This invention is concerned with the preparation of acrylic acid, and in particular with the continuous conversion of propionic acid to acrylic acid by steps involving the chlorination of propionic acid and the dehydrochlorination of the resulting chlorinated product. The process is rapid, efficient, and continuous. Pure anhydrous acrylic acid is produced in high yield with a minimum of by-products. The monomeric acrylic acid is highly stable on storage, and is particularly adapted to the direct production of esters and salts for subsequent polymerization.

The dehydrochlorination reaction employed involves simply heating of chloropropionic acid to boiling preferably under reduced pressure, with rapid removal and separation of the vapors and recovery of the acrylic acid. At about 135-165°C, beta-chloropropionic acid is dehydrochlorinated to acrylic acid and hydrogen chloride: alpha-chloropropionic acid remains unchanged. Hence it is desirable to carry out the preliminary chlorination of the propionic acid in such a way as to produce as high a proportion of the beta-chloro product as possible, with little or substantially no alpha-chloropropionic acid.

Previously described chlorinations of propionic acid have resulted in the production of relatively high ratios of alpha-chloro to beta-chloro propionic acid. The chlorination described by Hell, Volhard and Zelinsky is carried out at 100°C with a catalyst such as phosphorous or sulfur; alpha-chloropropionic acid is produced substantially exclusively. Other catalysts, such as propionyl chloride, have been stated to promote the formation of beta-chloropropionic acid; but the proportion of the alpha-substituted compound is still in the neighborhood of 30-40% of the total. The application of artificial light and of sunlight in bringing about the chlorination of the propionic acid in accordance with methods and procedures previously described has been found by us to produce mixtures of alpha and beta chlorinated propionic acid in the relative proportions ascribable to essentially random chlorination, and at rates much lower than called for in operations which are to be commercially successful. Thus, by no previously described method of which we are aware has it been possible rapidly and efficiently to produce more than about a 65-70% yield of beta-chloropropionic acid, with an accompanying yield of about 40-50% of the alpha-substituted product.

It is therefore an object of the present invention to provide a process for the production of acrylic acid from propionic acid showing improved efficiency over prior art processes. Another object is to provide pure anhydrous acrylic acid. A further object is to provide for the chlorination of propionic acid to monochloropropionic acid of which not more than about 10%, and preferably not more than about 5%, is alpha-chloropropionic acid and corresponding at least about 90% and preferably at least about 95% is beta-chloropropionic acid. A further object is to provide a continuous, rapid, efficient process for chlorinating propionic acid to beta-chloropropionic acid with minimum production of alpha-chloropropionic acid and for then dehydrochlorinating the beta-chloropropionic acid to acrylic acid. Other objects and advantages will be made apparent as the description proceeds.

In a preferred embodiment of our invention, gaseous or liquid chlorine in carefully controlled amount is continuously introduced into a mixture of pure uncontaminated propionic acid and a minor proportion of beta-chloropropionic acid, at a low temperature of the order of -20 to +20°C. The solution is exposed to actinic radiation, e.g. to the light from a mercury-vapor lamp having a high incidence of light at a wave length of approximately 3650 Angstroms. Chlorination occurs rapidly, the completion of the reaction being evidenced by an increase in temperature and by the disappearance of the greenish color of the initial solution. The components of a portion of the liquid are then separated by distillation, unreacted propionic acid is returned to the system for further chlorination, and the recovered beta-chloropropionic acid is heated to 135-165°C, preferably under vacuum, whereupon hydrogen chloride is split out to produce the desired acrylic acid.

The high yield of acrylic acid obtained with our novel process as above described is made possible mainly by the high proportion of beta-chloropropionic acid obtained during the chlorination, which in turn is a result of the specific radiation employed, the temperature and rate at which the reaction is carried out, the concentra-
tion of the reactants employed and the reaction products formed, the purity of the materials, and other conditions all as hereinafter to be set forth. The proportion of beta-chloropropionic acid is in all cases much higher than would be the case under conditions of random chlorination, and in many cases has been found to be well in excess of 90%, in some instances being as high as 95% or even higher.

