

Chapter - 1

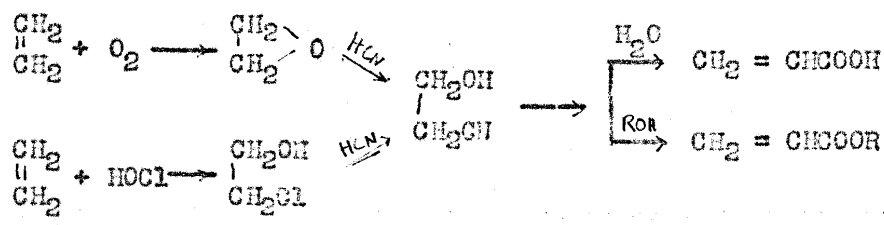
INTRODUCTION

Acrylic acid and its esters find wide industrial applications. They are used for manufacturing plastic sheet and moulding powders for signs, construction units and decorative emblems insignia; polymeric solutions are used as coatings, emulsion polymers are widely employed as textile, leather and paper finishes and in many processes in which the use of solvent might be hazardous or impractical. The solution polymers of acrylic esters find use as adhesives. The main advantage of these adhesives are that the films which are formed, transmit more than 90% of the visible light and are strong and flexible.

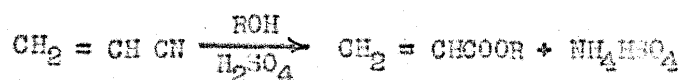
The demand for the acrylic acid and its esters has been great during the last decades and it promises a greater demand in future because of its manifold applications in industry.

Although a large number of methods of preparation of acrylic acid and its esters are reported in the literature, only a few have been exploited commercially. Some of the important methods are summarised below :-

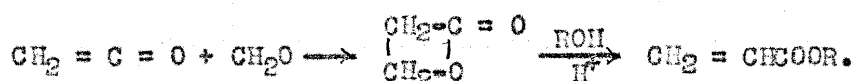
- (1) Ethylene cyanohydrin is allowed to react with water in acid medium to produce acrylic acid which is then converted to ester by direct esterification<sup>1</sup>.



(2) Acrylonitrile on hydrolysis in presence of sulphuric acid yields acrylic acid and in presence of sulphuric acid and alcohol gives acrylic esters :



(3)  $\beta$  - Propiolactone is obtained by reaction of ketene and formaldehyde. It may then be converted directly to acrylic esters by reaction with alcohols<sup>2</sup> :



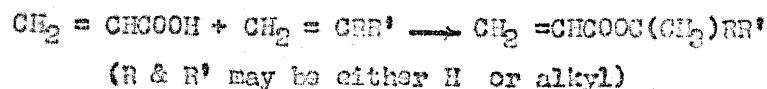
(4) The ester interchange process is also widely employed for the preparation of higher alkyl acrylates in presence of sulphuric acid as catalyst :



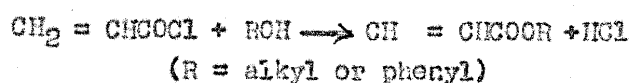
(5) Direct esterification of acrylic acid with alcohol in presence of sulphuric acid as a catalyst and benzene as a water entrainer, can also be effected in a batch process. This process may also be carried out on a continuous basis<sup>3,4</sup>. A vapour phase esterification over silica gel has also been reported<sup>5</sup>:



(6) Secondary and tertiary alkyl esters are made by the addition of acrylic acid to olefins<sup>6,7</sup>.



(7) Reaction with acrylyl chloride with alcohols and phenols yield acrylic esters<sup>8</sup>.

