July 3, 1945. L. COES, JR 2,379,625

MANUFACTURE OF METHACRYLIC ACID

Filed Aug. 16, 1940 2 Sheets-Sheet 1

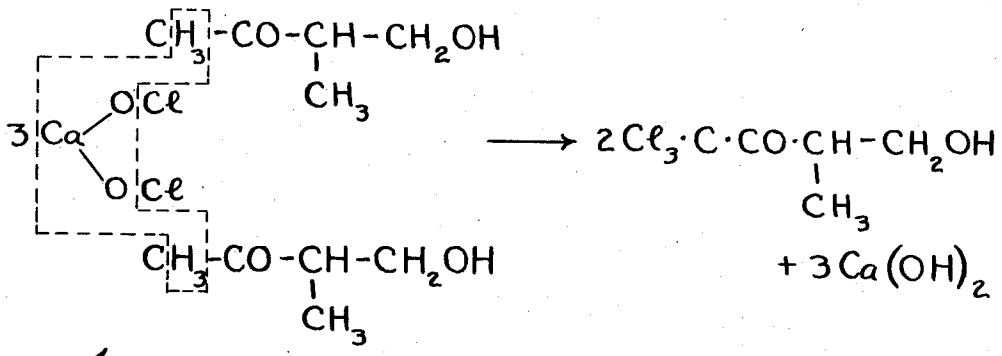


Fig. 1

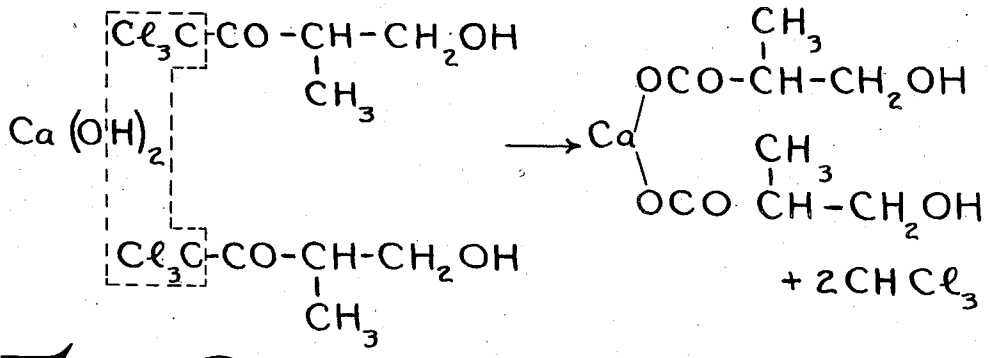


Fig. 2

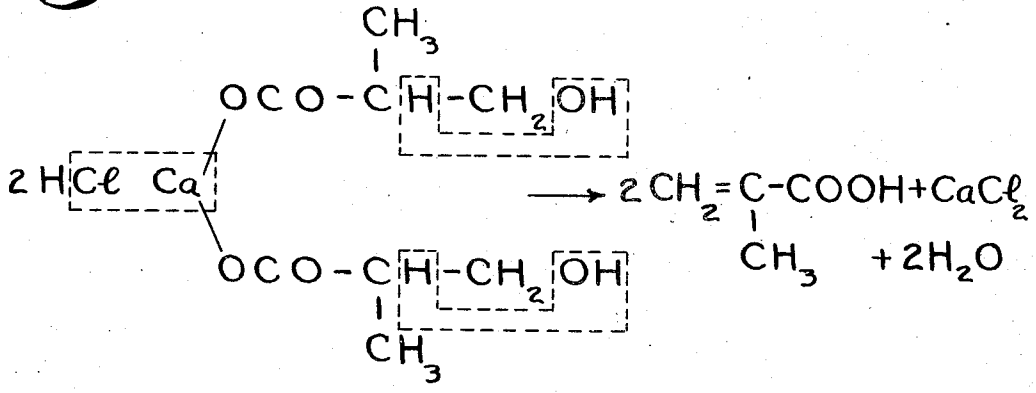


Fig. 3

Inventor

LORING COES JR.

