

CHAPTER 1

Copyright
IIT Kharagpur

CHAPTER 1

1.1 Introduction :

Since the discovery of the reaction between carbon monoxide and caustic alkali leading to the formation of formates by Berthelot in 1855, carbon monoxide has gained steady importance in chemical industries as a cheap raw material for the syntheses of various compounds. It is, especially, during the last thirty years, that the importance of carbon monoxide has become well evident and a number of new reactions of carbon monoxide of immense industrial potentiality has been discovered where it combines with another organic reagent, entering the molecule of the organic compound in the form of carbonyl group. Thus aldehydes, ketones, acids, esters etc. are produced in which a new oxygen-containing functional group is present.

High pressure reactions involving carbon monoxide leading to the synthesis of various organic compounds of technical importance can be categorised as (i) reactions with hydrogen; (ii) reactions with alcohols; (iii) reactions with olefins or olefinic compounds and water or compounds containing active hydrogen atoms; (iv) reactions of carbon monoxide, acetylene and water or other compounds containing active hydrogen atoms; (v) reactions with ethers; (vi) reactions with water, alcohols and aldehydes or ketones; (vii) reactions with primary and secondary amines;

- (viii) reactions with aryl halides and water or alcohols ² ;
- (ix) reactions with organo-metallic compounds.

i) Reactions of carbon monoxide and hydrogen :

These reactions lead to the synthesis of various hydrocarbons (Fischer Tropsh Synthesis), methanol, higher alcohols and various other compounds when the reaction conditions such as pressure, temperature, catalysts etc. are changed. The catalyst employed are generally (either supported or unsupported) oxides or reduced metals of transition group elements.

ii) The direction of the reactions of carbon monoxide with alcohols depends to a considerable extent on the nature of the catalysts used. Generally formates or higher carboxylic acids or their esters are obtained. A large number of acidic catalysts have been tried, mainly inorganic acids (boric, arsenic, molybdic, uranic, phosphoric, ³ tungstic and titanio etc.), hetero-acids (molybdo-phosphoric, molybdesilicic, tungstosilicic, etc.) and the acid salts of these acids ⁴. These catalysts are frequently used on carriers (carbon, graphite, coke or silica gel) and are promoted with various metals, chiefly those of group VIII, and also copper, manganese, chromium, vanadium and some group IV metals (titanium, zirconium, and thorium).

The mixture of a metal carbonyl and their halides have also been shown to be effective catalysts by Nagpe and co-workers, ⁵

in the synthesis of carboxylic acids from carbon monoxide and alcohols under a temperature range of 250-270° and a pressure range of 200-300 atm. The synthesis of carboxylic acids and esters from carbon monoxide and alcohols at 200-300° and 200-400 atm. with Ni, Co and Fe catalysts were studied in detail by Bhattacharyya and co-workers⁶ who tested a number of Ni and NiI₂ catalysts deposited on silica gel and found them to be highly active. The activity of these catalysts followed the order nickel > cobalt > iron, iodide > bromide > chloride.

In the synthesis of acetic/propionic acid from carbon monoxide, methanol/ethanol under optimum conditions (temp. 180-230°C and pressures 200 atm.) in presence of NiI₂ supported on silica gel, (NiI₂ = 84.2%) Bhattacharyya and co-workers⁷ obtained 46% conversion of methanol and 37.3% conversion of ethanol to acetic and propionic acids respectively. In both the cases corresponding yields of methyl and ethyl esters were quite low. Using nickel carbonyl as the catalyst Hatta and Pino⁸ obtained a 66.5% yield of acetic acid from methanol and carbon monoxide at 230-250°C and 400-600 atm. The same synthesis reaction has also been successfully tried with a catalyst consisting of a silver halide or its mixture with another metal halide⁹ in the presence of water at 300°C and 100 atm. Koch and Neef^{10,11} synthesised carboxylic acids by the reaction of alcohols (or alkenes) with formic acid at atmospheric pressure in the presence of a large excess of concentrated sulphuric acid, which serves both to dehydrate the formic acid and alcohols with the formation of carbon monoxide and alkenes respectively and

also to catalyse the addition of carbon monoxide to the alkenes.

(iii) Reactions of carbon monoxide, olefins or olefinic compounds, and water or compounds containing active hydrogen atoms, lead to the synthesis of saturated carboxylic acids and their derivatives, lactones and alcohols. Nickel and cobalt carbonyls or their salts of nickel and cobalt which are converted into carbonyls during the reaction have been widely used as catalysts in such reactions.