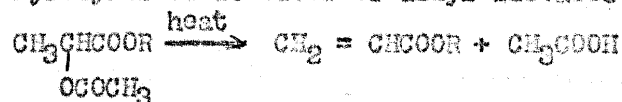


(8) From lactic acid esters:

(i) Dehydration of alkyl lactates<sup>9</sup>:



(ii) Pyrolysis of acetates of alkyl lactates<sup>10</sup>:



In recent years J.W. Reppe<sup>11,12</sup> discovered novel and newer methods of synthesising acrylic acid and its esters from acetylene, carbon monoxide and water or alcohols. He has developed two processes for his 'acrylic' synthesis; one is the stoichiometric route in which carbon monoxide supplier is a metal carbonyl and the reaction proceeds at milder conditions i.e. atmospheric pressure and 40°C. The other is the catalytic procedure in which acetylene, carbon monoxide and water or alcohols are allowed to react at elevated temperatures and moderately high pressures, in presence of carbonyl forming salts which serve as the catalysts. The stoichiometric procedure

is costly and hazardous whereas the catalytic procedure is economic and full of industrial promise.

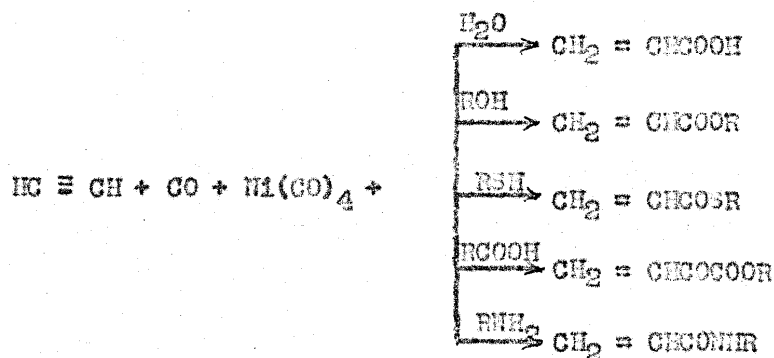
#### Scope of the work

Literature survey reveals that inspite of great technical importance of the acrylates, comprehensive data on the syntheses are not available. Most of the work was done in Germany under the direction of Reppe and was patented or kept as industrial secrets. Recently, Bhattacharyya and coworkers have published papers on the catalytic syntheses of acrylates. In view of the success achieved by them in the syntheses of methyl and ethyl acrylates from acetylene, carbon monoxide and methyl or ethyl alcohol and of great industrial potentiality of n-propyl and n-butyl acrylate, the work on their syntheses was undertaken by the present worker. The aim is to find out the optimum conditions necessary to get an appreciable yield of n-propyl and n-butyl acrylates, using various transition group metal salts as catalysts.

#### Literature survey

Following his success with vinylation, ethinylation and polymerisation of acetylene, Reppe in 1939 embarked upon an ambitious programme involving the reaction of acetylene with carbon monoxide. The outcome was the synthesis of acrylic acid which was formed when acetylene, carbon monoxide and water were allowed to react. Other compounds with active

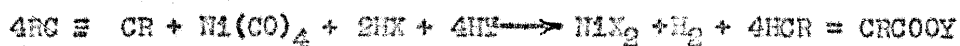
hydrogen atoms reacted in a similar way with acetylene and carbon monoxide and the transformations are shown below :



The reaction can be carried out either by the stoichiometric procedure with metal carbonyl or by purely catalytic method using carbonyl forming metals or their compounds as catalysts. Most of the work of Reppe is guarded by patents and the only sources of information being the F.I.A.F and D.I.O.S. reports.

#### Stoichiometric procedure

Reppe found that the reaction of acetylene with nickel carbonyl and aqueous hydrochloric acid and water at  $45^\circ - 50^\circ\text{C}$  gave acrylic acid, whereas in presence of alcohol, the corresponding acrylic esters were obtained. The reaction may be formulated as :

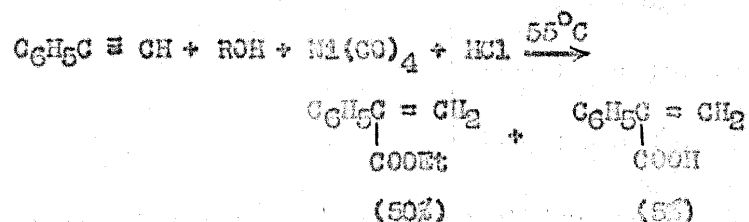


(where HX is an acid and HY is any compound containing reactive hydrogen atom).