By George Crompton

Attorney

July 3, 1945. L. COES, JR 2,379,625

MANUFACTURE OF METHACRYLIC ACID

Filed Aug. 16, 1940 2 Sheets-Sheet 2

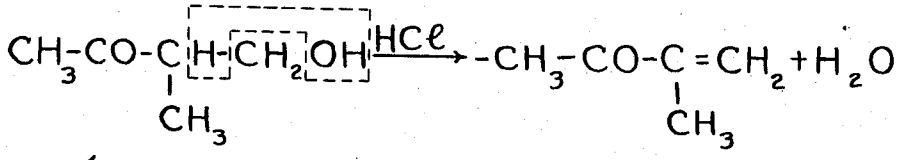


Fig. 4

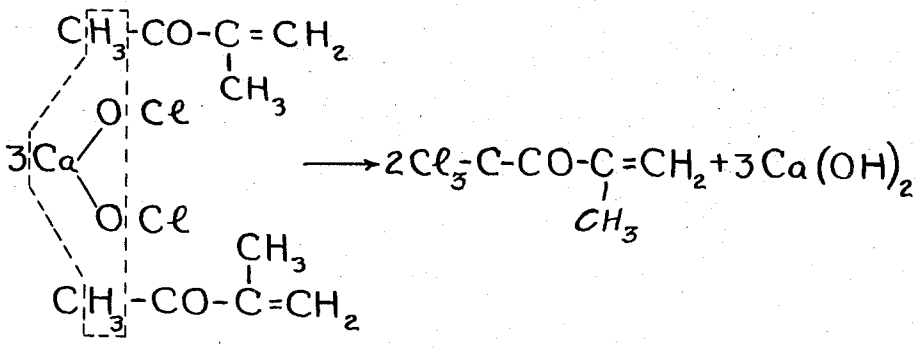


Fig. 5

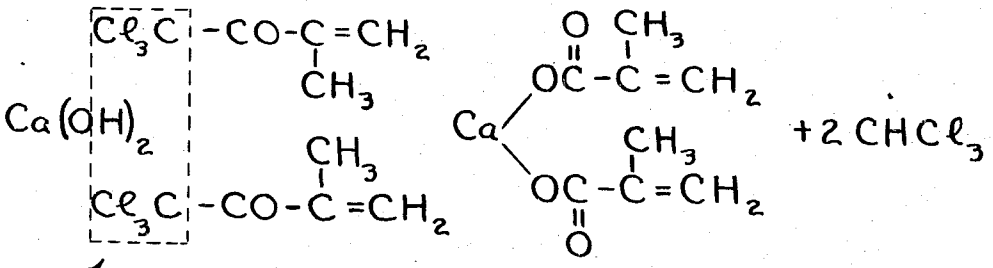


Fig. 6

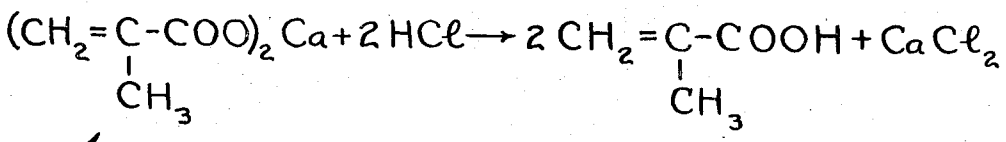


Fig. 7

Inventor

LORING COES JR.

By

Attorney

Patented July 3, 1945 2,379,625

UNITED STATES PATENT OFFICE

2,379,625

MANUFACTURE OF METHACRYLIC ACID

Loring Coes, Jr., Brookfield, Mass., assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application August 16, 1940, Serial No. 352,935

4 Claims. (Cl. 260—531)

The invention relates to the manufacture of methacrylic acid and its esters.

One object of the invention is to provide a simple process for making methacrylic acid. Another object of the invention is to provide a cheap process for making methacrylic acid. Another object of the invention is to provide a process for the manufacture of methyl methacrylate via preparation of methacrylic acid which shall be as cheap as or cheaper than any method heretofore known. Another object of the invention is to provide a cheap way of obtaining other derivatives of methacrylic acid, for example besides the methyl ester, ethyl, propyl and butyl and other alkyl esters, also phenol esters, metal salts, the anhydride of the acid, and many other derivatives of methacrylic acid. Another object is to provide a process of the type indicated free from the use of dangerous or poisonous chemicals. Other objects will be in part obvious or in part pointed out hereinafter.

