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PREPARATION OF ACRYLIC ACID

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4 Claims. (Cl. 260—526)

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

I have discovered that acrylic acid may be prepared by the thermal dehydration at a reduced pressure of hydracrylic acid in the presence of a dehydration catalyst. The reaction involved may be represented as follows:

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

The following specific examples, in which the proportions of reactants are given in parts by weight unless otherwise indicated, are illustrated only and it is not intended that the scope of the invention should be restricted to the details therein set forth.

Example 1

	Parts
85% phosphoric acid	68
Powdered copper metal	1
Hydracrylic acid	250

The phosphoric acid and copper powder are placed in a suitably equipped vessel and dehydrated by heating under a progressively decreased pressure until the temperature at 16 mm. pressure is 150° C.

With the above-prepared catalyst at a temperature of 150° C. and a pressure of 50 mm., the hydracrylic acid is allowed to flow gradually under the surface of the hot catalyst. The catalyst mass begins to boil immediately and a clear water-white liquid distills off. The distilling head temperature slowly rises from 37°–38° C. to 78° C. at 50 mm. During the course of the run, the pressure is gradually decreased to 26 mm. and the catalyst temperature increased to 170°–180° C. Under these conditions, the distilling head temperature varies from 65°–80° C.

The rate of addition of the hydracrylic acid is regulated so that the total volume of catalyst in the reaction vessel remains as nearly the same as possible. The total time consumed in adding the feed is about 1½ hours at the rate of about 70–100 drops per minute.

227 parts, representing a 90.8% weight recovery of the total hydracrylic acid feed, of a clear colorless liquid having a very strong, sharp odor are obtained. The weight loss as acrylic acid polymer and material retained in the catalyst is 23 parts or 9.2% of the weight of the feed.

The clear colorless liquid has a 72.2% acrylic acid content, therefore 163.9 parts of pure acrylic acid are produced. If it is assumed that the hydracrylic acid starting material is 100% pure, the yield of acrylic acid therefrom is 82%. It is more accurate, however, to calculate the yield of acrylic acid from the weight of the ethylene cyanohydrin which was used in the preparation of the hydracrylic acid according to the process of copending application Serial No. 462,050 filed October 14, 1942, now abandoned, and Patent No. 2,369,491 dated February 13, 1945. This is 77.4%.

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Pure acrylic acid is separated from the 72.2% aqueous solution by fractional distillation at reduced pressures. The following fractions comprise the pure acid:

Pressure, mm. Hg.	Boiling point, °C.
40	65
25	55–56
20	50–51
14	45

Example 2

	Parts
85% phosphoric acid	49
Copper powder	2
Hydracrylic acid	568

The phosphoric acid and copper powder are placed in a suitably equipped vessel and heated to 160° C. The pressure is then reduced to 40 mm. and the hydracrylic acid is allowed to drip slowly under the surface of the heated catalyst. The distilling head temperature rises rapidly, remains at 80°–90° C. for the major part of the run, and then rises almost to 110° C. at the end. A pressure of 40 mm. is held for the major part of the run but it is decreased to 30 mm. toward the end. The temperature of the catalyst is held at 180°–190° C. throughout the run. The total time consumed in adding the hydracrylic acid is about 4 hours at the rate of 70–120 drops per minute. The product is collected at about the same rate.

The product is 510 parts of a clear, colorless liquid which corresponds to 89.6% of the weight of the hydracylic acid. The liquid is 77% acrylic acid, representing a yield of 392.7 parts pure acid or 86.4% based on 100% pure hydracrylic acid. This figure corresponds to a yield of 76% based on the ethylene cyanohydrin from which the hydracrylic acid may be prepared.

Example 3

	Parts
95% sulfuric acid	300
Powdered metallic copper	5
Hydracrylic acid	1581

The mixture of sulfuric acid and copper is placed in a suitably equipped vessel and heated to 141° C. The pressure is then reduced to 35 mm. and the hydracrylic acid is allowed to drip below the surface of the heated catalyst.

