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## PREPARATION OF ESTERS OF ACRYLIC ACID

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This invention relates to the preparation of esters of acrylic acid. More particularly, the invention relates to the preparation of esters of acrylic acid from hydracrylic acid.

In the past, no completely satisfactory method for the preparation of esters of acrylic acid has been developed. It has been attempted to obtain these esters by direct esterification of acrylic acid with the appropriate alcohol. It has also been attempted to prepare acrylic acid esters by dehydration of the corresponding hydracrylic acid esters as described in the Bauer Patent No. 1,890,277. Poor yields of generally unsatisfactory products are obtained by such processes.

We have found that the disadvantages of the prior art processes for the manufacture of esters of acrylic acid may be overcome and acrylic acid esters of high purity obtained in good yield if hydracrylic acid is simultaneously esterified and dehydrated. The reaction may be represented by the following equation:

$$\begin{matrix} CH_2{-}OH \\ | \\ CH_2{-}COOH \end{matrix} + ROH \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH{-}COOR \end{matrix} + 2H_2O$$

The present invention will be described in greater detail in conjunction with the following specific examples in which the proportions are given in parts by weight unless otherwise indicated. These examples are merely illustrative, and it is not intended to limit the scope of the invention to the details therein set forth.

*Example 1*

| | Parts |
|---|---|
| Hydracrylic acid (4.4 mols) | 395 |
| Methanol (16.8 mols) | 538 |
| 85% phosphoric acid | 70 |
| Copper powder | 1 |

The phosphoric acid and copper powder are mixed together and placed in a reaction vessel suitably equipped with means for heating. The catalyst mixture is heated to about 155°–165° C., and a mixture of the hydracrylic acid and methanol is introduced under the surface of the heated catalyst. The hydracrylic acid and methanol are added at a rate of about 93 parts per hour, and reaction products distill off at the rate of about 79 parts per hour at a still head temperature of about 79°–81° C. The entire run takes about 10 hours.

Methyl acrylate is formed rapidly and boils out of the catalyst mixture with excess methanol, water, dimethyl ether formed by dehydration of part of the methanol, and small amounts of acrylic acid. 791 parts of product are collected,

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representing a 62.6% calculated minimum yield of methyl acrylate on the basis of 100% hydracrylic acid.

*Example 2*

| | Parts |
|---|---|
| Hydracrylic acid (46 mols) | 4140 |
| Methanol (142 mols) | 4516 |
| 95% sulfuric acid | 300 |
| Copper powder | 5 |

The sulfuric acid and copper powder are mixed together and placed in a vessel suitably equipped for heating. The catalyst mixture is heated to 135°–145° C. and a mixture of the hydracrylic acid and methanol is introduced under the surface of the heated catalyst. The acid and alcohol are added at a rate of about 412 parts per hour and the reaction products distill off at the rate of about 385 parts per hour at a still head temperature of about 80°–85° C. The entire run takes about 21 hours.

8039 parts of crude distillate comprising methyl acrylate, dimethyl ether, alcohol, acrylic acid and water, are collected and a 98.6% yield of methyl acrylate on the basis of 100% hydracrylic acid is obtained.

*Example 3*

| | Parts |
|---|---|
| Hydracrylic acid (13 mols) | 1170 |
| Ethanol (32.5 mols) | 1495 |
| Sulfuric acid (93% or 95%) | 128+ |
| Pyrogallol | 26 |

A converter unit comprising a 3-necked vessel to which is attached a feed device, a spent catalyst withdrawal device and a copper- and ceramic-packed column with catalyst inlet and reflux control is set up. The column is filled with concentrated sulfuric acid and the unit brought to a temperature of about 142° C.

A mixture of the hydracrylic acid, ethanol and 128 parts of sulfuric acid is added at a slowly increasing rate to the contents of the converter and a two-layered mixture of ethyl acrylate, ethanol, diethyl ether, water and acrylic acid distills off at a still head temperature of about 87°–88° C. This crude ethyl acrylate is collected in a vessel containing the pyrogallol polymerization inhibitor. After the reaction is well under way, spent catalyst is withdrawn continuously at such a rate that the level of catalyst in the converter is kept nearly constant and the total withdrawal per unit of feed is approximately twice the volume of its sulfuric acid catalyst.

The upper layer of the crude ester mixture comprises 1130 parts of ester, the lower layer 50

parts, representing a total yield of ethyl acrylate of 91.2% based on 100% hydracrylic acid.

*Example 4*

| | Parts |
|---|---|
| Hydracrylic acid (38.6 mols) | 3470 |
| Ethanol (77.2 mols) | 3551 |
| Sulfuric acid (93%–95%) | 380+ |
| Catechol | 77 |

The procedure of Example 3 is followed, the converter temperature being 142°–145° C. and the still head temperature 84°–86° C. A total recovery of 3270 parts ester in the upper layer and 60 parts in the lower layer represents a yield of 86.4% ethyl acrylate based on 100% hydracrylic acid.

