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Synthesis of Nitrogen-containing Compounds by the Interaction of Nitro-compounds with Carbon Monoxide

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The methods and catalysts for the synthesis of nitrogen-containing compounds (oximes, Schiff bases, amides, imides, amines, ureas, urethanes, isocyanates, and azo-compounds) by the interaction of nitro-compounds with carbon monoxide are considered. The reaction mechanisms are discussed and the characteristics of the synthesis of mono- and di-isocyanates are noted.
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I. INTRODUCTION

The catalytic interaction of nitro-compounds with carbon monoxide, which is a new and little investigated field of organic catalysis, has become in recent years one of the currently most important fields of industrial organic synthesis. The reason for this is that a whole series of industrially important compounds can be obtained from nitro-compounds and carbon monoxide in a single stage: azo-compounds, amides, amines, oximes, urethanes, ureas, and isocyanates.

The synthesis of oximes by the reduction of aliphatic nitro-compounds with carbon monoxide constitutes a new approach to the solution of the problem of synthesising intermediates in the manufacture of caprolactam. Urethanes and ureas are important final products and intermediates in the synthesis of fertilisers and pesticides and the development of a method of the direct synthesis of these compounds is of undoubted interest.

Aromatic mono- and di-isocyanates are valuable intermediates in the manufacture of pesticides, rigid and elastic polyurethane foam plastic (widely used in building, furniture, refrigeration, and transport industries), synthetic leather, adhesives, and coatings[1-3]. The world production of isocyanates during the period from 1970 to 1975 doubled and according to predictions will continue to grow at the same rate[4]. In the USA the annual increase is 9% and by 1980 the total production based on isocyanates will exceed 1 million tonnes annually[5]. However, the requirement for isocyanates is by no means fully satisfied, since their modern production is based on the obsolete method involving the treatment of amines with phosgene. In the course of the last decade intense research has therefore been prosecuted in order to develop a new and much more economical method of synthesising isocyanates by carbonylating nitro-compounds. The assembly of the first experimental plant is already being completed in Japan and in 1980 it is planned to begin the manufacture of isocyanates by the new method[6].

This review gives a systematic account of the advances in the last 7–10 years in the field of the catalytic synthesis of nitrogen-containing compounds (oximes, Schiff bases, amides, imides, amines, ureas, urethanes, isocyanates, and azo-compounds) by the interaction of CO and nitro-compounds. Attention is concentrated on the catalysts and the process conditions; furthermore the synthetic possibilities of the method involving the carbonylation of nitro-compounds and the prospects for its employment in organic synthesis are demonstrated.

II. THE PRINCIPAL FACTORS INFLUENCING THE INTERACTION OF NITRO-COMPOUNDS WITH CARBON MONOXIDE

When an attempt is made to arrange systematically the reactions of nitro-compounds with CO (see Table), two principal types of interactions can be distinguished: the reduction of nitro-compounds without the addition of CO to the latter and the addition of a CO molecule to the intermediates in the reduction process (carbonylation). The reaction pathway is in many respects determined by both the catalyst and the reaction conditions, on the one hand, and by the nature of the third component, which in most cases plays the role of the reaction medium, on the other.

The interaction of CO with nitro-compounds is a thermodynamically favourable process[7], but in the absence of a catalyst it proceeds with much difficulty. This is probably due to the high activation energy for the reaction with the reactants being readily activated when adsorbed on the catalyst.

By varying the nature of the catalyst, the reaction medium, and the reaction conditions (temperature, pressure, and reaction time), it is possible to alter both the reaction pathway and the yield of products and the selectivity of their formation. We shall consider the influence of the principal factors on the interaction of nitro-compounds with carbon monoxide.

Catalyst

Transition metals (as a rule Group VIII metals), copper salts, sulphur, and selenium and its compounds, which are capable of forming complexes with both CO and with the nitro-compound, catalyse the reactions of nitro-compounds with carbon monoxide. In the vast majority of cases the reaction proceeds in the liquid phase in the presence of homogeneous catalysts, although instances of the use of heterogeneous catalysts of analogous composition are known.

Despite the lack of data on the comparative activities of the known catalysts, analysis of the available publications (frequently contradictory) permits the conclusion that best results are obtained using palladium and rhodium compounds. Here one should note that the activity of the same compound is greatly influenced by the type of promoting additive and its amount, the nature of the third component, temperature, and carbon monoxide pressure. Tertiary amines, for example pyridine, quinoline, and their derivatives, quaternary ammonium salts, phenylphosphines, and salts of Group IIB, V, VI, and VIII transition metals, particularly vanadium, molybdenum, tungsten, copper, and iron, as well as lanthanide compounds can be used as activators of the palladium and rhodium catalysts.

Synthesis of nitrogen-containing compounds by the catalytic interaction of nitro-compounds with carbon monoxide.

Catalyst	Third component	t, °C	p, atm	Reaction product
—	—	250	3000	Azobenzene
$Fe(CO)_5$	—	200	100—200	Azo-compounds, amines
$Fe(CO)_5$	H_2	160	200	Amines
$Fe(CO)_5$	CH_3COOH	310	100	Acetanilide
$Ni(CO)_4$	CH_3COOH	310	100	Acetanilide
$Co_2(CO)_8$	CH_3COOH	310	100	Acetanilide
$Co_2(CO)_8$	—	190	200	Isocyanates
Copper salts*	—	85	1	Oximes, amines
Copper salts*	Piperidine	20	1	Ureas
Pd**	H_2	200	20	Ureas
Pd**	Alcohols	160	100	Urethanes
Pd**	—	200	900	Isocyanates
$PdCl_2$***	Amines	90	1	Ureas
$PdCl_2$***	Alcohols	150	100	Urethanes
$PdCl_2$***	—	150—200	50—100	Isocyanates
$RhCl_3$***	Water	150	50—120	Amines
$RhCl_3$***	Amines	190	205	Ureas
$RhCl_3$***	Alcohols	150	100—400	Urethanes
	—	120—200	1—300	Isocyanates
$Rh_6(CO)_{16}$****	Aldehydes	170	150	Schiff bases
$Rh_6(CO)_{16}$****	Dialdehyde	170	150	Acid amides
$Rh_6(CO)_{16}$****	Phthalic anhydride Acids and diphenylacetylene	170	120	Acid imides
$Rh_6(CO)_{16}$****	Water	150	50—120	Amines
$Rh_6(CO)_{16}$****	H_2	150—200	100—200	Ureas
$Rh_6(CO)_{16}$****	Alcohols	170	150	Urethanes
$Ru_3(CO)_{12}$	H_2	160	200	Amines, ureas
Se and its compounds	Alcohols	170	50	Urethanes

*In aqueous solutions of highly basic amines.
** On a carrier with added $FeCl_3$ and (or) pyridine.
*** With activating additives.
**** In pyridine.

The reduction and carbonylation reactions of nitro-compounds can also proceed stoichiometrically under mild conditions if CO is first bound in active carbonyl complexes, for example of the type of $Fe(CO)_5$ or iron acyl carbonyls.