Thus we have found, contrary to prior art teachings, that only a narrow band or radiation is of significance in the conversion of propionic acid to beta-chloropropionic acid. This specific radiation occurs at a wave length of about 3500 Angstroms, i.e., about 3600-3700 Angstroms. At 4000-5500 Angstroms, for example, and particularly above about 4500 Angstroms, no activation to beta-chloropropionic acid is observed at the low temperatures here employed. At higher temperatures, substantially random chlorination occurs, and chlorinations carried out under the influence of these longer wave length radiations have invariably resulted in the production of excessive ratios of alpha- to beta-chloropropionic acid. We find that high pressure mercury vapor lamps are a convenient source of the desired radiation. An incandescent tungsten filament type lamp, on the other hand, provided only a slow reaction and its use resulted in the formation of at least about 50% of alpha-chloropropionic acid. No observable chlorination was produced at low temperatures of the order of -20 to +20° C. when the reactant mixture was exposed to direct sunlight, at least at the latitude of St. Paul, Minnesota. At higher temperatures, e.g., 40° C., exposure to sunlight resulted in an undesirably high yield of the alpha-substituted product.

It is necessary, in attaining our improved results, to carry out the chlorination at a low temperature, preferably well below 30° C. For example, we have obtained good results by operating within the range of 20 to 28° C., although temperatures of 0° C. or even lower are at least equally desirable with regard to directing the course of the reaction. Since propionic acid solubilizes at about -20° C. it is desirable that the mixture be kept above such temperature. The hydrogen chloride liberated during the chlorination is continuously removed, desirably under vacuum.

The reaction between the propionic acid and chlorine is exothermic, and the products coming from the chlorination are therefore at a higher temperature than the inflowing mixture. Where the mixture is initially at 20° C., we control the extent of chlorination so as to permit the temperature to rise to not more than about 30° C., and preferably to not more than about 25° C., in order to obtain the desired high proportion of beta-chlorinated product. At lower initial temperatures, somewhat increased amounts of chlorine may be introduced, but we prefer to limit the amount of chlorine added in any cycle to not more than the amount required to convert about 1% of the propionic acid to chloropropionic acid. Thus the reaction mixture as it reaches the irradiation area may contain reactive chlorine in an amount equal to about 0.5% to 1.0%, or preferably about 0.1% to 0.3%, of the propionic acid.

With a suitable light source, such as the high-pressure mercury vapor lamp hereinafter previously identified, the reaction between chlorine and propionic acid is remarkably rapid and also remarkably selective. It is, however, necessary to provide for an adequate concentration of the radiation in the reactive mixture. We have also found that it is necessary carefully to exclude contaminants such as tin and other metallic ions, arsenic, sulfur, water and free oxygen. Metallic ions in particular have been found to retard or prevent chlorination, or to affect unfavorably the desired balance between the beta and alpha chlorinated products. This is particularly surprising in view of the frequent reliance of prior art workers on metallic catalysts for this and similar chlorinations.

Where "pure" propionic acid is specified, it will accordingly be understood that contaminants such as metallic ions, water, etc., are excluded. However the term is not to be considered as ruling out the presence of inert diluents, such as alpha-chloropropionic acid or other inert materials which do not act to inhibit the chlorination.

While each of the preceding details is important to the successful operation of our normal process, careful attention to the above identified, the reaction between chlorine and propionic acid is remarkably rapid and also remarkably selective. It is, however, necessary to provide for an adequate concentration of the radiation in the reactive mixture. We have also found that it is necessary carefully to exclude contaminants such as tin and other metallic ions, arsenic, sulfur, water and free oxygen. Metallic ions in particular have been found to retard or prevent chlorination, or to affect unfavorably the desired balance between the beta and alpha chlorinated products. This is particularly surprising in view of the frequent reliance of prior art workers on metallic catalysts for this and similar chlorinations.

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the dehydrochlorinator 5 and the purified acrylic acid being sent to storage tank 15. It will be apparent that storage or surge tanks may be provided between the chlorination and the dehydrochlorination units if desired, and that these reactor units may be operated independently of each other.