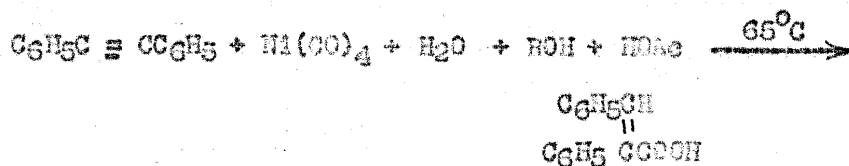
The carbonyl furnishes the carbon monoxide and the reaction was found vigorous and highly exothermic. Nickel

carbonyl was found to be the most active whereas the reaction fails completely with iron carbonyl.

The stoichiometric process with monosubstituted acetylenes has been studied by Jones and co-workers<sup>19</sup>. With phenyl acetylenes the reaction proceeded as follows :



They extended their studies to disubstituted acetylenes also and found the reaction to take the following course :



In this case, the decarboxylation of  $\alpha$ -phenyl cinnamic acid gave cis-stilbene showing that cis addition of -H and -COOH to the triple bond had taken place. The same workers extended their studies with  $\alpha,\beta$ -acetylene carbinols and acetylenic halides and some vinyl acetylenes. The results of their investigations on the stoichiometric procedure, the following conclusions were made :

(1) Depending on the nature of the acetylenic compound the reaction could either be quite fast or appreciably slow.

(iii) In these reactions cis addition of hydrogen and carboxyl group to the acetylenic compound occurred.

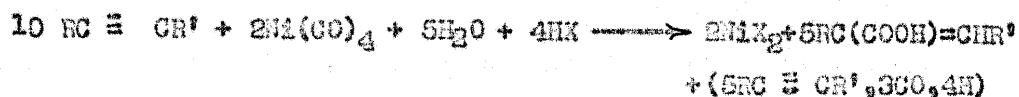
(iiii) The carbonyl group attacked that carbon atom which in acid, alkali or Hg catalysed hydration accepts the oxygen atom.

(iv) Each reaction was preceded by an induction period, which depended on the nature of the acetylenic compound, temperatures acid and the solvent.

(v) The nature of the solvent was relatively unimportant.

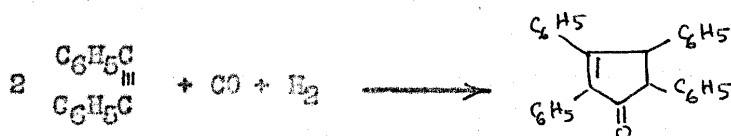
(vi) Under identical conditions the yield of the acid was much poorer with anhydrous reagents and even in alcoholic medium with acetic acid, *o*-methylene acid was the sole product. It was, therefore, concluded that water could participate as the HX component of the reaction, but the alcohols could not. In the absence of added water insitu formation of it from side reaction led to the formation of the acid.

(vii) The function of the acid was first thought to be the maintenance of a low pH value and that any acid would suffice. The failure of many organic acids indicated that the acid molecules rather than hydrogen atom participated in the reaction. Finally they correlated the above findings in the form of a general equation as follows :



(The last term representing the net composition of the very complex mixture of byproducts).

Mueller and McArtor<sup>23</sup> obtained 34% yield of ethyl- $\alpha$ -phenylcinnamate from diphenyl acetylene, nickel carbonyl and hydrogen chloride at 40°C in benzene-ethanol solvent. But, when dioxane and ethanol were used as solvents, the principal product was 2, 3, 4, 5 -tetraphenyl cyclopenta-2-en-1-one. The stoichiometry of the formation of this product may be represented as,



Most of the work in this field are guarded by patents.