Temperature

The process temperature is selected depending on the catalyst employed, the third component, and the CO pressure. For example, in the presence of $PdCl_2$ as the catalyst and activators, the carbonylation of nitro-compounds to give substituted ureas in solution in amines proceeds at 90 °C and atmospheric pressure; in order to synthesise isocyanates in an inert solvent or urethanes in alcohols, a temperature of 150—200° and a pressure of 50—100 atm are required. When $RhCl_3$ is employed as the catalyst in the presence of promoting agents, amines are formed at 150 °C (50—120 atm), ureas at 190 °C (200 atm), isocyanates at 120—200 °C (up to 300 atm), and urethanes at 150—230 °C (100—400 atm).

The process temperature influences in its turn both the degree of conversion of the initial nitro-compounds and the selectivity of its transformation. In the general case one should note that, in order to obtain practically acceptable yields of the desired product with a sufficiently high selectivity, the reaction must be performed at 100—200 °C under an increased CO pressure. At a lower temperature the rate of reaction is low, while an increase of temperature above 200 °C as a rule leads to undesirable side reactions, in particular to tar formation, which lowers the selectivity and deactivates the catalyst.

Carbon Monoxide Pressure

The working pressure depends on the nature of the nitro-compound, the catalyst, the third component, and the temperature. For example, mononitro-compounds are converted into isocyanates at a pressure of 50—100 atm, while, other conditions being equal, the dinitro-compounds require 200 to 300 atm. The reduction of nitro-compounds to amines, azo-compounds, amides, and imides proceeds at a lower pressure than their carbonylation to urethanes or isocyanates, which is apparently associated with the activating effect of the third component on the catalyst.

In addition, an increased CO pressure is necessary to maintain the catalytic complex in an active equilibrium state, which is characteristic of the majority of catalytic reactions of organic compounds involving carbon monoxide and occuring in the presence of carbonyl complexes of transition metals. In the synthesis of isocyanates by the carbonylation of nitro-compounds an increase of pressure (beyond the minimum value required for each catalyst) increases the productivity and makes it possible to reduce the reaction temperature to some extent.

The Third Component

The presence of the third component in the reaction system influences both the reaction pathway and the activity of the catalyst. The third component can be a reactant and (or) the reaction medium. Typical third components which are reactants in the reactions of nitro-compounds with CO are H_2 and aldehydes; hydrogen donors such as water, alcohols, and amines are also used as both the reactant and the reaction medium, while inert solvents, for example, aromatic and aliphatic hydrocarbons, chlorobenzene, or dichlorobenzene are used as inert solvents.

If the nitro-compound reacts with CO in an inert solvent, then mainly isocyanates are formed, two out of the three reacting CO molecules functioning as reductants. In the presence of H_2 in the reaction system, the nitro-compound is as a rule reduced to the amine; sometimes substituted ureas are formed together with the amine, possibly as a result of the carbonylation of the amine formed initially. Aldehydes and hydrogen donors such as amines and alcohols interact either with the catalyst in the complex with the deoxygenation product of the nitro-compound or with the isocyanate formed, giving rise to the corresponding derivatives. Stable compounds, for example, Schiff bases, ureas, and urethanes, can be isolated from the reaction mixture as the products; unstable compounds, for example carbamic acids or their anhydrides, which can be formed in water or acetic acid,

decompose with the evolution of CO_2 and the formation of carboxylic acid amides.

One should bear in mind that the majority of the known third components are effective complex-forming agents. When homogeneous metal-complex catalysts are used, they can therefore enter into the coordination sphere of the transition metal together with the nitro-compound and CO and thereby facilitate or hinder their activation. Consequently the third component can fulfill yet another function: it can regulate the activity and selectivity of the catalyst and can even alter the type of interaction of the nitro-compound with CO.

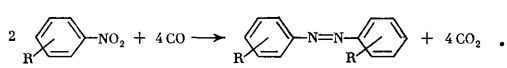
It would be premature to reach a final conclusion concerning the scientific justification of the subdivision of the catalytic reactions of nitro-compounds with CO into reduction without the addition of CO to the nitro-compound and carbonylation, because this new field of organic catalysis has been inadequately investigated. However, this approach permits a more clear-cut estimate of the fundamental achievements in this new field of industrial organic synthesis and a deeper understanding of the mechanism of the reactions of nitro-compounds and CO in the presence of catalysts and also enables one to outline ways of improving and developing the reactions under consideration.

III. REDUCTION OF NITRO-COMPOUNDS

1. Synthesis of Azo-Compounds

The interaction of carbon monoxide with nitro-compounds in the absence of a catalyst proceeds with much difficulty. Thus the conversion of nitrobenzene into azobenzene requires a high carbon monoxide pressure—3000 atm.[8] On the other hand, carbon monoxide bound in a carbonyl complex readily interacts with aromatic nitro-compounds, converting them into azobenzene derivatives[9,10]. The reaction takes place at atmospheric pressure. Under the influence of $Fe(CO)_5$, azobenzene, 2,2′-dimethyl-, 3,3′-dimethyl, and 4,4′-dimethylazobenzenes are formed in 48–76% yields from nitrobenzene and *o*, *m*, and *p*-nitrotoluenes respectively; 1,2-dinitrobenzene is converted to the extent of 11% into 2,2′-diaminoazobenzene.

Iron pentacarbonyl is an active catalyst of the reduction of nitro-compounds with carbon monoxide. In its presence the synthesis of azo-compounds from nitrobenzene and its derivatives takes place at 200 °C and a pressure of 100–200 atm [11]:



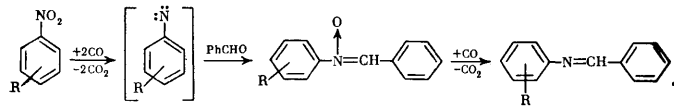
Azoxy-compounds are formed as intermediate. Nitrobenzene is reduced most selectively (the yield of azobenzene is 79%). 4-Chloro- and 4-bromonitrobenzenes are converted into 4,4′-dichloro-, and 4,4′-dibromo-azobenzenes to the extent of 55–56%. Azo-compounds are formed in yields of 18–32% from 4-fluoro- and 4-iodo-nitrobenzenes and in yields of 44–45% from 4-nitrotoluene and 4-nitroanisole[11].

2. Synthesis of Oximes

Nitropropane, nitrobutane, and nitrocyclohexane are reduced quantitatively by carbon monoxide to oximes in aqueous amine solutions of copper salts at 85 °C and atmospheric pressure. The reaction takes place only in the presence of highly basic amines, for example, ethylenediamine. Copper(I) salts are catalytically more active than copper(II) salts. Silver(I) salts are active only at an increased CO pressure, while mercury, cobalt, nickel, and manganese salts do not exhibit catalytic activity in this reaction[12–14].

3. Synthesis of Schiff Bases

The reduction of aromatic nitro-compounds (nitrobenzene, 4-nitroanisole, 4-nitro-*N*,*N*′-dimethylaniline, 2-, 3-, and 4-nitrotoluenes, and 4-nitrobiphenyl) by carbon monoxide under a pressure of 150 atm at 170 °C in the presence of benzaldehyde leads to the formation of Schiff bases in yields of 60–85%.[15] The reaction is catalysed by $Rh_6(CO)_{16}$ in pyridine. It is believed[15,16] that a nitrene is formed from the nitro-compound and CO in the first stage and then reacts with the aldehyde and carbon monoxide to give the final product:

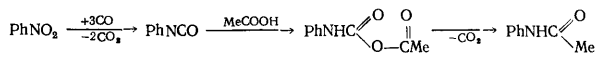


4. Synthesis of Amides and Imides

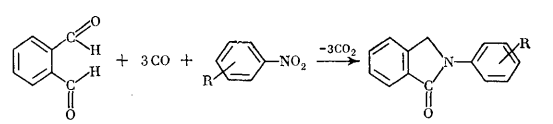
When primary and secondary aliphatic nitro-compounds are heated with iron pentacarbonyl in dry diglyme at 120 °C for 15 h, formamides are formed in low yields (3–20%). On replacing $Fe(CO)_5$ by $Fe_2(CO)_9$, the reaction takes place even at room temperature, but, instead of formamides, the nitrene complexes $(RN)_2Fe_3(CO)_9$, $(RN)_2Fe_2(CO)_6$, and $(RN)_2Fe_2(CO)_7$ are formed from the nitro-compounds and are then converted on heating in diglyme into formamides and urea derivatives[17].

