocyanate manufacture involves three steps and by-product hydrochloric acid which poses serious corrosion problems. On the other hand, the direct carbonylation route is single-step and does not involve corrosive components. It was therefore decided to undertake detailed investigations on the various aspects of the carbonylation route. The relevant literature on this subject is summarized in the following section.

1.2 SUMMARY OF LITERATURE ON ISOCYANATES FROM NITRO COMPOUNDS

Organic isocyanates are important raw materials in the manufacture of fibers, polyurethane foams, elastomers, adhesives, etc. Some of the industrially important isocyanates are phenylisocyanate, toluenediisocyanate (TDI), methylisocyanate and methylene diphenyl diisocyanate (MDI). It was in the 1950s that the combined efforts of scientists in West Germany and U.S.A. led to the development of commercial processes for flexible polymeric foams, fibers, coatings and

elastomers based on isocyanates. This created a strong demand for TDI and MDI.

Isocyanates have also important applications in flame retardent manufacture such as Estane (B.F. Godrich trade name) and Texin (Mobay trade name) which could be processed by extrusion or injection molding. The other uses of isocyanates include insecticides, herbicides, explosives and biologically active products. Due to the growing demand of isocyanates for various applications, developing a new viable technology will be always important. The commercial manufacture of isocyanate is normally via the phosgenation route. In the last few years, several attempts to develop a process via the carbonylation route have also been made. The literature on this new route as well as comparison with the phosgenation route are discussed in the following section.

1.3 PROCESS VIA PHOSGENATION ROUTE

Most of the commercial production of isocyanates is carried out from nitro compounds and this involves the following steps:



A description of the phosgenation^{process} is given in detail by Sittig [22].

Mainly the amines are produced via catalytic hydrogenation of nitro compounds and the process for this step varies depending on the nitro compound under consideration.

The second step for the preparation of phosgene (COCl_2) is normally carried out by passing equimolar quantities of CO and Cl_2 in an iron tube packed with carbon as catalyst. The resulting phosgene vapour is condensed to liquid phosgene [23]. The third step involving the phosgenation of amines is the most important one and is carried out in continuous gas-liquid reactors. In most of the processes, the phosgenation is carried out using a two stage reactor in a pressure range up to 15 atm of COCl_2 . The temperature range is normally 70-130°C.

1.4 CARBONYLATION ROUTE

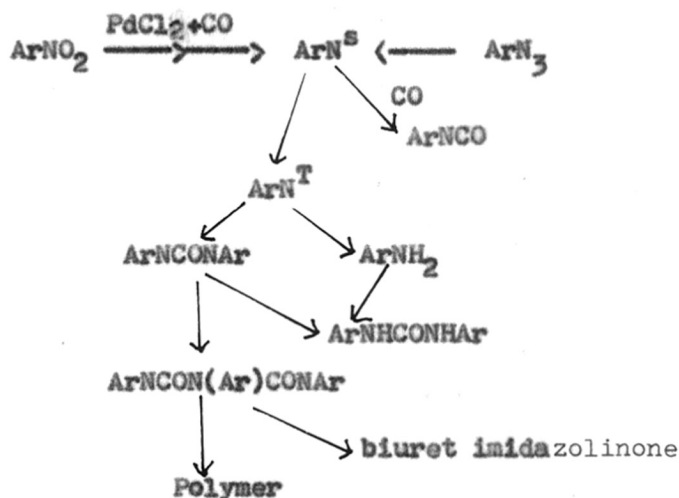
In the conventional phosgenation process there are several problems such as corrosion due to by-product hydrochloric acid. In the last few years, several attempts were made to eliminate COCl_2 as a raw material. In this direction M/s. Olin Mathison Corporation and du Pont have made major efforts in developing a route for isocyanates via carbonylation of nitro compounds. The various advantages of the carbonylation route are: (1) corrosive product HCl is eliminated; (2) energy intensive Cl_2 manufacture to prepare COCl_2 is avoided; and (3) carbonylation is a single-step

process as against the three-steps phosgenation route.

Hardy and Bennett [12] were the first to report the formation of phenylisocyanate via CO and nitrobenzene in the presence of Rh-C/FeCl₃ catalyst. This was followed by numerous patents claiming the feasibility of the direct carbonylation route for the manufacture of various aromatic isocyanates. A summary of the literature on the carbonylation route is presented in Table 1.1. This reaction is normally carried out in a high pressure reactor. The pressure and temperature ranges used are 80-200 atm and 170-200°C respectively. Normally a catalyst consisting of a transition metal complex with a metal oxide or chloride promoter is used. The catalyst systems consisting of palladium and rhodium complexes with N-containing heterocyclic ligands such as pyridine, quinoline and isoquinoline have been found to be effective.

Though most of the literature is patented, Arco and Mitsui Toatsu Chemicals [19] have already advanced to a stage of pilot plant for the manufacture of diisocyanates (TDI and MDI) via the carbonylation route.

Very few attempts to investigate the mechanism of carbonylation using the relevant catalyst (for example, Pd(Py)₂Cl₂) have been published in the literature. Weigert [13] has investigated the carbonylation of substituted nitro compound using Pd complex catalyst and has proposed the following speculative scheme of reactions:



where s = singlet and T = triplet

However, he has not investigated the nature of the intermediate catalytic species and the mechanism of carbonylation. Unverferth *et al* [16] reported that using $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ complex catalyst with MoCl_5 as a promoter, it is possible to convert nitro compounds to isocyanates at 100°C and 1 atm of CO. They have investigated the carbonylation of ortho substituted nitro compounds. This is the only study where a speculative mechanism is proposed for rhodium complex catalysed carbonylation. They have also found that the rate of conversion of nitro compound is directly proportional to the concentration of MoCl_5 and of the nitro compound, while the order with respect to the catalyst concentration was reported to be 0.5. However, no investigation on the kinetics and mechanism of the carbonylation of nitro compounds using

palladium complex catalyst has been reported in the literature.

1.5 SCOPE OF THE PRESENT WORK

From the published literature it was noted that little information is available on the role of various catalysts and process parameters on the activity of palladium complex catalysts for the carbonylation of nitro compounds to isocyanates. Also, no attempts to investigate the kinetics and the mechanism of this important reaction have been made so far. Therefore, the present work was undertaken with the following objectives.

PART-A

- (1) Investigations on the role of various ligands, promoters and solvents on the activity of palladium complex catalysed carbonylation of nitrobenzene to phenylisocyanate.
- (2) Influence of process parameters such as reactant concentration, catalyst concentration, temperature, etc. on conversion and selectivity in the carbonylation of nitrobenzene.
- (3) Determination of physico-chemical properties such as solubility of CO in monochlorobenzene and nitrobenzene, and gas-liquid mass transfer coefficient ($k_L a$).
- (4) Determination of the intrinsic kinetic parameters for the above reaction.

PART-B

Theoretical analysis of multiplicity and stability
in CSTR systems for homogeneously catalysed reactions.

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TABLE: 1.1

SUMMARY OF CATALYSTS AND PROMOTERS USED
IN CARBONYLATION OF NITRO COMPOUNDS

Sl. No.	Nitro compound	Catalyst	Promoter	Solvent	Temp., °C	CO, pressure psig	Contact time, hr	Conversion, %	Selectivity for isocyanate, %	Ref.
1	2	3	4	5	6	7	8	9	10	11
1.	2,4-dinitro toluene (28 gm)	Ni(ISOQ) ₂ I ₂ (9.0 gm)	-	o-dichloro-benzene (100 gm)	190	8000 psig	1.5	37	5	1
2.	2,4-dinitro toluene (28 gm)	Ni(ISOQ) ₂ I ₂ (9.0 gm)	MoO ₃ (2.0 gm)	o-dichloro benzene (100 gm)	190	8000 psig	1.5	-	25	1
3.	2,4-dinitro toluene (28 gm)	Ni(Py) ₂ I ₂	-	o-dichloro benzene	190	8000 psig	1.5	-	5	1
4.	2,4-dinitro toluene (25 gm)	PdCl ₂ (0.4 gm)	-	Aceto-nitrile (75 gm)	190	700 atm	6.0	71	85, 14(Toluene diisocyanate)	2
5.	m-dinitro benzene (25 gm)	PdCl ₂ (1.0 gm)	-	Aceto-nitrile (75 gm)	200	700 atm	4.0	73	86, 14(Toluene diisocyanate)	2
6.	1-chloro-4-nitrobenzene (25 gm)	PdCl ₂ (0.7 gm)	-	Aceto-nitrile (50 gm)	210	700 atm	8.0	-	45	2
7.	Nitrobenzene (100 gm)	CoI ₂ (1.0 gm)	-	-	200	2300 psig	3.0	-	-	3

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Table: 1.1 contd.

1	2	3	4	5	6	7	8	9	10	11
8.	Nitrobenzene (100 gm)	CoI ₂ (1.0 gm)	SO ₂ (125 gm)	-	200	2200 psig	4.0	-	-	3
9.	Nitrobenzene (40 gm)	Rh(PPh ₃) ₃ Cl (1.0 gm)	-	-	200	1160 psig	2.0	-	40	3
10.	Nitrobenzene (40 gm)	RhCl ₃ (1.0 gm)	-	-	200	1275 psig	2.0	-	No iso- cyanate	3
11.	Nitrobenzene (40 gm)	RhCl ₃ (5.0 gm)	Triphenyl phosphine (1.0 gm)	-	200	1350 psig	2.0	-	34	3
12.	Nitrobenzene (40 gm)	RhCl ₃ (0.5 gm)	[(C ₆ H ₅) ₃ PCl ₂] COOC ₂ H ₅ ⁺ Br ⁻	-	200	1310 psig	2.0	100	55	3
13.	Nitrobenzene (6.0 gm)	PdCl ₂ (3%, NB)	V ₂ O ₅ (2%, NB)	o-dichloro- benzene (5 ml) ⁺ COCl ₂ (2.5%, NB)	190	2800 psig	-	100	67	4
14.	2,4-dinitro- toluene (3.0 gm)	RhCl ₃ (3%, DNT)	V ₂ O ₅ (6%, DNT)	o-dichloro- benzene (5 ml) ⁺ COCl ₂ (2.5%, DNT)	190	2800 psig	-	33	51.5, 12(Toluene diisocyanate)	4
15.	Nitrobenzene (6.0 gm)	PdCl ₂ (3%, NB)	V ₂ O ₅ (2%, NB)	o-dichloro- benzene (5 ml) ⁺ SO ₂ Cl ₂ (2.5%, NB)	190	2800 psig	-	100	44.5	4

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Table: 1.1 contd.

	1	2	3	4	5	6	7	8	9	10	11
16. Nitrobenzene (6.0 gm)	PdCl ₂ (3%, NB)	V ₂ O ₅ (2%, NB)		o-dichloro-benzene (5 ml) + C ₆ H ₅ COCl (2.5%, NB)	190	2800 psig	-	100	69.2	4	
17. Nitrobenzene (6.0 gm)	PdCl ₂ (3%, NB)	V ₂ O ₅ (2%, NB)		o-dichloro-benzene (5 ml) + oxalylchloride (2.5%, NB)	190	2800 psig	-	42.3	72.6	4	
18. 2,4-dinitro-toluene (3.0 gm)	a) RhCl ₃ (3%, DNT)	MoO ₃ (12%, DNT)		o-dichloro-benzene (5 gm)	190	3830 psig	1.5	93.7	46, 20 (Toluene diisocyanate)	5	
	b) PdCl ₂ (3%, DNT)	CuBr ₂ (3%, DNT)		o-dichloro-benzene (5 gm)							
19. 2,4-dinitro-toluene (5.0 gm)	Pd(Py) ₂ Cl ₂ (0.75 gm)	GeCl ₄ (0.49 gm)		o-dichloro-benzene (5 gm)	190	3750 psig	-	94	55, 46 (Toluene diisocyanate)	6	
20. 2,4-dinitro-toluene (5.0 gm)	Pd(ISO) ₂ Cl ₂ (0.75 gm)	SnCl ₄		o-dichloro-benzene (5 gm)	190	3800 psig	-	93	47, 18 (Toluene diisocyanate)	6	
21. 2,4-dinitro-toluene (6.0 gm)	PdCl ₂ (2.0 m mole)	Pyridine (5.8 m mole) + FeBO ₃ (0.5 gm)		o-dichloro-benzene (20 gm)	200	3500 psig	4	95	40	7	



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Table: 1.1 contd.

	1	2	3	4	5	6	7	8	9	10	11
22.	2,4-dinitro- toluene	Pd(Py) ₂ Cl ₂	MoO ₃	o-dichloro- benzene	200	2500 psig	0.33	-	-	33	8
23.	2,4-dinitro- toluene	Pd(CO) ₂ Cl ₂	Isoquino- line	Benzene	190	227 atm	24	-	-	47	9
24.	2,4-dinitro- toluene	Pd(Py) ₂ Cl ₂	o-contai- ning oxidant	o-dichloro- benzene	200	10,000 psig	0.5	-	-	-	10
25.	2,4-dinitro- toluene	Pd(Py) ₂ Cl ₂	o-contai- ning compound	Cl-contai- ning compound	190	170 atm	-	-	-	21 to 3	11
26.	2,4-dinitro- toluene	Co ₂ (CO) ₈	-	-	190	200 atm	-	-	-	-	11
27.	2,4-dinitro- toluene	PdCl ₂ + isoquino- line or PdCl ₂ + pyridine	2-amino 4-nitro toluene	Benzene	167	100 2 kg/m	4	-	-	3.3	11
28.	2,4-dinitro- toluene	PdCl ₂ + pyridine in HCl	-	Benzene	180	150 2 kg/m	4	-	-	5.9	11
29.	Nitrobenzene	Rh/C-FeCl ₃	-	-	200	200 atm	-	-	-	Isocyanate formed	12
30.	4-chloro- nitrobenzene	PdCl ₂	-	Acetanitrile	225- 275	100- 400 atm	2-15	-	-	15-50	13
										

Table 1.1 contd.

1	2	3	4	5	6	7	8	9	10	11
31.	Nitrobenzene (3.6-9.0 gm)	Fe(CO) ₅ and Ni(CO) ₄	-	Acetic acid	285- 310	100 atm	2	-	0-6,1 gm	14
32.	Chloro-nitro- benzenes	PdCl ₂	Pyridine, isoquino- line and V ₂ O ₅	-	200	100 atm	-	67-100	38-92	15
33.	Nitro- mesitylene	Rh ₂ (CO) ₄ Cl ₂	MoCl ₅ , VCl ₄ and TiCl ₄ , etc.	o-dichloro- benzene	100	1 atm	0.5 - 2	3-50	1-26	16
34.	Nitrobenzene, etc.	Pd(Py) ₂ Cl ₂	Fe ₂ Mo ₇ O ₂₄	o-dichloro- benzene, aceto- nitrile	200	200 atm	3	8-100	7-62	17
35.	Phenylazide	RhCl(CO)(PPh ₃) ₂ [Rh (DFE) ₂]Cl	-	aniline, methanol	80	1 atm	-	-	> 98	18

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CHAPTER - 2

SCREENING OF PALLADIUM COMPLEX CATALYSTS
AND STUDY OF THE EFFECT OF PROCESS
VARIABLES ON THE CORBONYLATION OF
NITROBENZENE TO PHENYLISOCYANATE REACTION

CHAPTER-2

SCREENING OF PALLADIUM COMPLEX CATALYSTS AND STUDY OF THE EFFECT OF PROCESS VARIABLES ON THE CARBONYLATION OF NITROBENZENE TO PHENYLISOCYANATE REACTION

2.1 INTRODUCTION

In this chapter, the results on screening of catalysts and effect of process parameters on carbonylation of nitrobenzene to phenylisocyanate are presented. The relevant literature on this topic is summarized in Chapter 1.

From the published literature, though the feasibility of the carbonylation route has been established, very few systematic studies on the screening of catalysts and the parameters effecting their activity and selectivity have been reported. Considering the potential importance of the carbonylation route in isocyanate synthesis, it was thought desirable to investigate the various aspects of this reaction in detail. The objective of the present work was to study the activity of palladium complex catalysts (such as $\text{Pd X}_2 \text{Cl}_2$, where X is pyridine, isoquinoline, benzonitrile, triphenylphosphine or carbon monoxide) for the carbonylation of nitrobenzene to phenylisocyanate. The effect of solvents, ligands and oxide promoters on the activity of carbonylation has been studied. Besides the catalyst parameters, the process conditions also play an important role in determining the activity and selectivity

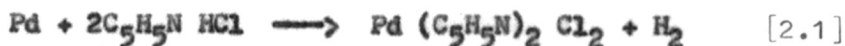
of the catalyst. Hence, the effect of carbon monoxide pressure, nitrobenzene concentration, catalyst concentration, promoter concentration and temperature has also been studied.

2.2 EXPERIMENTAL

2.2.1 Catalyst preparation

The catalyst used in the present work was a palladium complex of the formula $\text{Pd X}_2 \text{Cl}_2$, where X is either pyridine, isoquinoline, benzonitrile, triphenylphosphine or carbon monoxide. The procedure for the preparation of $\text{Pd(Py)}_2\text{Cl}_2$ (Py = pyridine) is given below.

Palladium chloride was dissolved in dilute hydrochloric acid solution and reduced to palladium black using hydrazine hydrate. Palladium black was then filtered, washed with distilled water and dried. In a typical experiment 0.075 gm of palladium black, stoichiometric quantity of pyridine hydrochloride, 0.5 cm³ concentrated nitric acid and 10 cm³ of monochlorobenzene were refluxed for 24 hr. The following reaction occurs:



After cooling, the reaction mixture was filtered and extracted with chloroform. During this treatment the complex was recovered as a chloroform solution. To this, petroleum ether (60-80°C) was added to precipitate the

complex. The yellow precipitate thus obtained was separated by filtration, washed with ether and dried under vacuum to give 0.232 gm of $\text{Pd}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$ complex. The elemental analysis of this complex indicated 36.2% C, 3.26% H, 8.38% N, and 23% Cl, which is consistent with the formula $\text{Pd}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$.

While $\text{Pd}(\text{Isoq})_2\text{Cl}_2$ complex was prepared by a similar procedure, the other complexes $\text{Pd}(\text{C}_7\text{H}_5\text{N})_2\text{Cl}_2$ [1], $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ [2] and $\text{Pd}(\text{CO})_2\text{Cl}_2$ [3] were prepared by the procedures described elsewhere.

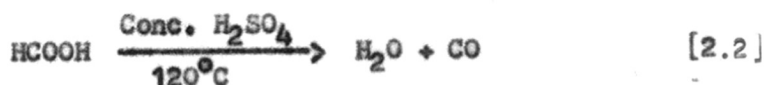
2.2.2 Materials

The oxides and solvents used were of AR grade. Freshly distilled and moisture freed solvents were used for the carbonylation experiments.

2.2.3 Apparatus and procedure

The carbonylation experiments were carried out using a 300 cm^3 pressure reactor (Parr Instrument Co.) made of S.S. 316 (shown in Fig. 2.1). This reactor had provision for temperature control, pressure recording, gas inlet, stirrer speed control and sampling.

The CO required for the present work was prepared by dehydration of formic acid by the following reaction:



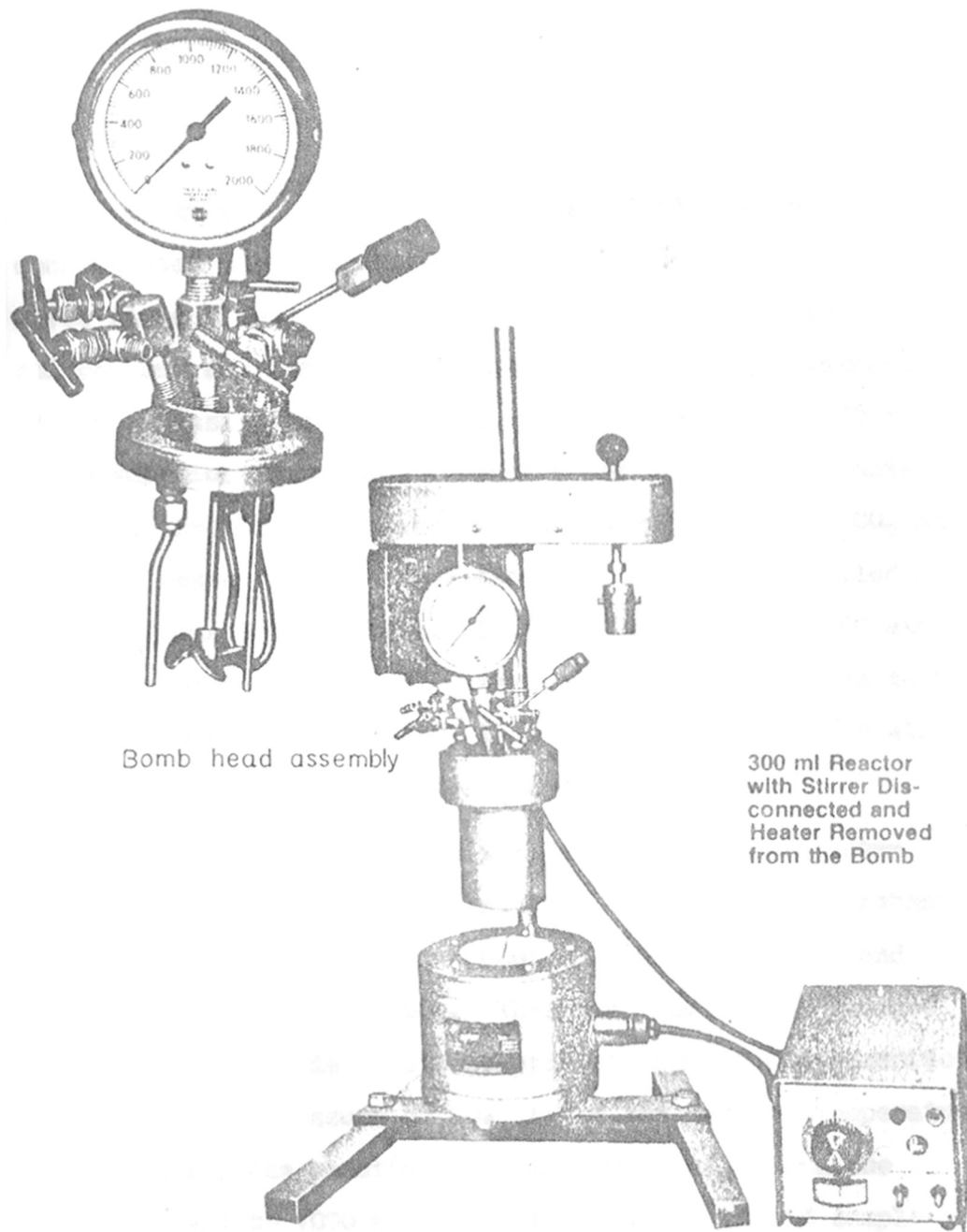
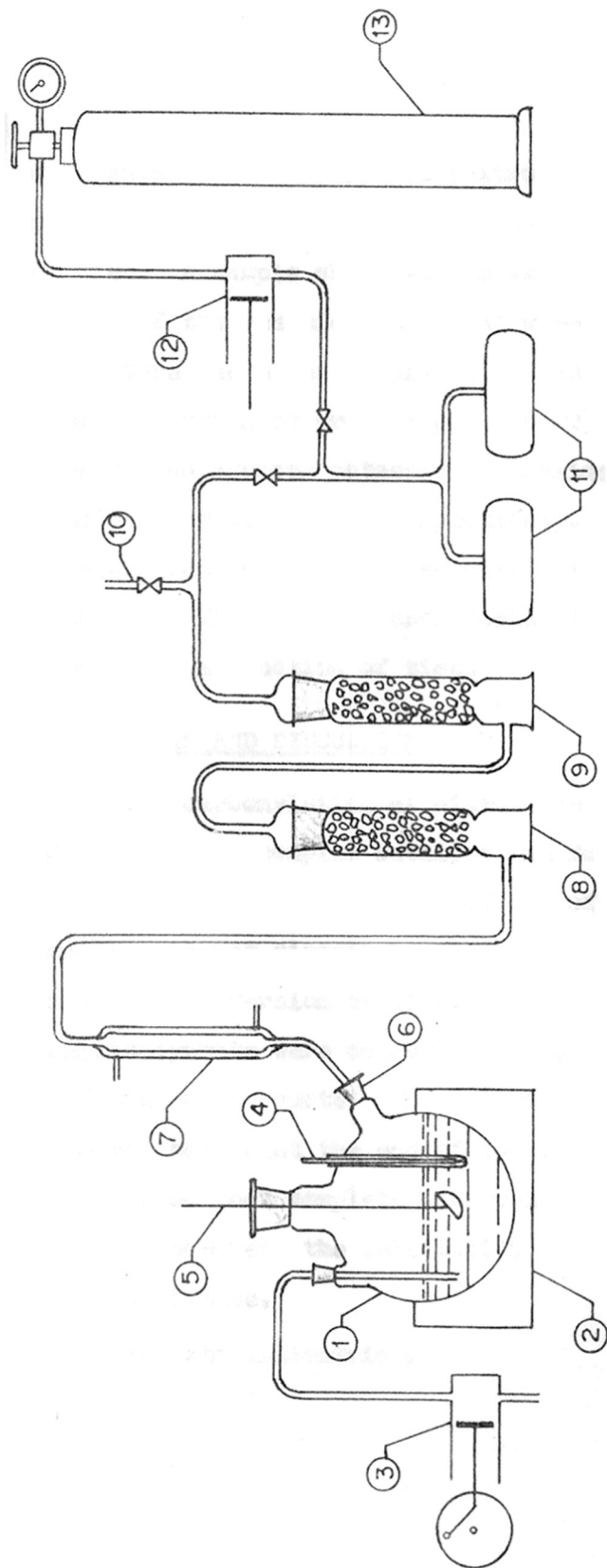


FIG. 2.1 REACTOR USED FOR CARBONYLATION EXPERIMENTS

The CO generation unit is shown schematically in Fig. 2.2. Concentrated sulphuric acid (AR grade) was charged to a three litre flask. This flask is provided with a teflon stirrer and was heated to 120°C. Formic acid was introduced into the flask by means of a liquid metering pump. CO formed by dehydration was passed through a series of traps containing potassium hydroxide pellets and silica gel to remove CO₂ and moisture respectively. Then the purified gas was filled into balloons and compressed into a cylinder up to 100 atm (Andreas Hofer compressor). The purity of the gas was tested using cuproammonium solution in an Orsat apparatus and also by gas chromatograph, and was found to be 99.5%.