12

Newitt and Momen obtained 46.6 % of propionic acid from ethylene, carbon monoxide and water in presence of reduced nickel and phosphoric acid, under a pressure of 150-400 atmosphere and a temperature of 250-300°C. It has also been found by them that ethanol, benzyl alcohol, ammonia and aniline, if used instead of water, can undergo similar reaction with ethylene and carbon monoxide.

13

Hardy obtained hydrocarbons as well as carboxylic acids by passing propylene, steam and carbon monoxide through phosphoric acid at 200°C and 200 atm. pressure.

The synthesis of propionic acid from ethylene, carbon monoxide and water has been thoroughly investigated by Bhattacharyya and co-workers in the presence of $\text{CoI}_2/\text{SiO}_2$ and $\text{NiI}_2/\text{SiO}_2(50:50)$ at 230-300°C and 300 atm. The yield of this acid after a residence period of 3 hours has been reported to be 7.3 % and 27.9 % respectively. Propionic acid has also been synthesised in 50-55 % yield

in the presence of cobalt propionate or butyrate in aqueous medium at 200-250°, 135-270 atm. and $C_2H_4 : CO = 1:3$.

When the formation of carboxylic acids from alkenes and carbon monoxide takes place in presence of alcohols, esters may predominate in the reaction products. Reppe and co-workers¹⁵ synthesized esters from alkenes, alcohols, and carbon monoxide in the presence of carbonyl forming metals. Hotta, Fino and their co-workers^{16,17} in the synthesis of esters from alkenes, carbon monoxide, and alcohols, made extensive use of catalysts based on cobalt. Chatterjee and co-workers¹⁸ used CoI_2 , NiI_2 and FeI_2 deposited on SiO_2 in the ratio 50:50. At 300 atm. and 230-300°, ethylene, carbon monoxide, and methanol gave methyl propionate in yields of 26.0, 26.0 and 27.1 % respectively. Ethyl propionate was obtained in yields of 25.1, 24.4 and 23.4 % when methanol was replaced by ethanol.

(iv) Reactions of carbon monoxide, acetylene and water or other compounds containing active hydrogen atoms, generally known as carbonylation of acetylene, lead to the synthesis of acrylic acid and its derivatives. This process may also be employed for any substituted acetylenes.

Reppe^{19,20} in 1939 synthesized acrylic acid and its esters from acetylene, carbon monoxide and water or alcohols. Other compounds with active hydrogen atom were found to react in a similar

way with acetylene and carbon monoxide. Thus amines gave acrylic amides, mercaptans gave acrylic acid thio esters or tautomeric thio acrylic esters.

The synthesis of acrylic acid and its esters from carbon monoxide, acetylene and water/alcohols in the presence of iodides, naphthenates and other salts of nickel, cobalt and iron has recently been investigated by Bhattacharyya and co-workers^{21,22} in detail. They have concluded from their experimental findings, that nickel salts exhibit superior catalytic activity over others.

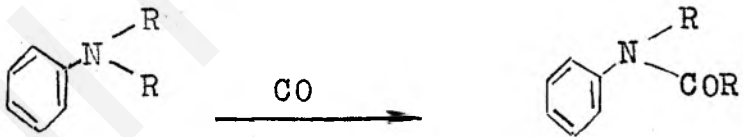
v) Reactions of carbon monoxide with cyclic and aliphatic ethers leading to the formation of carboxylic acids and esters have been investigated by Bhattacharyya and co-workers^{23,24}. They obtained a maximum yield of 23.3 % adipic acid from tetrahydrofuran and 28.9 % ethyl propionate from diethyl ether using iron, cobalt and nickel iodide supported on silica gel. Reppe²⁵ has also obtained quite good yields of esters from ether and carbon monoxide in presence of nickel ammonium complexes of phosphonium halides.

vi) Reactions of carbon monoxide with aliphatic aldehydes and water or alcohols leading to the formation of aliphatic hydroxy acids and its esters has been studied by Bhattacharyya and co-workers^{26,27,28} recently in great detail. They have published their findings on the synthesis of glycollic acid and lactic acid and their esters by utilising formaldehyde and acetaldehyde respectively. A patent by Leder²⁹ discloses a process which

involves the reactions, in the presence of a solvent and in the liquid phase, of carbon monoxide and a compound of the general formula RCH_2-CHO in which R represents H or an alkyl, aryl, cyclic or alicyclic radical, under super atmospheric pressure and at temperatures of 50-350°C.