Acetanilide, propionanilide, and benzanilide are obtained in high yields (68–86%) when nitrobenzene interacts with iron acyl carbonyls. The reaction proceeds at room temperature and in an inert atmosphere[18].

Acetanilide can be obtained catalytically in 68% yield from nitrobenzene in acetic acid in the presence of iron, cobalt, or nickel carbonyls at 310 °C and a pressure of 100 atm. With decrease of temperature, the yield of acetanilide falls sharply:



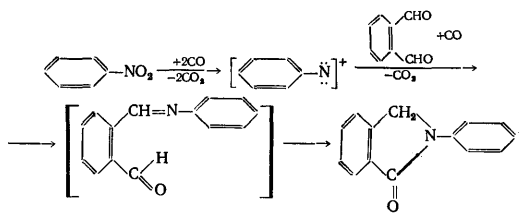
The carbonylation of nitrobenzene with carbon monoxide (150 atm, 170 °C) in the presence of *o*-phthalic aldehyde results in the formation of *N*-phenylisoindolinone[20]. Apart from nitrobenzene, 4-nitroanisole, 3- and 4-nitrotoluenes, and 3-chloronitrobenzene enter into this reaction:



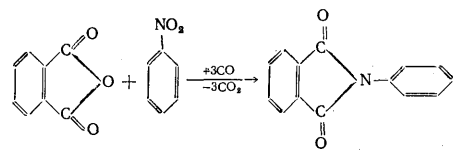
R = H (58%), 4-MeO (42%), 3-Cl (55%), 3-Me (40%), or 4-Me (46%).

The reaction is catalysed by $Rh_6(CO)_{16}$ in pyridine. It apparently proceeds via a stage involving the reduction of the nitro-compound to a nitrene complex, which interacts

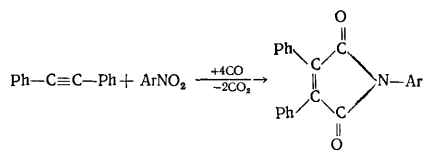
with one aldehyde group to form a Schiff base with subsequent ring closure:



The reduction of nitrobenzene with carbon monoxide (120 atm, 170 °C) in the presence of phthalic anhydride and the same catalyst [$Rh_6(CO)_{16}$ in pyridine] gave *N*-phenylphthalinide in 90% yield[16]:



In the presence of diphenylacetylene, the *N*-phenylimide of 2,3-diphenylmaleic acid is formed under the same conditions in 75% yield[16,21]. 3- and 4-Nitrotoluenes, 3-chloronitrobenzene, and 4-nitroanisole react similarly:



5. Synthesis of Amines

In the synthesis of azo-compounds from 2- or 3-nitrotoluene and $Fe(CO)_5$ in dibutyl ether, small amounts of 2- or 3-toluidine (6–13%) are formed as side products[10]. If the reaction is carried out in methanol which serves as a source of hydrogen, then aromatic amines can be obtained from nitrobenzenes and $Fe_3(CO)_{12}$ in 60–90% yield[22]. In the absence of methanol the reaction stops at the stage where the nitrene complex $(PhN)_2Fe_3(CO)_9$ is formed. The nitro-group is reduced both as a result of the oxidation of carbon monoxide to the dioxide; and as a result of the partial oxidation of iron. The reaction is undergone by 2- and 4-nitrotoluenes, 2- and 4-chloronitrobenzenes, 2-bromonitrobenzene, 1,3-dinitrobenzene, 3-nitroaniline, 4-nitrophenol, 4-nitroanisole, etc.[22]. In aqueous alkaline solutions 4-nitrotoluene, 4-chloronitrobenzene, 4-nitroanisole, and 4-acetoxynitrobenzene are also reduced to the amines under the influence of $Fe_3(CO)_{12}$ (yield 60–92%).

Nitro-compounds are reduced catalytically with carbon monoxide to amines using $Rh_6(CO)_{16}$, $[Rh(CO)_2Cl]_2$, Rh_2O_3, $RhCl_3$, $Ru_3(CO)_{12}$, $Fe(CO)_5$, and copper salts as catalysts.

In the reduction of 4-nitroaniline, 4-nitrophenol, α-nitronaphthalene, and 2-ethylnitrobenzene by carbon monoxide in the presence of $Fe(CO)_5$ in benzene (100–200 atm, 200 °C) the yield of amines is low (less than 30%)[11]. The addition of hydrogen to carbon monoxide to give proportions of 1:1 does not increase the yield. In the presence of $Ru_3(CO)_{12}$ the reaction of nitrobenzene is more selective: at 160 °C and a pressure of 200 atm of the 1:1 $CO + H_2$ mixture the yield of aniline reaches 66%; the yield falls with decrease of the hydrogen concentration[24]. Up to 85–95% of aniline is formed in the reduction of nitrobenzene in the presence of rhodium compounds [$RhCl_3$, $Rh_6(CO)_{16}$, etc] at 150 °C and a CO pressure in the range 50–120 atm in aqueous pyridine or *N*-methylpyrrolidine[25]. In methanol the reaction proceeds less effectively—the yield of aniline does not exceed 25%. It has been shown[26] that, when copper salts are used as catalysts, nitrobenzene, 2-nitroanisole, 2-chloronitrobenzene, 4-nitrobenzoic acid, and nitromethane are reduced only in highly basic amines containing water. The reduction of nitrobenzene with carbon monoxide to aniline (1 atm CO, 85 °C) takes place to the extent of 50% in aqueous ethylenediamine, 16% in aqueous 1,2- or 1,3-propylenediamine, and 30% in aqueous NH_4OH. The rate of reduction of nitrobenzene increases with increase of the concentration of the copper salt[26].

IV. CARBONYLATION OF NITRO-COMPOUNDS

1. Synthesis of Ureas

The formation of substituted ureas has been frequently observed in the carbonylation of nitro-compounds. For example, prolonged heating of nitroparaffins with a stoichiometric amount of $Fe(CO)_5$ at 130 °C results in the formation of up to 20% of ureas[17]. Diphenylurea has been synthesised in 86% yield by carbonylating nitrobenzene in an aqueous solution at 200 °C and a CO pressure of 70 atm in the presence of SCO.[27] When nitrobenzene, 4-nitroanisole, 4-chloronitrobenzene, 4-nitrotoluene, and nitrocyclohexane were allowed to react with $Fe(CO)_5$ and phenylmagnesium bromide at 0 °C and in an inert gas atmosphere, the corresponding symmetrical *N,N'*-substituted ureas were obtained in yields of 60–99%.[28] *N,N*-Dimethyl-*N'*-phenylurea was synthesised in 86% yield from nitrobenzene and $Me_2NCOSNHMe$ at atmospheric CO pressure[29].