The reaction solution was prepared in the reactor under nitrogen atmosphere. Catalyst, solvent and nitrobenzene in known quantities were introduced into the reactor and flushed with nitrogen twice. Then the reactor was flushed with carbon monoxide at atmospheric pressure and pressurised to the desired pressure of CO. After the desired temperature was attained, the reaction was started by adjusting the stirrer speed to 1000 rpm. At this stage a liquid sample was withdrawn. After this, the samples were withdrawn at different time intervals and analyzed for nitrobenzene and phenylisocyanate by GLC (HP 5840 model) using a FID detector (maintained at 350°C). A column three feet long and containing 5% SE-30 on chromosorb W was used to separate the



- | | | | |
|---|--|----|-------------------|
| 1 | RB REACTION FLASK | 7 | WATER CONDENSER |
| 2 | HEATING MANTLE | 8 | KOH COLUMN |
| 3 | FORMIC ACID FEED BY LIQUID METERING PUMP | 9 | SILICA GEL COLUMN |
| 4 | THERMOMETER | 10 | BY-PASS |
| 5 | STIRRER | 11 | RUBBER BALLOONS |
| 6 | GAS OUTLET | 12 | COMPRESSOR |
| | | 13 | GAS CYLINDER |

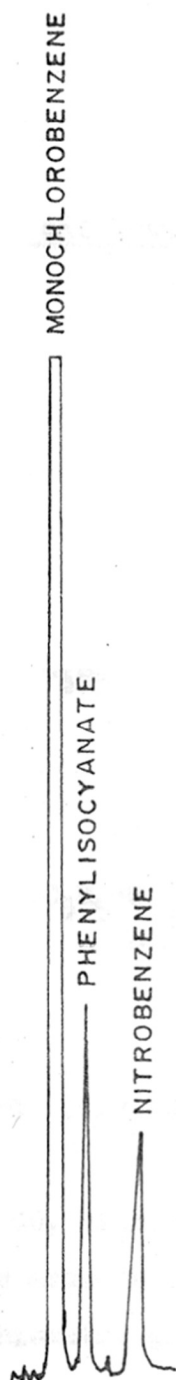
FIG. 2.2. CARBON MONOXIDE GENERATION UNIT

components. The carrier gas (nitrogen) flow rate was 20 cm³/minute, and temperature programming in the range of 110-150°C was used. A sample chromatogram is shown in Fig. 2.3. At the end of the reaction, the bomb was cooled to room temperature and a gas sample was withdrawn and analyzed for CO and CO₂ using an Orsat apparatus [9]. Ammonical cuprous chloride and aqueous potassium hydroxide were used as reacting solutions for CO and CO₂ respectively. The pressure was released, reactor was flushed with nitrogen and the contents withdrawn. The pressure drop during the reaction was also recorded as a function of time.

2.3 RESULTS AND DISCUSSION

The carbonylation of nitrobenzene to phenylisocyanate using palladium complex catalyst was found to be feasible at 190°C and a pressure of about 80 atm of CO. In each experiment the product distribution was noted as a function of time. The conversion of nitrobenzene and selectivity for phenylisocyanate were calculated based on the analysis of reactants and products. The material balance of CO and CO₂ was also checked at the end of the reaction. In general, it was observed that complete conversion of nitrobenzene was possible; however, the selectivity was found to be a complex function of time.

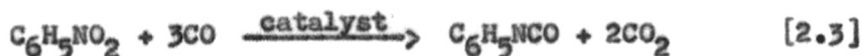
The stoichiometric reaction is



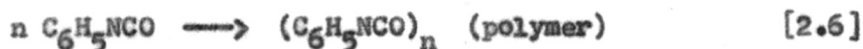
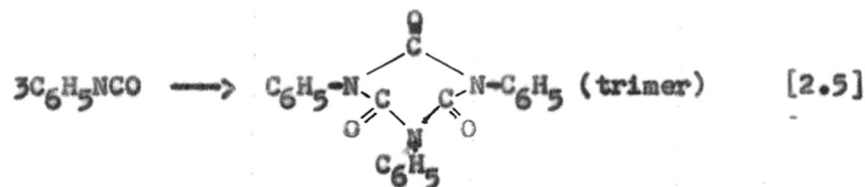
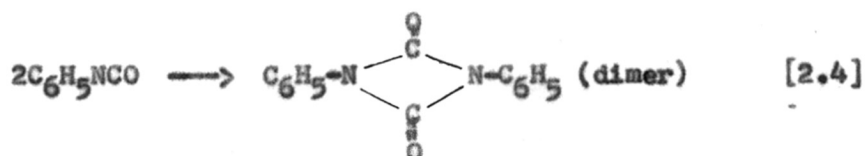
CONDITIONS -

TEMP 1	400	110	110
TIME 1	1.00		
RATE	20.00		
TEMP 2	400	150	
TIME 2	2.00		
INJ TEMP	400	200	200
FID TEMP	400	350	350
TCD TEMP	400	0	29
AUX TEMP	400	0	37
CHT SPD	1.00		
ZERO	10.0		
ATTN 2	10		
FID SGNL	A		
SLP SENS	0.10		
AREA REJ			0
FLOW A	20.0		19.8
FLOW B	20.0		19.9

FIG. 2.3. CHROMATOGRAM OF LIQUID COMPONENTS PRESENT IN THE CARBONYLATION OF NITROBENZENE REACTION MIXTURE



The drop in selectivity at higher conversion can be attributed mainly to the side products formed by consecutive reactions. The self condensation of phenylisocyanate (non-catalytic) by the following reactions is well known [4].



Material balances on CO, nitrobenzene, phenylisocyanate and CO₂ indicate that the amounts of nitrobenzene and CO reacted are as per the stoichiometry given by equation (2.3); however, the amount of phenylisocyanate formed does not correspond to the nitrobenzene reacted. This also indicates that further reactions [such as (2.4), (2.5) and (2.6)] are possible reasons for the drop in selectivity.

In order to understand the role of the various components of the catalyst system, a few preliminary experiments were carried out. An experiment carried out without catalyst but in the presence of CO produced no conversion of nitrobenzene. Similarly, carbonylation of nitrobenzene in the presence of oxide such as Fe_2O_3 , FeBO_3 , V_2O_5 , MoO_3 and Cr_2O_3 indicated no conversion of nitrobenzene. Experiments carried out using only a palladium complex catalyst in the absence of an oxide promoter indicated a significant conversion of nitrobenzene to phenylisocyanate. This suggests that the palladium complex is the main catalytic component and the oxide promoters are not essential for the reaction to occur.

The experimental data obtained for various catalysts, promoters and other operating conditions is given in Appendix-I.

2.3.1 Screening of catalysts

Effect of ligands : Several experiments were carried out to study the activity of palladium complexes as catalysts for the reduction of nitrobenzene using CO. The complexes studied were: (1) $\text{Pd}(\text{Py})_2\text{Cl}_2$, (2) $\text{Pd}(\text{Isoq})_2\text{Cl}_2$, (3) $\text{Pd}(\text{C}_7\text{H}_5\text{N})_2\text{Cl}_2$, (4) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and (5) $\text{Pd}(\text{CO})_2\text{Cl}_2$. The activity was tested at 190°C and 80 atm pressure of CO. The reaction was continued for a period of 5 hr and product distribution was recorded as a function of time. It was found that catalysts (1) and (2) were significantly active, while (3), (4) and (5) were inactive under the conditions used. This suggests that

the nitrogen containing heterocyclic compounds are the most suitable ligands. Also, the fact that $\text{Pd}(\text{CO})_2\text{Cl}_2$ is not active indicates that the first step in the catalytic cycle may not be the activation of CO. As it is known that PPh_3 and benzonitrile ligands are easily replaced by CO, the lower activity of the complexes (3), (4) and (5) can be explained.

The performances of catalysts (1) and (2) were found to be identical. Typical plots of concentration of nitrobenzene and of phenylisocyanate vs time are shown in Fig. 2.4. It can be seen that the initial period of formation of phenylisocyanate does not correspond to the nitrobenzene converted. This could be due to the initial activation of nitrobenzene to form an intermediate active complex or an intermediate such as nitrene [5]. The fact that the selectivity for phenylisocyanate increases later implies that the intermediates formed in the initial stages get converted to phenylisocyanate. A plot of selectivity for phenylisocyanate vs conversion of nitrobenzene is shown in Fig. 2.5. It can be seen that the selectivity is strongly dependent on the conversion of nitrobenzene and goes through a maximum for the $\text{Pd}(\text{Py})_2\text{Cl}_2$ catalyst system. Thus an optimum conversion of nitrobenzene exists for a given set of conditions. On the other hand, for $\text{Pd}(\text{Isoq})_2\text{Cl}_2$ the selectivity increases steadily with conversion of nitrobenzene.

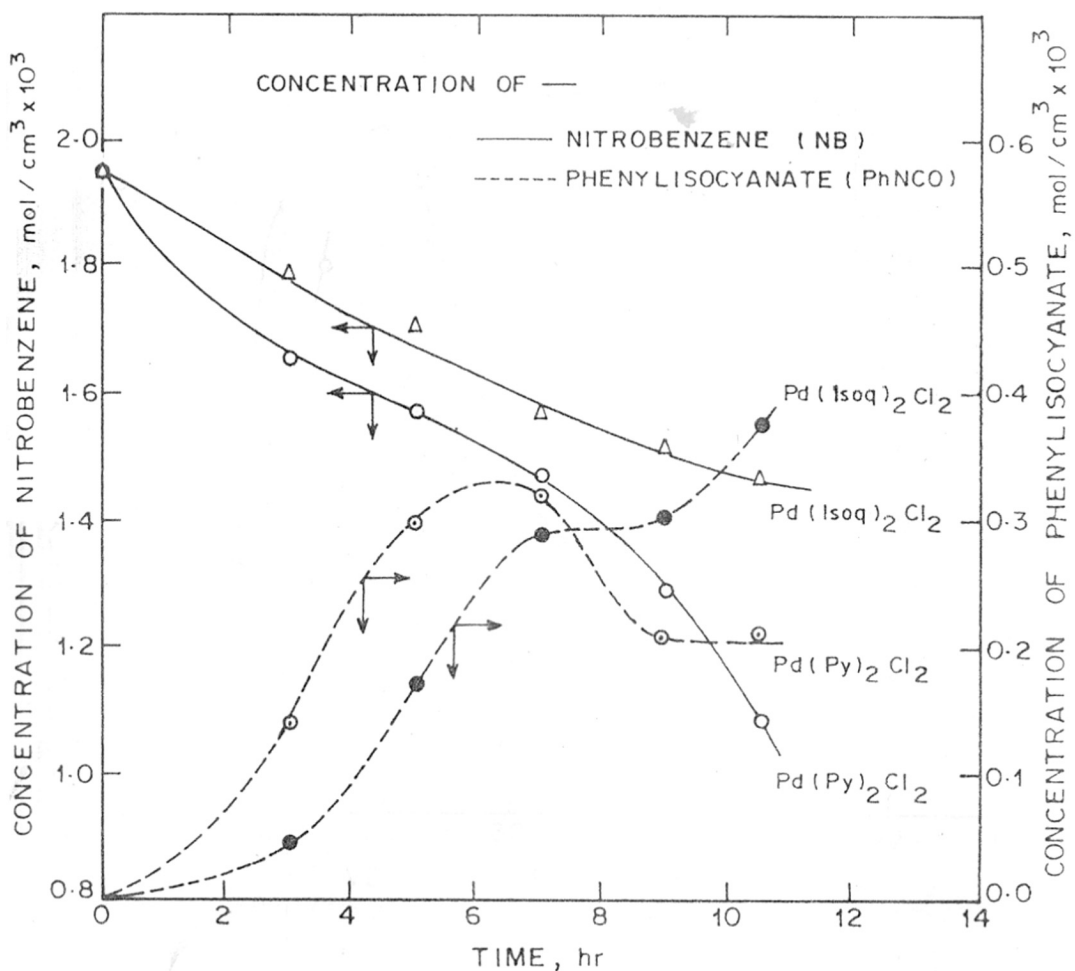


FIG. 2.4. CONCENTRATION VS TIME PLOTS FOR CATALYSTS (1) AND (2)

CONDITIONS: NB = 20 cm³, MCB = 80 cm³; TOTAL VOLUME = 100 cm³;
 CO PRESSURE = 80 atm; AGITATION = 1000 rpm;
 TEMPERATURE = 190°C; CATALYST = 3 × 10⁻⁵ mol/cm³

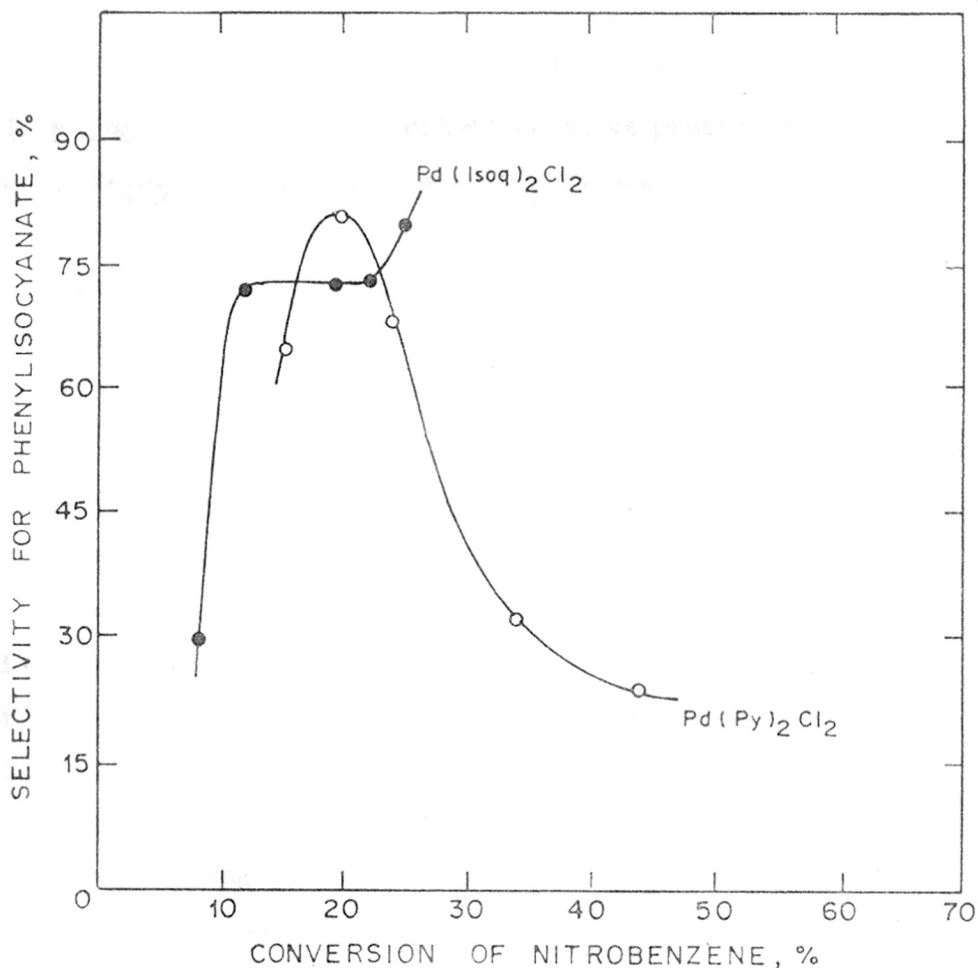


FIG. 2.5. SELECTIVITY VS CONVERSION PLOTS FOR CATALYSTS (1) AND (2)

CONDITIONS : NB = 20 cm³ ; MCB = 80 cm³ ; TOTAL VOLUME = 100 cm³
 CO PRESSURE = 80 atm ; AGITATION = 1000 rpm
 CONTACT TIME = 10.5 hr ; TEMPERATURE = 190 °C
 CATALYST = 3 x 10⁻⁵ mol / cm³

Effect of promoters: The effect of oxide promoters such as V_2O_5 , Fe_2O_3 , $FeBO_3$, Cr_2O_3 , and MoO_3 on the activity of catalysts (1) and (2) was studied under identical conditions. The conversion of nitrobenzene was found to increase with Fe_2O_3 , $FeBO_3$ and V_2O_5 marginally. However, the other oxides had no significant influence on the conversion of nitrobenzene.

The effect of promoters (Fe_2O_3 , $FeBO_3$ and V_2O_5) on the activity of catalyst (1) is shown in Fig. 2.6. This indicates that the oxide promoters have only a mild effect on the conversion rate of nitrobenzene. However, they have an interesting influence on the selectivity pattern. A plot of selectivity for phenylisocyanate vs conversion of nitrobenzene is shown in Fig. 2.7. As can be seen from this figure, Fe_2O_3 has no major influence on the selectivity pattern but V_2O_5 and $FeBO_3$ have interesting effects. While with V_2O_5 the selectivity increases with increase in conversion of nitrobenzene, with $FeBO_3$ a constant selectivity over a wider range of conversion of nitrobenzene has been achieved. This indicates that the promoters have no special advantage towards the activity of the catalyst, but improve the selectivity at higher conversions. From the observation that oxide promoters affect only the selectivity, it appears that these metal oxides influence the position of equilibrium in the self condensation reactions of phenyl isocyanate [reactions (2.4), (2.5) and (2.6)]. This perhaps explains the observed decline in selectivity at higher conversions as also the apparent 'stabilization' of phenylisocyanate in the presence of some oxide promoters.

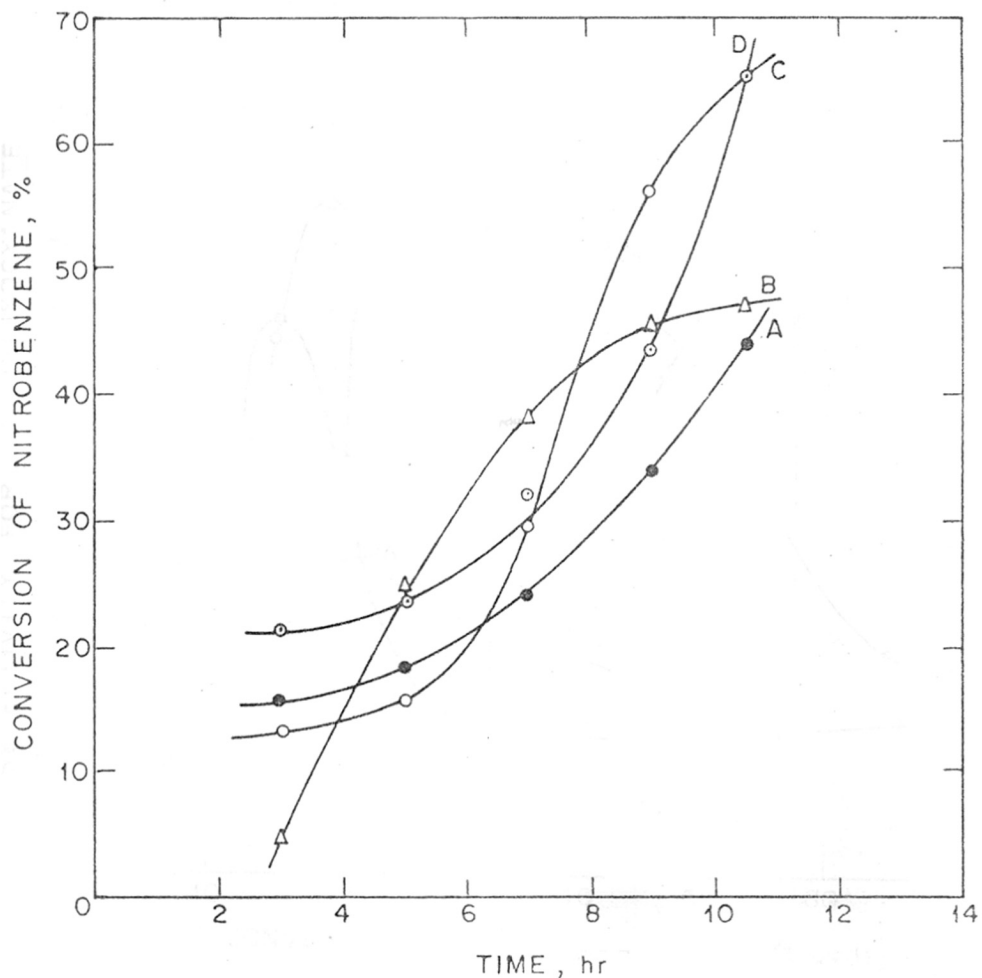


FIG. 2.6. EFFECT OF OXIDE PROMOTERS ON THE ACTIVITY OF $\text{Pd}(\text{Py})_2\text{Cl}_2$ CATALYSED CARBONYLATION OF NITROBENZENE

A) $\text{Pd}(\text{Py})_2\text{Cl}_2$; B) $\text{Pd}(\text{Py})_2\text{Cl}_2 + \text{V}_2\text{O}_5$

C) $\text{Pd}(\text{Py})_2\text{Cl}_2 + \text{Fe}_2\text{O}_3$; D) $\text{Pd}(\text{Py})_2\text{Cl}_2 + \text{FeBO}_3$

CONDITIONS : NB = 20 cm^3 ; MCB = 80 cm^3 ; TOTAL VOLUME = 100 cm^3 ;
 CO PRESSURE = 1173.75 psig ; $\text{Pd}(\text{Py})_2\text{Cl}_2 = 3 \times 10^{-5} \text{ mol / cm}^3$;
 PROMOTER = 0.5 gm ; AGITATION = 1000 rpm ;
 TEMPERATURE = 190°C

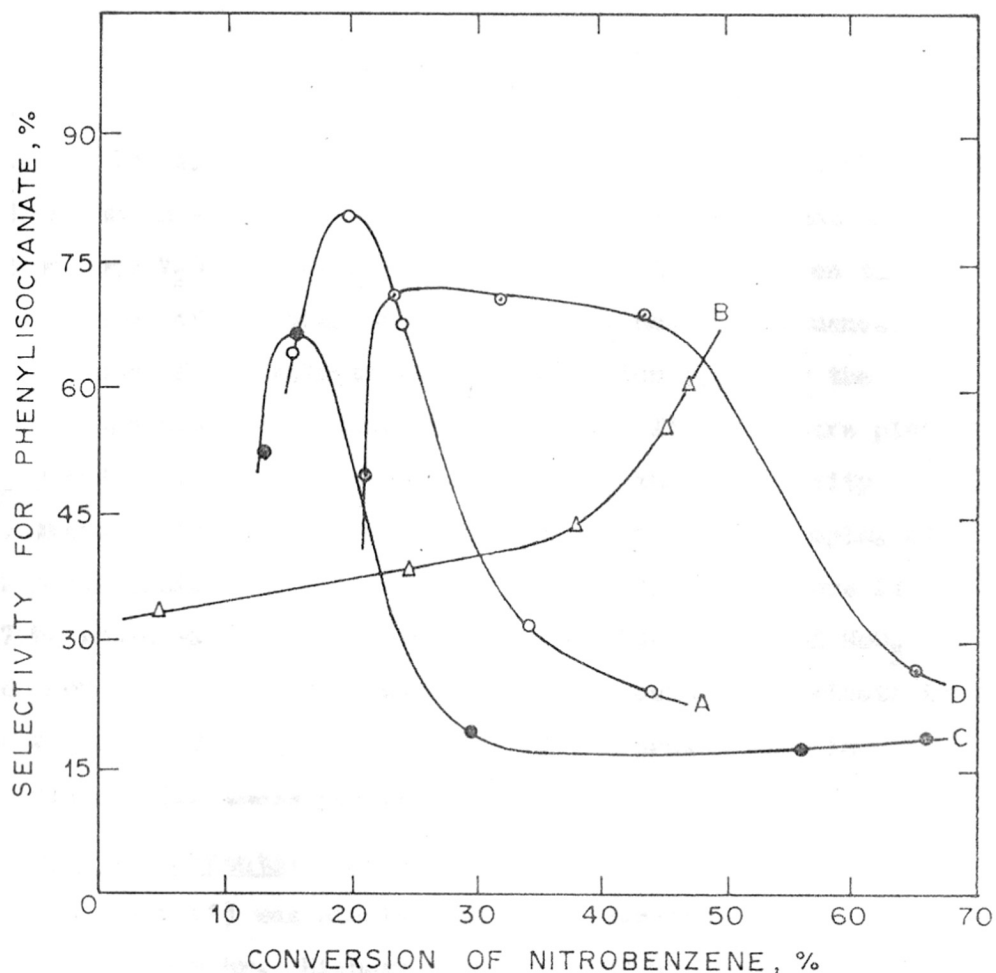


FIG. 2.7. EFFECT OF OXIDE PROMOTERS ON THE SELECTIVITY OF $\text{Pd}(\text{Py})_2\text{Cl}_2$ CATALYSED CARBONYLATION OF NITROBENZENE

A) $\text{Pd}(\text{Py})_2\text{Cl}_2$; B) $\text{Pd}(\text{Py})_2\text{Cl}_2 + \text{V}_2\text{O}_5$

C) $\text{Pd}(\text{Py})_2\text{Cl}_2 + \text{Fe}_2\text{O}_3$; D) $\text{Pd}(\text{Py})_2\text{Cl}_2 + \text{FeBO}_3$

CONDITIONS : $\text{NB} = 20\text{cm}^3$; $\text{MCB} = 80\text{cm}^3$; TOTAL VOLUME = 100cm^3
 CO PRESSURE = 1173.75 psig ; $\text{Pd}(\text{Py})_2\text{Cl}_2 = 3 \times 10^{-5}\text{mol}/\text{cm}^3$
 PROMOTER = 0.5 gm ; AGITATION = 1000 rpm ;
 TEMPERATURE = 190°C

The effect of promoters on the activity of catalyst (2) is shown in Fig. 2.8. It is interesting to note that the promoters V_2O_5 and MoO_3 have significant influence on the conversion of nitrobenzene, while $FeBO_3$ has no influence. The behaviour of the selectivity yg conversion plot for the promoters studied is shown in Fig. 2.9. If we compare plots (A) and (D), it is seen that with $FeBO_3$ the selectivity increases with conversion of nitrobenzene. For example, at 22% conversion the selectivity with catalyst (2) alone is 70%, while with $FeBO_3$ it is 90%. Promoters V_2O_5 and MoO_3 do not have any special advantage with respect to selectivity, but the trend of the selectivity yg conversion plot is different for these promoters.