The invention accordingly consists in the combinations of elements, arrangements of parts, and in the several steps and relation and order of each of said steps to one or more of the others thereof, all as will be illustratively described herein, and the scope of the application of which will be indicated in the following claims.

In the accompanying drawings illustrating an important step in two of many possible embodiments of my invention:

In Figures 1, 2 and 3 are chemical equations showing three reactions involved in one method according to the present invention;

Figures 4, 5, 6 and 7 are chemical equations showing the reactions involved in another method according to the present invention.

As a starting material, I use methyl ethyl ketone. In the cracking of petroleum, butanol 2 is produced. From this, methyl ethyl ketone can be readily manufactured in a well known manner. Methyl ethyl ketone in fairly pure form is readily available on the market and as of the present date has a price around five cents a pound.

Other ingredients used in my process are formaldehyde, chloride of lime, hydrochloric acid, and a small amount of sulphuric acid. Formaldehyde is inexpensive, being at present about seven cents per pound in a 40% solution in water. Ordinary bleaching powder is good enough chloride of lime and this at present has a price of about two cents a pound. Hydrochloric acid costs about two cents a pound and sulphuric acid, of which little is used, about one cent a pound. Therefore, the ingredients in the manufacture of methacrylic acid according to the present invention are all inexpensive. For the manufacture of methyl methacrylate, the most valuable product to be derived from the acid, methyl alcohol is used which is still relatively inexpensive, costing at present about five cents a pound.

Considering now in detail the manufacture of the acid, I take 500 grams of methyl ethyl ketone, 375 grams of 40% formaldehyde solution in water, and 10 cc. of 2 normal sodium hydroxide. I cool it to below 30° C. and let it stand for 24 hours. I distill this mixture and collect the fraction, boiling between 90° C. and 120° C. at 20 millimeters of mercury. This is beta methyl gamma keto butanol.

This is the first step in the process and the reaction may be indicated as follows:

$$CH_3COC_2H_5 + HCHO \longrightarrow CH_3{-}CO{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2OH$$

This reaction per se, however, is not novel.

The second step in the total process which is believed to be novel, as a whole, may be carried out as follows: I take 275 grams of commercial bleaching powder (an impure chloride of lime containing 33% of available chlorine) and suspend it in 800 cc. of water. I then add a solution of 40 grams of the foregoing beta methyl gamma keto butanol in 40 grams of water. The addition should be made gradually and the mixture should be stirred for about two hours at between 30° and 50° C.

To the foregoing mixture I then add 150 cc. of concentrated hydrochloric acid, keeping the temperature below 50° C. I then heat the mixture to approximately 75° C. for one hour and then extract continuously with ethyl ether. The ether extract is then distilled to drive off the ether and there remains methacrylic acid with some impurities. The methacrylic acid can be purified in known manners or else in the impure form it can be esterified to methyl methacrylate and the latter can be purified in known manners.

In carrying out the second step in the process, I provide a quantity of copper or other suitable inhibitor to prevent polymerization of the methacrylic acid during its manufacture. I believe the reactions will definitely convert all of the beta methyl gamma keto butanol to methacrylic acid, and the thing to be particularly guarded against is polymerization of the methacrylic acid. Since the reaction may proceed at low temperatures and polymerization is slower at low temperatures, it is possible to obtain a relatively high yield of

methacrylic acid in monomeric form. The use of copper as an inhibitor is a distinct aid in carrying out this step of the process. Other inhibitors which can be used are hydroquinone and pyrogallol.

In the foregoing, commercial bleaching powder has been selected as it is the cheapest of the group consisting of the alkaline earth hypochlorites and alkali hypochlorites that I know of. The process, however, can be carried out using an alkali hypochlorite such as sodium hypochloride NaOCl. Other alkali metals can be substituted, so also other alkaline earth metals. Also other halogens can be substituted for the chlorine. However, so far as I know, there is no advantage in using anything but the cheapest.

Other acid hydrolyzing and dehydrating agents besides HCl can be used, for example, sulphuric acid and phosphoric acid.