Substituted ureas can also be obtained by the catalytic carbonylation of nitro-compounds. Thus in the presence of $Rh_6(CO)_{16}$ as the catalyst in pyridine, nitrobenzene, 3- and 4-nitrotoluenes, and 4-nitrobiphenyl are converted into the corresponding symmetrical ureas in 70–80% yield at 150–200 °C and a pressure of 100–200 atm under the influence of the 25:1 $CO + H_2$ mixture[16]:

$$2ArNO_2 + 5CO + H_2 \rightarrow ArNHCONHAr + 4CO_2 .$$

When $Ru_3(CO)_{12}$ was used as the catalyst, the highest yield (54%) of *N,N'*-diphenylurea was obtained for the ratio of $CO : H_2 = 9 : 1$, the yield of urea decreasing with increase of the H_2 concentration[24]. Up to 80% of *N,N'*-diphenylurea is formed from nitrobenzene under the influence of the 10:1 $CO + H_2$ mixture in the presence of the 0.5% Pd/Al_2O_3-$FeCl_3$ catalyst[30]. The carbonylation of nitrobenzene in piperidine led to the isolation of *N*-pentamethylene-*N'*-phenylurea:

$$PhNO_2 + 5C_5H_{10}NH + 3CO \rightarrow PhNHCONC_5H_{10} + 2C_5H_{10}NCONC_5H_{10} + 2H_2O .$$

The reaction proceeds at atmospheric CO pressure in the presence of copper(I) salts. Nitrobenzene is reduced by piperidine, which is converted into the symmetrical *N,N'*-bispentamethyleneurea[31].

Palladium salts activated by triphenylphosphine and tetraethylammonium chloride permit the synthesis of substituted ureas by the catalytic carbonylation of aromatic nitro-compounds under mild conditions—at 90 °C and atmospheric pressure[32]. *N,N'*-Diphenylurea, *N,N'*-di(4-methylphenyl)urea, and *N,N'*-di(4-chlorophenyl)urea are formed respectively from nitrobenzene in aniline, from 4-nitrotoluene in 4-toluidine, and from 4-chloronitrobenzene in 4-chloroaniline. Carbonylation of 4-chloronitrobenzene in aniline leads to a

mixture of *N*-(4-chlorophenyl)-*N'*-phenylurea, *N,N'*-di(4-chlorophenyl)urea, and *N,N'*-diphenylurea; the carbonylation of the nitro-group may be accompanied by the carbonylation of the C–halogen bond, which leads to the formation of a further two products: the *N*-phenylamide of 4-nitrobenzoic acid and the corresponding urea 4-$PhNHCOC_6H_4NHCONHPh$.[33]

In the presence of $RhCl_3$ the carbonylation of nitrobenzene in aniline takes place at 190 °C and a CO pressure of 205 atm, *N,N'* diphenylurea being formed in 77% yield[34].

2. Synthesis of Urethanes

Urethanes are formed in the carbonylation of aromatic nitro-compounds in alcohols using palladium or rhodium compounds as well as metallic selenium as catalysts. The reaction is carried out for 0.3–20 h under a pressure of 50–400 atm at 150–230 °C:

$$ArNO_2 + 3CO + ROH \rightarrow ArNHCOOR + 2CO_2 \ .$$

In the presence of $RhCl_3$ the products obtained from nitrobenzene and 1-butanol are 4% of n-butyl *N*-phenylcarbamate, 34% of aniline, and 12% of a mixture of butylamines, while nitrobenzene and methanol give rise to 28% of methyl *N*-phenylcarbamate[35]. The addition of metallic iron[36] or $FeCl_3$ [37] to $RhCl_3$ (in proportions of 1:5) increases the yield of methyl *N*-phenylcarbamate to 54 and 81% respectively. The reaction can be carried out in toluene or in an excess of methanol[36,37]. In the presence of the cyclo-octadienylrhodium complex $[C_8H_{12}RhCl]_2$ activated with $FeCl_3$ (1:5), the yield of methyl *N*-phenylcarbamate is 47%.[38]

When $[Rh(CO)_2Cl]_2$ with added iron or copper chloride was used as the catalyst, phenyl *N*-phenylcarbamate was synthesised in 28% yield in phenol, in 1-butanol the product was n-butyl *N*-phenylcarbamate (82% yield), in methanol the product was methyl *N*-phenylcarbamate, while 1,3-dinitrobenzene in methanol gave rise to dimethyl 1,3-phenylenedicarbamate[39]. Ethyl *N*-phenylcarbamate is formed in a low yield (10%) on carbonylation of an ethanol solution of nitrobenzene containing $Rh_6(CO)_{16}$ and pyridine[15].

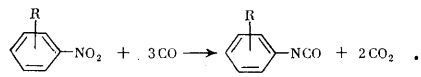
In the presence of the $PdCl_2$–pyridine (1:70) catalyst in ethanol, diethyl 2,4-tolylenedicarbamate was synthesised from 2,4-dinitrotoluene (yield 46–78%), while 1,5-dinitronaphthalene yielded diethyl 1,5-naphthylenedicarbamate. Carbonylation of 2,4-dinitrotoluene in phenol, pentyl alcohol, or ethylene glycol led to diphenyl or dipentyl 2,4-tolylenedicarbamate and ethylene 2,4-tolylenedicarbamate respectively[42–44]. The $Me(COO)_2Pd$–pyridine, $HRh(CO)(PPh_3)_3$, and PtO–pyridine catalysts are less effective.

In the presence of the 5% Pd/C and 5% Pd/Al_2O_3 heterogeneous catalysts activated with $FeCl_3$ carbonylation of nitrobenzene in methanol and of 2,4-dinitrotoluene in ethanol led to the synthesis of methyl *N*-phenylcarbamate (50%) [37] and diethyl 2,4-tolylenedicarbamate (89%) respectively[43,44]. In the presence of pyridine these catalysts are stable and can be used 10–16 times[45]. The analogous rhodium and ruthenium catalysts are less effective than the palladium catalysts (the yield of diurethane is 8–11%).[45] Apart from $FeCl_3$, copper and aluminium chlorides and copper bromide can be used as promoting agents. The carbonylation of ethanol solutions of nitrobenzene, 4-nitrotoluene, and 2,4-dinitrotoluene in the presence of the 5% Pd/C–$FeCl_3$–pyridine catalyst led to the synthesis of ethyl *N*-phenylcarbamate (yield 93%), ethyl *N*-(4-tolyl)carbamate (yield 92–95%), and diethyl 2,4-tolylenedicarbamate (yield 67–82%) respectively[45].