Effect of solvents: The effect of solvents on the activity of catalyst (1) was studied, with the duration of the run fixed at 10.5 hr. Highest conversion of nitrobenzene was achieved with o-dichlorobenzene (ODCB). The solvent effect on the conversion of nitrobenzene was found to be in the following order:



The highest conversion of nitrobenzene achieved with ODCB can be explained on the basis of the solubility of CO. For example, the solubility of CO in ODCB is twice that in xylene under the reaction conditions. The solubility values for CO in toluene and monochlorobenzene (MCB) lie in between.

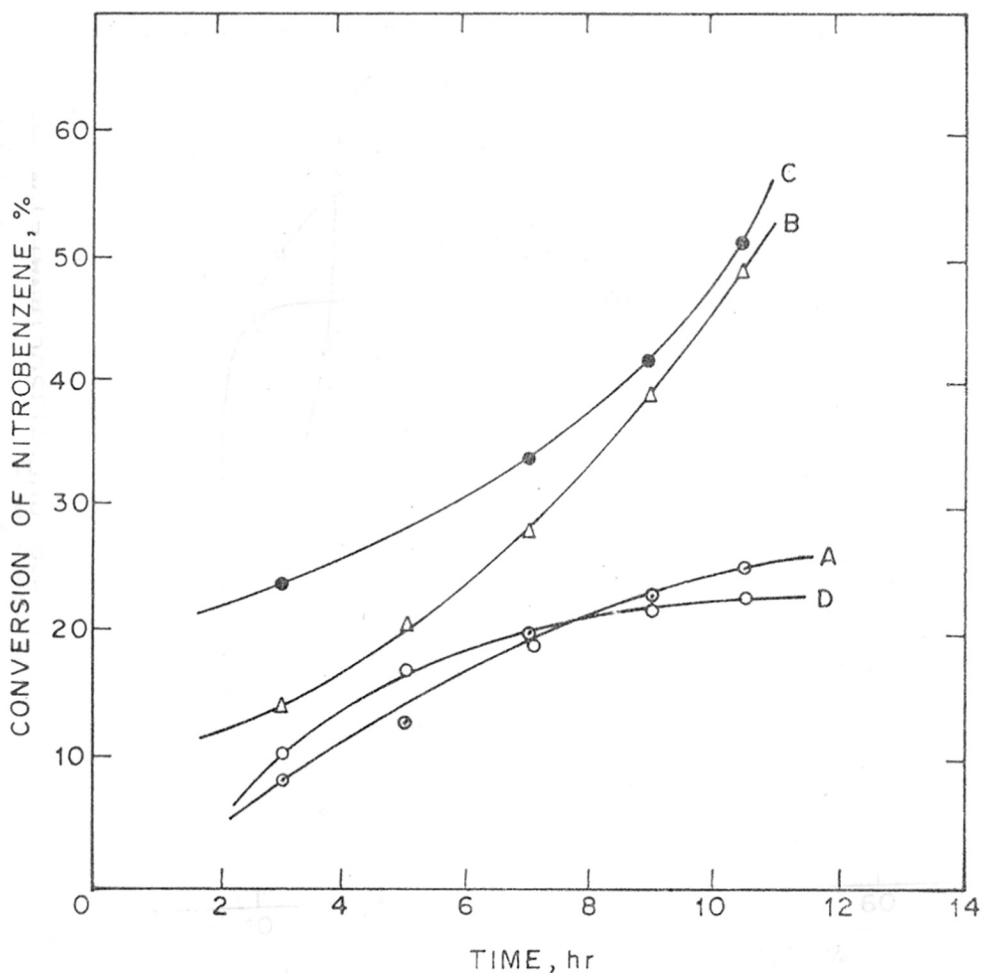


FIG. 2.8. EFFECT OF OXIDE PROMOTERS ON THE ACTIVITY OF $\text{Pd}(\text{Isoq})_2\text{Cl}_2$ CATALYSED CARBONYLATION OF NITROBENZENE

A) $\text{Pd}(\text{Isoq})_2\text{Cl}_2$; B) $\text{Pd}(\text{Isoq})_2\text{Cl}_2 + \text{V}_2\text{O}_5$

C) $\text{Pd}(\text{Isoq})_2\text{Cl}_2 + \text{MoO}_3$; D) $\text{Pd}(\text{Isoq})_2\text{Cl}_2 + \text{FeBO}_3$

CONDITIONS : $\text{NB} = 20 \text{ cm}^3$; $\text{MCB} = 80 \text{ cm}^3$; TOTAL VOLUME = 100 cm^3 ;
 CO PRESSURE = 1173.75 psig ; $\text{Pd}(\text{Isoq})_2\text{Cl}_2 = 3 \times 10^{-5} \text{ mol} / \text{cm}^3$;
 PROMOTER = 0.5 gm ; AGITATION = 1000 rpm ;
 TEMPERATURE = 190°C

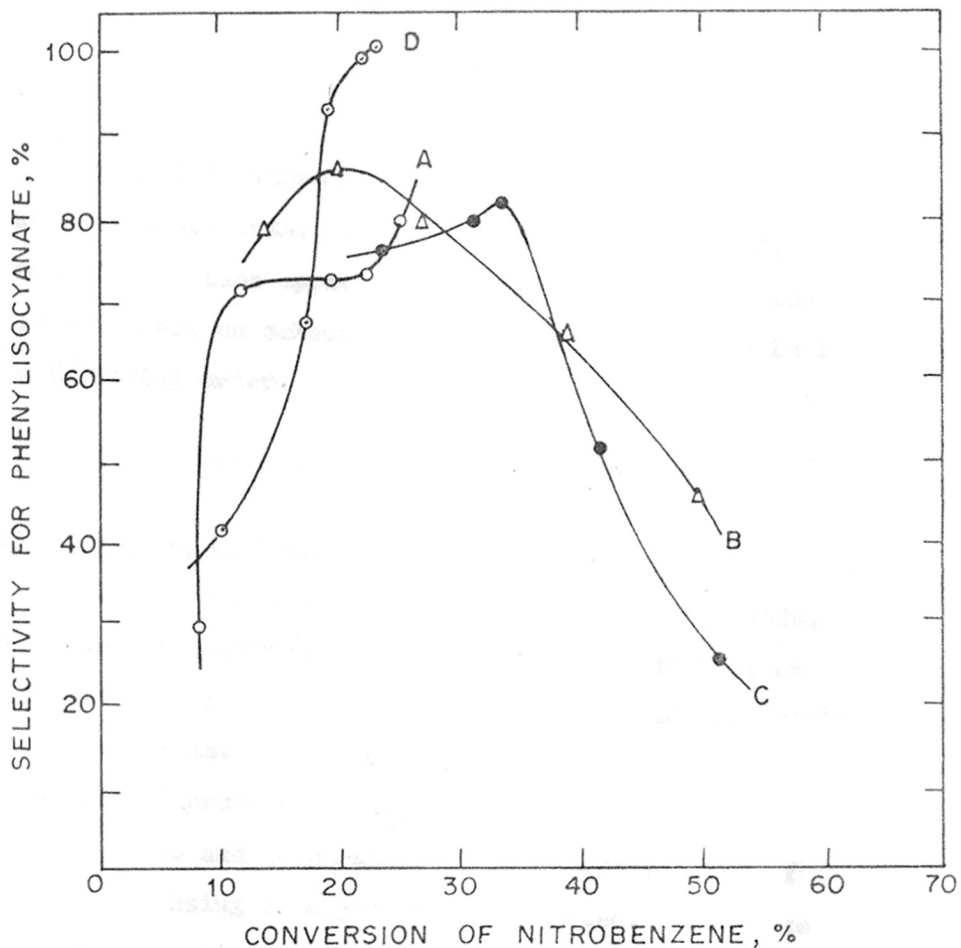


FIG. 2-9. EFFECT OF OXIDE PROMOTERS ON THE SELECTIVITY OF Pd (Isoq)₂ Cl₂ CATALYSED CARBONYLATION OF NITROBENZENE

A) Pd (Isoq)₂ Cl₂ ; B) Pd (Isoq)₂ Cl₂ + V₂O₅

C) Pd (Isoq)₂ Cl₂ + MoO₃ ; D) Pd (Isoq)₂ Cl₂ + FeBO₃

CONDITIONS : NB = 20 cm³ ; MCB = 80 cm³ ; TOTAL VOLUME = 100 cm³ ;

CO PRESSURE = 1173.75 psig ; Pd (Isoq)₂ Cl₂ = 3 x 10⁻⁵ mol / cm³

PROMOTER = 0.5 gm ; AGITATION = 1000 rpm ;

TEMPERATURE = 190°C

Fig. 2.10 shows a plot of selectivity vs conversion for various solvents. If we compare the selectivity at 25% conversion, xylene appears to be the best solvent, and the solvent effect on selectivity for phenylisocyanate is in the following order:

xylene > MCB > ODCB > toluene

2.3.2 Process variables

Besides the catalyst parameters such as ligands, promoters and solvents, process variables also play an important role in determining the activity and selectivity of the catalysts. Therefore, the influence of catalyst, proportion of promoter (V_2O_5), nitrobenzene concentration, pressure of CO and temperature on the carbonylation of nitrobenzene using catalyst (1) was studied. The ranges of variables investigated are given in Table 2.1. The results are discussed below.

Effect of CO pressure : The effect of CO pressure on the conversion vs time behaviour was studied in a batch reactor. In these experiments CO was charged only once during an experiment. The partial pressure changes with time for two reasons: (1) CO is consumed in the reaction, (2) carbon dioxide is generated as a gaseous product. Therefore, these experiments could not be carried out at a constant partial pressure of CO. However, some indications of the effect of CO pressure on the catalyst performance are interesting.

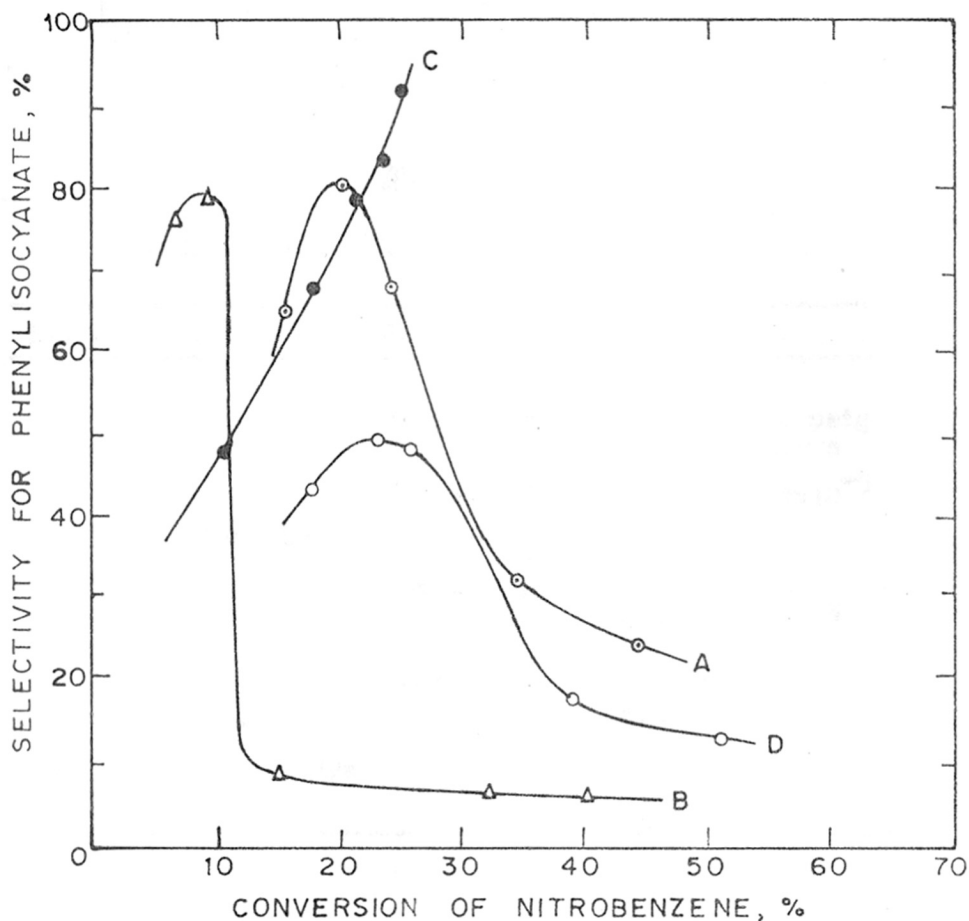


FIG. 2-10. EFFECT OF SOLVENTS ON THE SELECTIVITY OF $\text{Pd}(\text{Py})_2\text{Cl}_2$ CATALYSED CARBONYLATION OF NITROBENZENE

A) MONOCHLOROBENZENE ; B) TOLUENE
C) XYLENE ; D) ORTHODICHLOROBENZENE

CONDITIONS : NB = 20 cm^3 ; SOLVENT = 80 cm^3 ; TOTAL VOLUME = 100 cm^3
CO PRESSURE = 1173.75 psig ; $\text{Pd}(\text{Py})_2\text{Cl}_2 = 3 \times 10^{-5}\text{ mol/cm}^3$
AGITATION = 100 rpm ; TEMPERATURE = 190° C
CONTACT TIME = 10.5 hr

TABLE: 2.1VARIABLES AND THEIR RANGES STUDIED

S.No.	Variable	Range
1.	Carbon monoxide pressure	350 to 1650 psig total pressure
2.	$\text{Pd(Py)}_2\text{Cl}_2$ catalyst concentration	1×10^{-5} to 4×10^{-5} mol/cm^3
3.	Nitrobenzene concentra- tion	0.5×10^{-3} to 3×10^{-3} mol/cm^3
4.	V_2O_5 promoter concentra- tion	0.5 to 1.5 gm in 100 cm^3 solution
5.	Temperature	170 to 230°C

Fig. 2.11 shows a plot of conversion of nitrobenzene vs partial pressure of CO for two different durations. At lower pressures, (up to 1000 psig) the conversion is a strong function of pressure, while at higher pressures (above 1200 psig) it is independent of pressure. In low pressure experiments (350, 750 psig total pressure) the reaction stopped after a certain conversion equivalent to the CO charged initially.

The behaviour of the selectivity vs conversion plots observed at different pressures is shown in Fig. 2.12. It can be seen that for any given conversion, a higher selectivity is obtained at higher pressures. The possible explanation for this observation is that to achieve a certain conversion, the contact time required is dependent on pressure. At low pressures, the rate of phenylisocyanate is slower, while the contact time available for the side reactions of phenylisocyanate (self condensation reaction given in (2.4), (2.5) and (2.6)) to occur is very large, thus resulting in lower selectivity. At higher pressure, the rate of formation of phenylisocyanate being high, the contact time available is smaller and hence the selectivity is improved.

Effect of catalyst concentration: In order to study the influence of catalyst concentration on the carbonylation reaction, experiments were carried out over $\text{Pd}(\text{Py})_2\text{Cl}_2$ in the concentration range of 1 to 4×10^{-5} mol/cm³ keeping all other conditions constant. The results are shown in Fig. 2.13

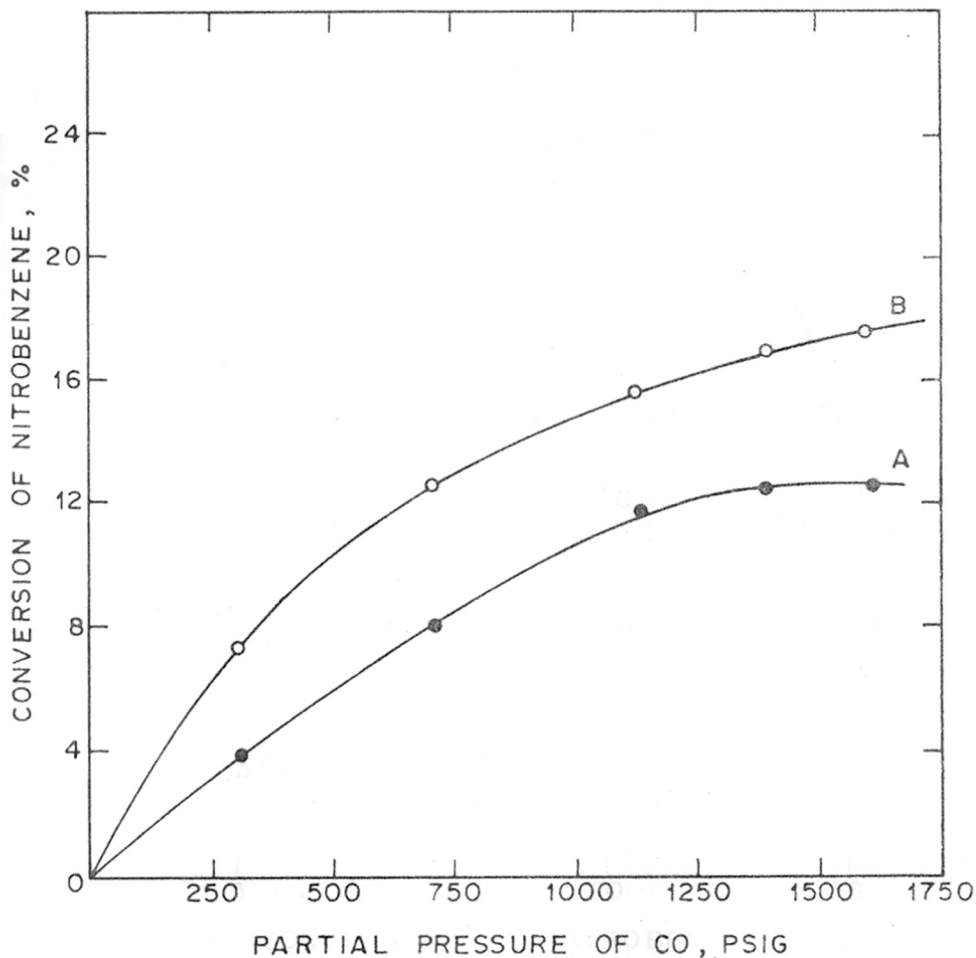


FIG. 2-11. EFFECT OF CARBON MONOXIDE PRESSURE ON THE ACTIVITY OF $\text{Pd}(\text{Py})_2\text{Cl}_2$ CATALYSED CARBONYLATION OF NITROBENZENE

DURATION: A) 1.75 hr; B) 2.5 hr

CONDITIONS: NB = 20 cm^3 ; MCB = 80 cm^3 ; TOTAL VOLUME = 100 cm^3
 $\text{Pd}(\text{Py})_2\text{Cl}_2 = 3 \times 10^{-5} \text{ mol/cm}^3$; CONTACT TIME = 4 hr
 AGITATION = 1000 rpm; TEMPERATURE = 190°C

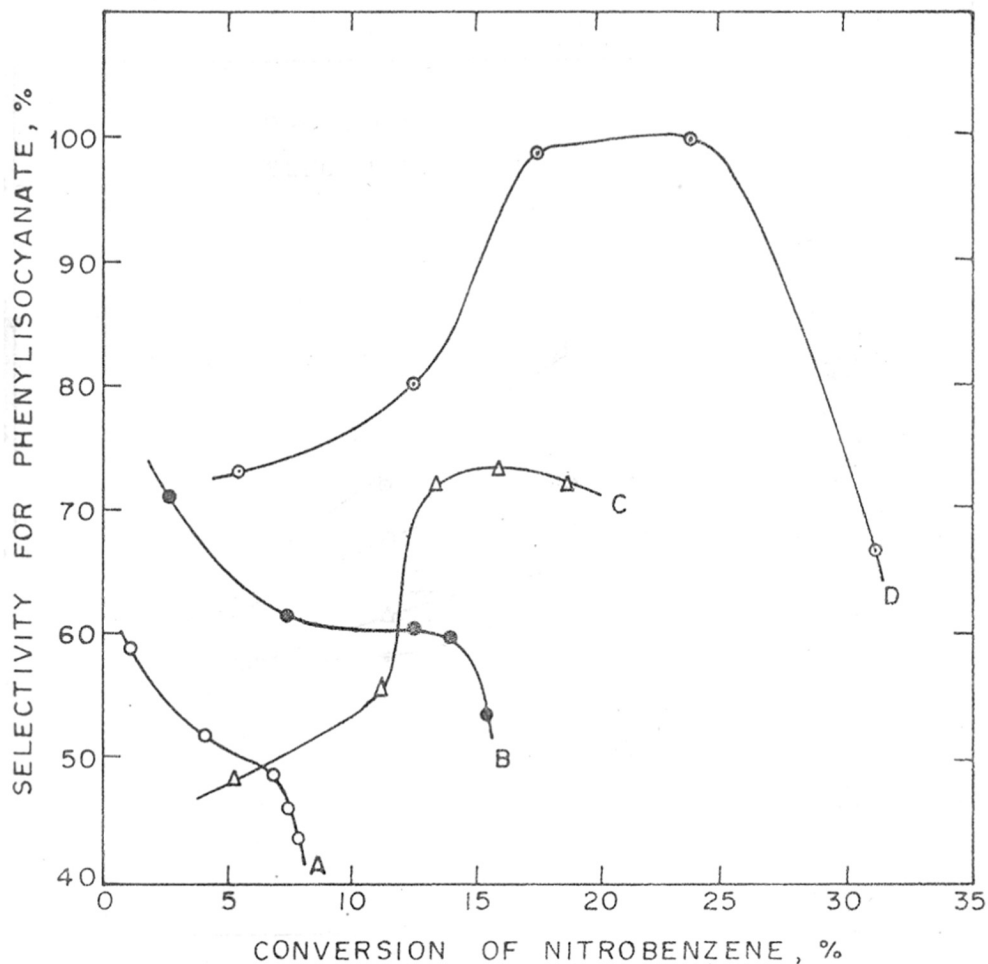


FIG. 2.12. EFFECT OF PARTIAL PRESSURE OF CARBON MONOXIDE ON THE SELECTIVITY VS CONVERSION PATTERN OF $\text{Pd}(\text{Py})_2\text{Cl}_2$ CATALYSED CARBONYLATION OF NITROBENZENE

PARTIAL PRESSURE : A) 303.75 psig B) 703.75 psig
 C) 1133.75 psig D) 1603.75 psig

CONDITIONS : NB = 20 cm^3 ; MCB = 80 cm^3 ; TOTAL VOLUME = 100 cm^3 ;
 $\text{Pd}(\text{Py})_2\text{Cl}_2 = 3 \times 10^{-5} \text{ mol/cm}^3$; AGITATION = 1000 rpm ;
 CONTACT TIME = 4 hr ; TEMPERATURE = 190°C

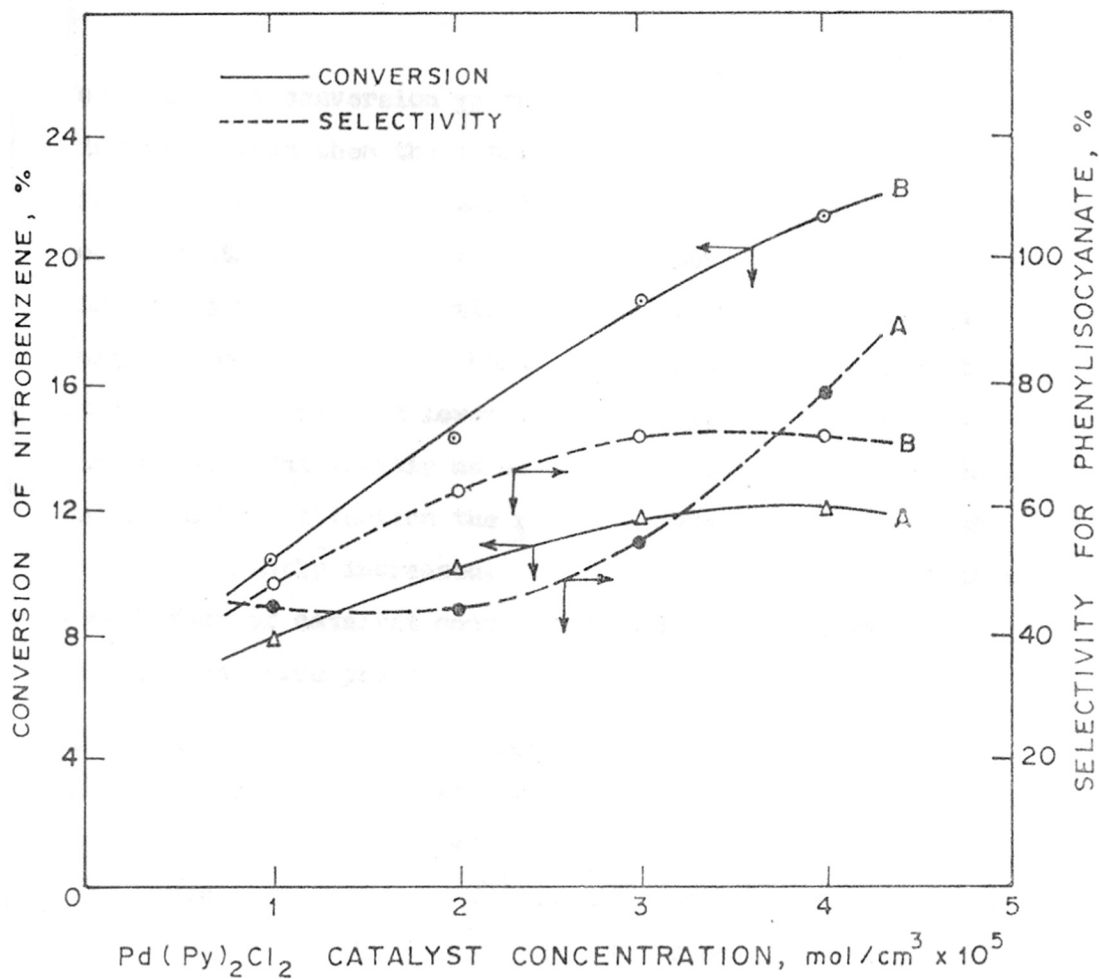


FIG. 2-13. EFFECT OF CATALYST CONCENTRATION ON THE CONVERSION AND SELECTIVITY OF CARBONYLATION

DURATION: A) 1.75 hr ; B) 4.0 hr

CONDITIONS: NB = 20 cm³ ; MCB = 80 cm³ ; TOTAL VOLUME = 100 cm³ ;

CO₂ PRESSURE = 1133.75 psig ; AGITATION = 1000 rpm

CONTACT TIME = 4 hr ; TEMPERATURE = 190° C

as a plot of conversion vs catalyst concentration. It indicates that when the catalyst concentration was changed fourfold the conversion was doubled. The influence of catalyst concentration on selectivity is also shown in Fig. 2.13, which indicates that the selectivity increases with increase in catalyst concentration. Here, the behaviour is dependent on the contact time. At lower contact time, the selectivity increases significantly as catalyst concentration is increased, since in this situation the relative rate of carbonylation is predominantly increased. However, at longer contact times, the effect of catalyst concentration is mild due to the significant side product formation.