It does not seem necessary to describe esterification of methacrylic acid to methyl methacrylate since this is now well known. Equally other monohydric alcohols can be used to obtain the corresponding esters of methacrylic acid and, in fact, other products can be made from it, such as the salts. By adding acetic anhydride, the anhydride of methacrylic acid can be produced. As set forth in co-pending application of Carl E. Barnes, Serial No. 326,974 filed March 30, 1940, a hard transparent resin highly useful for optical purposes, for windows and especially for airplanes, can be produced by copolymerizing methyl methacrylate with a small quantity of methacrylic anhydride.

Referring now to the accompanying drawings, Figure 1 shows a halogenation reaction in which beta methyl gamma keto butanol is converted to delta delta delta trichloro beta methyl gamma keto butanol. At the same time, three molecules of calcium hydroxide are formed. The delta delta delta trichloro beta methyl gamma keto butanol immediately breaks down, as shown in Figure 2, in a chloroform reaction, producing two molecules of chloroform and a molecule of calcium beta hydroxyisobutyrate. The reaction indicated in Figure 3 produces methacrylic acid, calcium chloride and water. This weak acid is liberated by treating the salt with a strong acid and dehydration occurs at the same time.

Other haloform reactions could be substituted for that shown in Figure 2 if for the hypochlorite a hypohalite having a halogen other than chlorine were selected.

A similar process for the manufacture of methacrylic acid within the scope of the present invention is illustrated in Figures 4 to 7 inclusive. Figure 4 illustrates the dehydrating of beta methyl gamma keto butanol to methyl isopropenyl ketone. As shown in Figures 5 and 6, this is then reacted with a hypohalite (using bleaching powder preferably) to produce calcium methacrylate which is then, as shown in Figure 7, reacted with a strong acid to produce the methacrylic acid. In the reaction shown in Figure 5, calcium hydroxide and trichloro-methyl isopropenyl ketone are produced from the calcium hypochlorite and methyl isopropenyl ketone. In the reaction shown in Figure 6 calcium methacrylate and chloroform are produced from the calcium hydroxide and trichloro-methyl isopropenyl ketone. As an example of this embodiment of the invention, I may take 40 grams of beta methyl gamma keto butanol, put it in a flask and warm it with 10 cc. of hydrochloric acid. I then add sodium carbonate to neutralize the HCl and then proceed as in the first example. However, from the metal methacrylate the esters may be made directly.

It will thus be seen that there has been provided by this invention methods and compositions of matter in which the various objects hereinabove set forth together with many thoroughly practical advantages are successfully achieved. As various possible embodiments might be made of the chemical features of the above invention and as the art herein described might be varied in various parts, all without departing from the scope of the invention, it is to be understood that all matter hereinbefore set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. In the process of producing methacrylic acid, the steps comprising reacting beta methyl gamma keto butanol and a hypohalite from the group consisting of alkaline and alkaline earth metal hypohalites, in an aqueous medium and, thereafter, treating said reaction mixture with an acid dehydrating agent from the group consisting of concentrated hydrochloric, sulfuric and phosphoric acids.

2. In the process of producing methacrylic acid, the steps comprising reacting beta methyl gamma keto butanol and calcium hypochlorite in an aqueous medium and, thereafter, treating said reaction mixture with concentrated hydrochloric acid.

3. In the process of producing methacrylic acid, the steps comprising reacting beta methyl gamma keto butanol and a hypohalite from the group consisting of alkaline and alkaline earth metal hypohalites, in an aqueous medium for at least about two hours at 30° C.–50° C. and, thereafter, adding to the reaction mixture an acid dehydrating agent from the group consisting of concentrated hydrochloric, sulfuric and phosphoric acids, and maintaining said reaction mixture at about 75° C. for at least about one hour.

4. In the process of producing methacrylic acid, the steps comprising reacting beta methyl gamma keto butanol and calcium hypochlorite in an aqueous medium for at least about two hours at 30° C.–50° C. and, thereafter, adding concentrated hydrochloric acid to the reaction mixture and maintaining said reaction mixture at about 75° C. for at least about one hour.

LORING COES, JR.