Selenium catalysts exhibit a high activity and selectivity in the synthesis of urethanes. In the presence of selenium and added aniline, trithylenediamine, diphenylurea, acetic acid, and potassium or sodium acetate, nitrobenzene and 2,4-dinitrotoluene in ethanol were converted into ethyl *N*-phenylcarbamate and diethyl 2,4-tolylenedicarbamate in 91–98% yield. The reaction proceeds rapidly (0.5 h) and under relatively mild conditions (50–70 atm, 170 °C).[46,47]

3. Synthesis of Aromatic Monoisocyanates

In 1967 Hardy and Bennett[48] reported for the first time that the carbonylation of aromatic nitro-compounds (nitrobenzene, 2- and 4-nitrotoluene, 3-chlorobenzene, and 3-trifluoromethylnitrobenzene) in benzene under a CO pressure of 500 atm and 190 °C in the presence of palladium and rhodium catalysts results in the formation of aromatic isocyanates (phenyl isocyanate, 2- and 4-tolyl isocyanates, 3-chlorophenyl isocyanate, and 3-trifluoromethylphenyl isocyanate respectively):



The reaction has a characteristic feature—the yield of the product passes through an extremum as a function of temperature, pressure, reaction time, and the amount of catalyst, which is due to the instability of the isocyanate under the conditions of the synthesis.

The catalyst plays a most important role in the formation of isocyanates from nitro-compounds and CO. A wide search has therefore been carried out for effective reaction catalysts. The following compounds were tested: CoI_2,[49] $Co_2(CO)_8$,[50–53] PdO,[54] $PdCl_2$,[55] $RhCl_3$,[56] $PdCl_2 + RhCl_3$ mixture[57], $Pd(PPh_3)_3.Cl_3$,[56] $Pd(C_5H_5N)_2Cl_3$, $Pd(quinoline)_2Cl_2$, $Pd(3,5\text{-dimethylpyridine})_2Cl_2$, and other pyridine complexes of palladium[58], as well as palladium, rhodium or ruthenium on a carrier (Al_2O_3, activated charcoal, $CaCO_3$, pumice, and $BaSO_4$).[59–63] The highest yields of phenyl isocyanate were obtained in the presence of $Co_2(CO)_8$ (46%), $Rh(PPh_3)_3Cl_3$ (40%), and $Pd(3,5\text{-dimethylpyridine})_2Cl_2$ (63%). Heterogeneous catalysts containing ruthenium, palladium, or rhodium on a carrier as well as the chlorides of these metals and PdO are catalytically relatively ineffective.

The activity of palladium and rhodium compounds increases when inorganic and organic compounds are added. In the carbonylation of nitrobenzene in the presence of $RhCl_3$ with added CoI_2 at 200 °C and a CO pressure of 100 atm, 21% of phenylisocyanate is formed[64]. In the presence of the $RhCl_3$–$CuBr_2$–V_2O_5 catalyst at 190 °C and 125 atm, the yield of the isocyanate is higher (45%), but the catalyst must be treated with carbon monoxide for 1–2 h under a pressure of 210 atm and at a temperature of 190 °C before the reaction[65]. The $PdCl_2$–V_2O_5 catalyst also requires a preliminary activation with carbon monoxide under pressure; In its presence the yield of phenyl isocyanate reaches 78–85% but the productivity of the catalyst is low (3–6 g of the product per gram of $PdCl_2$ per hour)[55]. Without preliminary activation with carbon monoxide, the selectivity of this catalyst is low (the yield of the isocyanate with respect to the reacted nitrobenzene is 58%)[66].

When 5% (relative to the weight of nitrobenzene) of phosphine, thionyl chloride, benzoyl chloride, sulphuryl chloride, or vanadium oxide chloride is introduced into the reaction system, and the $PdCl_2$–V_2O_5 catalyst not activated with carbon monoxide is used (190 °C, 145 atm), the yield of phenyl isocyanate is 45–70%.[66] Up to 68% of phenyl isocyanate is formed in the presence of $RhCl_3$–V_2O_5 with added $COCl_2$ or $POCl_3$.[67] In the presence of an excess of phosgene or thionyl chloride the carbonylation of nitrobenzene on the PdO,

$PdCl_2$, $PdCl_2$–$CoCl_2$, $TiCl_4$ and $SnCl_4$ catalysts under a CO pressure of 110–145 atm for 3–37 h leads to the formation of a mixture of isomers of dichloro- and trichloro-phenyl isocyanates with an overall yield of 10–28% instead of phenyl isocyanate[68]. Chlorophenyl isocyanates are also formed in the vapour-phase carbonylation of nitrobenzene in the presence of the catalyst comprising 5% $PdCl_2$–5% $CuCl_2$ on silicon carbide[69].

It has been suggested that aliphatic and aromatic nitriles, triphenylphosphine, quinoline, pyridine, alkyl and bromo-pyridines, and *N*-methylpyridinium iodide be used as organic activators. Patent data[57,70] concerning the activating effect of nitriles have not been confirmed; in fact the inhibiting effect of these additives has been noted[71]. When triphenylphosphine is added to PdO, $PtCl_4$, $RhCl_3$ and $PdCl_2$, the yield of phenyl isocyanate increases by a factor of 1.5–2.5 and amounts to 9–34%.[56,71]. The activity of $PdCl_2$ increases sharply after the introduction of quinoline, pyridine, and ethyl, methyl, dimethyl- and dibromo-pyridines: the degree of conversion of nitrobenzene and the yield of phenyl isocyanate increase by a factor of 4–8.[72] Triethylamine, urotropine, and 2,2-bipyridyl deactivated $PdCl_2$.[71]

The low activity of $PdCl_2$ when it is used without additives is due to the ease of conversion of this salt under the reaction conditions into a catalytically inactive form–the polynuclear carbonyl $[Pd(CO)Cl]_n$ [73,74] which decomposes in the presence of pyridine and is evidently converted into the catalytically active complex of the type $Pd(CO)_x(C_5H_5N)_yCl$:

$$\begin{array}{ccc} PdCl_2 & \xrightarrow{\text{pyridine}} & Pd(C_5H_5N)_2Cl_2 \\ \downarrow CO & & \downarrow CO \\ [Pd(CO)Cl]_n & \xrightleftharpoons{\text{pyridine}} & Pd(CO)_x(C_5H_5N)_yCl \end{array}.$$

Indeed the $[Pd(CO)Cl]_n$, which is inactive without additives, makes it possible to obtain phenyl isocyanate in 50% yield and with a nitrobenzene conversion of 64% in the presence of pyridine at 190° and a CO pressure of 100 atm. The $PdCl_2$–pyridine and $Pd(C_5H_5N)_2Cl_2$–pyridine catalysts give rise to similar results under these conditions[50]. When $PdCl_2$ is heated in chlorobenzene containing pyridine, the complex $Pd(C_5H_5N)_2Cl_2$ is formed readily and at an elevated CO pressure is apparently converted into $Pd(CO)_x(NC_5H_5)_yCl$. The catalytically active pyridine palladium carbonyl chloride complexes can be obtained also directly from $PdCl_2$ and pyridine under CO pressure[75].

Complexes having the general formula PdL_2Cl_2 [58] (L = pyridine and quinoline derivatives) are active in the synthesis of phenyl isocyanate and can be arranged in the following sequence in terms of the yield of the isocyanate: Pd(3,5-dimethylpyridine)$_2$Cl$_2$ (63%) >Pd(4-methylpyridine)$_2$Cl$_2$ (45%) >Pd(4-ethylpyridine)$_2$Cl$_2$ (38%) >Pd(pyridine)$_2$Cl$_2$ (28%) >Pd(2-methylpyridine)$_2$Cl$_2$ (16%) >Pd(2,3-dimethylpyridine)$_2$Cl$_2$ (11%) > Pd(quinoline)$_2$Cl$_2$ (10%) >Pd(2-methylquinoline)$_2$Cl$_2$ (5%) > Pd(2-ethylpyridine)$_2$Cl$_2$ (4%) >Pd(3,5-dibromopyridine)$_2$Cl$_2$ (0%), Pd(2,2-bipyridyl)Cl$_2$ (0%).