Recycling a portion of the chlorinated mixture through the reactor 4 serves two purposes. It permits greater flexibility in maintaining the desired low temperature. More importantly, it serves to provide the desired content of beta-chloropropionic acid in the mixture during further chlorination, thereby making possible increased yield of beta-chloropropionic acid and of acrylic acid.

Desirably, not more than about one percent of the propionic acid content is chlorinated and removed in each cycle, an equivalent quantity of fresh propionic acid being added. Higher percentages increase the rate at which heat is evolved, and it is desirable to restrict the temperature increase to not more than about 5–10° C. or even less. The diffusion of larger volumes of chlorine into the liquid and the removal of the resulting large volumes of HCl provide additional difficulties. Improved means of circulating the mixture, diffusing or dissolving the chlorine, and removing or neutralizing the HCl obviously may be devised so as to permit the chlorination of somewhat larger proportions of the acid during each cycle. Smaller amounts of chlorine may be used, but the expense of circulating and handling the larger volume of materials then becomes increasingly high. Furthermore the proportion of beta-chloropropionic acid produced during the chlorination has been found to be most advantageous when the initial percentage of chlorine is restricted to within the limits stated. Hence we have found it necessary to hold the proportion of chlorine added in each cycle to within the approximate limits of 0.65–1.0%, and more desirably about 0.1–0.3%, of the amount of propionic acid.

In one specific example, the chlorinator consists of a glass tube approximately 12 inches long and 4½ inches inside diameter, within which is axially sealed a smaller tube having an outside diameter of ¾ inches and containing a high-pressure 1 kw mercury-vapor lamp 12 inches long. The liquid mixture enters the annular chamber between the two tubes through an inlet tube placed near the bottom and at an angle to the axis so as to promote violent agitation, and is forced upward through the reactor and from an outlet tube located at the upper end at a rate of 3½ gallons per minute by suitable external pumps. Gaseous chlorine in carefully controlled amount is introduced into the liquid stream through glass diffusion disks just before the stream reaches the reactor. After the reaction has started, the greenish color of the reaction mixture appears within about 4 hours from the inlet end when the amount of chlorine is initially about 0.2% of the amount of the propionic acid as hereinabove specified. A concentration of at least about 0.2% chlorine is required to initiate the reaction. The temperature of the liquid increases during this operation, about 4–6° C., i.e., to about 25° C. The liquid then passes to a sump, where the hydrogen chloride is removed under slight vacuum, and from there through a series of cooling coils surrounded by cooling water, before returning to the chlorinator and reactor.

From the still 6 there is obtained a mixture of a small amount of alpha-chloropropionic acid, melting at −3° C. and boiling at 186° C., and a larger amount of beta-chloropropionic acid, melting at 37.5° C. and boiling at 204° C. We have observed that complete separation of these two components is difficult, due both to the closeness of boiling-points and to the formation of a eutectic; and this difficulty is believed to have contributed greatly to the observed inaccuracy of analytical determinations and to the melting point constants previously reported in this field. However it is possible to recover most of the beta-chloropropionic acid in pure form by distillation, leaving only a relatively insignificant proportion mixed with the residual small amount of alpha-chloropropionic acid. The pure beta-substituted acid is sent from the still 7 to the cracking unit 8.

In the cracking unit, the temperature is held at 160–165° C. by external heating and the beta-chloropropionic acid is converted to acrylic acid by splitting out of HCl, which is removed, all under reduced pressure. The products are distilled, the unconverted or reassociated beta-chloropropionic acid being returned to the cracking unit. The pure acrylic acid produced during this operation is anhydrous and remains unchanged even on prolonged storage.