Effect of promoter (V_2O_5) concentration: Since V_2O_5 was found to be the best oxide promoter from the studies on catalyst screening, the effect of different V_2O_5 concentrations was investigated at 2×10^{-5} mol/cm³ $Pd(Py)_2Cl_2$ concentration, 2M concentration of nitrobenzene, 190°C and 1180 psig total pressure (partial pressure 1133.75). The results are presented in Table 2.2. It can be seen that the conversion increases with increase in promoter concentration. If we compare the experiment in the absence of a promoter (Run No. 56) and those in the presence of promoters (Run Nos. 59, 60, 61) it can be seen that the selectivity first increases with increase in promoter concentration but drops on further increase in the concentration. An experiment was also carried out at 1×10^{-5} mol/cm³ $Pd(Py)_2Cl_2$ concentration and 0.5 gm of promoter concen-

TABLE: 2.2

EFFECT OF V₂O₅ ON Pd(Py)₂Cl₂ CATALYSED
CARBONYLATION OF NITROBENZENE TO PHENYLISOCYANATE

Conditions:

Monochlorobenzene	= 80 cm ³
Nitrobenzene	= 20 cm ³
Total volume	= 100 cm ³
Agitation speed	= 1000 rpm
Partial pressure of CO	= 1133.75 psig
Duration of the reaction	= 4 hr
Temperature	= 190°C

Run No.	Pd(Py) ₂ Cl ₂ catalyst concentration, x 10 ⁵ mol/cm ³	V ₂ O ₅ promoter concentration, gm	Conversion of NB, %	Selectivity for PhNCO, %
55	1	-	10.30	47.98
56	2	-	14.26	48.15
58	1	0.5	9.96	100.00
59	2	0.5	28.70	87.72
60	2	1.0	31.25	90.02
61	2	1.5	35.07	74.52

tration (Run No. 58) which indicates that the ratio of catalyst to promoter concentration plays an important role in determining the selectivity. For a ratio of catalyst to promoter concentration of 0.67 (wt/wt), highest selectivity (90-100%) for phenylisocyanate was obtained for a conversion up to 30% of nitrobenzene. This may be due to the stabilization of product at higher ratio of promoter to nitrobenzene.

Effect of nitrobenzene concentration: The effect of nitrobenzene concentration was studied at a catalyst concentration of 3×10^{-5} mol/cm³ of Pd(Py)₂Cl₂ and CO partial pressure of 1133.75 psig without using a promoter. From the results shown in Fig. 2.14, which is a plot of mol nitrobenzene reacted vs initial concentration of nitrobenzene, it can be seen that the rate of reaction is independent of nitrobenzene concentration.

Effect of temperature: The effect of temperature was studied in the range of 170 to 230°C at 3×10^{-5} mol/cm³ Pd(Py)₂Cl₂ concentration, 2M nitrobenzene concentration and 1133.75 psig CO partial pressure. Fig. 2.15 shows the effect of temperature on the conversion of nitrobenzene and selectivity for phenylisocyanate. As can be seen from this figure, the conversion of nitrobenzene increases with increase in temperature, while the selectivity drops from 100 to 7.94% in the temperature range studied. A drastic fall in selectivity at longer contact times and higher temperatures was perhaps due to the

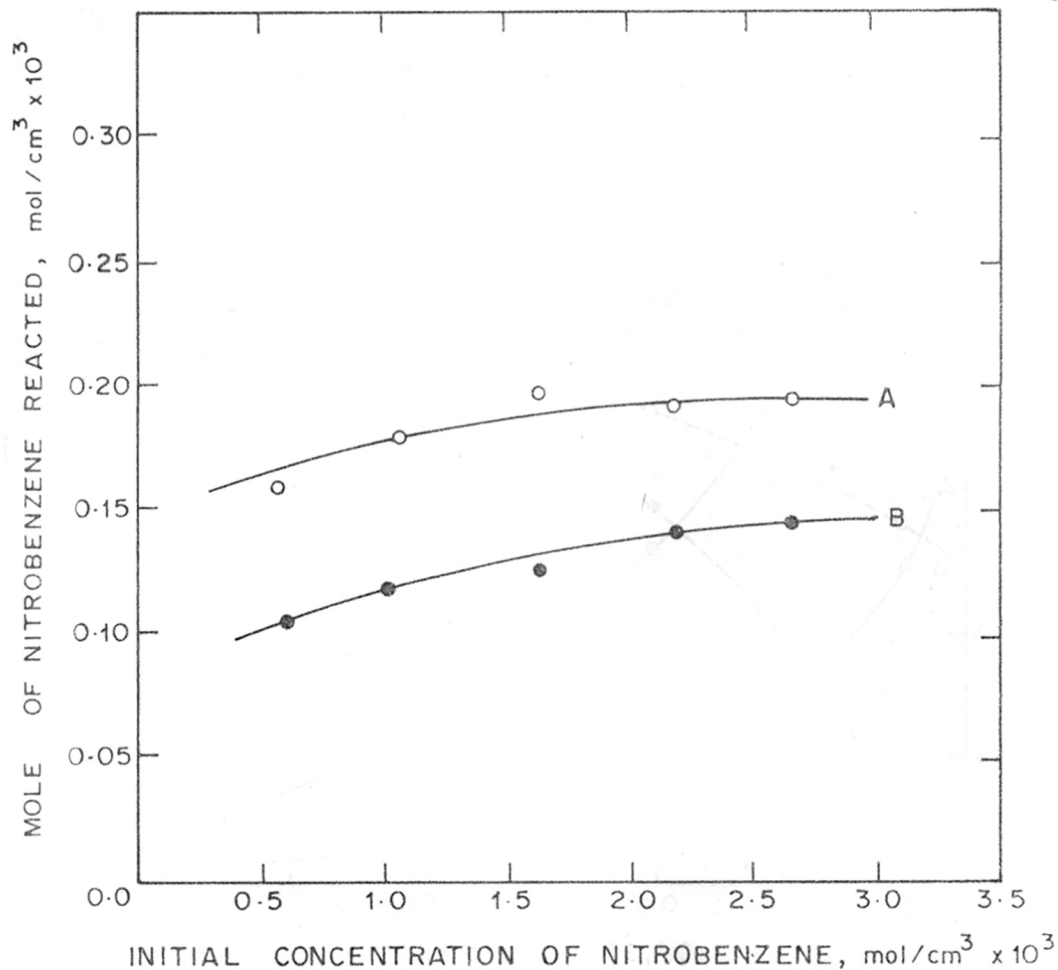


FIG. 2.14. EFFECT OF NITROBENZENE CONCENTRATION ON
Pd(Py)₂Cl₂ CATALYSED CARBONYLATION

DURATION: A) 1.75 hr ; B) 1.0 hr

CONDITIONS : CO PRESSURE = 1133.75 psig ; SOLVENT = MCB ;
TOTAL VOLUME = 100 cm³ ; Pd(Py)₂Cl₂ = 3 × 10⁵ mol / cm³
AGITATION = 1000 rpm ; CONTACT TIME = 4 hr ;
TEMPERATURE = 190 °C

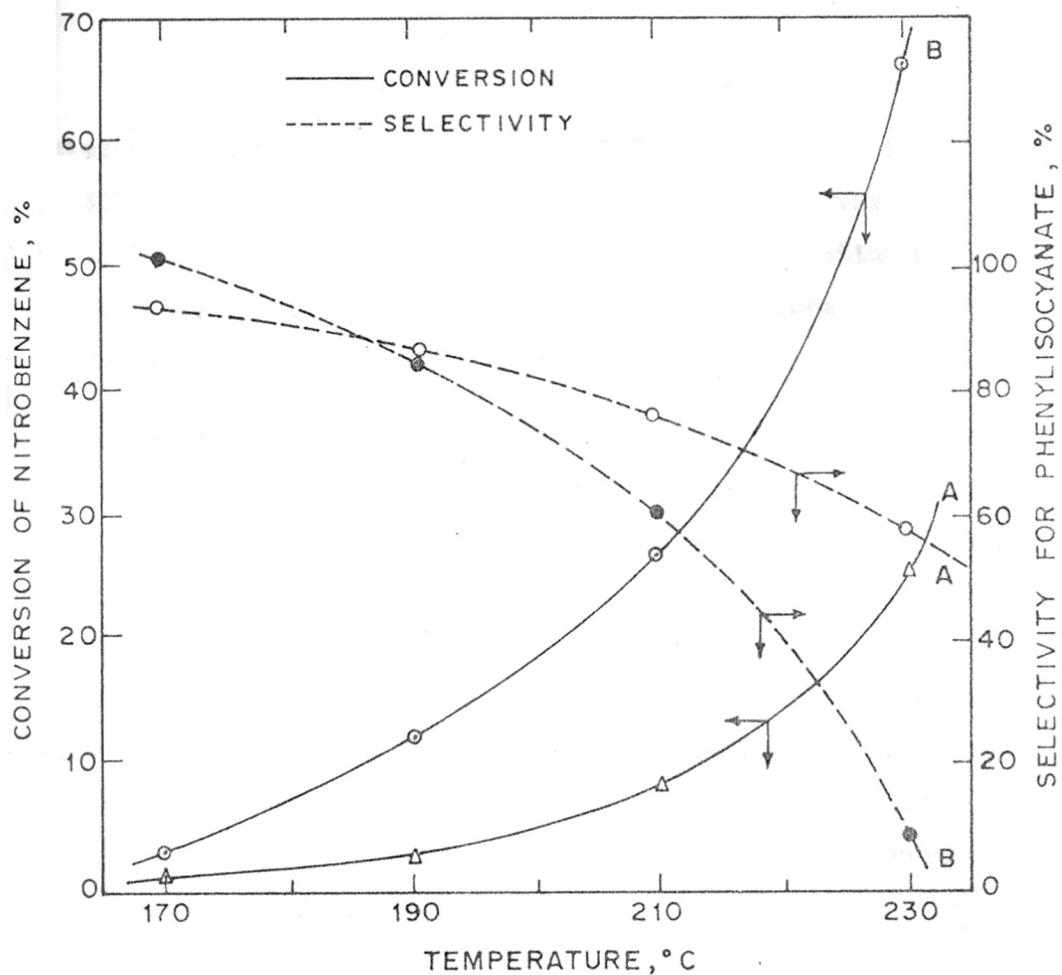


FIG. 2.15. EFFECT OF TEMPERATURE ON CONVERSION AND SELECTIVITY FOR $\text{Pd}(\text{Py})_2\text{Cl}_2$ CATALYSED CARBONYLATION OF NITROBENZENE

DURATION: A) 1.0 hr ; B) 4.0 hr

CONDITIONS: NB = 20 cm^3 ; MCB = 80 cm^3 ; TOTAL VOLUME = 100 cm^3 ;

CO PRESSURE = 1133.75 psig; AGITATION = 1000 rpm;

$\text{Pd}(\text{Py})_2\text{Cl}_2 = 3 \times 10^{-5} \text{ mol} / \text{cm}^3$; CONTACT TIME = 4 hr

relatively high rates of side product formation under these conditions compared to the carbonylation rate. In these conditions, the product solution at the end of reaction was found to be highly viscous which indicates the formation of polymeric side products.

2.3.3 Possible reaction mechanism

In order to throw some light on the reaction mechanism and the nature of the active species, an analysis of the complex $\text{Pd}(\text{Py})_2\text{Cl}_2$ and the catalyst residue recovered from the reaction mixture was carried out. The catalyst residue from the reaction mixture was isolated by precipitating with petroleum ether (60-80°C range). The important IR frequencies are shown in Fig. 2.16. The elemental analysis of the residue was: 60.65% C, 4.06% H, 12.05% N and 23.14% Pd. This corresponds to a structure of the type $\text{Pd}(\text{Py})_2(\text{RN})_2$. The other supporting evidences for this structure are:

- (1) IR frequency (see Fig. 2.16) for Pd-Cl bonding (355 cm^{-1}) in the original complex has disappeared in the residue.
- (2) Pd-N bonding IR frequency (470 cm^{-1}) is retained in the residue at 500 cm^{-1} ; generally Pd-N bonding frequencies are in the range of $450\text{-}550\text{ cm}^{-1}$.
- (3) IR frequencies corresponding to N-containing aromatics (e.g. pyridine) are seen in both the original catalyst and residue; this indicates that the pyridine ligand is not replaced during carbonylation.

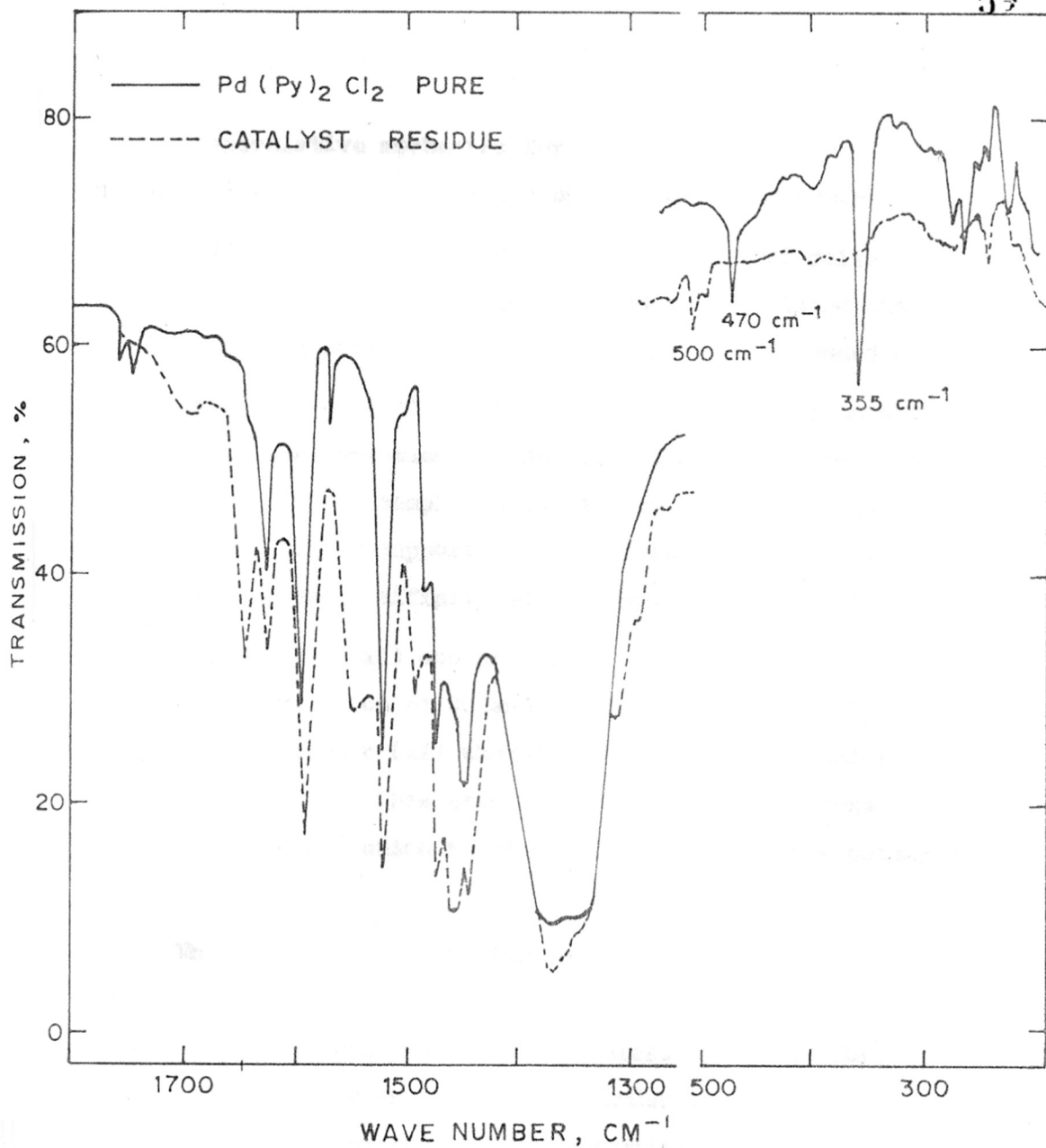
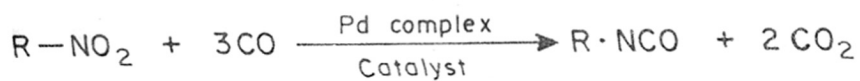


FIG. 2-16. IR SPECTRUM OF PURE $\text{Pd}(\text{Py})_2\text{Cl}_2$ CATALYST AND CATALYST RESIDUE SEPARATED FROM THE REACTION MIXTURE

A speculative mechanism for the reaction is proposed in Fig. 2.17. This is supported by the following observations:

- (i) The fact that the carbonyl complex of palladium is not active suggests that the CO ligand hinders the activation of $R-NO_2$ by attack on bonded chlorine.
- (ii) The activation of $R-NO_2$ is likely to be through the formation of the nitrene radical (6-8) and further complexation to form species such as (B). This is supported by the fact that chlorine has greater affinity towards bonded oxygen than CO.
- (iii) Point (ii) appears to be reasonable, since the oxidation of CO and CO_2 can be explained by reaction (II) wherein ClO_2 is a strong oxidizing agent. This step is necessary for the regeneration of Cl^- which is required to complete the catalytic cycle.

While the above mechanism is speculative at this stage, there is sufficient justification based on the evidences reported to accept it as ^a basis for kinetic studies. However, further work on this subject is necessary in order to establish the mechanism of this reaction firmly and understand the nature of the active species. Attempts should be made to investigate the nature of the catalytic species by in situ IR spectroscopy, molecular weight determination and different temperature NMR studies.



L = Pyridine, R = -C₆H₅

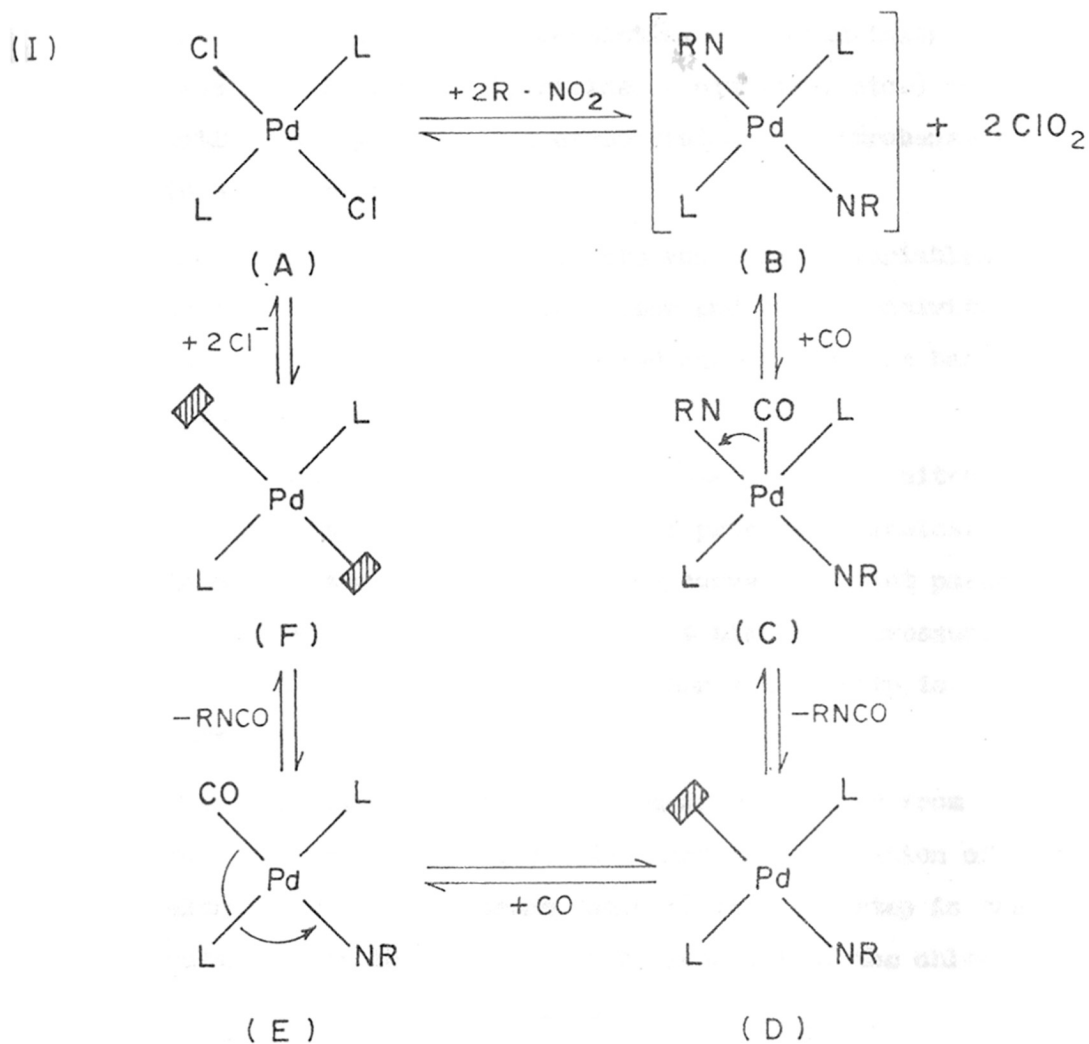


FIG. 2-17. MECHANISM OF CARBONYLATION OF NITROBENZENE

2.4 CONCLUSIONS

1. The palladium complexes consisting of N-containing heterocyclic ligands (pyridine, isoquiline, etc.) are active catalysts for the carbonylation of nitrobenzene to phenylisocyanate.
2. The effect of various catalysts and process variables on the conversion of nitrobenzene and the selectivity for phenylisocyanate was studied and a mechanism has been proposed.
3. The selectivity for phenylisocyanate (based on nitrobenzene) is a complex function of process variables. In most cases the selectivity vs conversion plot passes through a maximum. In general, at higher CO pressures and catalyst concentrations, higher selectivity is obtained.
4. The analysis of the catalytic residue isolated from the reaction mixture indicates that the activation of nitrobenzene (via nitrene radical) is a key step in the catalytic cycle and involves replacement of the chlorine ligand rather than pyridine.

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CHAPTER - 3

SOLUBILITY OF CO IN SOLVENT MIXTURES

CHAPTER-3SOLUBILITY OF CO IN SOLVENT MIXTURES3.1 INTRODUCTION

In any study of the intrinsic kinetics of gas-liquid reactions, data on the solubility of the gas phase reactant in the liquid medium is necessary. For the system studied in the present work (carbonylation of nitrobenzene to phenylisocyanate catalysed by $\text{Pd}(\text{Py})_2\text{Cl}_2$ complex), data on the solubility of CO in nitrobenzene, monochlorobenzene (solvent) and their mixtures at higher pressures and temperatures was required. As no published information was available on this system in the range of conditions used in the kinetic studies, these data were obtained experimentally using a specially designed solubility apparatus.