The reaction of carbon monoxide with higher ketones has met with little success. It has been observed by Hardy³⁰ that when a mixture of acetone and water vapour was led with carbon monoxide through liquid phosphoric acid at 200 to 210°C a mixture of acetic and pivalic acids was formed in the molar ratio of 2:1.

vii) Primary and secondary amines react with carbon monoxide or a wide variety of metal carbonyls forming the N-formyl derivatives and ureas. Many of these reactions take place even at room temperature and pressure. The behaviour of tertiary amines on carbonylation is very interesting. Aliphatic tertiary amines on carbonylation are reported^{31,32} to give N, N-dialkyl formamides; the fate of the alkyl is not reported. Aryl tertiary amines on the other hand are reported to react as shown where R is an alkyl group.



It has been reported by Sampson³³ that hydrazine hydrate reacts with iron penta-carbonyl at 45° under a carbon monoxide

pressure of 900 atmospheres to give semicarbazide, while at 100° and 500 atmospheres both urea and semicarbazide are formed. However, totally different products are obtained from hydrazine hydrate and carbon monoxide in the absence of a catalyst³⁴.

viii) The conversion of aryl halides into aryl carboxylic acids using metal carbonyls or carbon monoxide has been attempted in order to devise a method of synthesizing the industrially important terephthalic acid. The literature on this subject is, however, extremely meagre. There is not even a single published paper on the synthesis of aryl carboxylic acids and its derivatives from aryl halides and carbon monoxide. Only a few patent literature could be traced.

A thorough literature survey reveals that the treatment of an aryl halide with nickel carbonyl, aqueous acid, and carbon monoxide at temperatures around 300°C and carbon monoxide pressure of about 600 atmospheres gives the corresponding aryl acid in around 30% yield. A patent by Bliss and Southworth³⁵ discloses the use of iron and cobalt carbonyls apart from nickel carbonyl in the above reaction. The carbonylation of aryl halides using a copper-zinc catalyst has been patented³⁶, but whether this involves a metal carbonyl intermediate is uncertain. It has been reported that if in the carbonylation of aryl halides instead of water, an anhydrous alcohol^{37,38} or lower ester³⁷, such as methyl formate is used as reaction medium, the corresponding esters are obtained.

ix) Reactions of carbon monoxide and organometallic compounds such as Grignard's reagent³⁹, metal alkyls have also been utilised to synthesise various aliphatic as well as aromatic compounds of industrial importance such as ketones, unsaturated hydrocarbons, alcohols, acids, aldehydes etc.

Mechanism of carboxylation reactions:

The mechanism of carboxylation naturally depends to a considerable extent on the catalyst used. In a discussion of the mechanism of the carboxylation of acetylene in the presence of nickel carbonyl, Reppe¹⁵ considers the possibility that the CO reacts with the iso-form of acetylene with the intermediate formation of methylene-keten which subsequently can react readily with water or alcohol to give acrylic acid or its esters :



The keten scheme cannot, however, explain either the reactivity of symmetrically disubstituted acetylenes or the formation of two reaction products.

40

A mechanism was proposed, according to which the reagent with labile hydrogen reacts with the metal carbonyl catalyst to give intermediate compounds which in turn react with alkenes to form new intermediate compounds in which one carbon atom in the alkene is joined directly to the central atom of the metal carbonyl.

41

When it was suggested that cobalt carbonyl hydride $\text{Co}(\text{CO})_3\text{COH}$ is formed as an intermediate product in the oxo-process and it was pointed out that the reaction of cobalt carbonyl with carbon monoxide precedes its reaction with a reagent containing labile hydrogen, Natta and Pino suggested a new mechanism for the carboxylation of alkenes with carbon monoxide in the presence of a catalyst based on metallic cobalt. According to their scheme, the active catalyst is the intermediate cobalt carbonyl hydride $\text{Co}(\text{CO})_3\text{COH}$. This adds on to the double bond of the alkene to form an intermediate compound which then reacts with the compound containing labile hydrogen.

42

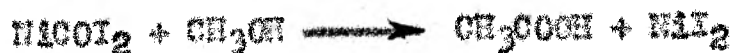
43

The formation of cobalt carbonyl hydride does not require the presence of large quantities of hydrogen, and small quantities of water or hydrogen sulphide are sufficient.

44

For carboxylation reactions in the presence of metallic nickel and nickel halides on carriers, Chattacharye proposed two basic schemes with intermediate metal carbonyl halide complexes or carbonium ions. The first scheme gives complexes of the type $\text{M}(\text{CO})\text{I}_2$ (where $\text{M} = \text{Co}, \text{Fe}, \text{Ni}$), which subsequently react with other reagents; CO may be added on with the liberation of halogen. For example,

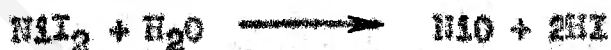
45



Here NiI_2 is regenerated.