Shortly after the beginning of the reaction, the pressure is decreased to 25 mm. and is held at 23–26 mm. throughout the run. The temperature of the catalyst is held at 125°–135° C. during the first half of the run and raised to 140°–150° C. during the last half.

A total of about 5 hours is required for addition of all the hydracrylic acid at the rate of 400–500 cc. per hour for about 3½ hours and 200–300 cc. per hour for the remaining period of time.

1264.5 parts of clear, colorless liquid product, equivalent to 80% of the total weight of the feed, is obtained. The product is 81.4% acrylic acid or 1029.3 parts of the pure acid, a yield from assumed 100% pure hydracrylic acid of 81.3% and from ethylene cyanohydrin 76.1%.

The hydracrylic acid used as starting material in the preceding examples was obtained from ethylene cyanohydrin according to the process disclosed and claimed in Patent No. 2,369,491 issued February 13, 1945, and copending application Serial No. 462,050 filed October 14, 1942, but hydracrylic acid from any other source may be used in the process of the invention.

Dehydration catalysts other than phosphoric and sulfuric acids may be used. For example, boric acid, zinc chloride, benzene sulfonic acid, and p-toluene sulfonic acid are equally as effective. Similarly, the copper powder may be replaced by other polymerization inhibitors such as bronze powder, chromium, manganous salts, hydroquinone, catechol, ferric sulfate, etc., without departing from the spiirt of the invention.

The dehydration reaction is carried out below atmospheric pressure to avoid polymer formation and thereby provide good yields of acrylic acid. Pressures below 100 mm. of Hg and especially around 20–60 mm. of Hg are preferred.

The dehydration temperature giving best results will vary somewhat with the particular catalyst employed, but in general I have found it advantageous to carry out the reaction at temperatures of between about 130° C. and 190° C.

It is an advantage of the present invention that hydracrylic acid may be continuously dehydrated to produce good yields of acrylic acid. Moreover, the water-white product obtained which contains no impurity other than about 20% water may be used for many purposes without further purification.

I claim:

1. In the process of preparing acrylic acid by dehydration of hydracrylic acid, the steps which comprise adding the hydracrylic acid gradually to an acid dehydration catalyst maintained at dehydration temperatures of between about 130° to 190° C. under pressures below 100 mm. of Hg to form an aqueous solution of acrylic acid and distilling off the aqueous acrylic acid as formed, the rate of addition of hydracrylic acid being so regulated that the total volume of catalyst remains nearly constant.

2. In the process of preparing acrylic acid by dehydration of hydracrylic acid, the steps which comprise adding the hydracrylic acid gradually to an acid dehydration catalyst maintained at dehydration temperatures of between about 130° to 190° C. under pressures below 100 mm. of Hg to form an aqueous solution of acrylic acid, distilling off the aqueous acrylic acid as formed, the rate of addition of hydracrylic acid being so regulated that the total volume of catalyst remains nearly constant, and recovering pure acrylic acid from the aqueous solution thereof by fractional distillation at reduced pressures.

3. The process of preparing acrylic acid which comprises adding hydracrylic acid gradually to concentrated phosphoric acid maintained at a temperature of about 150°–190° C. and a pressure of about 26–50 mm. of Hg in the presence of powdered metallic copper and separating the aqueous acrylic acid formed from the catalyst by distillation.

4. The process of preparing acrylic acid which comprises heating a mixture of concentrated sulfuric acid and powdered metallic copper to about 140° C., reducing the pressure to about 35 mm. of Hg, gradually adding hydracrylic acid, controlling the temperature and pressure throughout the addition so the temperature remains between 125° C. and 150° C. and the pressure between 23 mm. and 26 mm. of Hg, and separating the aqueous acrylic acid formed from the catalyst by distillation.

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