In one experiment, the specific chlorinating apparatus just described and starting with pure redistilled propionic acid, the mixture was wholly recycled and the progress of the chlorination was determined periodically by careful analysis. Chlorine was added at a constant rate, initially at about 0.1–0.3% of the total, the percentage based on the propionic acid thus gradually increasing as propionic acid became gradually converted to monochloropropionic acid. Shortly after the start of the reaction, the ratio of beta to alpha chloropropionic acid was found to be about 7:3 or even lower, extrapolation indicating the initial ratio to be approximately the ratio of random chlorination, viz., 6:4. With continued recycling, the ratio of beta to alpha chlorinated acid rose to 9:2 at about 20% total chlorination, at which point the maximum proportion of betachloropropionic acid, 16.3 mols of propionic acid, 16.3 mols of beta-chloropropionic acid, and 3.7 mols of alpha-chloropropionic acid. This represents a considerably higher proportion of the beta acid than is obtainable either by random chlorination or by catalytically directed chlorination processes or other processes previously known, as far as we have been able to ascertain.

In the same experiment, it was found that the most favorable results in terms of a high ratio of beta to alpha chlorinated acid produced in the chlorination reaction were obtained when the percentage of monochlorinated acid in the reaction mixture was above about 5% and about 20%. At higher percentages, up to about 40%, the ratio was found to be slightly less favorable. Within the preferred range, the percentage of beta-chloropropionic acid was between about 3% and about 16% of the total. Under somewhat different operating conditions, e.g. with a substantial proportion of beta-chloropropionic acid present in the initial reaction mixture, the maintaining of substantially higher proportions of beta-chloropropionic acid in the reaction mixture results in still more favorable ratios.

By starting with a mixture consisting exclusively of a major proportion of pure propionic acid and a minor proportion of beta-chloropropionic acid, still higher yields of the beta acid are obtained, ratios of as high as 9:1 or even 95:5.
beta to alpha chlor being frequently reached. This represents a very much higher proportional yield of beta-chloropropionic acid than any obtainable by prior art chlorination processes with which we are familiar, and provides a basis for the economical commercial conversion of propionic acid to acrylic acid.

The particular apparatus hereinabove described has given excellent results, but our invention is not to be considered as restricted to any specific apparatus, since many other combinations of radiation sources, radiation cells, agitation equipment, etc., have proven equally suitable when operated in conformity with the principles herein set forth.

In one such alternative apparatus, the liquid mixture is contained in an open glass jar having a diameter of 10 inches and containing an axially located 2-inch diameter "Pyrex" glass closed tube enclosing a 125-watt high-pressure mercury vapor lamp. Chlorine is continuously introduced through a diffusion disc located at the bottom of the cylinder, and the liquid is vigorously agitated by means of a motor-driven propeller-type stirrer. When the starting liquid is pure propionic acid, a chlorine concentration slightly higher than about 1% is required before reaction will start, and substantially random-chlorination ratios of the beta-chloroacids are at first obtained. The ratio of beta to alpha acid increases as the reaction continues and the content of beta-chloropropionic acid increases, at least while the beta-chloropropionic acid remains in a minor proportion and the unchlorinated propionic acid at a major proportion. Where these proportions are reversed, e.g. at 65 percent beta-chlorinated acid and 35 percent propionic acid, chlorination to dichloropropionic becomes troublesome. At still higher percentages of the beta acid, e.g. at about 85 percent, the mixture changes from a free-flowing liquid to a crystalline mush. Best results are obtained when the starting liquid contains an appreciable but minor proportion of beta-chloropropionic acid.

The above apparatus is particularly useful for laboratory investigations, preferably by direct radiation, or may be speeded up by immersing a cooling coil in the liquid. The hydrogen chloride liberated during the chlorination may be allowed to escape from the open cylinder. The presence of a liquid-air interface does not appear to inhibit the chlorination, although bubbling air into the liquid, as by too rapid agitation, has been found to have an adverse effect.

Still another form of reactor has been investigated. In this apparatus, the 125-watt mercury-vapor lamp was contained within a "Pyrex" glass bulb sealed within an outer bulb carrying an inlet tube and an outlet tube at opposite sides and so situated that liquid entering the outer bulb at the inlet would flow over the inner bulb by gravity in a uniform thin film before leaving the bulb at the outlet. Chlorine was introduced through a small glass tube into the free space between inner and outer bulbs. The liquid was circulated by an external pump. When this apparatus was tested, it was found that the chlorination reaction would not proceed even though the amount of chlorine eventually absorbed was far in excess of the chloropropionic acid. Apparently the liquid layer was not sufficiently thick to absorb an effective concentration of the incident radiation. However, when the direction of liquid flow was reversed so that the liquid filled the space between the two bulbs and was therefore in a layer approximately one-half to one inch thick, the light was adequately absorbed, and the reaction started and proceeded at much lower levels of chlorine concentration.