Catalytic method of producing acrylates :

Acrylic acid and its esters can be produced by the reaction of acetylene, carbon monoxide and an alcohol in the presence of catalysts and at a temperature of 130-150°C and a pressure of 30 atm. Since under these conditions acrylic acid and esters are likely to polymerise, attempts were made by Reppe to find more active catalysts which would enable the reaction to proceed under milder condition.

As a result of his extensive investigations on the acrylate synthesis, Reppe found that nickel and cobalt salts, specially their halides and  $\gamma$ -nickel sulphide exhibited catalytic properties.

Reppe<sup>24</sup> disclosed that the inert solvent like



tetrahydrofuran, dioxan acetone etc. is a preferred medium. Various catalysts were tried among which nickel acetate<sup>25</sup>, nickel chloride activated by cupric chloride, a mixture of nickel carbonyl and iodine etc appeared to be more active.

Pino, Migliorina and Pietra<sup>63-64</sup> have studied the synthesis of methyl acrylate in a batch reactor using cobalt carbonyl as catalyst. At a reaction temperature of 90-100°C, and reaction pressure of 200-300 atm, besides methyl acrylate, number of products such as dimethyl succinate, dimethyl fumarate etc. have been detected.

In a recent patent by Jacobsen and Spathe<sup>26</sup>, the use of Palladium with iodine as a catalyst has been recommended for the synthesis of acrylates.

T.P.Forboth<sup>27</sup> dissolved acetylene in tetrahydrofuran and allowed it to react with carbon monoxide and water at 80 atm and 390°F in presence of nickel salts as catalysts to produce acrylic acid.

Recently, a patent by J.T.Dunn<sup>28</sup>, disclosed that the mixture of nickel halides and nitrogen containing phenol were catalysts for the acrylate synthesis.

Most of the literature in this field are patented. The most systematic and exhaustive work in the catalytic procedure for the syntheses of methyl and ethyl acrylates has been published by Bhattacharyya and Sen<sup>17,18</sup>. Of the various

catalysts studied by them nickel halides, particularly the iodide was the most active. Using nickel iodide on silica gel (Ni : SiO<sub>2</sub> = 50 : 50), they obtained maximum yield of 61.34% of ethyl acrylate and 47.26% of methyl acrylate, based on input acetylene.

Besides the stoichiometric and catalytic processes for the synthesis of acrylic acid and esters, a semi-catalytic process having the industrial potentiality has been evolved<sup>33-35</sup>. The essential feature of this process is that nickel carbonyl is used as the source of carbon monoxide initially, whereas at the later stages gaseous carbon monoxide itself serves as the source; the nickel compound functioning merely as catalyst. The conditions required are milder than that of catalytic procedure, which lessens the danger of explosive decomposition of acetylene.

#### Raw material supply :

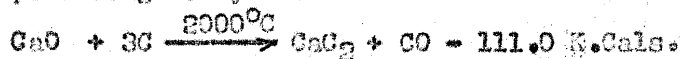
##### Acetylene :

For the preparation of acetylene derivatives it is essential to have a cheap and abundant supply of acetylene. The important methods for the manufacture of acetylene are given below.

##### (i) From calcium carbide :

It is the best known and most exploited process for generating acetylene. Calcium carbide, is manufactured in electric furnace by fusing together coke and limestone by means of an electric arc. This carbide reacts with water

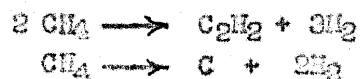
producing acetylene :



Although the raw materials are cheap, the process suffers from a drawback that it requires 10 to 11 Kwh of electrical energy per Kg of acetylene and high purity of carbon electrodes (25 to 50 Kg per metric ton of carbide). The acetylene so generated is relatively of high purity.