Electron-donating alkyl substituents in the β- and γ-positions in the ligand of this complex increase and those in the α-position decrease the degree of conversion of nitrobenzene and the yield of phenyl isocyanate. In the presence of palladium complexes with ligands more bulky than pyridine (quinoline and 2-methylquinoline) the yields of isocyanate are lower by factors of 2.8 and 5.6 respectively. When an electron-accepting substituent, for example, bromine, is introduced in the β-position of the pyridine ligand, nitrobenzene is not carbonylated.

Bulky substituents in the α-position of the pyridine ring should reduce, like electron-accepting substituents, the capacity for coordination, the former due to steric hindrance and the latter due to the decrease of the electron density at the nitrogen atom. Evidently equilibrium is established under carbonylation conditions between the catalytically active pyridinepalladium carbonyl chloride complexes and the inactive $[Pd(CO)Cl]_n$; the greater the capacity of the ligand for coordination to palladium, the greater the displacement of the equilibrium in the direction of the active complexes, and the higher the degree of conversion of the nitrobenzene and the yield of phenyl isocyanate. The introduction of an excess of the free ligand into the reaction mixture should also increase the amount of the catalytically active complexes and hence the degree of conversion of the nitro-compound and the yield of the isocyanate. Indeed the addition of a sevenfold excess of the ligand L to the PdL_2Cl_2 complexes and to the $PdCl_2$–pyridine system (molar ratio 1:2) increases their activity[58,71]. Under these conditions, the effect of the excess ligand is manifested particularly sharply for complexes which give rise to a small yield of the isocyanate in the absence of the free ligand. Thus the yield of phenyl isocyanate in the presence of the complexes Pd(2-ethylpyridine)$_2$.Cl_2, Pd(quinoline)$_2$Cl$_2$, and Pd(pyridine)$_2$Cl$_2$ increases by factors of 14, 4, and 1.7 following the addition of the corresponding ligand, while in the case of the complex Pd(3,5-dibromopyridine)$_2$Cl$_2$ the yield increases from 0% to 50%. The addition of the excess ligand to the palladium complexes with 4-methyl, 4-ethyl, and 3,5-dimethyl-pyridines results in an increase of the yield of phenyl isocyanate only by a factor of 1.1–1.6.[58]

2,2′-Bipyridyl forms stable chelate complexes which are evidently incapable of being converted into catalytically active complexes under the influence of carbon monoxide. The addition of 2,2′-bipyridyl therefore not only does not activate the complex Pd(2,2′-bipyridyl)Cl$_2$,[58] but actually fully deactivates $PdCl_2$ and the $PdCl_2$–pyridine catalyst[71].

The activity of $PdCl_2$ increases sharply in the presence of *N*-methylpyridinium iodide or the pyridine–MeI mixture capable of forming a salt[76], which makes it possible to synthesise phenyl isocyanate in a high yield (76–90%) at 160 °C and a CO pressure of 100 atm. The promoting effect of *N*-methylpyridinium iodide is evidently based on the formation of complexes preventing the conversion of $PdCl_2$ into the catalytically inactive state $[Pd(CO)Cl]_n$ and on the decomposition of the palladium carbonyl chloride already formed (the effect is similar to that of other ammonium salts)[74].

Among all the known catalysts of the carbonylation of nitrobenzene, the three-component catalysts of the type $PdCl_2$–pyridine–inorganic activator (V_2O_5, V_2O_4, MoO_3, and lanthanide molybdates) are the most active and selective in the synthesis of phenyl isocyanate.

The dependence of the activity of the $PdCl_2$–pyridine–metal oxide catalytic system on the nature of the transition metal oxides has been studied systematically[77] and it has been established that the effect of the oxide of the metal in each transition series of the Periodic System changes consistently: with increase of the number of the Group from III to V and VI, the degree of conversion of nitrobenzene and the yield of phenyl isocyanate increase. The maximum degree of conversion of the nitro-compound and the maximum yield of the isocyanate were obtained in the presence of the oxides V_2O_4 and V_2O_5 [Group (V)]in the first transition series, Nb_2O_5 and MoO_3 (Groups V and VI) in the second transition series, and Ta_2O_5 and WO_3 (Groups V and VI) in the third transition series. With further increase of the number of the Group, the activity in the metal oxide in the

first transition series falls: the degree of conversion of nitrobenzene and the yield of phenyl isocyanate also decrease.

All the metal oxides investigated can be divided into three groups in terms of the activity of the catalyst of the type of $PdCl_2$–pyridine: 1) oxides activating the catalyst (V_2O_4, V_2O_5, MoO_3, and also certain lanthanide molybdates, which increase the rate of carbonylation of nitrobenzene by a factor of 3–4); 2) oxides which do not have an appreciable influence on the activity of the catalyst (Cr_2O_3, Fe_2O_3); 3) oxides which reduce the activity of the catalyst—a large group which includes the remaining transition metal oxides[77,78].

In the presence of the best catalysts, for example $PdCl_2$–pyridine–MoO_3 (or V_2O_5, $La_2O_3.4MoO_3$, $Nd_2O_3.MoO_3$, and $Pr_2O_3.2MoO_3$) the selectivity of the synthesis of phenyl isocyanate at 185–200 °C and a pressure of 100 atm reaches 90–98%.[72,78] These catalysts are active also in the synthesis of substituted phenyl isocyanates: in their presence at 200 °C and a pressure of 100 atm, 2-, 3-, and 4-nitrotoluenes are converted into 2-, 3-, and 4-tolyl isocyanates in yields of 82 to 90% respectively, while 2-, 3-, and 4-chloronitrobenzenes, 3,4-dichloronitrobenzene, and 4-bromonitrobenzene are converted respectively into 2-, 3-, and 4-chlorophenyl isocyanates (yield 70–90%)[74,80–85], 3,4-dichlorophenyl isocyanate (83%), and 4-bromophenyl isocyanate (32%).

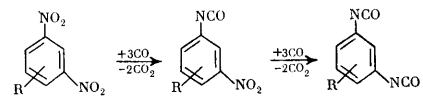
A whole series of monoisocyanates have been synthesised in yields less than 25% by carbonylating 2,4,5- and 2,4,6-trichloronitrobenzenes, 4-fluoronitrobenzene, 3-trifluoromethylnitrobenzene, 2-nitrofuran, 4-nitroanisole, 2-nitronaphthalene, and 5-nitropyrimidine in the presence of $PdCl_2$ and 5% Pd/Al_2O_3 at a high CO pressure (700–1000 atm)[59,61,70,79]. In the absence of activators the palladium catalysts are ineffective at low CO pressures; even in the presence of added activators (pyridine and metal oxides) it is impossible to synthesise isocyanates at atmospheric pressure. A single catalyst, namely $[RhCl(CO)_2]_2$–$MoCl_5$, active in the synthesis of isocyanates at a pressure of 1 atm, is known. Di-, tri-, and tetra-methylphenyl isocyanates are formed in its presence at 120 °C with a low selectivity (less than 50%) from the corresponding nitrobenzenes[86]. Carbonylation is accompanied by the reduction of the nitro-compounds to the amines.