What we claim is as follows:

1. In the chlorination of propionic acid to monochloropropionic acid by actinic irradiation of a mixture of propionic acid and chlorine, that improvement which comprises carrying out the chlorination at an initial temperature not higher than about +20° C. under irradiation with light of a wave length of about 3650 Angstroms, in a liquid mixture comprising chlorine, a major proportion of pure propionic acid, and a minor proportion of beta-chloropropionic acid, the amount of chlorine present in the mixture prior to reaction being within the range of about 0.05-1.0% of the amount of propionic acid; whereby to obtain a yield of beta-chloropropionic acid in excess of that obtainable through random chlorination.

2. The process of claim 1 in which the amount of chlorine prior to reaction is within the range of about 0.1-0.3% of the amount of propionic acid.

3. Process for initiating and carrying out the continuous preparation of beta-chloropropionic acid in high yield comprising the steps of: (1) mixing together 100 parts of pure propionic acid and about 1.00 part of chlorine; (2) absorbobly exposing the liquid mixture at a temperature not higher than about 30° C. to ultraviolet light at a wave length of about 3650 Angstroms; (3) recycling at least a portion of the resulting reacted mixture, with addition of further propionic acid sufficient to maintain the total propionic acid content in major proportion and the beta-chloropropionic acid in minor proportion, and with addition of further chlorine in an amount equal to about 0.05-1.0% of the said total amount of propionic acid; (4) withdrawing at least a portion of the said reacted mixture from the cycle; and (5) separating pure beta-chloropropionic acid from the portion withdrawn.

4. In the continuous chlorination of propionic acid to monochloropropionic acid with production of the beta-chlorinated acid in high yield, the process comprising the steps of: (1) mixing together a mixture comprising a major proportion of pure propionic acid and a minor proportion of beta-chloropropionic acid, and chlorine in an amount equal to about 0.05-1.0% of said pure propionic acid; (2) absorbably exposing the resulting reactive liquid mixture, at a temperature not higher than about 20° C., to ultraviolet light at a wave length of about 3650 Angstroms; (3) recycling at least a portion of the resulting reacted mixture, with addition of further propionic acid sufficient to maintain the total propionic acid content in major proportion and the beta-chloropropionic acid content in minor proportion, and with addition of further chlorine in an amount equal to about 0.05-1.0% of the said total amount of propionic acid; (4) withdrawing at least a portion of the said reacted mixture from the cycle; and (5) separating pure beta-chloropropionic acid from the portion withdrawn.

5. In the continuous chlorination of propionic acid to monochloropropionic acid with production of the beta-chlorinated acid in high yield, the process comprising the steps of: (1) providing a chlorination mixture comprising at least about 50 percent of pure propionic acid, about 5-20 parts of beta-chloropropionic acid based on...
100 parts of said pure propionic acid, and about 0.05–1.0 part of chlorine based on 100 parts of said pure propionic acid; (2) absorbably exposing said chlorination mixture, at a temperature not higher than about 20° C., to ultraviolet light at a wave length of about 3650 Angstroms; (3) recycling at least a portion of the resulting reacted mixture with addition of further pure propionic acid sufficient to maintain the total propionic acid content at least about 50 percent of the total and the beta-chloropropionic acid about 5–20 parts per 100 of said total propionic acid, and with addition of further chlorine in an amount equal to about 0.05–1.0% of the said total amount of propionic acid; (4) withdrawing at least a portion of the said reacted mixture from the cycle; and (5) separating pure beta-chloropropionic acid from the portion withdrawn.

6. Process of claim 5 in which the amount of beta-chloropropionic acid prior to chlorination is about 5–15 parts for each 100 parts of propionic acid.

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