INTRODUCTION

The uses of organic esters in different fields of chemical industries need no elaboration. They are primarily used as solvents (in the extraction of naturally occuring substances and in the paint industries), as plasticizers, as perfuming and flavouring agents in the cosmetics and soap industries, as artificial food preservents and as medicines.

Considering the large scale uses of esters, a number of methods have been utilised from time to time for their syntheses. Of these some are industrially and economically feasible and others have only academic interest.

The most general method for the preparation of esters involves in the esterification of the respective acids and alcohols in liquid phase, using mineral acid as catalyst :

 $RCOOH + R'OH = H^+ RCOOR' + H_2O$

The extent of esterification in most cases is not satisfactory. In order to make the process more economical either, the alcohol to acid ratio should be kept very high, or, one of the reaction products, generally water, should be removed from the reaction phase. Maintenance of these conditions in most cases become very difficult and expensive too in industry. Vapour phase catalytic 'esterfication⁽¹⁻³⁾ is a definite improvement over the liquid phase process just described. Extensive research in this field has revealed that silica gel, zirconium dioxide, activated charcoal, potassium hydrogen sulphate, potassium and sodium alcoholate and difficultly reducible oxides $(Al_2O_3, ThO_2, CaO \text{ etc.})$ supported on silica gel, silicon carbide and alumina have pronounced catalytic activity. But much has to be done still, to push this process to the industrial arena.

Other compounds instead of acids can also be used for esterification. They are acid anhydride, acyl chlorides and ketenes. The reactions are shown below :

(a) R = CO R = CO R = CO R = COR = CO

(b) $RCOC1 + R'OH \longrightarrow RCOOR' + HC1$

(c) $CH_2 = C = 0 + ROH \longrightarrow CH_3COOR$

These reactions are irreversible and proceed very smoothly to completion. But as these compounds are rather costly, the methods involving them as reactants do not promise industrial significance.

For the preparation of methyl esters, methyl halides, dimethyl sulphate and diazomethane have been reported to be used conveniently as methylating agents.

Other methods for the syntheses of esters are :

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1) Dehydrogenation of alcohol^(4,5) over promoted copper catalyst :

 $2C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2$

2) Condensation of aldehydes in presence of alkoxide catalyst⁽⁶⁾:

 $2CH_3CHO \longrightarrow CH_3COOC_2H_5$

3) Direct esterification of acid amides or nitriles : $RCONH_2 + R'OH \longrightarrow RCOOR' + NH_3$ $RCN + R'OH + H_2O \longrightarrow RCOOR' + NH_3$

4) Action of silver salt of acids with alkyl halides : RCOOAg + R'X ----> RCOOR' + AgX

5) Ester-alcohol, ester-acid and ester-ester interchanges : R'COOR'' + ROH → R'COOR + R''OH R'COOR'' + RCOOH → RCOOR'' + R'COOH R'COOR'' + RCOOR → RCOOR'' + R'COOR

From the industrial standpoint, methods (1) and (2) have got immense potentiality and are being studied extensively, particularly in Russia.

The general trend at present in the field of chemical industry is to utilise the relatively cheap coal and petroleum chemicals for synthesising useful organic compounds. Extensive researches in this field by a number of workers led to the discoveries of some new and novel methods of synthesising organic esters by carbonylation of simple molecules such as alcohols, olefins, ethers etc., with carbonmonoxide (7-28). The outstanding contributions by Bhattacharyya and his school in this field have successfully established the following methods :

(i) The reaction of carbonmonoxide with alcohols (9-11) to form carboxylic acids and esters under high pressure in

presence of nickel, cobalt and iron halides as catalysts.

 $RCH_2OH + CO \longrightarrow RCH_2COOH$

 $RCH_2OH + RCH_2COOH \longrightarrow RCH_2COOCH_2R + H_2O$

(ii) Reaction of carbonmonoxide with alcohols under high pressure in presence of basic catalyst to give formates (12-14).

 $RCH_2OH + CO \longrightarrow HCOOCH_2R$

(iii) Reaction of carbonmonoxide with ethers to form esters and also acids as by-products (15).

 $ROR^{\dagger} + CO \longrightarrow RCOOR^{\dagger}$

(iv) Reaction of carbonmonoxide and ethylene with alcohols to form esters, corresponding acids being formed as by-products (18)

 $ROH + CO + C_2H_4 \longrightarrow RCOOC_2H_5$

(v) Reaction of carbonmonoxide and acetylene with alcohols/water to form esters/acids⁽¹⁹⁾.