*Example 5*

The crude ethyl acrylate from Examples 3 and 4 is purified as follows:

(1) The crude ester is subjected to rapid steam distillation to remove diethyl ether. When the vapor temperature starts to rise above 36 C., the reflux ratio is increased and the throughput decreased until a vapor temperature of 65° C. is obtained.

(2) The distillation column is now operated with no reflux and with high throughput until the vapor temperature rises above 85° C. when the removal of ester from the residue which contains acrylic acid and β-ethoxyethyl propionate is complete.

(3) The ethyl acrylate fraction from (2) is given a two-step counter-current washing with water, 1.2 weights of water being used for each unit weight of ethyl acrylate, about 10% excess over the theoretical amount needed to produce a raffinate of about 95–96% ethyl acrylate and an extract containing a maximum of ethanol for a minimum of water. The raffinate, which is the final, purified product, contains about 90% of the ester content of the ethyl acrylate fraction as 95–96% ethyl acrylate. The extract contains the rest of the ester and about 95% of the ethanol content of the fraction.

(4) The extract from (3) is fractionated to recover the ester and the ethanol therefrom. Ethanol and ethyl acrylate froms an ill-defined azeotrope with water which boils between 77° and 78° C. and is hence difficult to separate from the ethanol-water binary which boils at 78° C. The fraction distilling in the range 77°–78° C. which has a high density is rich in ester and the fraction with low density is rich in ethanol.

(5) The ester-rich fraction from (4) is combined with the ethyl acrylate fraction from (2); the ethanol-rich fraction is concentrated to about 92% ethanol by weight and recycled into the feed.

If desired, the crude ethyl acrylate may be treated before steam distillation with calcium carbonate to neutralize any free acrylic acid present.

*Example 6*

| | Parts |
|---|---|
| Hydracrylic acid (50 mols) | 4500 |
| N-butanol (100 mols) | 7400 |
| Phosphoric acid (85%) | 1500+ |
| Water | 500 |
| Catechol | 2.2 |

The procedure of Example 3 is followed, the feed being prepared by adding 1500 parts of phosphoric acid to the n-butanol, blending well, adding the hydracrylic acid with good stirring and finally adding the water. The feed is introduced into the converter when the temperature of the catalyst therein is about 160°–163° C. The vapor temperature in the head is kept at about 95° C.



11,800 parts of two-layered distillate are obtained, the n-butyl acrylate contents of which represent an 86% yield of the ester.

The crude n-butyl acrylate is purified by multistage washing to remove acrylic acid and some other impurities followed by vacuum distillation which removes the butyl ether present and separates the azeotropic fractions, i. e., (1) water, butyl ether, butanol, butyl acrylate boiling at 34°–36° C., (2) butanol, butyl acrylate boiling at 58° C., both at 54 mm. pressure, from each other and each from the butyl acrylate fraction boiling at 71°–72° C. An overall recovery of about 80% of ester of 90% purity is obtained.

The hydracrylic acid used in the preceding examples may be prepared according to the processes described in Patent No. 2,369,491, copending application Serial No. 462,050 filed October 14, 1942, now abandoned, and copending applications Serial Nos. 470,236, 470,237, both now abandoned and 470,238, now Patent No. 2,410,776, dated November 5, 1946 and all filed on December 26, 1942. Other methods of preparation of the acid may of course be substituted therefor.

Other esters of acrylic acid than the one described in the specific examples may be prepared. The methanol, ethanol and n-butanol may be replaced in the reaction mixture by other alcohols, such as propanol, isopropanol, isobutanol, hexanol, octanol, dodecyl alcohol, isoamyl alcohol, n-amyl alcohol, benzyl alcohol, phenylethyl alcohol, etc.

Our invention is not limited to the use of any particular dehydration catalyst. We may use an acid catalyst such as phosphoric acid, sulfuric acid, alkyl sulfuric acids (methyl, ethyl, butyl, etc.), zinc chloride, sodium bisulfate, boric acid, boric anhydride, phosphorus pentoxide, etc., a neutral catalyst such as alumina, bauxite, ferric oxide, titania, thoria, etc., or a basic catalyst such as calcium oxide, calcium hydroxide, magnesium oxide, borax, disodium sulfate, sodium methoxide, etc. In general we prefer to use an acidic catalyst such as phosphoric or sulfuric acid, but this preference is merely a specific embodiment of our invention and other dehydration catalysts of the types listed may be used to advantage.