3.2 APPARATUS

The solubility of a gas in a liquid at higher pressures and temperatures is generally obtained by taking out a known amount of saturated solution and measuring the dissolved gas in the liquid. The amount of gas dissolved can be measured either by chemical, GLC or volumetric method. In the chemical and GLC methods there is a possibility of losing the dissolved gas during the handling of the samples and hence these methods are not always suitable. In this work, the volumetric method was used to determine the solubility of CO in monochlorobenzene, nitrobenzene and their

mixtures, as this method has been found to be quite accurate by many investigators (Battino and Clever [2], Chaudhari et al [3]).

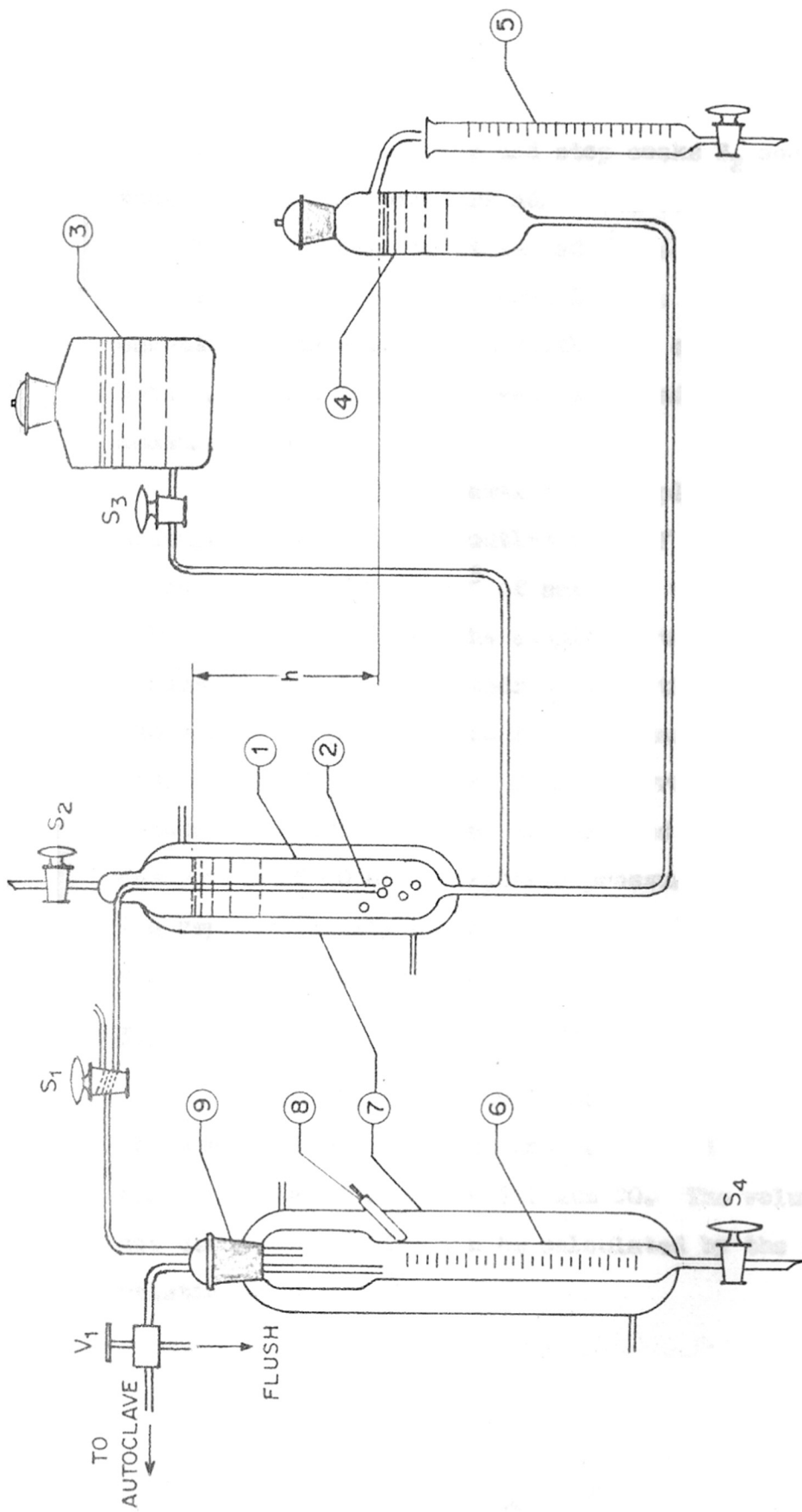
Apparatus for determining the solubilities by the volumetric method has been described by Battino [1]. The solubility apparatus used in the present work is shown schematically in Fig. 3.1. It consists essentially of two parts: one, the sample burette in which the desorption of the dissolved gas from saturated liquid occurs at atmospheric pressure; and, second, the gas collecting and measuring unit. The sample collecting burette and the gas collector are provided with a water jacket for keeping the temperature constant during an experiment.

3.3 MATERIALS

Freshly distilled and degassed solvents were used in solubility determinations.

3.4 EXPERIMENTAL PROCEDURE

The solvent was equilibrated with CO at a known pressure and temperature for about one hour in a reactor shown in Fig. 2.1 at a stirrer speed of 1000 rpm. After connecting the solubility apparatus to the reactor, the sample collecting burette was flushed with CO and the stop cocks S_1 and S_4 were closed. Water in the gas collector and reservoir was saturated with CO before use. The gas collector was completely filled with water by using the



- 1 GAS COLLECTOR
- 2 GAS INLET TUBE
- 3 WATER RESERVOIR
- 4 PRESSURE ADJUSTING DEVICE
- 5 GRADUATED BURETTE
- 6 SAMPLE BURETTE
- 7 WATER JACKET
- 8 THERMOWELL
- 9 B-19 COPPER METAL JOINT

FIG. 3-1. CO SOLUBILITY APPARATUS

pressure adjusting device and stop cocks S_2 and S_3 were then closed. The pressure adjusting device was lowered and the water level in it was adjusted to that of the tip of the gas inlet tube as shown in Fig. 3.1. The sample burette was then connected to the gas collector using stop cock S_4 . Thus the system was made ready for solubility measurements.

Before the withdrawal of a sample for solubility measurement, the liquid outlet tube of the reactor was flushed with about 10 cm^3 of solution using a three-way valve V_1 . After this, the sample of the saturated liquid (about $10\text{-}15 \text{ cm}^3$) was withdrawn into the sample burette. The volume of gas desorbed from the sample displaced an equivalent volume of water from reservoir, which was measured. Sufficient time was allowed for the complete desorption of CO at atmospheric pressure and room temperature. The reproducibility of the data as confirmed by repeating some experiments 3-4 times was found to be within 2%.

3.5 EXPERIMENTAL DATA

The solubility of CO in monochlorobenzene, nitrobenzene and their mixtures was determined in a temperature range of $150\text{-}230^\circ\text{C}$ and $20\text{-}110 \text{ atm CO}$. The volume of the gas desorbed (at STP) can be calculated by the following relationship:

$$X = \frac{v - v_1}{v_1} \frac{P - P_w - \frac{h}{13.6} \times 298}{760 \times T_w} \quad [3.1]$$

where, X = amount of gas desorbed, cm^3/cm^3

v = volume of water displaced, cm^3

v_1 = volume of liquid sample, cm^3

P = atmospheric pressure, mm of Hg

P_w = vapour pressure of water at the temperature of gas collector

h = height of water column (as shown in Fig. 3.1), mm of Hg

and

T_w = temperature of gas collector, K

As the solubility of CO measured excludes the solubility at atmospheric pressure, the following correction was made to get the actual solubility under the conditions employed to equilibrate the gas with the solvent:

$$S = X + S_1 \quad [3.2]$$

where, S = actual solubility of CO, cm^3/cm^3

X = observed solubility of CO, cm^3/cm^3

and

S_1 = solubility of CO at atmospheric pressure, cm^3/cm^3

The solubility of CO in a mixture of monochlorobenzene (MCB) and nitrobenzene (NB) at different temperatures were determined

and expressed in terms of Henry's constant (gm/lit/atm) and the results are presented in Table 3.1.

3.6 CORRELATION OF DATA

The types of equations normally used to fit the solubility data to establish the temperature dependence of solubility have been summarised by Battino and Clever [2]. Some of these are given below.

$$\ln S = a + \frac{b}{T} + C \ln T \quad [3.3]$$

$$\ln S = a + \frac{b}{T} + \frac{C}{T^2} \quad [3.4]$$

$$\ln S = a + b \ln T \quad [3.5]$$

To establish the dependence of S on nitrobenzene concentration in the mixtures of nitrobenzene and monochlorobenzene, the following modified equation was used:

$$\ln S = a + \frac{b}{T} + C \ln (1 - dx) \quad [3.6]$$

where S = solubility of CO, gm/lit/atm

x = mole fraction of nitrobenzene

T = equilibrium temperature, K

and

a, b, c and d = constants in the equations (3.3 to 3.6)

The above equation was found to fit the data on CO solubility in mixtures of solvents with an error of less than

TABLE: 3.1SOLUBILITY OF CO IN A MIXTURE OF
MONOCHLOROBENZENE (MCB) AND NITROBENZENE (NB)

Composition (by volume)		Henry's constant (gm/lit/atm)				
		150°C	170°C	190°C	210°C	230°C
NB, %	MCB, %					
0	100	0.2100	0.2286	0.2400	0.2647	0.2710
5	95	-	0.2145	0.2220	0.2310	-
10	90	-	0.2032	0.2130	0.2150	-
15	85	-	0.1925	0.1990	0.2035	-
20	80	-	0.1835	0.1860	0.1920	-
30	70	-	0.1712	0.1740	0.1790	-
50	50	-	0.1530	0.1590	0.1620	-
70	30	-	0.1380	0.1430	0.1472	-
80	20	-	0.1315	0.1390	0.1410	-
90	10	-	0.1275	0.1340	0.1372	-
100	0	0.1200	0.1232	0.1300	0.1330	0.1420

3%. The values of the constants obtained are given below.

$$\begin{aligned} a &= -0.8407 \\ b &= -321.538 \\ c &= 5.3573 \\ &\text{and} \\ d &= 0.1 \end{aligned}$$

3.7 CONCLUSIONS

The solubility of CO in monochlorobenzene, nitrobenzene and their mixtures at higher pressures and temperatures was determined experimentally using a suitably designed apparatus. The solubility of CO was correlated using an empirical equation and the estimated error was found to be less than 3%. As these data were obtained under actual reaction conditions, they can be directly used in interpreting the kinetics of the carbonylation of nitrobenzene catalysed by soluble $\text{Pd}(\text{Py})_2\text{Cl}_2$ complex catalyst.

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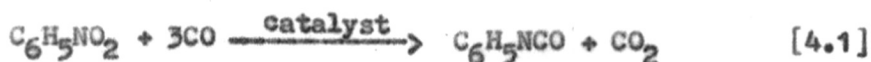
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CHAPTER - 4

KINETIC STUDY OF CARBONYLATION OF
NITROBENZENE TO PHENYLISOCYANATE

CHAPTER-4KINETIC STUDY OF CARBONYLATION
OF NITROBENZENE TO PHENYLISOCYANATE4.1 INTRODUCTION

Carbonylation of nitro compounds is an industrially important reaction as it provides a novel route for the synthesis of isocyanates in a single step. This reaction is normally carried out in the presence of homogeneous transition metal complex catalysts in high pressure reactors. The stoichiometric reaction is:



A detailed literature survey on this reaction is presented in Chapter-1, while the investigations on the screening of catalysts and the effect of process parameters on their activity and selectivity have been reviewed in Chapter-2. It has been found that the complex $\text{Pd}(\text{Py})_2\text{Cl}_2$ gives consistent activity and high selectivity in the carbonylation of nitro compounds to isocyanates. Besides, the information on the activity of different catalysts, a knowledge of the reaction kinetics is useful in understanding the mechanism as also in the design of commercial reactors. However, no attempt to investigate the kinetics of this reaction has so far been made. The purpose of the present work was to study the intrinsic kinetics of this reaction with $\text{Pd}(\text{Py})_2\text{Cl}_2$ complex

as catalyst in chlorobenzene solvent using a high pressure stirred reactor. As part of this study the gas-liquid mass transfer coefficients were also measured for the high pressure reactor system used.

4.2 EXPERIMENTAL

4.2.1 Reactor

The reactor used was a high pressure stirred autoclave supplied by M/s. Parr Instrument Company, which is shown in Fig. 2.1. This unit had provision for automatic temperature control and for withdrawing the liquid samples. The reactor had a volume of $3 \times 10^{-4} \text{ m}^3$ and diameter of $6.4 \times 10^{-2} \text{ m}$. The stirrer used was a two bladed turbine impeller with a width of $3.9 \times 10^{-2} \text{ m}$.

4.2.2 Materials

The complex $\text{Pd}(\text{Py})_2\text{Cl}_2$ prepared according to the procedure explained in Chapter-2 was used directly for kinetic experiments. The solvents used were freshly distilled and dried.

4.2.3 Procedure for kinetic experiments

The solution of reactant (nitrobenzene) and catalyst ($\text{Pd}(\text{Py})_2\text{Cl}_2$) was charged into the reactor and the system was flushed with nitrogen. Then the system was flushed with CO at atmospheric pressure. When the desired temperature was attained, the reactor was pressurized by CO to the required level. At this stage the reaction was started by adjusting

the stirrer speed at 1000 rpm. The pressure readings were recorded at regular intervals of time. Most of the runs were continued atleast for a period of 1.5 hours. At the end of each run, the gas sample was analysed for CO and CO₂. Also, the liquid samples withdrawn at zero time and at the end of a run were analyzed for nitrobenzene and phenylisocyanate as explained in Chapter-2. The results on pressure drop vs. time are presented in Appendix-II. From these data, the initial rate of reaction of CO was calculated. Due to the formation of CO₂ as a by-product (2 moles per mole of product), the pressure drop observed would correspond to 1/3 of the actual consumption of CO. The CO₂ solubility under the conditions studied was found to be negligible.

4.3 RESULTS AND DISCUSSION

The reaction between CO and nitrobenzene using a homogeneous Pd(Py)₂Cl₂ complex catalyst gives mainly two products, phenylisocyanate and carbon dioxide. This type of reaction can occur in different regimes depending on the relative rates of mass transfer and chemical reaction under the conditions employed. For the purpose of kinetic analysis it is important to ensure that gas-liquid mass transfer resistance is absent. This requires a knowledge of the gas-liquid mass transfer coefficient ($k_L a$) and solubility. These data were obtained experimentally and the results on solubility data are discussed in Chapter-3, while the results on gas-liquid mass transfer coefficient for the reactor used are discussed below.

4.3.1 Gas-liquid mass transfer

Various correlations for gas-liquid mass transfer coefficient in an agitated reactor have been reported in the literature [1-4]. However, no attempts to measure $k_L a$ in a high pressure stirred reactor have been made so far. Therefore it was considered necessary to measure $k_L a$ in the equipment used in this work. The $k_L a$ measurements were carried out by the dynamic physical absorption method. The system used was CO-chlorobenzene and experiments were conducted at 26°C and 55.42 atm CO. In these measurements pressure drop vs. time data were obtained. From the pressure drop, the amount of CO absorbed over a given time interval (and thus the concentration of CO in the liquid bulk) was calculated. Then the results were plotted as: $\ln \left[1 - \frac{(A_1)}{(A)} \right]$ vs. t. From the slope of this plot (equal to $-k_L a$), $k_L a$ values were calculated. The final results are presented in Fig. 4.1, which is a plot of $k_L a$ vs. agitation speed. These results indicate that $k_L a$ is proportional to $N^{2.44}$ which is in agreement with the results of Yagi and Yoshida [4], who reported the exponent of N as 2.2.

As $k_L a$ measurements could not be carried out in the range of temperature (170-230°C) used in this work due to experimental difficulties, corrections were made to the values obtained at 26°C by using the relationship,

$$(k_L a)_T = (k_L a)_{26^\circ\text{C}} \frac{D_T}{D_{26^\circ\text{C}}} \quad [4.2]$$

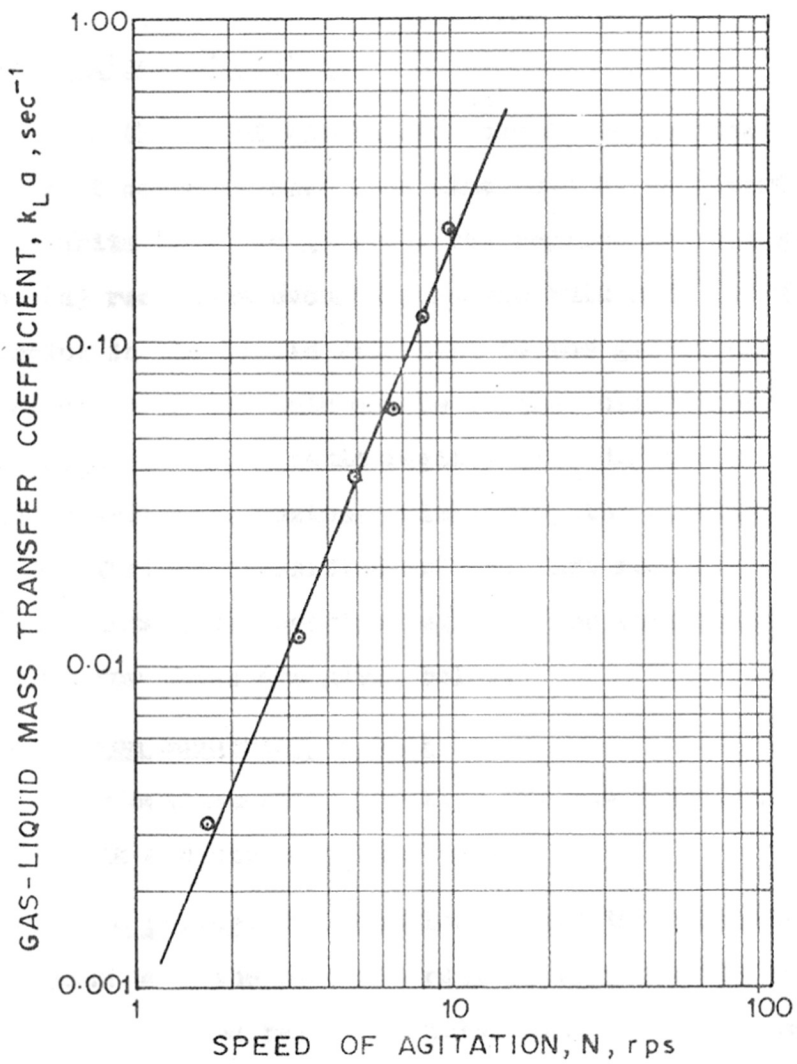


FIG. 4.1. EFFECT OF AGITATION SPEED ON $k_L a$ VALUE

4.3.2 Regimes of control

The theory of gas-liquid reactions, and the various regimes of control, have been discussed by Danckwerts [6] and Astarita [7]. In general, the regimes are classified into: (a) reactions occurring in the bulk and (b) reactions occurring in the liquid film next to the gas-liquid interface. The reaction in the bulk can be further classified into three regimes: (i) kinetic regime, (ii) diffusion regime, and (iii) intermediate regime. Similarly, the reactions in the film are further classified as: (i) fast reaction regime, and (ii) instantaneous reaction regime. The rate equations and criteria for these are given below.

(a) Reaction occurring in bulk

The concentration profiles for the reactions occurring in the bulk are shown in Fig. 4.2.

(i) Kinetic regime: The reaction is said to be kinetically controlled when the reaction rate is very slow in comparison with the diffusion rate. In this situation, the specific rate of absorption of the gas is the same as the reaction rate and the liquid phase is essentially saturated with the absorbing gas. In this regime, the concentration of the gaseous species in the liquid phase is given by its solubility (which is the same as the interfacial concentration). The specific rate of absorption is given by

$$R_A = k A^{m} B_{\circ}^n C_{\circ}^p \quad [4.3]$$

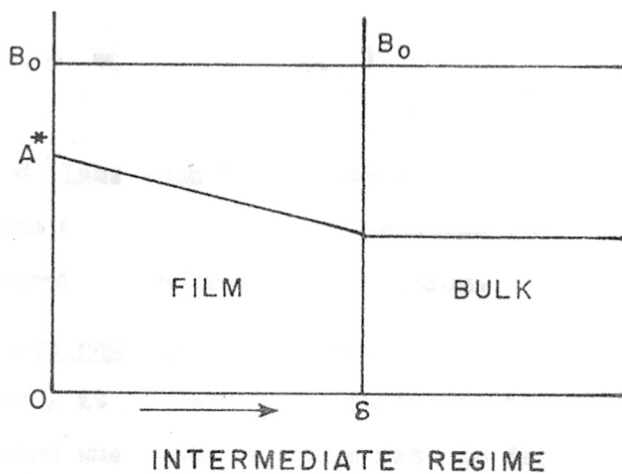
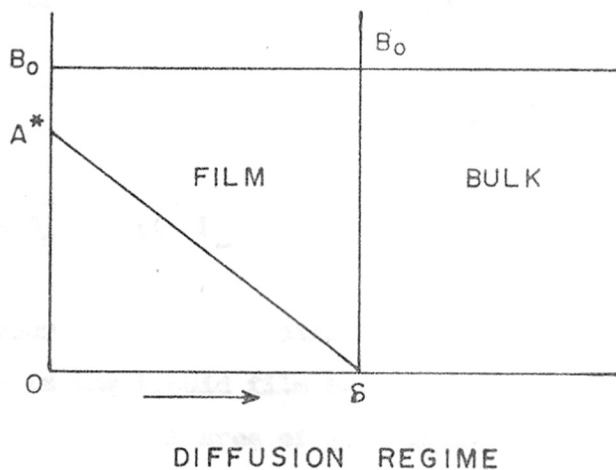
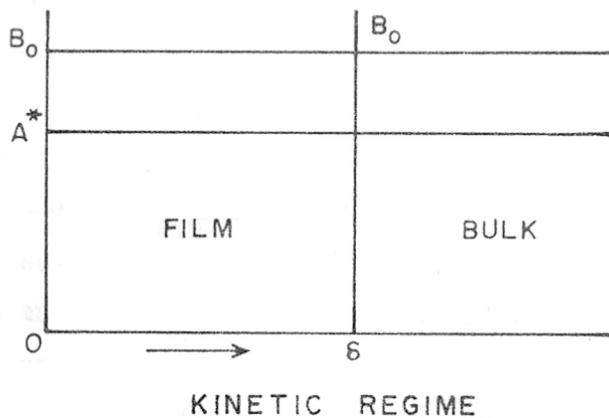


FIG. 4.2. CONCENTRATION PROFILES OF THE REACTING SPECIES FOR VARIOUS REGIMES

where k is the rate constant $[(\text{cm}^3/\text{mol})^{m+n+p-1} \text{sec}^{-1}]$; A^* is the concentration of CO at the gas-liquid interface; B_o , C_o are the bulk concentrations of nitrobenzene and $\text{Pd(Py)}_2\text{Cl}_2$ catalyst respectively (mol/cm^3); and m , n , p are the reaction orders with respect to A^* , B_o and C_o respectively.

The criteria for kinetic control can be given as:

$$\frac{1}{k} A^{*m-1} B_o^n C_o^p \ll k_L a, \quad m \neq 1 \quad [4.4]$$

and

$$\frac{1}{k} B_o^n C_o^p \ll k_L a, \quad m = 1 \quad [4.5]$$

where $\frac{1}{k}$ represents the fractional hold-up of the liquid phase; k_L is the liquid film mass transfer coefficient; and a is the interfacial area of gas-liquid contact.

A parameter α is defined as

$$\alpha = \frac{R_A}{k_L a A^*} \ll 1 \quad [4.6]$$

Value of α less than 0.1 is not adequate for the kinetic regime. The criterion given in equation (4.6) does not require a prior knowledge of reaction kinetics.

(b) Diffusion regime: If the reaction is very fast compared to diffusion, it is said to be diffusion controlled. This is the situation where the reaction rate is fast enough to maintain the bulk concentration of the diffusing gas almost at zero and slow enough to occur in the film, and thus the

concentration of the gaseous species is not the same as that at the interface. In this regime, the rate of absorption of A is governed by its transport and is represented as

$$R'_A = k_L a A^* \quad [4.7]$$

The criteria for diffusion control can be given as

$$R'_A \ll R_A \quad [4.8]$$

or

$$k_L a \ll \frac{1}{\tau} k A^{*m-1} B_0^n C_0^p, \quad m \neq 1 \quad [4.9]$$

and

$$k_L a \ll \frac{1}{\tau} k B_0^n C_0^p, \quad m = 1 \quad [4.10]$$

It is also necessary to ensure that there is no reaction occurring in the film and as such the following condition has to be satisfied:

$$\frac{D_A k B_0^n C_0^p}{k_L^2} \ll 1 \quad [4.11]$$

where D_A is the diffusion coefficient of CO in the reacting solution.

When the absorption is entirely diffusion controlled, the mass transfer coefficients with and without chemical reaction are the same indicating that there is no enhancement in the absorption due to reaction. On this basis, the following condition can also be postulated for the diffusion regime:

$$\alpha = 1 \quad [4.12]$$

(iii) Intermediate regime : When the concentration of the gaseous species in the bulk is not the same as the interfacial concentrations but also not zero, a situation exists when the reaction and the diffusion rates are comparable and both are important. The specific rate of A is given as

$$R_A = k_L a (A^* - A_0) \quad [4.13]$$

and

$$R_A = \frac{1}{2} k A_0^m B_0^n C_0^p \quad [4.14]$$

where A_0 is the concentration of CO in the liquid bulk.