(ii) Arc Process :

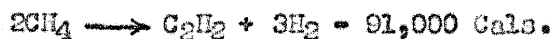
Natural gas, byproduct gas from coal hydrogenation or mixtures thereof are suitable for the manufacture of acetylene by arc process. The gas is compressed to 1.4 atm and passed through an electric arc. The electric arc transforms 7,000 Kw of electrical energy at 8,300 Volts and 850 amps d.c. into heat, producing a temperature of about 3000°C. The temperature of the gas coming out of the furnace is between 1600-2000°C. At this point the gas is quenched with water spray to about 150 to 200°C to prevent further cracking. The main reactions are,



The conversion to acetylene is about 50% per pass. Together with acetylene detectable amounts of diacetylene, methyl acetylene etc. are produced. These impurities are separated by scrubbing with oil or by low temperature fractionation<sup>36-38</sup>.

(iii) Partial combustion of methane (Sachsse Process) :-

Acetylene may also be prepared by thermal cracking of methane:



The energy required by this endothermic process is supplied by the partial combustion of methane with air or oxygen. In real practice 800 m<sup>3</sup>/hr of methane and 400 to 500 m<sup>3</sup>/hr of oxygen are heated separately to 500°C and then mixed and burned in a burner. The temperature of the gases reaches about 1400°C due to partial combustion, and is rapidly cooled to about 80°C by quenching with water. The yield of acetylene is about 31.0%.

The main advantage of this process is that it does not require electrical energy and it produces carbon monoxide and hydrogen in the ratio of 1 : 2, an ideal ratio for utilization in other synthesis.

A novel and possibly significant approach to the conversion of hydrocarbons to acetylene has been described by Schallus and Goetz<sup>39</sup>. Preheated hydrogen (1000°C) is led through an electric arc where it is further heated to such a temperature that it is partially or completely decomposed into its atoms. The hydrocarbon feed is then mixed with this plasma outside the arc where the recombination of hydrogen atoms to the molecular hydrogen provides the energy necessary for the cracking of the hydrocarbon to acetylene. It is claimed that in case of propane feed, 80% of the carbon content of the hydrocarbon is converted to acetylene, 7.3% to propylene, 9.0% ethylene and 3.6% methane.

Leutnar and Stokes<sup>40</sup> reported that using a low voltage argon plasma jet, they were able to convert methane to acetylene with yields of 80.0% based on the carbon in the hydrocarbon feed.

It has also been suggested that the use of shock-wave techniques, which provide temperatures as high as the arc and plasma process, may find commercial application for this type of processing<sup>41</sup>.

#### Carbon monoxide :

Carbon monoxide being the incomplete combustion product of carbonaceous material, has a very large availability as a cheap raw material<sup>42-43</sup>. Its largest sources are the gases made from coal and coke by various methods. The gases obtained are blue water gas (37-42.8% CO), producer gas (27-26% CO) and blast furnace gas (26-28% CO). Coke oven gas and the gas from carbide furnaces also contain carbon monoxide. Blue water gas is sometimes used as the source of pure carbon monoxide industrially. Almost pure carbon monoxide can be produced in large scale by simply blowing the water gas set with only CO<sub>2</sub> instead of steam.

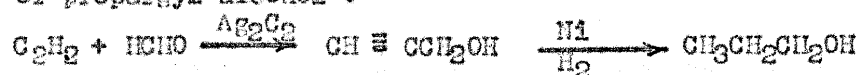
#### Alcohols

##### n-propanol :

Industrially it is obtained as a byproduct in the manufacture of ethanol by fermentation process. The crude ethanol obtained after fermentation on distillation yields fusel oil

(final runnings) which contains a mixture of higher alcohols mainly n-propyl, n-butyl and n-amyl alcohol.

A more recent method is by the catalytic reduction of propargyl alcohol :



### n-Butanol

Starch or molasses on fermentation with the micro-organism, *clostridium acetobutylicum*, whereupon acetone and n-butanol are obtained and they are separated by fractional distillation.

Synthetically it may be made from acetaldehyde as follows :-