4. Synthesis of Aromatic Di-isocyanates

Group VIII metal compounds have been patented as the main components of catalysts of the synthesis of di-isocyanates by the carbonylation of aromatic dinitro-compounds, but di-isocyanates have been obtained only using catalysts based on palladium and rhodium compounds. Thus the carbonylation of dinitronaphthalene, di(3-nitrophenyl)methane, and di(3-methyl-4-nitrophenyl)methane in the presence of the 5% Pd/Al_2O_3 catalyst results in the formation of a mixture of the corresponding mono- and di-isocyanates[87], while the carbonylation of 1,3-dinitrobenzene in the presence of $PdCl_2$ gives 14% of phenylene 1,3-di-isocyanate[88].

1,3-Phenylene di-isocyanate, 1,4-phenylene di-isocyanate, 2,4-tolylene di-isocyanate, 1,5-dimethyl-2,4-phenylene di-isocyanate, 1,3,5-dimethyl-2,4-phenylene di-isocyanate, and 1,2,4,5-tetramethylene-3,6-phenylene di-isocyanate have been synthesised in yields of 32–75% by the carbonylation of the corresponding 1,3- and 1,4-dinitro-compounds in the presence of the PdO, MoO_3, and Fe_2O_3/Al_2O_3–pyridine catalysts[89]. The yield of the di-isocyanate depends on the relative positions of the nitro-groups in the aromatic ring of the initial compound: di-isocyanates have been obtained from *meta*-dinitro-compounds in yields twice as great as those from *para*-dinitro-compounds.

The synthesis of di-isocyanates proceeds via the intermediate formation of mononitromonoisocyanates, which can be isolated in yields up to 50%:



The yield of di-isocyanates passed through an extremum as a function of temperature, CO pressure, amount of catalyst, and the concentration of the nitro-compound[90,91], which is apparently due to the instability of the di-isocyanates. The optimum conditions for the formation of di-isocyanates in the presence of different catalysts are various: 300 atm and 210 °C for the PdO, Fe_2O_3, and MoO_3/Al_2O_3–pyridine catalysts, 300 atm and 170 °C for the $PdCl_2$–pyridine–Fe_2O_3–MoO_3 catalyst, and 250 atm and 260 °C for the $Pd(pyridine)_2.Cl_2$–Fe_2O_3–V_2O_5 catalyst. Under conditions milder than the optimum conditions, mononitromonoisocyanates are formed, while under more severe conditions tar is produced[90,91].

Among the di-isocyanates, 2,4-tolylene di-isocyanate is of greatest practical importance and the principal data concerning the development of catalysts for the synthesis of di-isocyanates have therefore been obtained for the carbonylation of 2,4-dinitrotoluene. $Co_2(CO)_8$, NiI_2, and $Ni(quinoline)_2I_2$, which have been tested as catalysts of the carbonylation of 2,4-dinitrotoluene with carbon monoxide[92,93], give rise to the mononitromonoisocyanate in a low yield (less than 25%) instead of the di-isocyanate, when $Fe(CO)_5$ is used, isocyanates are not formed at all[10].

At 150–200 °C and a pressure of 175–300 atm the salts $PdCl_2$ and $RhCl_3$ are relatively ineffective in the absence of promoting agents. A number of organic compounds, introduced into the reaction mixture together with the solvent in amounts of 1–10 moles per mole of the catalyst, are used to activate palladium and rhodium chlorides. Compounds such as thiophen, thionaphthene, benzothiophen, dimethyl sulphoxide, diphenyl sulphoxide, sodium sulphite and thiosulphate[94,95], derivatives of furan[96], carbodi-imide[97], aniline[98], formamide and urea[99], cyanamide[100], as well as isocyanates[97], nitroso-compounds[101], and mononitriles[57,70] proved to be relatively ineffective. In their presence less than 10% of 2,4-tolylene di-isocyanate is formed. Activation of $PdCl_2$ by aromatic dinitriles increases the yield to 24%.[102] The best organic activator of $PdCl_2$ is pyridine, whose introduction into the reaction mixture increases the yield of 2,4-tolylene di-isocyanate to 50–68%.[90] Inorganic compounds have a weak activating effect on $PdCl_2$ and $RhCl_3$. Thus, when $PdCl_2$ with added iron, molybdenum, or vanadium oxides, the CuBr–MoO_3 and Fe_2O_3–MoO_3 mixtures, as well as the iron molyb-

dates $Fe_2Mo_7O_{24}$ and $Fe_2(MoO_4)_3$ are used, the yield of di-isocyanates formed from 2,4-dinitrotoluene is 10–20%.[55,65,103] The $PdCl_2$–MoO_3–$CuBr_2$ catalyst subjected to preliminary activation with carbon monoxide in the presence of phosgene makes it possible to obtain up to 40% of 2,4-tolylene di-isocyanate[65]. The attempts to activate palladium and rhodium chlorides with organoelemental derivatives of lead, silicon, germanium, boron, and copper, in the presence of which the yield of di-isocyanate does not exceed 32%, were relatively unsuccessful[54].

The joint use of organic and inorganic activators proved to be the most effective. When chromium, iron, or molybdenum oxides, the Fe_2O_3–MoO_3 mixture, or a mixture of iron (manganese) molybdates is added to the $PdCl_2$–pyridine catalyst, the yield of 2,4-tolylene di-isocyanate is 60%,[104–106] 75%, 85%, 92%, and 73–78%[103] respectively.

Apart from palladium and rhodium chlorides, certain other complexes of the above elements are used as catalysts for the synthesis of 2,4-tolylene di-isocyanates. The complexes $Pd(pyridine)_2(NCS)_2$, $Pd(pyridine)_2(NCO)_2$, $Pd(isoquinoline)_2.(NCS)_2$, $Pd(isoquinoline)_2Cl_2$, and $Rh(pyridine)_3Cl_3$ are relatively inactive without additives; in their presence the yield of the di-isocyanate does not exceed 10%.[107–109]. The complexes of $PdCl_2$ with dimethylcyanamide, dibenzylcyanamide, and diphenylcyanamide made it possible to obtain 4, 5, and 31% of di-isocyanate respectively[100,110]. In the presence of $Pd(pyridine)_2Cl_2$, $Pd(CO)_2Cl_2$, $Pd(CO)(pyridine)Cl_2$, $Pd(CO).(pyridine\ oxide)Cl_2$, $Pd(CO)(2,5\text{-lutidine})_2Cl_2$ and $Pd(CO).(isoquinoline)Cl_2$, 20–40% of 2,4-tolylene di-isocyanate is formed[109,111–114]. It has been suggested that the complexes $Pd(pyridine)_2Cl_2$, $Pd(isoquinoline)_2Cl_2$, and $Rh(pyridine)_3Cl_3$ be activated[108] with hydrogen, water, and formic, oxalic, hydrochloric, and boric acids, which, however, are relatively ineffective (the yield of di-isocyanate is not greater than 44%). Up to 57% of 2,4-tolylene di-isocyanate is obtained in the presence of $Pd(pyridine)_2Cl_2$–MoO_3 to which diphenyl carbonate has been added[115], while in the presence of added diarylurea the yield is only 23%.[116]

One of the most active and selective catalysts of the carbonylation of 2,4-dinitrotoluene with carbon monoxide is the $Pd(pyridine)_2Cl_2$–Fe_2O_3–V_2O_5 system (the yield of di-isocyanate is up to 90%).[117]

Metal chlorides have been tested as activators of the catalyst $Pd(isoquinoline)_2Cl_2$[118]; They can be arranged in the following sequence in terms of the yield of the di-isocyanate: $SbCl_5$ (2%) < $ZnCl_2$ (4–10%) < $PbCl_2$ (11%) < $BiCl_3$ (15%) < $CrCl_3$ (18%) < $MoCl_5$(20%) < VCl_4 (23%) < $TiCl_4$ (25%) < $FeCl_3$ (26%) < $HgCl_2$ (27%) < $ZrCl_4$ (28%) < $MnCl_2$ (32%) < $GeCl_4$ (56%). When Fe_2O_3–CrO_3, CrO_3, or $Cr(CO)_6$–MoO_3 is added to the complex $Pd(isoquinoline)_2Cl_2$, the yield of 2,4-tolylene di-isocyanate increases to 54–65%.[119,120].