At the beginning of the addition of the hydracrylic acid-alcohol mixture to the catalyst, an exothermic reaction of short duration occurs. During the initial stages of the reaction dialkyl ether is produced almost exclusively. Since the passage of alcohol alone through the heated catalyst produces an initial exothermic reaction and dialkyl ether, the catalyst may be preconditioned if it is desired to avoid the high temperatures caused by the exothermic reaction during the actual dehydration and esterification and to minimize the amount of ether produced. This preconditioning is effected by passing alcohol containing 1 mol of water per mol of acid catalyst through the catalytic mixture at the desired reaction temperature until the initial exothermic reaction is over and the alcohol begins to distill freely. The addition of alcohol is then discontinued and the catalyst mixture heated to a temperature of about 10° C. above the actual temperature to eliminate as much of the free alcohol remaining in the catalyst as is practicable.

A noticeable increase in the volume of the catalyst due to the accumulation of material in the feed is noted in nearly all cases. Since the hot

material remaining in the reaction vessel immediately following the termination of a run usually has a slight odor of acrylic acid formed either by direct dehydration of the hydracrylic acid in the feed without subsequent esterification or by the hydrolysis of the acrylate already formed, a small amount of the alcohol may be passed through the heated catalyst mass after the feed mixture has been added. By bringing about combination of the acrylic acid by-product with this extra alcohol, there results a definite decrease in catalyst volume and consequent increase in yield of acrylic acid ester.

In order that the hydracrylic acid alcohol feed mixture be homogeneous, it is sometimes desirable to add a little of the catalytic acid to the feed. In some cases, as in the case of the preparation of n-butyl acrylate, plain water will serve to homogenize the feed and at the same time aid in the final purification by azeotropic distillation. It is also possible to use a mixture of acid and water as a homogenizer.

The temperature at which the process of our invention is carried out is preferably the lowest possible temperature at which a continuous esterification or dehydration can be maintained. Obviously this temperature will not be constant but will depend upon the particular alcohol with which it is desired to esterify the hydracrylic acid, the particular catalyst employed, or other variable factors. In general, the dehydrating catalyst should be maintained at a temperature of about 130–170° C. More specifically, we prefer a temperature of from about 135–145° C. when sulfuric acid is the catalyst and a temperature of about 155–165° C. when phosphoric acid is the catalyst.

Various polymerization inhibitors may be used in our process. These may be admixed with the dehydration catalyst prior to the reaction or the ester produced may be collected in the presence of the inhibitor. Examples of suitable polymerization inhibitors include ferrous sulfate, copper, manganese and manganese salts, chromium and chromium salts, hydroquinone, pyrogallol, catechol, etc.

According to the equation representing the reaction of the present invention, the hydracrylic acid and alcohol should react in a molal proportion of 1:1. However, in order to obtain good yields of a pure product we have found it advisable to use an excess of alcohol. In general the proportion should be somewhere in the neighborhood of 2:1 to 4:1 alcohol to hydracrylic acid. When hydracrylic acid is esterified and dehydrated in the presence of ethanol and n-butanol, for example, the ratio of alcohol to acid should be about 2:1 to 2.5:1. On the other hand it is advantageous to use a 3- or 4-fold excess of methanol when methylacrylate is the product desired.

It is an advantage of the present invention that the simultaneous esterification and dehydration process may be carried out continuously. As the mixture of alcohol and acid is fed into the heated catalyst, reaction products and unconverted reactants are continuously distilled off. The unconverted reactants may be recycled. The spent catalyst is continuously withdrawn and it may be regenerated by blowing with air or by some other suitable means.

We claim:

1. The process of preparing an ester of acrylic acid which comprises passing a mixture including hydracrylic acid and an alcohol having the formula ROH in which R is a member of the group consisting of alkyl and aralkyl radicals through an acidic dehydrating catalyst heated to a temperature of about 130°–170° C., said catalyst being selected from the group consisting of concentrated sulfuric acid and concentrated phosphoric acid, and collecting the acrylic acid ester formed in the simultaneous esterification and dehydration reaction.

2. A process according to claim 1 in which an excess of alcohol is used.

3. A process according to claim 1 in which a polymerization inhibitor is mixed with the dehydrating catalyst.

4. A process according to claim 1 which is operated continuously, unconverted materials being recycled through the heated catalyst and spent catalyst being continuously withdrawn.

5. The process of preparing methyl acrylate which comprises passing a mixture including hydracrylic acid and methanol through a quantity of concentrated sulfuric acid containing powdered copper and heated to about 135°–145° C., and separating the methyl acrylate from the products which distill off from the heated catalyst.

6. The process of preparing ethyl acrylate which comprises passing a mixture including hydracrylic acid and ethanol through a quantity of concentrated sulfuric acid heated to about 142°–145° C., collecting the products which distill off from the heated catalyst in the presence of a polymerization inhibitor and separating pure ethyl acrylate from said products.

7. The process of preparing n-butyl acrylate which comprises passing a mixture including hydracylic acid and n-butanol through a quantity of concentrated phosphoric acid heated to about 160°–163° C., collecting the products, and separating pure n-butyl acrylate from said products.

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