ROH + C_2H_2 + $CO \longrightarrow CH_2$ = CHCOOR C_2H_2 + CO + $H_2O \longrightarrow CH_2$ = CHCOOH Besides these there are several other reactions studied leading to the formation of diabasic acids, hydroxy acids, etc. (20-22).

Scope of the present work

Though all the methods described above appear at the first sight to be very alluring, they are still at the research stage. In the present investigation the author suggests another general method for the synthesis of esters by the reaction of organic acids directly with olefins in presence of acid type catalysts. There are some definite advantages of this direct esterification method (organic acids + olefins) over the conventional commercial process where alcohols are used instead of the corresponding olefins :

(i) In the present days alcohols are prepared from the respective olefins and hence esterification by alcohols seems to involve a superfluous step when compared to direct esterification by olefins.

(ii) Another serious drawback of the commercial process is that the yield of ester appreciably falls when high molecular weight alcohols are used. It has been observed for example that about 6% butyl acetate is obtained when butyl alcohol is used, whereas the yield of ester is as high as 70%

in the case of ethyl acetate.

(iii) The direct esterification process is faster and may be made to completion if an efficient catalyst is selected.

(iv) The ester produced may be recovered more easily as the question of seperation of water does not arise. If a high olefin to acid ratio is used in the manufacturing process one may expect to get very pure ester directly.

With the ever increasing availability of olefins at a cheaper rates from cracked petroleum gases and other sources, this process will be a definite preference in near future. Over and above the operational advantages described above, there are reasons more than one to choose the three lowest homologous members of saturated aliphatic acids, acetic, propionic and n-butyric, for direct esterification with ethylene.

Firstly, the studies on this homologous series are sure to give a proper indication as to the dependence of esterification on the chain bulk of the acid.

Secondly, the studies on the lower acids will naturally be simpler.

Last but not the least, is the industrial importance of the esters derived especially from these acids. The impor-• tant uses of these esters are given below : Ethyl acetate :- As solvent, in the manufacture of photographic film, rayon, inks, lacquer etc.; as chemical in the manufacture of synthetic dyes, drug intermediates, ethyl acetoacetate etc.

Ethyl propionate :- In the preparation of food flavours; as fruit syrup; in the synthetic chemical industries; when it is admixed with ethyl or methyl acetate it can be used as a good solvent.

Ethyl butyrate :- As solvent for esters and ethers of cellulose and natural and synthetic resins, as an artificial flavouring agent.

Literature survey

This type of esterification reaction has been known for many years. But a thorough survey of the literature on this subject reveals only a few references, most of the work on the subject being guarded by patents. As early as 1933, Frolich and Young⁽²⁹⁾ reported the formation of esters from olefins and anhydrous aliphatic acids in presence of sulphuric acid catalyst. In other patent literatures⁽³⁰⁻³³⁾ it was found that the catalysts used were chlorides, bromides, phosphates and sulphates of aluminium, zinc, copper etc., relatively non-volatile inorganic acids e.g. sulphuric acid, phosphoric acid and the metal acid salts, and alkyl and aryl derivatives of these acids e.g. sodium

hydrogen sulphate, ethyl sulphonic acid etc. Acid phosphates of calcium, barium, strontium, manganese and boron (34) have also been tried as catalysts for direct esterification with ethylene, propylene and butylene in the temperature range of 100 - 150°C under pressures higher than atmospheric. In the vapour phase interaction of ethylene with acetic acid at the temperature ranging 150 - 350°C and under a pressure ranging 10 - 500 atmosphere, Lazier⁽³⁵⁾ used heteropoly acids as catalysts. Dreyfus⁽³⁶⁾ did not mention any catalyst used in his attempt of the synthesis of ethyl acetate from ethylene and acetic acid at a temperature of 350°C and under a pressure of 5 atmosphere. Evans et al⁽³⁷⁾ reported the formation of esters from olefins and organic acids under pressure in presence of sulphuric acid as catalyst. Altschul studied the reversible esterification of isobutylene with acetic acid, benzoic acid, p-nitrobenzoic acid. He studied also the reaction of trimethyl butylene with henzoic acid at 25°C and 35°C using sulphuric acid as catalyst and dioxane as solvent. 60% yield of sec-butyl acetate from 2-butene and acetic acid was obtained by Brooks (39) at a temperature of 115 - 120°C under pressure using 10% sulphuric acid as catalyst. In many of attempts for direct esterification boronfluoride, boronfluoride hydrate, hydrofluoric acid, mixture of boronfluoride and hydrofluoric acid, BF3, Et20 complex have been tried as catalysts⁽⁴⁰⁻⁴⁶⁾. Bearse and Morin⁽⁴⁷⁾ obtained 72% and 40% yield of isopropyl acetate and ethyl acetate respectively