The known heterogeneous catalysts of the carbonylation of 2,4-dinitrotoluene are less effective than the homogeneous-heterogeneous catalysts examined above[90,117]. The yield of di-isocyanate on the 9% $RhCl_3/C$-V_2O_5 catalyst in the presence of phosgene does not exceed 29%.[121] The complex $Pd(pyridine)_2Cl_2$ deposited on CrO_3/Al_2O_3 is still less selective (the yield of di-isocyanate is 15%).[122] Not more than 10% of di-isocyanate is formed in the presence of $Pd(pyridine)_2Cl_2$ adsorbed on the copolymer of divinylbenzene, styrene, and 4-vinylpyridine[123,124]. Less than 13% of 2,4-tolylene di-isocyanate has been obtained in the presence of a catalyst containing palladium or rhodium on Al_2O_3, silica gel, activated charcoal[97,125], or $CuBr_2/MoO_3$.[65,126] The heterogeneous catalyst PdO–MoO_3–Fe_2O_3/Al_2O_3 promoted with pyridine exhibits the highest activity and selectivity; in its presence 2,4-tolylene di-isocyanate is formed at a rate of 70 g/g Pd h and with a yield of 70%.[89]

V. THE MECHANISM OF THE TRANSFORMATION OF NITRO-COMPOUNDS UNDER THE INFLUENCE OF CARBON MONOXIDE

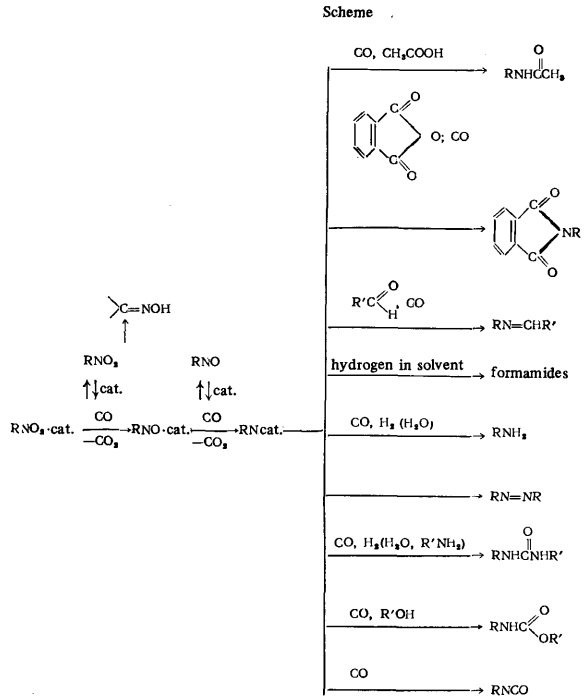
The mechanism of the interaction of CO with nitro-compounds has so far been inadequately studied and it would be premature to reach final conclusions. However, the available data make it possible to formulate a working hypothesis which explains the fundamental features of the process and enables one to outline ways of seeking effective catalysts and new reaction pathways.

In the synthesis of the majority of nitrogen-containing substances (amines, amides, imides, Schiff bases, azo-compounds, substituted ureas, and isocyanates) by the carbonylation of nitro-compounds, one of the intermediates is believed to be a nitrene in a free state or in the form of complexes. Nitrenes are highly reactive short-lived species which exist in the singlet or triplet (biradical) states. The formation of nitrenes is usually inferred from the final reaction products, but it is sometimes possible to detect them in the form of unstable complexes. Thus the nitrene complexes $(RN)_2Fe_2(CO)_6$, $(RN)_2Fe_2(CO)_7$, and $(RN)_2Fe_3(CO)_9$ were isolated in the reduction of aliphatic nitro-compounds with iron nonacarbonyl $Fe_2(CO)_9$; on heating they are converted into formamide and ureas[17]. Under the influence of $Fe_3(CO)_{12}$, nitrobenzene also gives rise to the nitrene complex $(RN)_2Fe_3.(CO)_9$, which is converted into aniline in the presence of a source of hydrogen[22].

The catalytic reduction of aromatic nitro-compounds in the presence of $Fe(CO)_5$, leading to the formation of amines and (or) azo-compounds (depending on the reaction conditions and the nature of the nitro-compound), evidently also proceeds via the intermediate formation of nitrene complexes with iron carbonyl. This is indicated by the formation of side products specific to the nitrene mechanism (carbazole, etc.)[11]. An analogy has been established between the catalytic (on $PdCl_2$) carbonylation of nitro-compounds and the reactions of aryl azides (a classical source of nitrenes): the selectivity of the synthesis of isocyanates increases with increase of the CO pressure and identical side products are formed[79,127]. Indirect evidence for the nitrene mechanism has also been obtained in the carbonylation of nitrobenzenes on rhodium catalysts. It was found (see Table) that the reaction pathway depends on the composition of the reaction medium: under identical conditions, in the presence of hydrogen in the gas phase, ureas are formed, in ethanol a mixture of an amine, urea, and urethane is obtained, in the presence of mono- or di-aldehydes Schiff bases and amides are isolated respectively, while in the presence of diphenylacetylene the products are the *N*-arylimides of 2,3-diphenylmaleic acid[15,16,20,21,25].

On the basis of the data available at the present time, the overall mechanism of the carbonylation of nitro-compounds can apparently be represented as follows. Under the influence of the reducing medium (CO), the metal complex catalyst is converted into one of its reduced forms, for example $[HFe(CO)_{11}]$,[23] $[RhCl(CO)_2]_2$,[86] and $Pd(CO)_x(pyridine)_yCl$,[58] and interacts with the nitro-compound and then with the nitroso-compound, forming a charge-transfer complex[86,128], in which an electron is transferred to the nitro-, or nitroso-group. As a result of deoxygenation within the coordination sphere, a nitrene complex is then formed, and depending on the reaction medium, the nature of the central atom, the ligands in the complex, temperature, and CO pressure is converted into the final products (see the Scheme).

Scheme



Thus the catalytic reduction of nitro-compounds by carbon monoxide makes it possible to obtain a whole series of valuable nitrogen-containing products. This field in the chemistry of nitro-compounds is still not adequately investigated, but the results already obtained indicate the great synthetic possibilities of the carbonylation methods. In the first place the development of an industrial method of synthesising isocyanates is at present of practical importance. There is no doubt about the importance of the above reactions for the theory of homogeneous and heterogeneous catalysis and also for nitrene chemistry.

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