Eliminating the unknown A_0 from equations (4.13) and (4.14) we get the following relationship for the specific rate of absorption of A :

$$R_A = \frac{\frac{1}{2} k A^* B_0^n C_0^p}{1 + \frac{\frac{1}{2} k B_0^n C_0^p}{k_L a}} \quad [4.15]$$

Equations (4.3) and (4.7) are the two asymptotes of equation (4.15) and the condition to be satisfied for the intermediate regime is

$$1 + k_B C_O \approx k_L a, \quad m \neq 1 \quad [4.16]$$

When the values of α are in the range 0.2-0.9, it is quite likely that the absorption would be in the intermediate regime. A digrammatic presentation of all the three regimes is shown in Fig. 4.3, which is a long-log plot of α vs. $\frac{k_L a}{1 + k_B^n C_O^p}$. The transition from the kinetic to the diffusion regime can be clearly seen in the figure.

(b) Reaction occurring in the film

(i) Fast reaction regime: In this situation, the reaction of the dissolved gas is completed entirely in the liquid film. Here, a simultaneous diffusion and reaction of the gaseous reactant occurs, while the concentration of the liquid reactant is not depleted in the film. This situation is also referred as pseudo-fast reaction regime. The rate equations and criteria for identification of this regime are given by Danckwerts [6]. In this situation there is an enhancement in the rate of gas absorption due to chemical reaction, and the factor α is greater than unity.

(ii) Instantaneous reaction regime : In this case, the reaction between the gases and the liquid reactant occurs

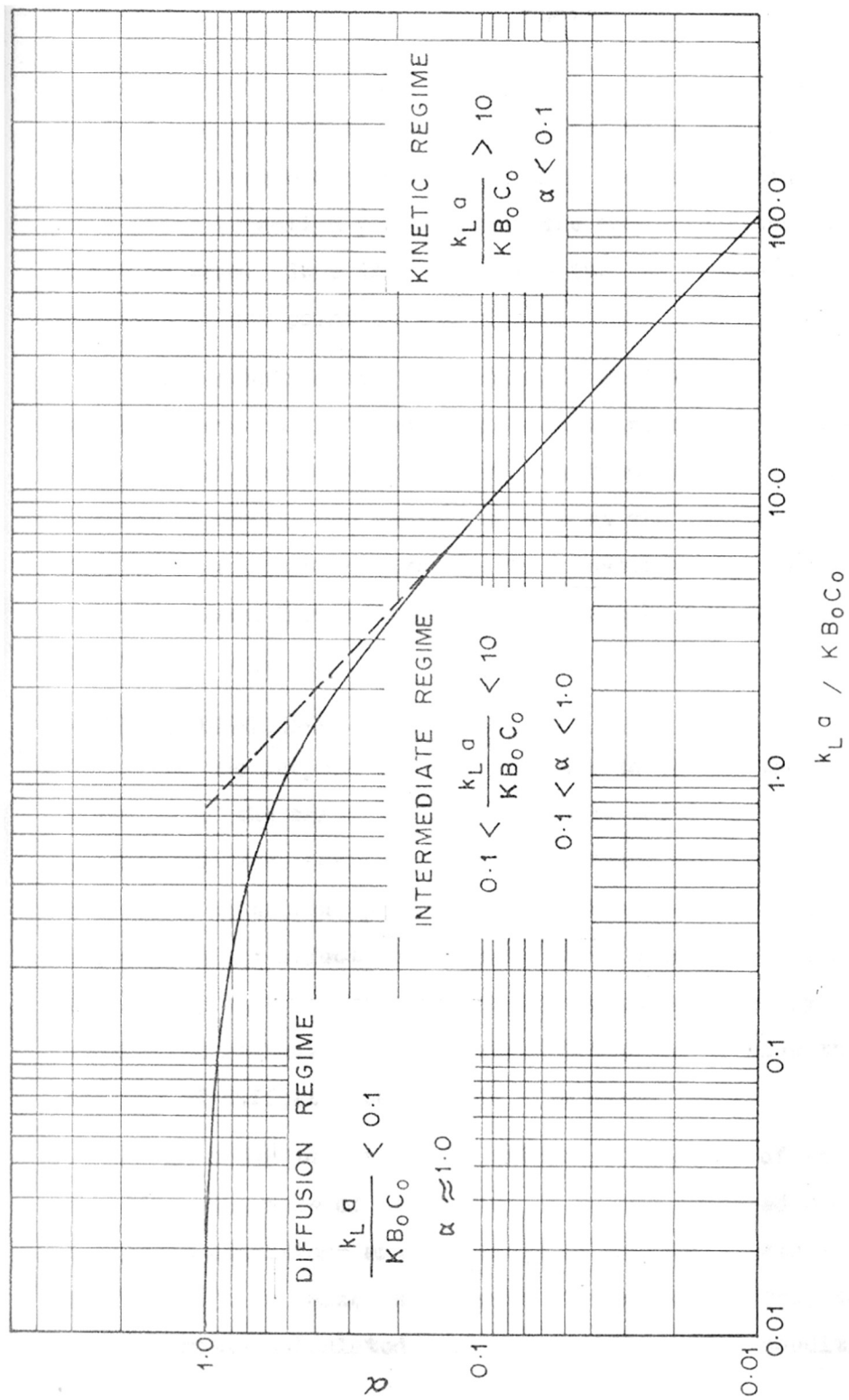


FIG. 4-3. TRANSITION FROM KINETIC TO THE DIFFUSIONAL REGIME 79

instantaneously within the film. Here, both species A and B diffuse to each other within the film and the reaction occurs at a point (reaction plane) where the concentrations of A and B drops to zero. Thus in this regime the two reactants do not co-exist at any point in the liquid.

The reaction can also occur in an intermediate regime which is between fast and instantaneous reaction regimes. Here, simultaneous diffusion and reaction of both A and B becomes important and depletion of B at the gas-liquid interface is significant unlike the fast reaction regime. The rate equations for these have been given by Astarita [7] and Danckwerts [6].

4.3.3 Kinetic study

As the purpose of this work was to obtain the intrinsic kinetics of the carbonylation reaction, initially a few experiments were carried out under extreme conditions at different agitation speeds. It was observed that agitation has negligible effect on the rate of CO absorption, thus suggesting that the reaction occurs in the chemically controlled regime. A quantitative criterion to show the absence of diffusion control is also given later.

In order to obtain the intrinsic kinetics of the reaction, the rate of absorption of CO was observed under different conditions and the range of variables used is given in Table 4.1. In these experiments it was ensured that the initial rates calculated were under differential conditions,

TABLE: 4.1VARIABLES AND THEIR RANGES

Agitation speed	100-1000, rev/min
CO pressure, P_{CO}	23-94, atm
$Pd(Py)_2Cl_2$ concentration	$1-8 \times 10^{-5}$, mol/cm ³
Nitrobenzene concentration	$4.89-48.9 \times 10^{-4}$, mol/cm ³
Temperature	170-230°C

since the kinetic analysis was based on initial rates. The reproducibility of the rate data was found to be within 5% as confirmed by carrying out some runs in triplicate. To ensure that the reaction is kinetically controlled, conditions (4.4) - (4.6) were verified for each run by ensuring that the second order rate constant is much lower than $k_L a$ and the enhancement factor is much less than unity. This can be clearly seen from Table 4.2.

The effect of various parameters on the rate of absorption of CO is discussed below.

Effect of catalyst concentration: The effect of $\text{Pd}(\text{Py})_2\text{Cl}_2$ concentration on the rate of absorption was studied at 190°C , $19.5 \times 10^{-4} \text{ mol/cm}^3$ nitrobenzene concentration and 76.08 atm CO. The results are presented in Fig. 4.4. It can be seen that the rate of CO absorption is directly proportional to the catalyst concentration up to a concentration of $5 \times 10^{-5} \text{ mol/cm}^3$. Then, up to a concentration of $7 \times 10^{-5} \text{ mol/cm}^3$, the dependence of the rate of absorption is not linear, and beyond this value the rate becomes almost independent of catalyst concentration. Such behaviour is possible under the following situations: (a) when the transport of the gaseous reactant (CO) to the liquid phase is rate controlling, or (b) when all the catalyst is not available in the reaction medium (due to solubility limitations, for example). Under the conditions used in this work the mass transfer resistances were found to be absent as mentioned earlier. However, to

TABLE:4.2

EXPERIMENTAL CONDITIONS AND KINETIC CONSTANTS
 FOR THE CARBOXYLATION OF NITROBENZENE TO PHENYLISOCYANATE
 CATALYSED BY BIS-PYRIDINE PALLADIUM(II) CHLORIDE CATALYST

Run No.	Temp., K	Reactant concentration, mol/cm ³		Rate of CO absorption, RA x 10 ⁷ mol/cm ³ /sec		Reaction rate constant, k sec ⁻¹	Physical rate of absorption, RA x 10 ⁵ mol/cm ³ /sec	Enhancement factor, E = $\frac{RA}{RA_0}$
		Nitrobenzene, A x 10 ⁴	CO, B x 10 ²	Pd(Py) ₂ Cl ₂ , C x 10 ⁵	RA x 10 ⁷			
		3	4	5	6	7	8	9
101	463	19.56	5.054	1	0.93	9 x 10 ⁻³	4.118	0.226
102	"	"	"	2	1.80	"	"	0.437
103	"	"	"	3	2.72	"	"	0.660
104	"	"	"	4	3.58	"	"	0.870
105	"	"	"	6	4.43	"	"	1.076
106	"	"	"	8	5.10	"	"	1.238
107	463	19.56	9.320	3	3.64	5.36x10 ⁻⁶	4.118	0.884
108	"	"	8.304	"	3.62	"	"	0.879
109	"	"	7.404	"	3.50	"	"	0.850
110	"	"	6.229	"	3.20	"	"	0.777

.....

Table A-2 contd.

1	2	3	4	5	6	7	8	9
111	463	19.56	5.054	3	2.72	5.36×10^{-6}	4.118	0.661
112	"	"	4.286	"	2.26	"	"	0.549
113	"	"	3.337	"	1.76	"	"	0.427
114	"	"	1.484	"	0.82	"	"	0.199
115	463	4.89	5.054	3	2.68	2.72×10^{-7}	4.118	0.651
116	"	9.78	"	"	2.70	"	"	0.655
117	"	14.67	"	"	2.76	"	"	0.670
118	"	19.56	"	"	2.72	"	"	0.660
119	"	29.34	"	"	2.70	"	"	0.655
120	"	48.90	"	"	2.72	"	"	0.660
121	443	19.56	"	"	1.40	"	"	0.340
122	463	"	"	"	2.72	"	"	0.660
123	483	"	"	"	4.82	"	"	1.170
124	503	"	"	"	8.45	"	"	2.052

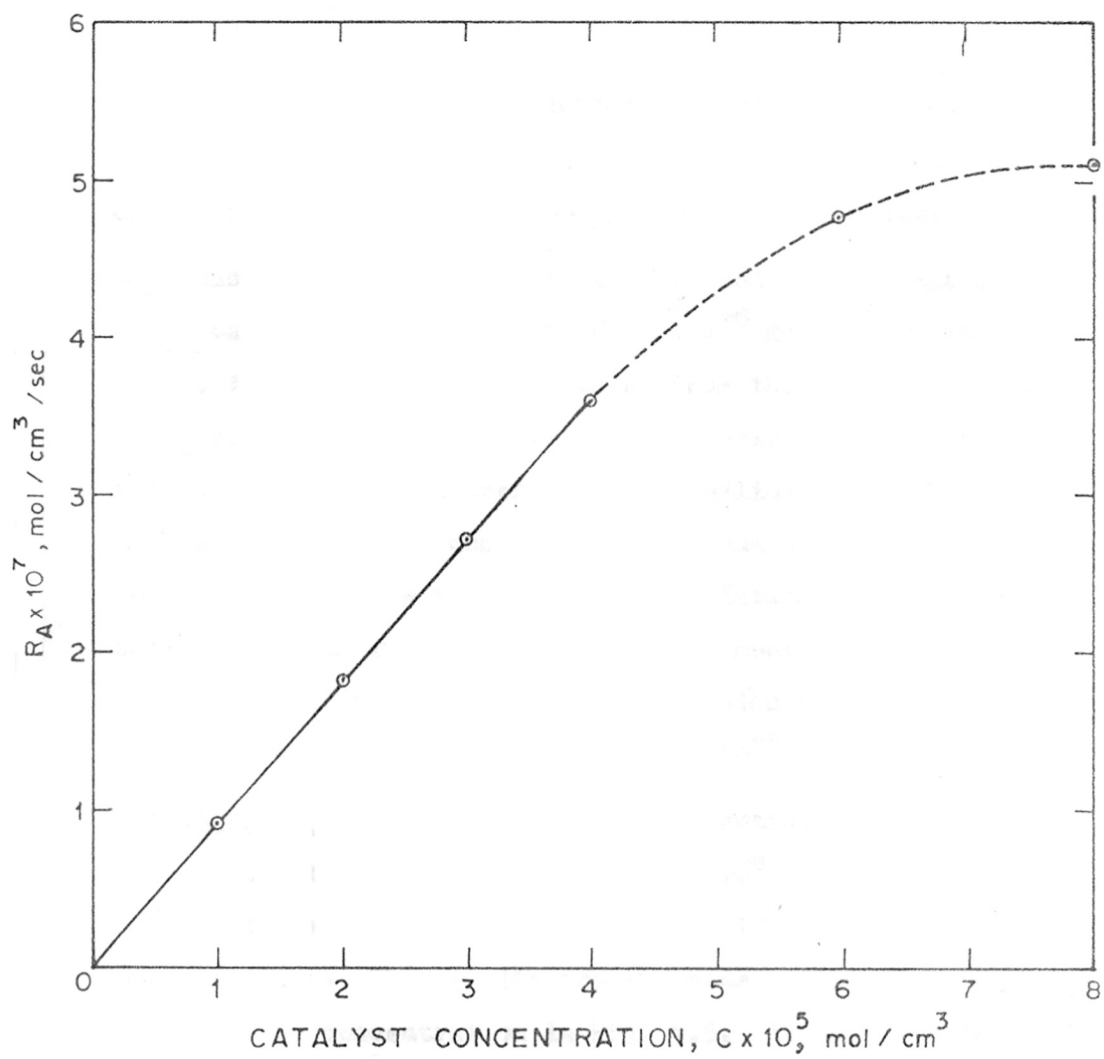


FIG. 4.4. EFFECT OF CATALYST CONCENTRATION ON THE RATE OF REACTION

ensure this a quantitative criterion reported by Chaudhari and Doraiswamy [5] was also used. According to this criterion a factor $\alpha = \frac{R_A}{k_L a(A^*)}$ should be less than 0.1 for the reaction to be in the kinetically controlled regime. For a catalyst concentration of $8 \times 10^{-5} \text{ mol/cm}^3$ (highest used), the value of α calculated from the observed value of R_A was 0.0025, which suggests that mass transfer effects are not important. Therefore, the non-linear dependence of the rate on catalyst concentration beyond $5 \times 10^{-5} \text{ mol/cm}^3$ would be mainly due to solubility limitations. This was also confirmed by an independent solubility measurement of $\text{Pd(Py)}_2\text{Cl}_2$ in chlorobenzene at 190°C which indicated that the solubility of the complex was $5.562 \times 10^{-5} \text{ mol/cm}^3$.

Effect of CO pressure : Effect of CO partial pressure on the rate of CO absorption was studied at 190°C , $19.4 \times 10^{-4} \text{ mol/cm}^3$ nitrobenzene concentration and $3 \times 10^{-5} \text{ mol/cm}^3$ catalyst concentration. The results are shown as a plot of R_A vs. dissolved CO concentration in Fig. 4.5. It may be noted that the rate of CO absorption is directly proportional to CO concentration, thus suggesting that the reaction is first order with respect to CO concentration.

Effect of nitrobenzene concentration: The effect of nitrobenzene concentration on the rate of CO absorption was studied at 190°C , 76.08 atm CO and $3 \times 10^{-5} \text{ mol/cm}^3$ catalyst concentration. The results are shown in Fig. 4.6 which is a plot of R_A vs. nitrobenzene concentration. The rate is clearly independent of nitrobenzene concentration.

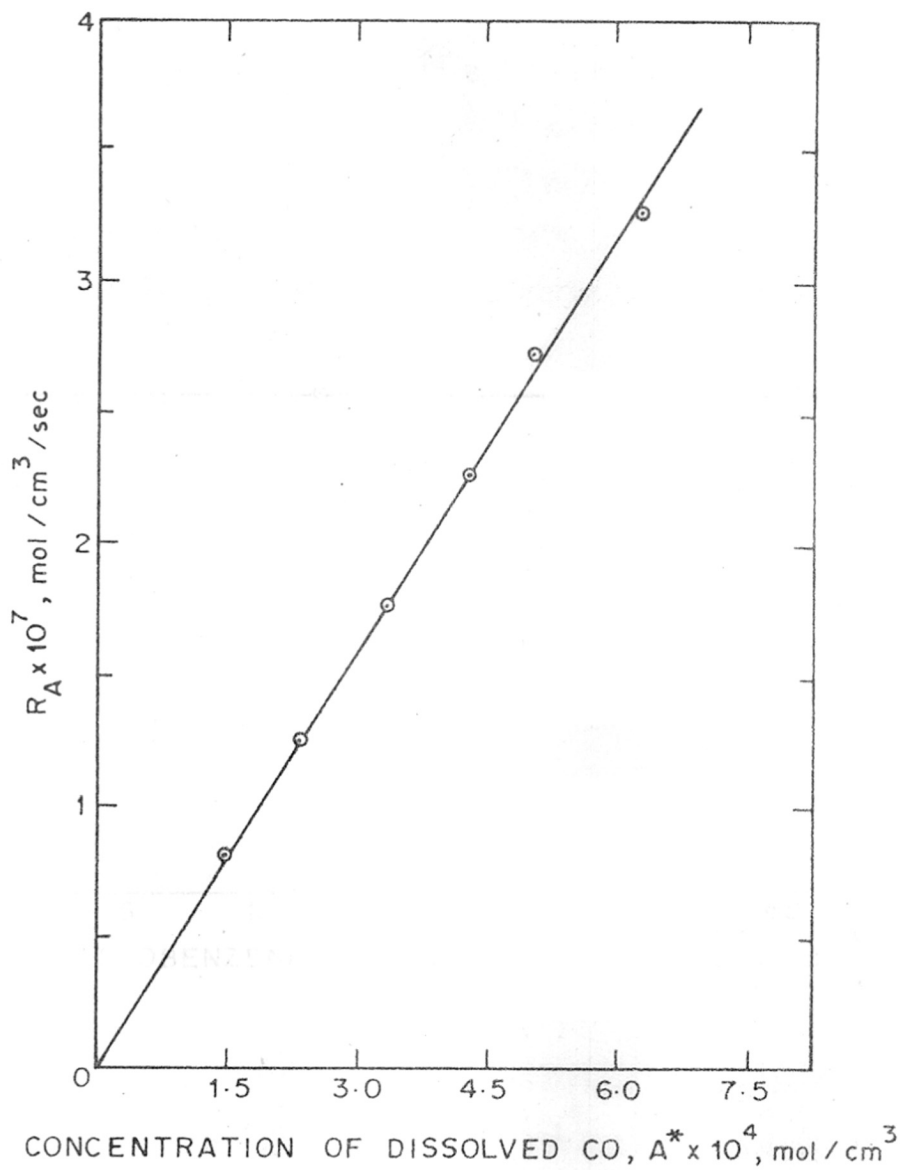


FIG. 4.5. EFFECT OF DISSOLVED CO CONCENTRATION ON THE RATE OF REACTION

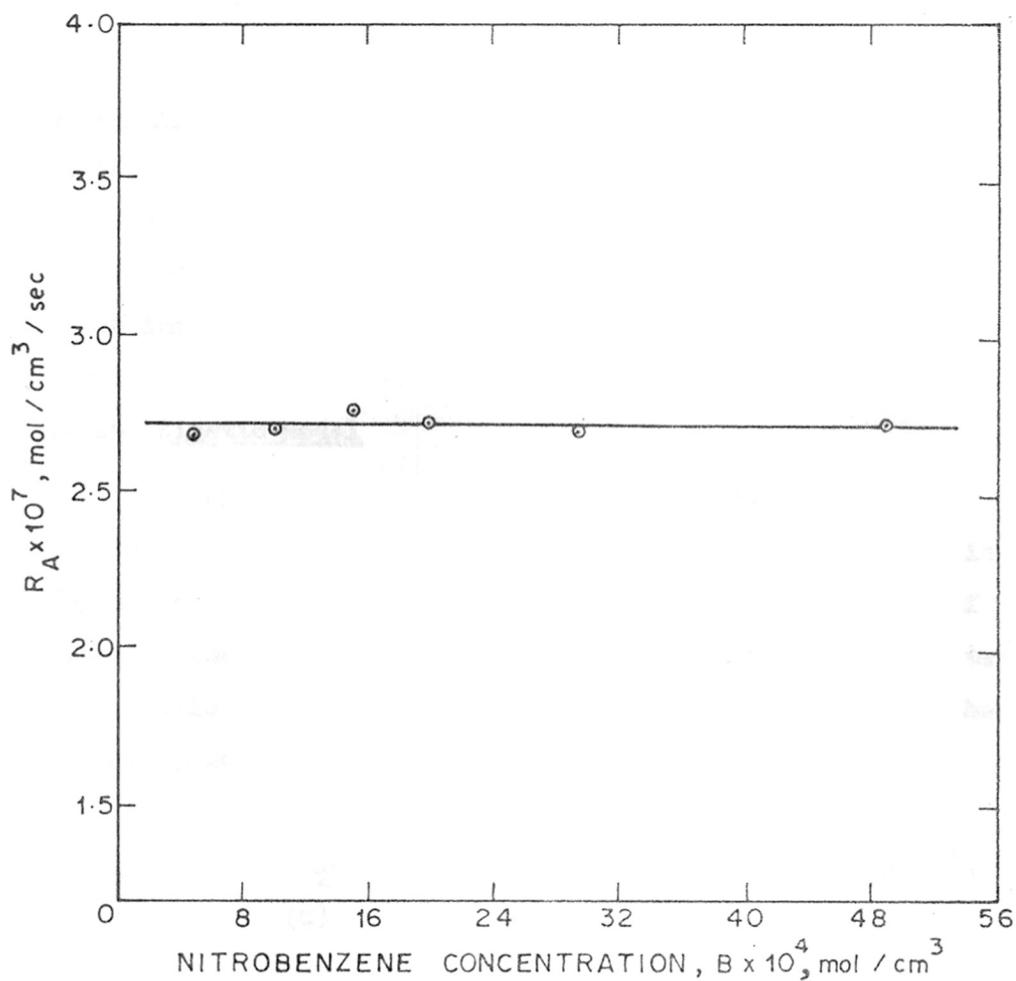
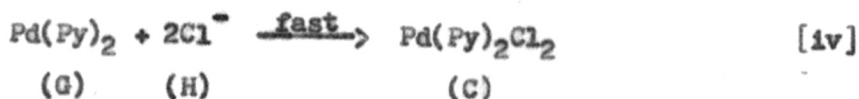
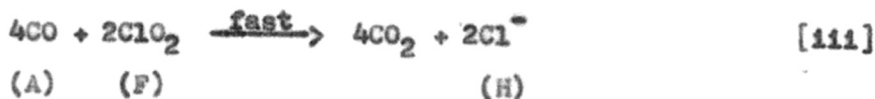
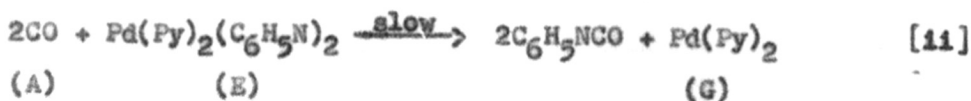
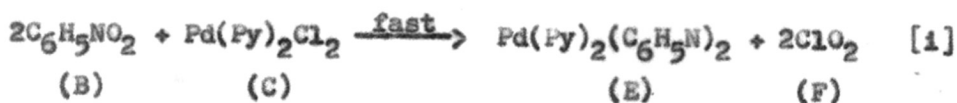


FIG. 4.6. EFFECT OF NITROBENZENE CONCENTRATION ON THE RATE OF REACTION

Effect of temperature: The rate of CO absorption was observed at different temperatures at 3×10^{-5} mol/cm³ catalyst concentration, 76.08 atm CO and 19.4×10^{-4} mol/cm³ nitrobenzene concentration. A plot of $\ln R_A$ vs $1/T$ is shown in Fig. 4.7 which indicates that the rate is strongly dependent on temperature.

