Patented June 3, 1941

2,244,389

UNITED STATES PATENT OFFICE

2,244,389

PROCESS OF PREPARING ESTERS OF METHACRYLIC ACID

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No Drawing. Application December 1, 1939, Serial No. 307,146

9 Claims. (Cl. 260—486)

This invention relates to a process of preparing esters of alpha-methacrylic acid (more commonly known simply as methacrylic acid) and has for its object the production of high yields of such esters from the corresponding esters of alpha-hydroxy isobutyric acid by an economical method which avoids the difficulties heretofore attendant the preparation of alpha-methacrylic esters from the said isobutyric esters.

It was known prior to my invention that esters of alpha-methacrylic acid could be prepared by dehydrating alpha-hydroxy isobutyric esters with the aid of phosphorus pentoxide (P_2O_5) as a dehydrating agent. However, the prior methods have not been entirely satisfactory. In solventless processes, solid meta phosphoric acid precipitates from the reaction mass. This precipitate is a relatively poor conductor of heat, and makes difficult or more costly the effective and uniform heating of the reaction mass. Further, the precipitate coats the phosphorus pentoxide and decreases its dehydrating efficiency. Considerable difficulty also is encountered in cleaning the reaction vessel of such solid residues. When the higher alkyl alpha-hydroxy isobutyric esters are treated with phosphorus pentoxide in the absence of a solvent, further complications occur in that the phosphorus pentoxide causes excessive decomposition of the higher alkyl methacrylates at the high temperatures required for separating them from the reaction mass. To avoid this excessive decomposition certain inert solvents boiling below 200° C. at atmospheric pressure have been suggested as mediums in which the reaction may be carried out, specifically octane, cyclohexane, low-boiling petroleum ether or naphtha, benzene, toluene, xylene, solvent naphtha, chlorobenzenes, tri- and tetra-chloroethanes, ethylene dichloride and carbon tetrachloride. These inert solvents have been of some aid in carrying out the dehydration, but this technique still required the step of removing undissolved particles, as by filtration.

I have discovered that high yields of alpha-methacrylic esters can be obtained, without any difficulties during dehydration and without the necessity for a filtration step prior to distillation, by effecting reaction between the corresponding alpha-hydroxy isobutyric ester and phosphorus pentoxide while admixed with a phosphate ester, e. g., aliphatic phosphate ester such as the tributyl phosphates, cycloaliphatic phosphate esters such as the tricyclohexyl phosphates and aromatic phosphate esters such as the tricresyl phosphates. Mixtures of phosphate esters also may be used. The mixed phosphate esters may be of the same class or of different classes. Thus, in certain cases I may use, for example, mixtures of different aromatic phosphate esters or I may use mixtures of aromatic phosphate esters with either or both aliphatic phosphate esters and cycloaliphatic phosphate esters.

Additional examples of suitable phosphate esters are:

	Boiling point, °C.
Tri ethyl phosphate	211 (92–95 at 10 mm. pressure)
Tri-phenyl phosphate	220 at 5 mm. pressure
Di-para-tertiary butyl phenyl monophenyl phosphate	260–275 at 5 mm. pressure
Diphenyl mono-ortho, xenyl phosphate	250–285 at 5 mm. pressure
Di-ortho-xenyl monophenyl phosphate	285–300 at 5 mm. pressure
Tri-para-tertiary butyl phenyl phosphate	320 at 5 mm. pressure

In some cases tri-methyl phosphate (boiling point 193° C. at atmospheric pressure) may be used, but in general a phosphate ester boiling substantially above 200° C. at atmospheric pressure is to be preferred. Best results also are obtained when the chosen phosphate ester has a boiling point differing by at least 30° C. from that of the particular methacyclic ester being prepared.

