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TREATING PROPIOLACTONE WITH HEATED PHOSPHORIC ACID TO PRODUCE ACRYLIC ACID

Arthur W. Schnizer and Edward N. Wheeler, Corpus Christi, Tex., assignors to Celanese Corporation of America, New York, N.Y., a corporation of Delaware
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This invention relates to the production of unsaturated acids and relates more particularly to the production of acrylic acid.

It is an object of this invention to provide a new and highly efficient method for the production of acrylic acid from propiolactone.

Other objects of this invention will be apparent from the following detailed description and claims.

In accordance with one aspect of this invention, propiolactone is brought into contact with heated phosphoric acid to produce vapors of acrylic acid. While we do not wish to be bound by any particular theory we believe that the propiolactone forms a complex or adduct with the phosphoric acid (e.g. an adduct of the formula $(\text{HO})_2\text{PO}-\text{O}-\text{CH}_2\text{CH}_2\text{COOH}$), and that the complex then breaks down thermally to produce acrylic acid and regenerate the phosphoric acid.

In a preferred form of the invention liquid propiolactone is forced continuously into contact with a hot liquid mass of the phosphoric acid while vapors of acrylic acid are taken off continuously overhead. Best results are obtained when the phosphoric acid is maintained at a subatmospheric pressure since this makes possible the use of lower temperatures in the process. The use of reduced pressure also results in a lower concentration of acrylic acid in the reaction mass which reduces the tendency of the material to polymerize. Pressures below about 200 mm. Hg A are particularly suitable. Economically it is not advantageous to reduce the pressure below about 20 mm. Hg A, because of the difficulty of subsequently condensing the acrylic acid vapors at such pressures, if condensers operating at about room temperature are employed.

It is preferable to operate under such conditions that the difference between the temperature of the phosphoric acid and the boiling point of the acrylic acid at the operating pressure is at least about 50° C.; this makes for rapid flashing of the acrylic acid vapors from the mass of phosphoric acid. The temperature is advantageously about 140° C., preferably above about 150° C. Since phosphoric acid becomes increasingly corrosive to ordinary reactor materials as the temperature increases, it is desirable to operate at temperatures below about 220° C., preferably below about 180° C.

The choice of the best feed rate depends on the temperatures and pressures used; desirably it is such that the acrylic acid is volatilized at a rate approximately corresponding to the rate of feed, so that there is little if any buildup of acrylic acid in the phosphoric acid during operation. For example, a preferred rate of feed is less than 0.4, preferably less than 0.2, gram of propiolactone per gram of H_3PO_4 per hour.

It is advantageous to introduce a stream of liquid propiolactone blow the upper level of a thoroughly agitated mass of the phosphoric acid; thorough agitation can be obtained, for example, by the use of a mechanical stirrer.

To obtain highest purity acrylic acid it is desirable to use relatively pure propiolactone in the feed. For example, when propiolactone of 98% purity is used the product contains 96%, or more, of acrylic acid, without

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further purification. However, the propiolactone need not be of high purity. For example, monomeric propiolactone containing appreciable proportions of acetic acid, acetic anhydride or other acetoxy compounds, or propiolactone polymers, may be used. Acetic anhydride in the feed is primarily hydrolyzed to acetic acid during the reaction while propiolactone dimer and other propiolactone polymers are converted to acrylic acid.

For most purposes it is desirable that acrylic acid contain little if any water. We have found that the water content of the product depends in large measure on the water content of the phosphoric acid; thus, by reducing the water content of the phosphoric acid until its empirical composition is about 100% H_3PO_4 , or $\text{P}_2\text{O}_5(\text{H}_2\text{O})_3$, we can reduce the water content of the acrylic acid vapors to a very low value. A suitable phosphoric acid for this purpose may be prepared conveniently by removing water from aqueous phosphoric acid (e.g. commercial phosphoric acid containing 70–75% phosphoric acid), as by evaporation while heating under subatmospheric pressure. The phosphoric acid in the dehydrated product is present as a mixture of orthophosphoric acid, pyrophosphoric acid and higher molecular weight phosphoric acids, depending on the extent of dehydration. Thus, the dehydration may be continued until there is much less water present than is represented by the empirical formula for orthophosphoric acid, $\text{P}_2\text{O}_5(\text{H}_2\text{O})_3$. The dehydration may proceed further during continuous operation with the result that the catalyst may tend to become more viscous and, eventually to become a difficultly handled mass, solid at the reaction temperature. We have found that the catalyst can be maintained in a liquid condition by the continual addition of water thereto. This is conveniently effected by continual removal of a portion of the catalyst (e.g. about 5 to 20% at daily intervals) and replacement thereof with liquid phosphoric acid (e.g. of 50 to 85% concentration) or by the incorporation of a small amount of water (e.g. ½%) into the propiolactone feed. Alternatively, water can be added directly to the thickened catalyst. Conveniently the liquid phosphoric acid used for the above-mentioned continual replacement is obtained by adding sufficient water to a portion of the thickened catalyst to thin said catalyst to a filterable viscosity; we have found that this causes any carbonaceous impurities present to agglomerate, after which the catalyst can be filtered and reused.