4.3.4 Kinetic model

In order to obtain a rate equation representing the intrinsic kinetics, a knowledge of the reaction mechanism is necessary. A speculative mechanism on the carbonylation of nitrobenzene to phenylisocyanate has been proposed in Chapter-2. The reaction of CO with nitrobenzene can be described by the following scheme:



Based on the investigations presented in Chapter-2 on the

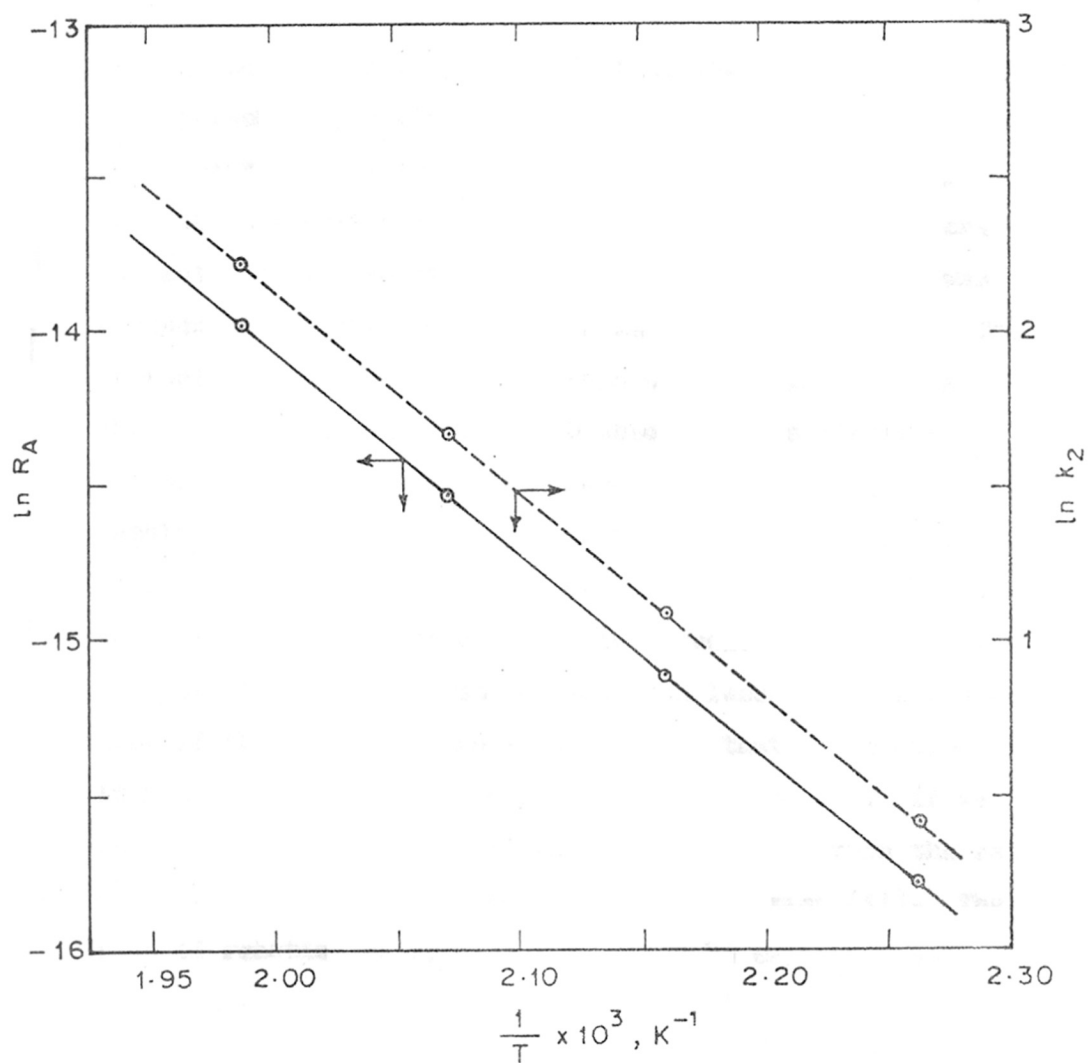


FIG. 4.7. EFFECT OF TEMPERATURE ON THE RATE OF REACTION

intermediate species, it appears that the catalyst precursor C is present as species E $[\text{Pd}(\text{Py})_2(\text{C}_6\text{H}_5\text{N})_2]$, thus suggesting that reaction (ii) is perhaps the rate controlling step. From the observations on the effect of various parameters on the rate of CO absorption, it was found that the rate was independent of nitrobenzene (species B) concentration. This indicates that step (i) is perhaps not rate controlling. The observation that the rate of CO absorption is directly proportional to [A] (partial pressure of CO) and [C] ($\text{Pd}(\text{Py})_2\text{Cl}_2$ catalyst concentration) suggests that reaction (ii) is likely to be the rate controlling step. Here, it is important to note that in the range of variables studied in this work, the concentration of catalyst [C] was much less than the concentration of [B] (nitrobenzene). This means that if reaction (i) is fast, [E] will be directly proportional to [C]. If we assume that reactions (iii) and (iv) are fast, then the rate of carbonylation will be controlled by reaction (ii). The rate of reaction of species E can then be expressed as:

$$R_A = k_2 [A] [E] \quad [4.17]$$

Considering the fact that for every mole of E reacting 6 moles of CO are consumed, the rate of CO absorption will be given by:

$$R_A = 6 k_2 [A] [E] \quad [4.18]$$

As reaction (iii) is assumed to be fast, the species F (ClO_2 concentration) generated in reaction (i) will be consumed and hence the concentration of species E will be the same as catalyst concentration C. Hence R_A can be expressed as:

$$R_A = 6 k_2 [A] [C] \quad [4.19]$$

This rate model is also consistent with the observed data. For this purpose, the rate data up to a catalyst concentration of $5.5 \times 10^{-5} \text{ mol/cm}^3$ was used, as beyond this the catalyst was not completely soluble. First order dependence on CO and catalyst concentrations and zero order dependence on nitrobenzene concentration can also be seen from Figs. 4.4, 4.5 and 4.6.

Using equation (4.19) and the experimental data, values of the second order reaction rate constant k_2 were calculated for different temperatures. The values at 190°C obtained for a number of measurements were within 5-10% of one another, thus indicating that the data are well represented by equation (4.19). The temperature dependence of the reaction rate constant is shown in Fig. 4.7 as a plot of $\ln k_2$ vs $1/T$. From the slope of this plot, an activation energy of 29.87 kcal/mol was obtained. The magnitude of activation energy also indicates that the carbonylation of nitrobenzene to phenylisocyanate occurs in the kinetic regime.

4.4 CONCLUSIONS

Carbonylation of nitrobenzene to phenylisocyanate was studied in a high pressure stirred reactor using $\text{Pd(Py)}_2\text{Cl}_2$ complex catalyst. It was found that the absorption of CO was kinetically controlled in the range of conditions studied. A rate equation has been proposed and an activation energy of 29.87 kcal/mol obtained from the temperature dependence of the reaction rate constant. An interesting observation was that beyond a catalyst concentration of 5.5×10^{-5} mol/cm³, the dependence of the rate was non-linear; this was found to be due to the limiting solubility of the catalytic complex. Based on these observations, and a probable mechanism presented in Chapter-2, it has been proposed that the reaction of CO with the intermediate complex $[\text{Pd(Py)}_2(\text{C}_6\text{H}_5\text{N})_2]$ is the rate controlling step.

NOTATION

a	effective interfacial area, cm^{-1}
A^*	concentration of CO in the gas-liquid interface, mol/cm^3
A_0	concentration of CO in the liquid bulk, mol/cm^3
A_1	concentration of dissolved CO in bulk liquid phase mol/cm^3
B_0	concentration of nitrobenzene in the liquid bulk, mol/cm^3
C_0	concentration of $\text{Pd}(\text{Py})_2\text{Cl}_2$ catalyst in the liquid bulk, mol/cm^3
D_A	diffusion coefficient, cm^2/sec
E	active species in the kinetic scheme
k	rate constant
k_2	second order rate constant, $\text{cm}^3/\text{mol}/\text{sec}$
k_L	liquid film mass transfer coefficient, cm/sec
$k_{L,a}$	gas-liquid mass transfer coefficient, sec^{-1}
m	order of a reaction with respect to CO
N	agitation, rps
n	order of a reaction with respect to nitrobenzene
p	order of a reaction with respect to $\text{Pd}(\text{Py})_2\text{Cl}_2$ catalyst
R_A	rate of absorption of CO, $\text{mol}/\text{cm}^3/\text{sec}$
R_A'	rate of physical absorption, $\text{mol}/\text{cm}^3/\text{sec}$
t	time, sec

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- $\bar{1}$ fractional holdup of the liquid phase
- T temperature, K
- α parameter defined by equation (4.6)

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CHAPTER - 5

THEORETICAL ANALYSIS OF MULTIPLICITY AND STABILITY IN CSTR SYSTEMS FOR HOMOGENEOUSLY CATALYSED REACTIONS

CHAPTER-5

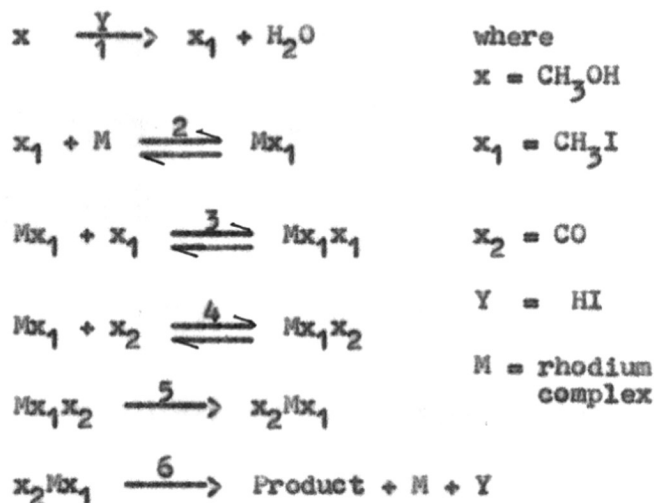
THEORETICAL ANALYSIS OF MULTIPLICITY AND STABILITY IN CSTR SYSTEMS FOR HOMOGENEOUSLY CATALYSED REACTIONS

5.1 INTRODUCTION

In recent years, organometallic complexes of transition metals have been found to be excellent homogeneous catalysts for a number of chemical reactions. Typical examples include rhodium complex catalysed carbonylation of methanol to acetic acid, cobalt complex catalysed oxo-synthesis (olefins to aldehydes) and palladium chloride catalysed oxidation of ethylene to acetaldehyde. These metal complexes are finding extensive applications because of their remarkable activity and specificity in converting the reactant to the desired product. Many homogeneously catalysed reactions follow a complex kinetic scheme and do not obey simple power law type rate models. The formulation of the rate model taking into account the complete reaction scheme frequently results in complex non-linear rate form which attains a maximum at some intermediate finite value of the reactant concentration. Multiplicity of states is therefore possible and the present work analyses a typical rate form in a CSTR to establish the condition for their occurrence and the stability of the resulting states.

5.2 KINETIC SCHEME

A typical kinetic scheme for the carbonylation of methanol suggested by Roth et.al. [5] is represented as:



The mass balance equations for the above kinetic scheme can be written as:

$$V \frac{dx}{dt} = F(x_0 - x) - V k_1 x \quad [5.1]$$

$$\begin{aligned}
 V \frac{dx_1}{dt} = F(0 - x_1) - V & \left[k_2(x_1)(M) - k_{-2}(Mx_1) \right] \\
 - V & \left[k_3(Mx_1)(x_1) - V k_{-3}(Mx_2) \right] - k_1 x
 \end{aligned} \quad [5.2]$$

$$V \frac{dx_2}{dt} = F(x_{2,0} - x_2) - V k_4 (Mx_1) (x_2) \quad [5.3]$$

$$\begin{aligned}
 V \frac{dM}{dt} = -V & \left[k_2(x_1)(M) - k_{-2}(Mx_1) \right] \\
 + V k_6 & (x_2Mx_1)
 \end{aligned} \quad [5.4]$$

$$\begin{aligned}
 V \frac{d(Mx_1)}{dt} &= V \left[k_2 (x_1)(M) - k_{-2} (Mx_1) \right] \\
 &- V \left[k_3 (x_1) + k_4 x_2 (Mx_1) \right] \\
 &+ V k_{-3} (Mx_2)
 \end{aligned}
 \tag{5.5}$$

$$V \frac{d(Mx_2)}{dt} = V k_3 (Mx_1)(x_1) - V k_{-3} (Mx_2)
 \tag{5.6}$$

$$V \frac{d(Mx_1 x_2)}{dt} = V \left[k_4 (Mx_1)(x_2) - k_5 (Mx_1 x_2) \right]
 \tag{5.7}$$

$$V \frac{d(x_2 Mx_1)}{dt} = V \left[k_5 (Mx_1 x_2) - k_6 (x_2 Mx_1) \right]
 \tag{5.8}$$

Assuming pseudo steady state for equations (5.4)-(5.8), we obtain

$$(x_2 Mx_1) = \frac{k_5}{k_6} (Mx_1 x_2)
 \tag{5.9}$$

$$(Mx_1 x_2) = \frac{k_4}{k_5} (Mx_1)(x_2)
 \tag{5.10}$$

$$(Mx_2) = \frac{k_3}{k_{-3}} (Mx_1)(x_1)
 \tag{5.11}$$

$$(Mx_1) = \frac{k_2(M)(x_1)}{k_{-2} + k_4 x_2}
 \tag{5.12}$$

Substituting the value of (Mx_1x_2) from equation (5.10) in equation (5.9) we have:

$$(x_2Mx_1) = \frac{k_4}{k_6} (Mx_1)(x_2) \quad [5.13]$$

The value of M (rhodium complex concentration) can be obtained as:

$$M = M_0 - (x_2Mx_1) - (Mx_1x_2) - (Mx_2) - (Mx_1) \quad [5.14]$$

where M_0 = initial concentration of rhodium complex.

Substituting the values of (x_2Mx_1) , (Mx_1x_2) , (Mx_2) and (Mx_1) in equation (5.14), the value of M will be

$$M = M_0 - \left[\left(\frac{k_4}{k_6} + \frac{k_4}{k_5} \right) x_2 + \frac{k_3}{k_{-3}} x_1 + 1 \right] \frac{k_2 x_1}{k_{-2} + k_4 x_2} \quad [5.15]$$

or

$$M = \frac{M_0}{1 + \frac{k_2 x_1}{k_{-2} + k_4 x_2} \left[\left(\frac{k_4}{k_6} + \frac{k_4}{k_5} \right) x_2 + \frac{k_3}{k_{-3}} x_1 + 1 \right]} \quad [5.16]$$

Substituting this value of M in equations (5.2) and (5.3) we obtain

$$V \frac{dx_1}{dt} = -F x_1 + V k_1 x - V \left[\frac{k_2 k_4 x_1 x_2}{k_{-2} + k_4 x_2} \right] \frac{M_0}{1 + \frac{k_2 x_1}{k_{-2} + k_4 x_2} \left[\left(\frac{k_4}{k_6} + \frac{k_4}{k_5} \right) x_2 + \frac{k_3}{k_{-3}} x_1 + 1 \right]}$$

and

[5.17]

$$V \frac{dx_2}{dt} = F (x_2, 0 - x_2) - \frac{V k_2 k_4 x_1 x_2}{k_{-2} + k_4 x_2} \left[\frac{M_0}{1 + \frac{k_2 x_1}{k_{-2} + k_4 x_2} \left[\left(\frac{k_4}{k_6} + \frac{k_4}{k_5} \right) x_2 + \frac{k_3}{k_{-3}} x_1 + 1 \right]} \right]$$

[5.18]

On the assumption that the rate of change of intermediate species involving the metal complex is zero, the overall rate with respect to the species x_1 and x_2 can be written from the carbonylation scheme as:

$$r(x_1, x_2) = k_4 (Mx_1) (x_2) (M) (x_1) \quad [5.19]$$

Substituting the values of (Mx_1) and (M) from equations (5.12) and (5.16) in equation (5.19), the resulting rate equation is

$$r(x_1, x_2) = \frac{k_2 k_4 M_0}{k_{-2} + k_4 x_2} \left[\frac{x_1 x_2}{1 + \frac{k_2 x_1}{k_{-2} + k_4 x_2} \left[1 + x_2 \left(\frac{k_4}{k_5} + \frac{k_4}{k_6} \right) + \frac{k_3}{k_{-3}} x_1 \right]} \right] \quad [5.20]$$

At steady state we therefore can write

$$-F x_1 + V k_1 x = F (x_{2,0} - x_2) \quad [5.21]$$

or

$$x_2 = \frac{F (x_{2,0} + x_1) - V k_1 x}{F} \quad [5.22]$$

and

$$x = \frac{F x_0}{F + V k_1} \quad [5.23]$$

Substituting the value of x from equation (5.23) in equation (5.22), the value of x_2 can be written as

$$x_2 = \frac{1}{F} \left(F x_{2,0} - \frac{F V k_1}{F + V k_1} x_0 + F x_1 \right) \quad [5.24]$$

or

$$x_2 = a + x_1 \quad [5.25]$$

where

$$a = x_{2,0} - C_1 \quad [5.26]$$

$$C_1 = \frac{V k_1 x_0}{F + V k_1} \quad [5.27]$$

Substituting the value of x_2 from equation (5.25) in equation (5.20), the rate at steady state can be written as:

$$r_{s.s} = \frac{k_2 k_4 M_0 [x_1 (\alpha + x_1)]}{k_{-2} + k_4 (\alpha + x_1) + k_2 x_1 \left[1 + (\alpha + x_1) \left(\frac{k_4}{k_5} + \frac{k_4}{k_6} \right) + \frac{k_3}{k_{-3}} x_1 \right]}$$

[5.28]

The above equation (5.28) after expansion and rearrangement reduces to the following form:

$$r_{s.s} = \frac{k_2 k_4 M_0 \alpha x_1 + k_2 k_4 M_0 x_1^2}{k_2 \left[\frac{k_4}{k_5} + \frac{k_4}{k_6} + \frac{k_3}{k_{-3}} \right] x_1^2 + \left[k_4 + k_2 \left[1 + \alpha \left(\frac{k_4}{k_5} + \frac{k_4}{k_6} \right) \right] \right] x_1 + [k_{-2} + k_4 \alpha]}$$

[5.29]

The typical rate of the equation (5.29) can be written in the following form:

$$r_A = \frac{a_1 x_1 + a_2 x_1^2}{a_3 x_1^2 + a_4 x_1 + a_5}$$

[5.30]

$$\text{where } a_1 = k_2 k_4 M_0^\alpha \quad [5.31]$$

$$a_2 = k_2 k_4 M_0 \quad [5.32]$$

$$a_3 = k_2 \left[\frac{k_4}{k_5} + \frac{k_4}{k_6} + \frac{k_3}{k_{-3}} \right] \quad [5.33]$$

$$a_4 = k_4 + k_2 \left[1 + \alpha \frac{k_4}{k_5} + \frac{k_4}{k_6} \right] \quad [5.34]$$

$$a_5 = k_{-2} + k_4 \alpha \quad [5.35]$$

A similar kinetic scheme arises in a number of homogeneously catalysed reactions and examples of these are available in the literature [1-4]. Under certain conditions the reaction rate given by equation (5.30) attains a maximum at a certain intermediate value of the concentration of the reacting species and therefore shows the possibility of existence of multiplicity. It is important to identify the values of the kinetic and operating parameters within which the multiplicity of states exists so that a rational analysis of the experimental data is possible. Such information is also useful in the design and operation of CSTR for homogeneously catalysed reactions.

5.3 THEORY

The conservation equation for the promoter x_1 (methyl iodide concentration) in rhodium complex catalysed carbonylation of methanol carried out in CSTR for the kinetics given by equation (5.30) can be written as:

$$-Fx_1 + \frac{Vk_1 Fx_0}{F + Vk_1} = V \frac{a_1 x_1 + a_2 x_1^2}{a_3 x_1^2 + a_4 x_1 + a_5} \quad [5.36]$$

where F is the flow rate, V is the volume of the reactor, x_0 represents the concentration of methanol at the reactor inlet and x_1 refers to concentration of methyl iodide in the reactor.

Equation (5.36) can be written in dimensionless form as:

$$\psi [C_1 - x_1] = \frac{x_1 + \delta x_1^2}{1 + \beta x_1 + \gamma x_1^2} \quad [5.37]$$

where

$$\beta = \frac{a_4}{a_5} \quad [5.38]$$

$$\gamma = \frac{a_3}{a_5} \quad [5.39]$$

$$\delta = \frac{a_2}{a_1} \quad [5.40]$$

$$\psi = \frac{a_5}{a_1} \times \frac{F}{V} \quad [5.41]$$

The conservation equation given by equation (5.36) assumes that there are no external mass transfer limitations.

In order to determine the region of multiplicity consider a graphical solution to equation (5.37). Fig. 5.1

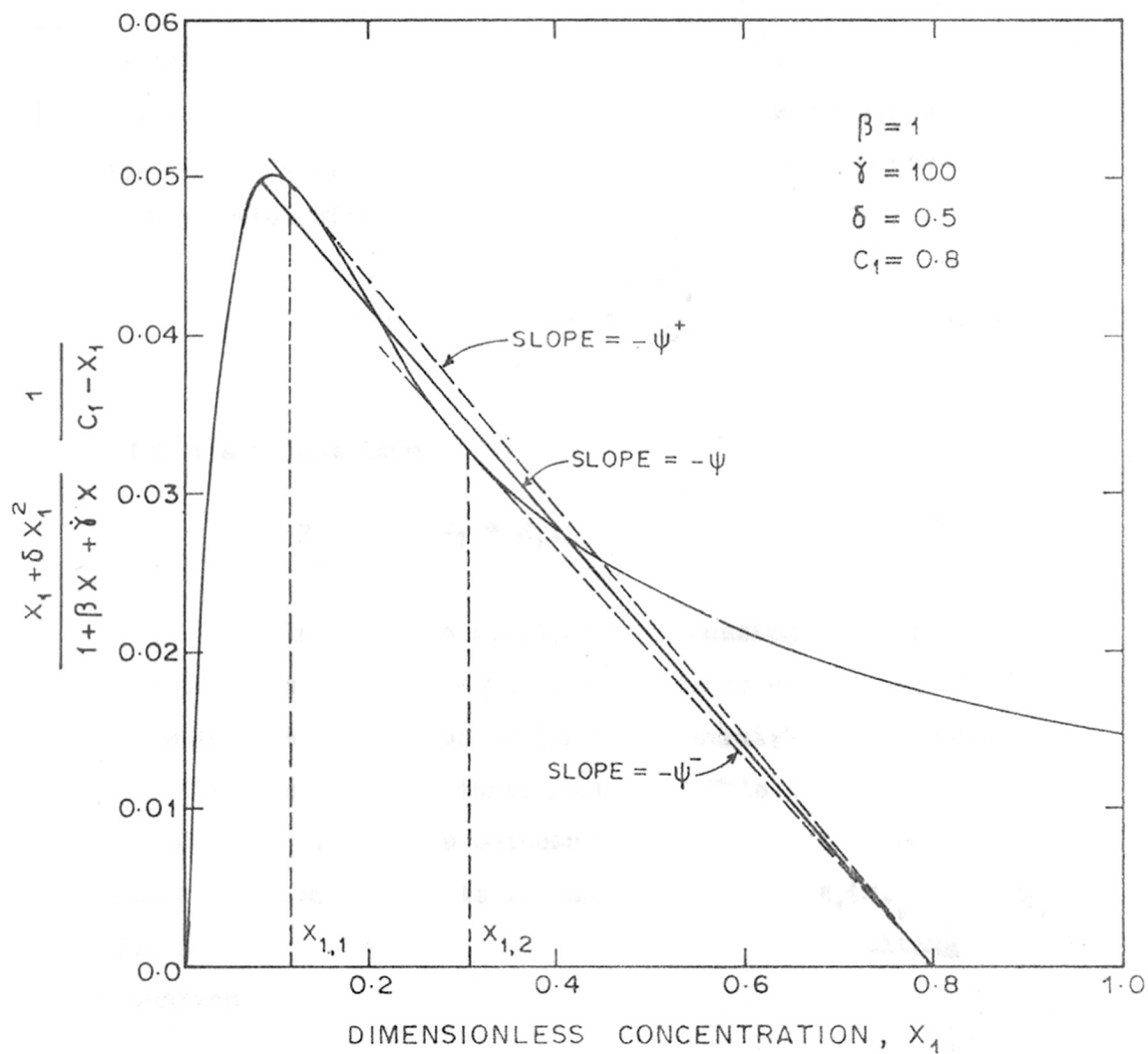


FIG. 5.1. ILLUSTRATION OF THE REGION OF MULTIPLE STEADY STATES

illustrates the procedure for a set of parameter values ($C_1 = 0.8$, $\beta = 1$, $\gamma = 100$ and $\delta = 0.5$). The possible solutions of equation (5.37) correspond to the points of intersection of the rate curve

$$y = \frac{x_1 + \delta x_1^2}{1 + \beta x_1 + \gamma x_1^2} \times \frac{1}{C_1 - x_1} \quad \text{[RHS of equation (5.37)]}$$

with a straight line

$$y = \psi [C_1 - x_1] \quad \text{[LHS of equation (5.37)]}$$

The latter is a straight line passing through $(0.8, 0)$ and having a slope of $-\psi$. The existence of multiplicity depends on the value of ψ (that is, straight line should cut the rate curve at three points). This implies that the slope ($-\psi$) should be between the slopes of the two dotted lines which are tangents to the rate curve, $x_1(x_{1,1}$ and $x_{1,2})$ can be obtained by equating the slope of the resulting equation is

$$6x_1^4 + 2x_1^3 + \left[\frac{C_1(\beta\delta - \gamma) + \beta - \delta}{\gamma} \right] x_1^2 + \frac{2\delta C_1}{\gamma} x_1 + \frac{C_1}{\gamma} = 0$$

[5.42]

Hence the necessary condition for the existence of multiplicity can be stated as that equation (5.42) should have two real roots in the region 0 to 0.8. Due to the quartic nature of equation

(5.42) it is difficult to derive analytical criterion. However, numerical identification of the parameters β , γ and δ to ensure the existence of multiplicity can be easily obtained by noting whether the quantity on LHS of equation (5.42) changes sign twice as x_1 is incremented in stepwise manner in the range of 0 to 0.8. The results of these calculations for various ranges of parameters are presented in Table 5.1. It is seen that for a given value of β and δ there exists a minimum value of γ below which multiplicity is absent.