By reacting the chosen ester of alpha-hydroxy isobutyric acid with phosphorus pentoxide while admixed with a suitable amount of a phosphate ester, there results a solution which is clear (unless a polymerization inhibitor that is insoluble in the reaction mass is employed) and which can be distilled directly to obtain the methacrylic ester without the necessity of filtering the mass prior to distillation. This clarity is believed to be due to the greater affinity and dissolving power of the phosphate esters for P_2O_5 and for the products of the reaction of P_2O_5 with esters of alpha-hydroxy isobutyric acid than the mediums heretofore known or suggested for use as modifiers of the above reactants while effecting reaction therebetween. It is also possible that the phosphate ester may react with products of the main reaction in some reversible or irreversible manner, e. g., by an ester exchange process between the added phosphate ester and the intermediate phosphates derived from P_2O_5 and the alpha-hydroxy isobutyric ester, thereby enhancing the homogeneity of the solution through mutual solubility characteristics. Whatever the explanation may be, the fact remains that when the reaction between the described components is carried out in the presence of a suitable

amount of a phosphate ester, the reaction mass need not be filtered before distillation, with obvious economies in operation, and the yields of methacrylic ester are higher than when ordinary inert solvents boiling below 200° C. are employed.

The amount and kind of phosphate ester may be varied widely, the preferred amount and kind depending upon such influencing variable as the nature of the chosen hydroxy isobutyric ester, the structure and properties of the phosphate ester, for example the number of carbon atoms which it contains, whether it is aliphatic, cycloaliphatic or aromatic, the structure of the ester radical, etc. For example, a cyclic phosphate ester preferably is employed in dehydrating an aromatic hydroxy isobutyric ester. The amount of phosphorus pentoxide employed also influences the optimum amount of phosphate ester to be used. When other factors are the same, the higher the molar amount of P_2O_5 with respect to the hydroxy isobutyric ester, the more phosphate ester ordinarily should be employed. In general, the amount of phosphate ester should be at least sufficient to dissolve and to keep in solution the reactants and the reaction products, thereby rendering unnecessary the step of filtering the reaction mass prior to separation of the alpha-methacrylic ester therefrom. Preferably the amount of phosphate ester is at least equal in volume to the amount of hydroxy butyric ester. While in some cases it may be desirable to use an amount of phosphate ester as much as ten times the volume of hydroxy butyric ester, no particular advantage appears to accrue from using more than three or four volumes of phosphate ester per volume hydroxy butyric ester.

The amount of phosphorus pentoxide also may be varied widely, good results being obtained with from ¼ to ½ mols P_2O_5 per mol alpha-hydroxy isobutyric ester. Optimum results are obtained when the phosphorus pentoxide is used in the ratio of from ⅓ to ⅖ mols P_2O_5 per mol of the chosen hydroxy isobutyric ester. The use of lower or higher molar amounts of P_2O_5 is not precluded, as for example from about 0.1 to 1.0 mol P_2O_5 per mol alpha-hydroxy isobutyric ester, but such mol ratios are less desirable. In general, when less than about ¼ mol P_2O_5 is used the yield of methacrylic ester tends to be lower because of the higher amount of hydroxy isobutyric ester which remains undehydrated and distils over with the methacrylic ester. On the other hand, when more than ½ mol P_2O_5 per mol alpha-hydroxy isobutyric ester is employed, there is a tendency toward decomposition of the methacrylic ester as it forms, thus reducing yields and resulting in monomeric esters of inferior quality, that is, esters which are more difficult to polymerize.

In carrying my invention into effect, it is desirable to cause reaction between the phosphorus pentoxide and the alpha-hydroxy isobutyric ester while these reactants are admixed with an inhibitor of polymerization of the methacrylic ester which forms. The separation of the methacrylic ester from the reaction mass, as by distillation, also preferably is carried out without initially removing the polymerization inhibitor from the said mass. The inhibitor may or may not be soluble in the reaction mixture. Examples of inhibitors which may be used are copper, copper bronze, copper acetate, phenol, cresol, pyrogallol, hydroquinone, resorcinol, tannic acid, sulfur, selenium, etc., or mixtures of inhibitors, e. g., a mixture of selenium and copper.