from the corresponding olefins and acetic acid in presence of boronfluoride and hydrofluoric acid mixture as catalyst. A pressure of 1800 psig., a temperature ranging $150-170^{\circ}$ C and a residence period of 3 hours were reported to be the optimum values for the reaction of ethylene and acetic acid. With propylene the reaction was more rapidly accomplished. Very recently cation exchange resins have been reported to be good catalysts in the addition reaction of olefins with organic acids.

Raw material supply

The following raw materials have been used in the present course of investigation :-

- (a) Ethylene
- (b) n-Butyric acid
- (c) Propionic acid
- (d) Acetic acid

Ethylene :- Ethylene is the starting material for the synthesis of various organic compounds and several methods of its production are followed in industry. The most important method is the pyrolysis of petroleum fractions. Sometimes petroleum refinery gases contain as high as 40% ethylene. The recovery and purification of ethylene from the cracked gases play an important part in its manufacture. The methods are as follows :

(i) low temperature, low pressure straight fractionation,

(ii) low temperature, high pressure straight fractionation,

- (iii) low temperature absorption and fractionation,
 - (iv) hyper absorption, and
 - (v) solvent extraction.

The other sources of ethylene production are hydrogenation of acetylene, dehydration of alcohol or ether, controlled hydrogenation of carbonmonoxide⁽⁴⁹⁾, etc.

n-Butyric acid :- One of the most important commercial methods of production of n-butyric acid is the oxidation of n-butyl alcohol or butyraldehyde. About 90% yield of n-butyric acid is obtained when butyraldehyde is oxidised by air or oxygen over a wide range of temperature in presence of an efficient catalyst. Butyraldehyde in turn is manufactured from acetylene the steps being given below⁽⁵⁰⁾:

 $\begin{array}{c} \text{CH } \equiv \text{ CH} \xrightarrow{\text{Hydration}} & \text{CH}_3\text{CHO} \xrightarrow{\text{Condensation}} & \text{CH}_3\text{CHOHCH}_2\text{CHO} \\ \text{Acetylene} & \text{Acetaldehyde} & \text{Aldol} \end{array}$

 $\begin{array}{c} \text{CH}_{3}\text{CHOHCH}_{2}\text{CHO} \xrightarrow{\text{Dehydration}} \text{CH}_{3}\text{CH} : \text{CHCHO} \xrightarrow{\text{Hydrogenation}} \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CHO} \\ \hline \text{Aldol} & \text{Croton aldehyde} & \text{Butyraldehyde} \end{array}$

Fermentation of starchy materials by certain microorganisms produces n-butyric acid along with lactic acid. It may be obtained as a by-product in production of synthetic gasoline⁽⁵²⁾.

Propionic acid : It is menufactured from carbonmonoxide and ethyl alcohol when they are reacted in presence of borontrifluoride catalyst at pressures of 350 - 700 atmospheres and temperatures of 180 - 350°C. Ethylene, steam and carbonmonoxide can be reacted together in the similar manner to produce propionic acid. Another method of industrial production of propionic acid is the dehydrogenation of n-propyl alcohol and subsequent oxidation of propionaldehyde produced. The other sources of propionic acid are mentioned below :-

Natural gas, the Hydrocol version of Fieser-Tropsch process for synthesising gasoline, hard wood carbonization, various carbohydrates such as molasses⁽⁵¹⁾.

Acetic acid :- There are several methods for the manufacture of acetic acid. Bacterial oxidation of ethyl alcohol (quick vinegar process) produces acetic acid. Pyroligneous acid obtained from the destructive distillation of wood contains 5 - 6% acetic acid. Now-a-days acetic acid is manufactured synthetically from acetylene.

 $CH \equiv CH \xrightarrow{Hydration} CH_3CHO \xrightarrow{Oxidation} CH_3COOH$ Acetylene Acetaldehyde Acetic acid

Oxidation of lower hydrocarbons also gives acetic acid along with other by-products.