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The application of high pressure operations to chemical processes has been one of the most outstanding contributions of chemical technologists to modern industry. In pressure, the chemist has discovered a valuable tool that has rapidly opened up vast fields of new development, particularly in the manufacture of ammonia, urea, methanol, polyethylene, gasolines, synthetic petrol and lubricating oils.

A number of other technically important high pressure reactions are known and are reported to be of economic significance. They include a number of hydrogenation reactions, oxidations reactions and various other synthesis processes. As examples may be cited the hydrogenation of unsaturated hydrocarbons, of resin oils, of nitrobenzene to aniline, of hydroxynitroparaffins to aminohydroxy compounds, of nitrobenzene or aniline to cyclohexylamine, of p-nitrophenol to p-aminophenol or aminocyclohexanol, of naphthalene to tetralin, of phenols and cresols to aromatic hydrocarbons, of alpha-naphthol to tetrol and tetralin, of phenol to methylcyclopentane and by-products, of fats to higher alcohols, of beta-naphthol to aci-tetralol, of beta-ar-tetralol to beta-decalol, of benzene to cyclohexane, of diphenyl ether to cyclohexane and cyclohexanol, of oxo-process aldehydes to mixed alcohols, of crotonaldehyde to n-butanol, of aldol to n-butanol and 1,3-butanediol, of 1,3-butanediol to n-butanol

and iso-butanol, of glycollic acid to ethylene glycol, of carbon monoxide to hydrocarbons, methanol and higher mono-hydroxy and polyhydroxy alcohols, of 1,4-butylene glycol to 1,4-butanediol, of furfural to furfuryl alcohol, of furfuryl alcohol to di- and tetrahydro derivatives, of propargyl alcohol to allyl alcohol and by-products, of 2-ethyl-2-hexenal to 2-ethyl-1-hexanol, of phenol to cyclohexanol, of methyl ester of rosin to hydroabietyl alcohol, and of butyraldehyde and ammonia to n-butylamine.

Among the oxidation reactions are oxidation of methane to formaldehyde and of ammonia to nitric acid. Hydration reactions include that of alpha-ar-tetralol to decalin and cis-decalol. Ammonolysis of propylene oxide to iso-propanolamines, and of resorcinol to m-aminophenol are carried out at high pressures. Isomerisation of low octane pentanes and hexanes, thermal alkylation of propane and butane, hydroforming of n-heptane to toluene, saponification of fatty acids to industrial soaps, vapour phase nitration of saturated hydrocarbons, dealkylation of diethylbenzene to monoethyl benzene, hydrolysis of bis (o-(chloromethyl) phenyl) carbonate to salicyl alcohol, and manufacture of nickel carbonyl from nickel and carbon monoxide are among other such processes.

Numerous other reactions are conducted at

high pressures. Among them may be mentioned the syntheses of toluene from methanol and benzene, of alkylbenzenes from benzene and olefins, of n-butanol from ethanol or acetaldehyde, of 1,4-butanediol and n-butanol from 1,4-butyne-1,3-diol, of higher alcohols from ethanol and acetaldehyde, of iso-butanol from isobutyl chloride, of butyraldehyde from crotonaldehyde, of aromatic aldehydes from benzene and carbon monoxide, of ketones and aliphatic aldehydes from hydrocarbons and carbon monoxide, of carboxylic acids and esters from carbon monoxide and a large number of organic compounds, of salicylic acid from sodium phenate and carbon dioxide, of 2-hydroxyethyl aryl ethers from ethylene oxide and phenol, of n-alkylaminophenols from amines and resorcinol, of polyamides from diamines and dibasic acids, of hydrazine hydrate from sodium hypochlorite and ammonia, of guanidine nitrate from ammonium nitrate and dicyanamide, of urea derivatives from carbon dioxide and aniline type compounds, and of benzoic and toluic acids from carbon dioxide and hydrocarbons.

A number of high pressure reactions utilise ammonia as a reactant. As examples may be cited the syntheses of o-chloroaniline from o-dichlorobenzene, of aniline and diphenylamine from monochlorobenzene, of methylamine and isobutylamine from methanol and isobutylamine, of ethylamines from ethyl alcohols or ethyl ether, of n-propylamine from n-propanol and hydrogen, of isopropylamines from acetone and hydrogen, of

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butylamines from butanol and hydrogen, of ethylene amines from 1,2-dichloroethane, of ethanolamines from ethylene oxide and of aromatic amines from phenols.

Other reactions of note are oxo-syntheses of alcohols, aldehydes and ketones, manufacture of trichloroethylene-vinyl chloride polymers, production of stable rosin oil from rosin, and preparation of alkali salts of naphthalene sulphonic acids.

In addition, a very large number of reactions, based on the chemistry of acetylene developed by Reppe and his coworkers¹⁻³ during World War II in Germany, are known. These relate to the preparation of vinyl ethers, alcohols, adipic acid and numerous other materials of industrial importance from acetylene and carbon monoxide. Also known are many reactions at high pressure which have^{as} yet only a theoretical interest and have not been used in industrial practice.

Among the old materials that have found new and exciting uses as a result of the development of high pressure chemistry is carbon monoxide^{4,5}. That carbon monoxide should interest the high pressure technologist is not surprising, considering that for synthetic methanol and higher alcohols, for synthetic fuel by the Fischer-Tropsch method, and for synthesis of carboxylic acids, carbon monoxide is an essential basic material.