To prevent polymerization of the acrylic acid in the reaction vessel it is desirable to have present a polymerization inhibition. Such materials are well known in the art. For example, copper powder may be mixed with the phosphoric acid, or the walls of the reaction vessel may be made of copper, which acts as an inhibitor.

This invention makes it possible to produce acrylic acid of high purity directly at very high efficiencies. The catalyst can be used for long periods without loss of its activity. In contrast to the known process of making acrylic acid from propiolactone by polymerization followed by thermal depolymerization the process of this invention requires only a single step, with an attendant saving in equipment for processing and handling the reactants and a reduction in losses of material. In addition, the acrylic acid produced by the pyrolysis of propiolactone polymer is generally contaminated with propiolactone dimer which must be removed by distillation; the present invention makes it possible to avoid such distillation, since, as previously discussed, propiolactone dimer is decomposed by the phosphoric acid catalyst.

To insure maximum recovery of the acrylic acid produced it is desirable to prevent polymerization of the acrylic acid. As another aspect of this invention, we have found that polymerization results upon the liquefac-

tion (condensation) of vapors of uninhibited acrylic acid. We have also discovered that such polymerization may be prevented by maintaining the vapors in superheated condition, preventing liquefaction until the superheated vapors have been mixed with a volatile polymerization inhibitor, and then condensing the vapors and inhibitor together. Particularly suitable inhibitors are phenolic materials such as hydroquinone and the monomethyl ether of hydroquinone. An especially effective method for supplying the inhibitor is by flashing a liquid solution thereof in acrylic acid into the superheated vapors of acrylic acid. For example, a 0.1 to 10% solution of the volatile inhibitor in acrylic acid may be introduced into the superheated vapors of acrylic acid in an amount sufficient to provide a concentration of about 10 to 200 p.p.m. of inhibitor in the resulting mixture. Thereafter the mixture can be liquefied, as by cooling, or by increasing the pressure.

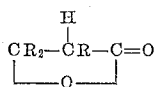
The following example is given to illustrate this invention further.

Example

Aqueous phosphoric acid (of 85% concentration) was dehydrated by heating it, in known manner, until its empirical composition was 100% H_3PO_4 . 2% based on the weight of the dehydrated phosphoric acid of copper powder was added and then liquid beta-propiolactone (of about 97% purity) mixed with 0.5% of its weight of water was pumped continuously into the hot liquid dehydrated phosphoric acid, beneath the surface of the phosphoric acid, while the latter was stirred and maintained at a temperature of 170° C. under a pressure of 100 mm. Hg A. The rate of feed of the propiolactone was 0.116 gram per gram H_3PO_4 per hour. Superheated acrylic acid distilled from the liquid phosphoric acid. After passing from the reaction zone, the stream of acrylic acid was treated by spraying into it continuously a 0.1% solution of mono methyl ether of hydroquinone in liquid acrylic acid, in an amount such as to provide a concentration of 100 p.p.m. of the hydroquinone ether in the resulting mixture. The resulting gaseous stream was then passed through a condenser at a temperature of about 15° C. Liquid acrylic acid of 97% purity was obtained in a yield of 101% based on the propiolactone present in the feed. The yield above 100% was due to the fact that the lactone feed contained minor proportions of impurities (such as, acryloxypropionic acid, acrylic anhydride and hydroxypropionic acid) which were also converted to acrylic acid in the process. The walls of the reactor and of conduits with which the uninhibited acrylic acid vapors came into contact were maintained heated, at a temperature of 170° C.; this is above the dew point of the acrylic acid at the pressure in the system and thus prevents condensation of acrylic acid on said walls.

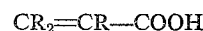
It was found that after 290 hours of continuous operation the phosphoric acid catalyst still had not lost its activity. The catalyst at this point was a semi-solid when cooled to room temperature.