In the reaction of Fe and Co halides under pressure, complexes of composition $\text{Co}(\text{CO})\text{I}_2$, $\text{Fe}(\text{CO})_2\text{I}_2$, $\left[\text{Fe}(\text{CO})_3\text{Br}_2 \right]_3$ etc. are formed. $\text{Co}(\text{CO})\text{I}_2$ is obtained at 200 atm. and 100° in the form of a dark red crystalline substance with a very high CO dissociation pressure even at room temperature. The analogous nickel complexes could not be isolated, although they may be formed as unstable intermediate products. The electronic configuration of Ni, Co, and Fe indicate that the stability of these complexes decreases in the order $\text{Fe} > \text{Co} > \text{Ni}$. On the one hand, the Ni complexes are the least stable and hence more reactive and on the other hand, iodide forms complexes more readily than bromide and chloride. The Scheme involving intermediate carbonyl halide complexes cannot, however, explain the activating action of traces of water on the catalyst. The other scheme, based on the carbonium-ion theory, is therefore more probable, in view of the acidic character of the catalysts on silica gel.

It was mentioned above that the presence of traces of water is necessary to preserve the activity of the NiI_2 catalysts. This is evidently required for the formation of HI according to the reaction



or, according to Reppe,



Traces of nickel oxide are in fact detected in the spent catalyst. The function of the HI may be to displace the extremely active CO from the nickel carbonyl with regeneration of NiI_2 :



or to activate other components of the reaction



The resulting carbonium ion reacts with CO :



Water, then reacts with the formation of acetic acid :



The H^+ then attacks another alcohol molecule and the reaction continues. The mechanism of other reactions involving the formation of acids and esters may be represented in this way. ^{47,48}

1.2 Scope of the Present Work :

Chlorobenzene, technically made by treating benzene with chlorine in presence of halogen carriers as iron, iodine etc. is utilised for the production of various compounds of commercial importance, as synthetic phenol, aniline and D.D.T. etc. Another important reaction of chlorobenzene and iodobenzene, disclosed in

a few patents, is that they react with carbon monoxide and water/ alcohol to produce benzoic acid or its esters. Unfortunately the details of the operational procedure, catalysts etc. are, as usual, not disclosed. A thorough search of literature revealed no published paper which reports in details the synthesis of benzoic acid and its esters by such a method.

In view of the ever increasing importance of benzoic acid and its esters, as evident from the following table showing the annual production and demand in U.S.A. and India, their syntheses from chlorobenzene and carbon monoxide seem to be of immense industrial potentialities.

U.S.A.

1917 - 219, 210 lbs. of benzoic acid

1920 - 743, 113 lb. of acid and 812, 193 lb. of sodium benzoate

Subsequent trend for the production of sodium benzoate is ;

1925 - 800, 841 lbs.

1933 - 1, 113, 449 lbs.

1945 - 3, 448, 000 lbs.

In India, however, the trend for the production of Benzoic acid is as given below.

1957	1958	1959	1960	1961
Qty. value	Qty. value	Qty. value	Qty. value	Qty. value
26 1.08	29 1.22	30 1.27	42 1.71	62 2.30

Qty. : in tons, Value : in rupees in lakhs.

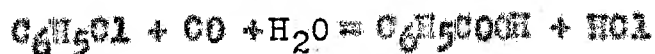
In India, the synthesis of benzoic acid or its esters from chlorobenzene, carbon monoxide and water or alcohols may successfully be exploited by industry as these raw materials or other materials required for their productions, are readily available. Carbon monoxide is the product of incomplete combustion of carbonaceous materials and its chief sources are the gases obtained from coal and coke by various methods. Chlorobenzene may be produced by the chlorination of benzene, which may be available in huge amounts in India. Methanol may be manufactured by reacting carbon monoxide and hydrogen at elevated pressures, or by oxidising hydrocarbons.

In view of this situation, the extensive and intensive investigation on the syntheses of benzoic acid and its ester such as methyl ester has been undertaken both in the presence and absence of catalysts. The results of the investigations have been embodied in the thesis.

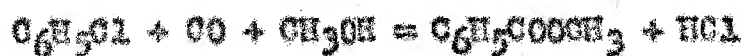
The thesis has been divided into seven chapters.

Chapter 2 and 3 deal with the experimental techniques and thermodynamics of the reactions.

Chapter 4 deals with the results on the synthesis of benzoic acid from chlorobenzene, carbon monoxide and water :



Chapter 5 deals with the synthesis of methyl benzoate :



Chapter 6 describes the probable mechanism of the reactions studied and finally the thesis concludes in Chapter 7 with a summary of the results of the investigations.

Copyright
IIT Kharagpur