The results of Table 5.1 represent only the necessary condition for the existence of multiplicity. In order to obtain a sufficiency criterion we note from Fig. 5.1 that the value of ψ must lie between (ψ^+) and (ψ^-) which correspond to the negative slopes of the two tangents shown by the dotted lines to the rate curve. Thus if $x_{1,1}$ and $x_{1,2}$ are the two roots to equation (5.42) in the region $0 < x_1 < 0.8$ then ψ^+ and ψ^- are given as

$$\psi^+ = \frac{x_{1,1} + \delta x_{1,1}}{1 + \beta x_{1,1} + \gamma x_{1,1}^2} \times \frac{1}{C_1 - x_{1,1}} \quad [5.43]$$

$$\psi^- = \frac{x_{1,2} + \delta x_{1,2}}{1 + \beta x_{1,2} + \gamma x_{1,2}^2} \times \frac{1}{C_1 - x_{1,2}} \quad [5.44]$$

Thus the sufficiency condition can be written as

$$\psi^- < \psi < \psi^+ \quad [5.45]$$

TABLE: 5.1

MINIMUM VALUES OF γ REQUIRED FOR THE
EXISTENCE OF MULTIPLICITY FOR VARIOUS
VALUES OF β AND δ WHERE $C_1 = 0.8$

$\delta \backslash \beta$	γ , values							
	0.1	1.0	2.0	5.0	10.0	20.0	50.0	100.0
0	42.6	45.9	49.4	59.1	73.8	100.1	169.1	271.0
1	79.7	84.8	90.3	105.7	129.5	172.9	288.3	461.0
5	252.6	264.4	277.2	314.1	372.1	480.1	773.3	1218.8
10	513.9	533.5	555.0	617.3	716.4	902.7	1413.3	2193.7

5.4 CRITERIA FOR STABILITY OF STATES

For the stability analysis the unsteady state equations for the reaction under consideration can be written in dimensional form as:

$$\frac{dx}{dt} = \frac{F}{V} (x_0 - x) - k_1 x \quad [5.46]$$

$$\frac{dx_1}{dt} = \frac{F}{V} x_1 + k_1 x - r \quad [5.47]$$

$$\frac{dx_2}{dt} = \frac{F}{V} (x_{2,0} - x_2) - r \quad [5.48]$$

where r is the overall rate of reaction with respect to the species x_1 and x_2 given by equation (5.20). The present case represents a three components system and the Jacobian matrix to test the asymptotic stability of the states can be formulated as:

$$M = \begin{bmatrix} -\frac{F}{V} - k_1 & 0 & 0 \\ k_1 & -\frac{F}{V} \frac{\partial r}{\partial x_2} - \frac{\partial r}{\partial x_2} \\ 0 & -\frac{\partial r}{\partial x_2} - \frac{F}{V} - \frac{\partial r}{\partial x_2} \end{bmatrix} \quad [5.49]$$

The characteristic equation of this system can then be obtained as:

$$\lambda^3 + m\lambda^2 + n\lambda + P = 0 \quad [5.50]$$

$$\text{where } m = \left[\frac{F}{V} + k_1 \right] + 2 \frac{F}{V} + \frac{\partial r}{\partial x_1} + \frac{\partial r}{\partial x_2} \quad [5.51]$$

$$\begin{aligned} n = & \left[\frac{F}{V} \right]^2 + \frac{F}{V} \left[\frac{\partial r}{\partial x_1} + \frac{\partial r}{\partial x_2} \right] + 2 \frac{F}{V} \left[\frac{F}{V} + k_1 \right] \\ & + \left[\frac{F}{V} + k_1 \right] \left[\frac{\partial r}{\partial x_1} + \frac{\partial r}{\partial x_2} \right] \end{aligned} \quad [5.52]$$

$$P = \left[\frac{F}{V} \right]^2 \left[\frac{F}{V} + k_1 \right] + \frac{F}{V} \left[\frac{F}{V} + k_1 \right] \left[\frac{\partial r}{\partial x_1} + \frac{\partial r}{\partial x_2} \right] \quad [5.53]$$

and

λ = characteristic root

For the asymptotic stability of the steady states the necessary conditions can be obtained employing Routh-Herwitz criteria as:

$$\frac{\partial r}{\partial x_1} + \frac{\partial r}{\partial x_2} > 0 \quad [5.54]$$

$$\text{and } [x_1 + x_2] > \frac{x_1 x_2 [k_2(1+x_2 b + Cx_1) + k_2 Cx_1 + k_4 + k_2 b x_1]}{k_{-2} + k_4 x_2 + k_2 x_1 [1 + x_2 b + Cx_1]} \quad [5.55]$$

$$\text{where } a = k_2 k_4 M_0 \quad [5.56]$$

$$b = \frac{k_4}{k_5} + \frac{k_4}{k_6} \quad [5.57]$$

$$c = \frac{k_3}{k_{-3}} \quad [5.58]$$

and x_1, x_2 appearing in this equation are steady state values of equations (5.46)-(5.48) and (5.20).

For a given set of parameter values (β, γ, δ etc.) the necessary condition for the existence of multiplicity can be checked using Table 5.1. The sufficiency conditions can then be tested to see if multiplicity really exists. Finally the stability of the steady states can be checked using equations (5.54)-(5.55). The procedure is illustrated in the next section.

5.5 ILLUSTRATIVE EXAMPLE

To illustrate the above procedure consider the following parameters ($\beta = 1, \delta = 0.5, \gamma = 100, C_1 = 0.8$ and $\psi = 0.07$). From Table 5.1 it is obvious that minimum value of γ required for the existence of multiplicity is already met for this case. We now test for the sufficiency conditions given by equations (5.43) and (5.44). For this purpose the solution to equation (5.42) is obtained and is found to have two real roots in the interval 0 to 0.8. The actual values of the roots were obtained as:

$$x_{1,1} = 0.1352$$

$$x_{1,2} = 0.3144$$

Substituting these values in equations (5.43) and (5.44) the values of ψ^+ and ψ^- are obtained as:

$$\psi^+ = 0.1029$$

$$\psi^- = 0.0867$$

The sufficiency condition for the existence of multiplicity for the present case can thus be written as:

$$0.0867 < \psi < 0.1029$$

For the parameter value of ψ employed, it is seen that sufficiency condition is violated for the present example. We therefore have a unique solution. In order to ensure that the unique solution is stable we test for the asymptotic stability of the solution using equations (5.54) and (5.55). The actual values obtained are:

$$\frac{\partial r}{\partial x_1} + \frac{\partial r}{\partial x_2} = 13.6505$$

and LHS of equation (5.55) = 2.2704

RHS of equation (5.55) = 1.1032

It is seen from this that the solution obtained is unique and stable.

To obtain the global stability of the state, equations (5.46)-(5.48) have been integrated using a fourth order Runge-Kutta method. The phase plot of dimensionless concentration

of x_2 vs. dimensionless concentration of x_1 is shown in Fig. 5.2. The parameters used in Fig. 5.2, ($\beta = 1$, $\delta = 0.5$, $\gamma = 100$, $C_1 = 0.8$ and $\psi = 0.07$) were the same as those used previously. The dimensional constants used for the above case have the values $k_1 = 1$, $k_2 = 20$, $k_{-2} = 46.5$, $k_3 = 2.85$, $k_{-3} = 1$, $k_4 = 2.5$, $k_5 = 10$, $k_6 = 5.2631$, $\frac{F}{V} = 1$, $\alpha = 2$, $x_0 = 1.6$, $x_{2,0} = 2.8$ and $M_0 = 7.357$.

From the phase plot shown in Fig. 5.2, it is apparent that the trajectories converge to a single steady state solution in conformity with the analytical criteria developed.

5.6 CONCLUSIONS

For the reaction scheme considered, the necessary and sufficient conditions for the existence of multiplicity have been obtained for a class of homogeneously catalysed reactions. The parameter values for the existence of necessary conditions of multiplicity have been listed in Table 5.1. Procedures for calculation of the sufficiency condition and the asymptotic stability of the steady state are illustrated by considering a simple example. The stability analysis is then presented in the form of a phase plot to confirm the analytical criteria derived. The results obtained should be useful in the a priori determination of the region of multiplicity and stability of states for homogeneously catalysed reactions.

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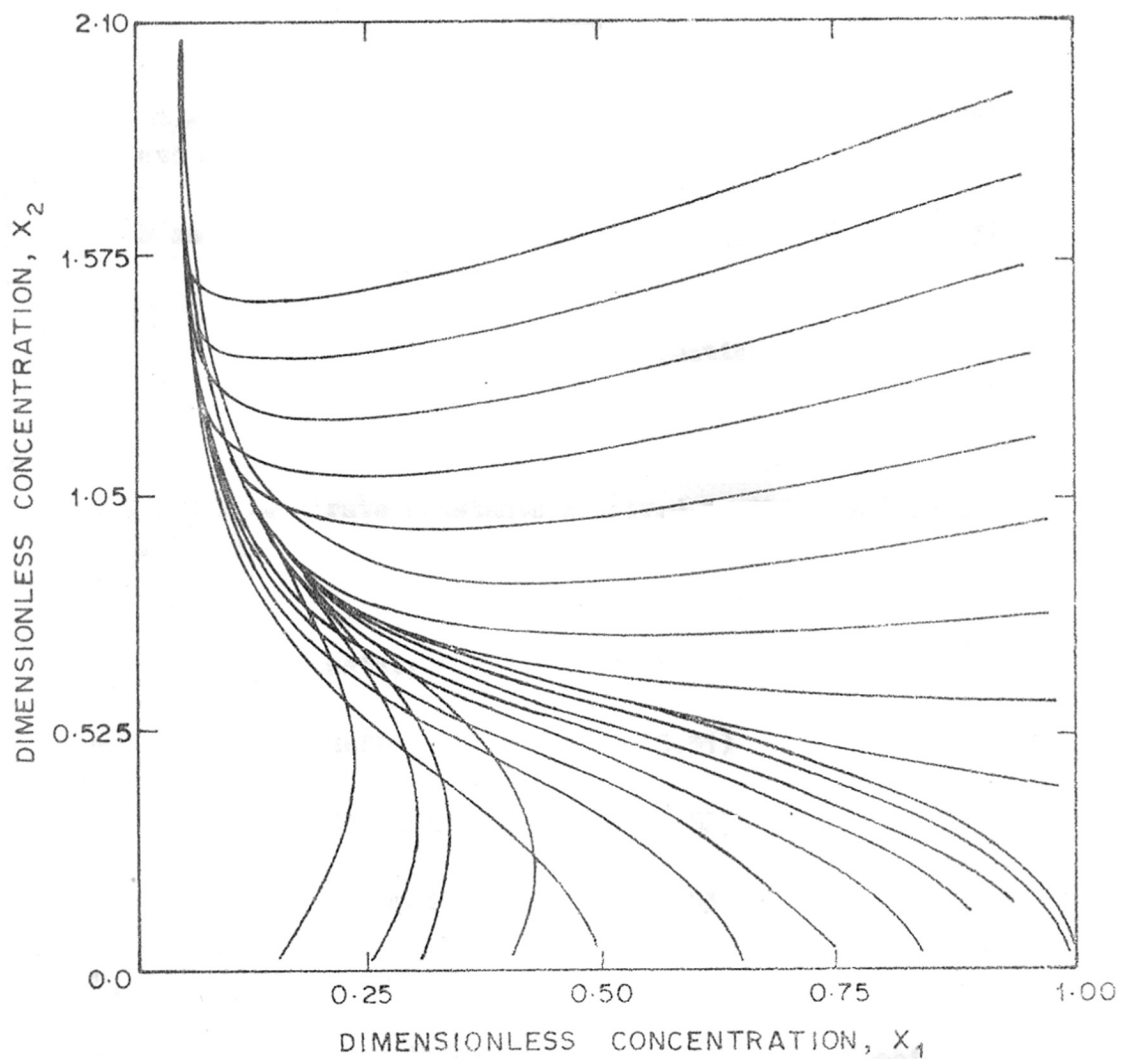


FIG. 5.2. PHASE PLANE PLOT

NOTATION

a_1, a_2, a_3 a_4 and a_5	constants defined by equation (5.31)-(5.35) respectively
a, b and C	constants defined by equations (5.56)-(5.58) respectively
C_1	constant defined by equation (5.27)
F	flow rate of reactant
$k_1, k_2, k_{-2},$ k_{-3}, k_4, k_5 and k_6	rate constants involved in the reaction scheme
M_0	catalyst concentration
m	defined by equation (5.51)
n	defined by equation (5.52)
P	defined by equation (5.53)
r_A	rate of disappearance of species x ,
r	overall rate with respect to the species x_1 & x_2
V	volume of the CSTR system
x, x_1, x_2	concentrations of methanol, methyl iodide and carbon monoxide in solution respectively

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$x_{1,0}, x_{2,0}$	inlet concentration of species x_1 and x_2 respectively
$x_{1,1}, x_{1,2}$	points at which the tangent touch the rate curve
Y	concentration of hydroiodic acid

Greek letters

ψ	defined by equation (5.41)
ψ^+, ψ^-	defined by equations (5.43) and (5.44) respectively
α	defined by equation (5.26)
β	defined by equation (5.38)
γ	defined by equation (5.39)
δ	defined by equation (5.40)
λ	characteristic root of equation (5.50)

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APPENDICES
EXPERIMENTAL DATA

APPENDIX - I

EXPERIMENTAL DATA ON SCREENING OF CATALYSTS

APPENDIX-IEXPERIMENTAL DATA ON SCREENING OF CATALYSTS[A] Effect of ligands on the catalyst activity for carbonylation of nitrobenzene to phenylisocyanateCatalyst concentration = 3×10^{-5} mol/cm³

Duration of the reaction = 5 hr

Complex	Conversion of nitrobenzene, %	Selectivity for phenylisocyanate, %
Pd(Py) ₂ Cl ₂	19.23	80.69
Pd(Isoq) ₂ Cl ₂	12.31	71.13
Pd(C ₇ H ₅ N) ₂ Cl ₂	-	-
Pd(PPh ₃) ₂ Cl ₂	-	-
Pd(CO) ₂ Cl ₂	-	-

[B] Effect of oxide promoters on Pd(Py)₂Cl₂ and Pd(Isoq)₂Cl₂ catalysed carbonylation of nitrobenzene to phenylisocyanate

Conditions:

- 1) Nitrobenzene (NB) = 20 cm³
- 2) Chlorobenzene (MCB) = 80 cm³
- 3) Total volume = 100 cm³
- 4) Temperature = 190°C
- 5) Catalyst concentration = 3x10⁵ mol/cm³
- 6) Promoter concentration = 0.5 gm
- 7) CO partial pressure = 1173.75 psig
- 8) Agitation speed = 670 rpm

Run No.	Catalyst	Promoter	Duration of the reaction, hr	Conversion of NB, %	Selectivity for PhNCO, %
1	2	3	4	5	6
21.	Pd(Py) ₂ Cl ₂	-	3	15.33	64.21
			5	19.23	80.69
			7	24.26	67.23
			9	33.79	31.99
			10.5	44.36	25.23
22.	Pd(Py) ₂ Cl ₂	V ₂ O ₅	3	04.61	33.30
			5	24.60	38.57
			7	37.90	44.32
			9	45.64	55.06
			10.5	46.80	61.20
23.	Pd(Py) ₂ Cl ₂	Fe ₂ O ₃	3	13.00	51.94
			5	15.54	65.56
			7	29.40	19.00
			9	55.90	17.20
			10.5	65.56	19.11

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1	2	3	4	5	6
24.	Pd(Py) ₂ Cl ₂	FeBO ₃	3	21.02	49.46
			5	23.59	71.57
			7	31.85	71.03
			9	43.44	69.18
			10.5	65.23	27.40
25.	Pd(Isoq) ₂ Cl ₂	-	3	08.21	29.44
			5	12.31	71.13
			7	19.49	71.50
			9	22.05	71.86
			10.5	24.62	78.75
26.	Pd(Isoq) ₂ Cl ₂	V ₂ O ₅	3	13.85	78.75
			5	20.51	85.35
			7	26.92	79.53
			9	39.13	65.37
			10.5	48.74	44.87
27.	Pd(Isoq) ₂ Cl ₂	MoO ₃	3	23.64	75.12
			5	30.97	78.97
			7	33.64	80.94
			9	41.64	51.23
			10.5	51.18	24.85
28.	Pd(Isoq) ₂ Cl ₂	FeBO ₃	3	10.10	41.62
			5	16.92	66.97
			7	18.77	93.16
			9	21.79	99.77
			10.5	22.97	100.00

[C] Effect of solvents on Pd(Py)₂Cl₂ catalysed carbonylation of nitrobenzene to phenylisocyanate (PhNCO)

Conditions:

- 1) Nitrobenzene (NB) = 20 cm³
- 2) Solvent = 80 cm³
- 3) Total volume = 100 cm³
- 4) Temperature = 190°C
- 5) Pd(Py)₂Cl₂ concn. = 3 x 10⁻⁵ mol/cm³
- 6) CO, partial pressure = 1173.75 psig
- 7) Agitation speed = 670 rpm

Run No.	Solvent	Duration of the reaction, hr	Conversion of NB, %	Selectivity for PhNCO, %
21.	Chlorobenzene	3	15.33	64.21
		5	19.23	80.69
		7	24.26	67.23
		9	33.79	31.99
		10.5	44.36	25.23
31.	Toluene	3	7.03	75.69
		5	9.13	78.26
		7	15.02	8.84
		9	32.46	7.16
		10.5	39.95	6.65
32.	Xylene	3	10.26	47.25
		5	16.51	67.52
		7	20.82	78.69
		9	24.10	82.04
		10.5	25.13	91.55
33.	o-dichlorobenzene	3	17.69	44.00
		5	23.05	49.36
		7	25.64	48.34
		9	39.28	18.35
		10.5	51.12	14.11

[D] Effect of process variables on Pd(Py)₂Cl₂ catalysed carbonylation of nitrobenzene to phenylisocyanate

Conditions:

- (1) Solvent = Monochlorobenzene (MCB)
- (2) Reactant = Nitrobenzene (NB)
- (3) Total volume = 100 cm³
- (4) Agitation speed = 1000 rpm
- (5) Product = Phenylisocyanate (PhNCO)

Run No.	Initial concn. of NB -x10 ³ mol/cm ³	Partial pressure of CO, psig	Pd(Py) ₂ Cl ₂ catalyst concn., -x10 ⁵ mol/cm ³	V ₂ O ₅ concn., g	Temp- rature, °C	Duration of the reaction, hr	Mol of NB present, -x10 ³ mol/cm ³	Mol of NB reacted, -x10 ³ mol/cm ³	Mol of PhNCO formed, -x10 ³ mol/cm ³	Conversion of NB, %	Conver- sion of NB, %	Selec- tivity for PhNCO, %
1	2	3	4	5	6	7	8	9	10	11	12	
51.	1.974	303.75	3	-	190	1.00	1.952	0.022	0.012	1.11	58.69	
						1.75	1.897	0.077	0.039	3.90	51.30	
						2.50	1.831	0.143	0.070	7.24	48.95	
						3.25	1.828	0.146	0.066	7.40	45.75	
						4.00	1.824	0.150	0.064	7.60	43.25	
52.	1.969	703.75	3	-	190	1.00	1.914	0.054	0.038	2.76	70.94	
						1.75	1.844	0.123	0.075	6.28	61.31	
						2.50	1.721	0.247	0.151	12.55	61.30	
						3.25	1.694	0.274	0.169	13.94	61.90	
						4.00	1.670	0.298	0.158	15.14	53.15	

	1	2	3	4	5	6	7	8	9	10	11	12
58.	2.068	1133.75	1	0.5	190	3.25	4.00	1.607	0.347	0.261	17.76	75.22
						4.00		1.539	0.415	0.294	21.24	71.03
						1.00	1.00	2.042	0.025	0.025	1.21	100.00
						1.75	1.75	2.003	0.065	0.065	3.14	100.00
						2.50	2.50	1.927	0.141	0.141	6.82	100.00
						3.25	3.25	1.919	0.149	0.149	7.20	100.00
						4.00	4.00	1.862	0.206	0.206	9.96	100.00
59.	1.958	1133.75	2	0.5	190	1.00	1.00	1.843	0.115	0.108	5.87	94.36
						1.75	1.75	1.724	0.234	0.205	11.95	87.95
						2.50	2.50	1.601	0.357	0.313	18.23	87.80
						3.25	3.25	1.467	0.491	0.430	25.08	87.76
						4.00	4.00	1.396	0.562	0.493	28.70	87.72
60.	1.859	1133.75	2	1.0	190	1.00	1.00	1.770	0.089	0.089	4.79	100.00
						1.75	1.75	1.697	0.162	0.162	8.71	100.00
						2.50	2.50	1.550	0.309	0.309	16.62	100.00
						3.25	3.25	1.425	0.434	0.434	23.35	100.00
						4.00	4.00	1.278	0.581	0.523	31.25	90.02
61.	2.039	1133.75	2	1.5	190	1.00	1.00	1.847	0.192	0.179	9.42	93.23
						1.75	1.75	1.740	0.299	0.273	14.66	91.51
						2.50	2.50	1.544	0.495	0.433	24.28	87.47
						3.25	3.25	1.478	0.561	0.470	27.51	83.82
						4.00	4.00	1.324	0.715	0.532	35.07	74.52

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	1	2	3	4	5	6	7	8	9	10	11	12
67.	2.043	1133.75	3	-	210	1.00	1.890	1.858	0.041	0.040	2.16	99.35
						4.00	1.846	1.846	0.053	0.053	2.76	100.00
						1.75	1.775	1.775	0.153	0.114	7.52	74.97
						2.50	1.627	1.627	0.416	0.178	13.12	66.70
						3.25	1.552	1.552	0.491	0.249	20.36	59.95
						4.00	1.511	1.511	0.532	0.293	24.03	59.73
						1.00	1.438	1.438	0.493	0.316	26.04	59.44
68.	1.931	1133.75	3	-	230	1.75	1.234	1.234	0.697	0.281	25.53	57.13
						2.50	1.146	1.146	0.785	0.354	36.10	50.83
						3.25	0.885	0.885	1.046	0.322	40.65	41.02
						4.00	0.655	0.655	1.276	0.209	54.17	20.03
										0.101	66.08	07.97

APPENDIX - II
EXPERIMENTAL DATA ON KINETIC STUDIES

[B] Effect of Pd(Py)₂Cl₂ catalyst concentration on the rate of carbonylation of nitrobenzene

CONDITIONS:
 Nitrobenzene = 20 cm³ CO pressure = 1150 psig
 Chlorobenzene = 80 cm³ Temperature = 190°C
 Total volume = 100 cm³ Agitation = 1000 rpm

Run No.	107	108	109	110	111
Pd(Py) ₂ Cl ₂ concentration } mol/cm ³	1x10 ⁻⁵	2x10 ⁻⁵	4x10 ⁻⁵	6x10 ⁻⁵	8x10 ⁻⁵
Time, min	CO pressure, psig	Time, min	CO pressure, psig	Time, min	CO pressure, psig
0	1150	0	1150	0	1150
15	1148	15	1130	15	1125
30	1140	30	1140	30	1110
45	1130	45	1130	45	1090
60	1110	60	1120	60	1070
75	1095	75	1110	75	1050
90	1085	90	1105	90	1025
105	1080	105	1100	105	995
120	1075	120	1095	120	965

[C] Effect of nitrobenzene concentration on the rate of carbonylation of nitrobenzene

CONDITIONS:

Solvent = chlorobenzene Temperature = 190°C
 Total volume 100 cm³ CO pressure = 1150 psig
 Pd(Py)₂Cl₂ = 3 x 10⁻⁵ mol/cm³ Agitation = 1000 cm³

Run No.	112	113	114	115	116
Nitrobenzene - x 10 ⁻⁴ mol/cm ³	4.89	9.78	14.67	29.34	48.90
Time, min	0	15	30	45	60
CO pressure, psig	1150	1130	1120	1115	1100
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1120	1110	1100
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1115	1105	1100
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1115	1105	1090
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1115	1105	1040
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1115	1095	1000
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1115	1075	980
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1115	1065	960
Time, min	0	15	30	45	60
CO pressure, psig	1150	1140	1115	1055	940

[D] Effect of temperature on the rate of carbonylation of nitrobenzene

CONDITIONS :

Nitrobenzene = 20 cm³ Pd(Py)₂Cl₂ = 3x10⁻⁵ mol/cm³
 Chlorobenzene = 80 cm³ CO pressure = 1150 psig
 Total volume = 100 cm³ Agitation = 1000 rpm

Run No.	117	118	119
Temperature =	170°C	210°C	230°C
Time, min	CO pressure, psig	Time, min	CO pressure, psig
0	1150	0	1150
15	1145	5	1135
30	1140	10	1120
45	1120	15	1105
60	1105	20	1090
75	1100	25	1075
90	1090	30	1060
105	1080	35	1030
120	1070	40	1010
			980

[E] Data on mass transfer coefficient ($K_L a$) determination

CONDITIONS: Solvent = chlorobenzene, Temperature = 26°C, CO pressure = 800 psig

Agitation=600 rpm		500 rpm		400 rpm		300 rpm		200 rpm		100 rpm	
Time, sec	CO pressure, psig	Time, sec	CO pressure, psig	Time, sec	CO pressure, psig	Time, sec	CO pressure, psig	Time, sec	CO pressure, psig	Time, sec	CO pressure, psig
0	800	0	800	0	800	0	800	0	800	0	800
1	790	1	795	3	795	10	795	10	795	75	795
2	780	2	790	7	790	25	790	30	790	150	790
3	775	4	785	10	785	40	785	50	785	195	785
4	770	6	780	18	780	60	780	70	780	360	780
5	765	8	775	23	775	80	775	120	775	540	775
-	-	10	770	30	770	100	770	150	770	690	770
-	-	15	765	40	765	120	765	180	765	900	765