In order that those skilled in the art better may understand how the present invention may be carried into effect, the following illustrative example thereof is given:

	Parts by weight
Ethyl alpha-hydroxy isobutyrate	60.0
Tricresyl phosphate	180.0
Phosphorus pentoxide	21.5
Copper bronze (polymerization inhibitor)	0.2

The tricresyl phosphate was poured into a suitable reaction vessel provided with a stirrer, a temperature recorder, a reflux condenser convertible into a distillation condenser and means for heating the vessel, for example a liquid bath or a steam jacket. The phosphorus pentoxide and powdered copper bronze were added, followed by the slow addition of the ethyl alpha-hydroxy isobutyrate. Although in most cases no undue rise in temperature occurs, the temperature preferably is not allowed to exceed substantially 65° C. until all the hydroxy ester has been added. Simultaneously with active stirring, heat was applied to the mixture so that the temperature of the mass remained at about 80° to 100° C. for approximately 4 to 8 hours. A homogeneous solution of reaction products containing the copper bronze dispersed throughout the mass was obtained. This mixture need not be filtered prior to distillation to obtain the ethyl ester of alpha-methacrylic acid. Filtration of a sample through a filtering medium showed copper bronze to be the only insoluble material in the solution. The filtrate was clear.

The apparatus was converted to a distillation system and there was obtained 46.6 to 48.1 parts of a distillate boiling at 116° to 120° C. and consisting of practically pure ethyl alpha-methacrylate. This is approximately 90 to 92.8 per cent of the theoretical yield.

This distillate may be further purified, if desired, by washing it with solutions of sodium carbonate or sodium chloride, followed by drying and redistillation.

In a similar manner any of the other esters of alpha-methacrylic acid may be prepared. Illustrative of such esters are those ranging from the lower aliphatic esters such as methyl, propyl, isopropyl, butyl, isobutyl, amyl, isomeric amyl to the higher aliphatic esters such as decyl, dodecyl, tetradecyl, cetyl and octadecyl, and aromatic alpha-methacrylic esters, e. g., phenyl, cresyl, tolyl, benzyl, resorcinyl, naphthyl, etc.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of making esters of alpha-methacrylic acid which comprises reacting the corresponding ester of alpha-hydroxy isobutyric acid with phosphorus pentoxide while admixed with a phosphate ester and separating the ester of alpha-methacrylic acid from the reaction mass.

2. The method of making esters of alpha-methacrylic acid which comprises effecting reaction between 1 mol of the corresponding ester of alpha-hydroxy isobutyric acid and from about 0.1 to 1 mol phosphorus pentoxide while admixed with a phosphate ester in an amount at least sufficient to dissolve and to keep in solution the reactants and the reaction products, and distilling the reaction mass to separate therefrom the ester of alpha-methacrylic acid.

3. The method of making esters of alpha-methacrylic acid which comprises effecting re-

action between 1 mol of the corresponding ester of alpha-hydroxy isobutyric acid and from about ¼ to ½ mol phosphorus pentoxide while admixed with a phosphate ester differing in boiling point by at least 30° C. from that of the particular methacrylic ester being prepared, and distilling the reaction mass to obtain the ester of alpha-methacrylic acid.

4. The method of making esters of alpha-methacrylic acid which consists in effecting reaction between 1 mol of the corresponding ester of alpha-hydroxy isobutyric acid and from about ¼ to ½ mol phosphorus pentoxide while admixed with a polymerization inhibitor and an alkyl phosphate ester, and distilling the reaction mass to separate therefrom the ester of alpha-methacrylic acid.

5. A method as in claim 4 wherein the alkyl phosphate ester is a tributyl phosphate.

6. The method of making esters of alpha-methacrylic acid which consists in effecting reaction between 1 mol of the corresponding ester of alpha-hydroxy isobutyric acid and from about ¼ to ½ mol phosphorus pentoxide while admixed with a polymerization inhibitor and a cycloaliphatic phosphate ester, and distilling the reaction mass to obtain the ester of alpha-methacrylic acid.

7. A method as in claim 6 wherein the cycloaliphatic phosphate ester is a tricyclohexyl phosphate.

8. The method of making esters of alpha-methacrylic acid which consists in effecting reaction between 1 mol of the corresponding ester of alpha-hydroxy isobutyric acid and from about ¼ to ½ mol phosphorus pentoxide while admixed with a polymerization inhibitor and an aromatic phosphate ester in an amount at least sufficient to dissolve and to keep in solution the reactance and the reaction products, and distilling the reaction mass to separate therefrom the ester of alpha-methacrylic acid.

9. A method as in claim 8 wherein the aromatic phosphate ester is a tricresyl phosphate.

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