While the invention has been described in detail in relation to the production of acrylic acid from propiolactone it may be used for the production of other, substituted, acrylic acids from the corresponding substituted lactones of monocarboxylic acids having at least one unsubstituted hydrogen atom on the alpha carbon and containing only unreactive hydrocarbon substituents, such lactones having the formula:



where each R may be hydrogen or an unreactive hydrocarbon radical such as an alkyl, aryl alkyl or a cycloalkyl radical. Examples of lactones are beta-hydroxy butyric acid lactone, alpha-methyl hydracrylic acid lactone, beta-hydroxy n-valeric acid lactone, beta-hydroxy alpha methyl butyric acid lactone, alpha-ethyl hydra-

rylic acid lactone, beta-hydroxy isovaleric acid lactone, beta-hydroxy n-capric acid lactone, beta-hydroxy alpha-methyl valeric acid lactone, beta-methyl beta-ethyl hydracrylic acid lactone, alpha-methyl beta-ethyl hydracrylic acid lactone, alpha-methyl beta-methyl hydracrylic acid lactone, alpha-propyl hydracrylic acid lactone, alpha-butyl hydracrylic acid lactone, beta-methyl beta-propyl hydracrylic acid lactone and the like; the beta lactones of aryl substituted carboxylic acids such as beta-phenyl hydracrylic acid lactone, alpha-phenyl hydracrylic acid lactone and the like and other beta lactones of substituted carboxylic acids such as beta-cyclohexyl hydracrylic acid lactone, beta-benzyl hydracrylic acid lactone and the like. The treatment of this invention produces the alpha- beta unsaturated acid having the same number of carbon atoms as the lactone, and having the formula



As pointed out previously, the present invention is operable with the lactone in monomeric or polymeric form, and it will be understood that the reference to "lactone" in the claims refer to both the monomeric and polymeric forms unless otherwise specified.

In the specific working example given in column 3 above the lactone is essentially monomeric, its 97% purity being based on the content of monomeric lactone.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention what we desire to secure by Letters Patent is:

1. Process for making acrylic acid from beta-propiolactone which comprises bringing beta-propiolactone into contact with heated phosphoric acid to produce vapors of said acrylic acid.

2. Process for making acrylic acid, which comprises bringing monomeric beta-propiolactone into contact with heated phosphoric acid to produce vapors of acrylic acid.

3. Process as set forth in claim 2 in which propiolactone is forced continuously into a heated liquid mass of said phosphoric acid and vapors of acrylic acid are taken off continuously.

4. Process as set forth in claim 2 in which the phosphoric acid is maintained at a temperature of at least about 50° C. above the boiling temperature of the acrylic acid at the pressure on said liquid phosphoric acid.

5. Process as set forth in claim 4 in which the water content of said phosphoric acid is at most about equal to the water content of 100% H_3PO_4 .

6. Process as set forth in claim 5 in which water is added continually to said phosphoric acid to replace combined water removed during said process.

7. Process as set forth in claim 6 in which said addition of water is effected by continual replacement of a portion of said phosphoric acid by phosphoric acid of higher combined water content than said replaced portion.

8. Process as set forth in claim 6 in which said addition of water is effected by addition of minor proportions of water to the propiolactone feed.

9. Process as set forth in claim 3 in which the phosphoric acid is maintained at subatmospheric pressure and a temperature of at least about 140° C., and in which water is added continually to said phosphoric acid to replace combined water removed during said process.

10. Process as set forth in claim 9 in which said phosphoric acid contains an inhibitor of the polymerization of acrylic acid.

11. Process as set forth in claim 10 in which the inhibitor is copper.

12. Process as set forth in claim 1 in which the phosphoric acid is maintained at a temperature of about 140 to 180° C. and a pressure of about 20 to 200 mm. Hg A.

13. Process as set forth in claim 1 in which said phos-

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phoric acid contains an inhibitor of the polymerization of acrylic acid.

14. Process for making monomeric acrylic acid of low water content from propiolactone, which comprises forcing liquid monomeric propiolactone continuously into a heated liquid mass of phosphoric acid maintained under subatmospheric pressure, and driving off superheated vapors of acrylic acid continuously from said mass, said phosphoric acid having a water content which is at most about equal to that of 100% H_3PO_4 , said phosphoric acid

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being at a temperature at least about 50° C. above the boiling temperature of said acrylic acid at said pressure.

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