The chemical reactivity of this important

industrial gas, that makes possible its participation in a wide variety of reactions, is generally attributed to the existence of free electrons in the molecule. Pauling⁶ has postulated the structure of carbon monoxide to be represented by resonance between



with structures (a), (b) and (c) contributing about equally to the normal state of the molecule. The various reactions of carbon monoxide under pressure may be grouped as follows :-

I. Reactions of carbon monoxide and hydrogen: These are summarised in Table No.I.

II. Reactions of carbon monoxide, acetylene and water or other compounds containing active hydrogen atoms,--the so-called carboxylation of acetylene which leads to the synthesis of acrylic acid and its derivatives. The development of this type of reactions was marked by the use of carbonyls of cobalt, nickel and iron as catalysts. These new reactions and new catalysts are of great interest and potential value. They permit the production of numerous derivatives of acrylic acid, such as esters, amides, acid anhydrides, thioesters, etc.

TABLE - I

Reactions of Carbon Monoxide and Hydrogen

Process	Catalysts	Promoters	Temperature	Pressure	Products
Fischer-Tropsch Synthetic	Fe, Co, Ni	ThO ₂ , MgO Al ₂ O ₃ , K ₂ O	150-350°C	1-30 atm.	Paraffinic and olefinic hydrocarbons varying from methane to waxes; small to large quantities of oxygenated compounds.
	Ru		150-250°C	100-1000 atm.	
Methanol Synthesis	ZnO, Cu, MnO Cr ₂ O ₃		200-400°C	100-1000 atm.	Methanol
Higher Alcohol Synthesis	ZnO, Cu, MnO Cr ₂ O ₃	alkali	300-450°C	100-400 atm.	Methanol and higher alcohols.
Iso Synthesis	ThO ₂ , ZrO Al ₂ O ₃	K ₂ O	400-500°C	100-1000 atm.	Saturated branched hydrocarbons

The process may also be employed for any substituted acetylenes.

III. Reactions of carbon monoxide, olefins or olefinic compounds, and water or compounds containing active hydrogen atoms: These reactions lead to the synthesis of saturated carboxylic acids and their derivatives, lactones and alcohols. The type of catalysts used is the same as that used for acetylene and acetylenic compounds.

IV. Reactions of carbon monoxide with water, alcohols, aldehydes, etc., to give saturated carboxylic acids: In this type

of reaction, which has been utilised for the work presented in this thesis, carbon monoxide reacts with water and/or an organic compound to produce saturated carboxylic acids and esters⁷⁻¹⁵. As examples may be cited the syntheses of formic acid from water¹⁶⁻³¹, acetic acid from methanol³²⁻⁴³, propionic acid from ethanol⁴⁴⁻⁴⁶, adipic acid from tetrahydrofuran⁴⁷, glycollic acid from formaldehyde and water⁴⁸⁻⁵⁶, lactic acid from acetaldehyde and water⁵⁷⁻⁵⁹, benzoic acid from chlorobenzene and water⁶⁰, iso-butyric acid from n- or iso-propanol and water⁶², propionoxyacetic acid from formaldehyde and propionic acid⁶³, chloroacetic acid from formaldehyde and hydrochloric acid⁶⁴, etc. In a number of similar reactions, substitution of water by alcohols produces corresponding esters of carboxylic acids^{65,66}.

Among the catalysts that have been used for such syntheses are: mineral acids like hydrochloric acid and sulphuric acid; acid salts like potassium acid sulphate and sodium acid phosphate; phosphoric acid, phosphates, phospho-molybdates; boron trifluoride, fluoboric acid and other complexes of boric acid with hydrofluoric acid; halogen gases, especially chlorine; activated carbon; heavy metal salts such as zinc and cuprous chlorides; oxides and silicates of chromium, molybdenum, tungsten, etc.; oxides of thorium, zirconium, titanium, aluminium, magnesium, vanadium, boron and alkali and alkaline

earth metals; aliphatic carboxylic acids like formic, acetic acids, etc.; ammonium halides; metal carbonyls with small quantities of halides; metallic halides and hydriodic acid; cobalt, iron, nickel in the reduced state, etc.

In the present work, the syntheses of glycollic acid from formaldehyde, carbon monoxide and water, of methyl glycollate from formaldehyde, carbon monoxide and methanol, and of ethyl glycollate from formaldehyde, carbon monoxide and ethanol, have been carried out in the presence of nickel, cobalt and iron, particularly their halides, as catalysts. Temperatures upto 275°C . and pressures upto 8,700 pounds per square inch have been used for the purpose. In addition, the thermal decomposition under pressure, uncatalysed and in the presence of iodide catalysts, has been studied in the case of carbon monoxide, paraformaldehyde, commercial formaldehyde solutions, methyl alcohol, ethyl alcohol, glycollic acid solution and ethyl glycollate. Some physico-chemical studies, based on the technique of differential thermal analysis, have been made on the iodide catalysts.

Part I of this thesis presents a short general introduction to the subject. Details of apparatus, reactants, catalysts, procedure, analysis of products and calculations have been grouped in Part II. The next three parts of the thesis

pertain to the synthesis of glycollic acid in the presence of nickel, cobalt and iron catalysts. Part VI and Part VII describe the syntheses of methyl glycollate and ethyl glycollate. Then follow decomposition studies and physico-chemical investigations based upon the technique of differential thermal analysis, forming Part VIII and Part IX, respectively, of this thesis. The thesis concludes with a short summary of the work done.