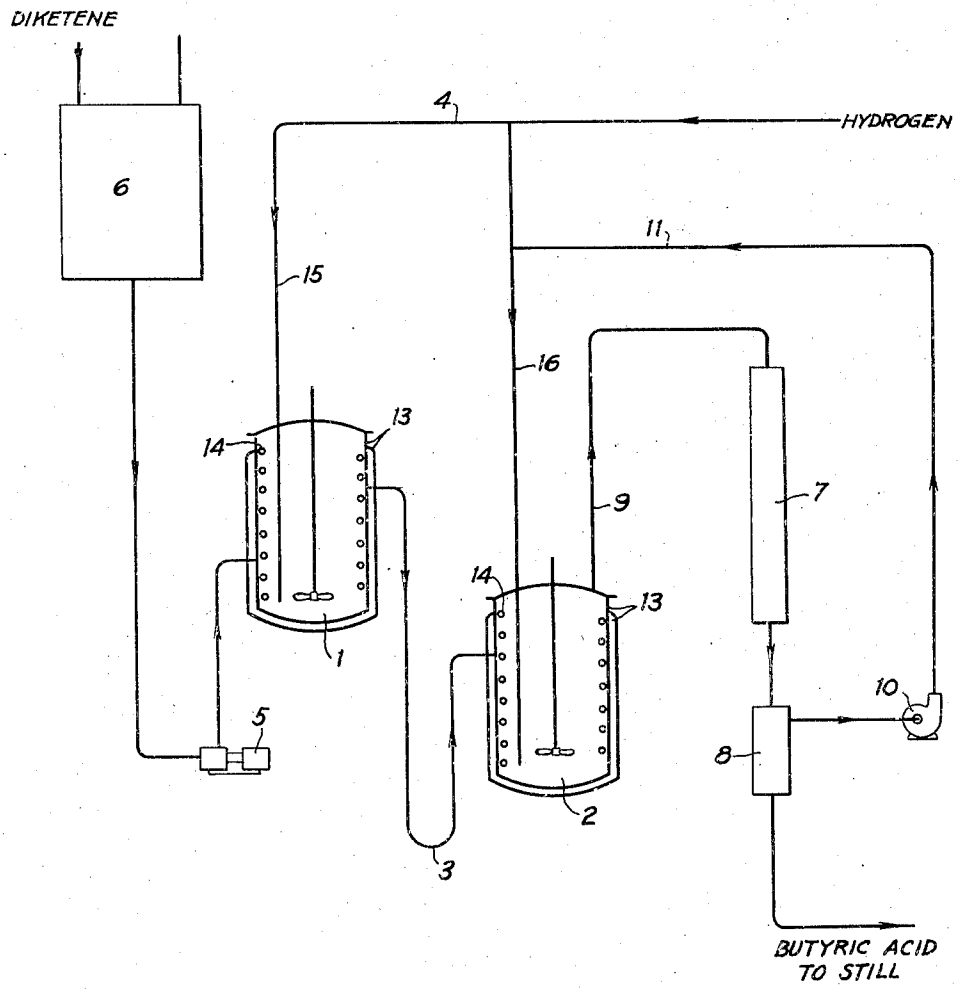
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PREPARATION OF BUTYRIC ACID

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PREPARATION OF BUTYRIC ACID

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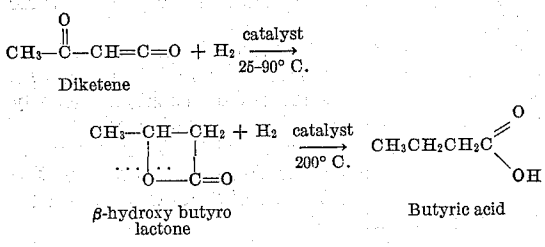
5 Claims. (Cl. 260—540)

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This invention relates to a method of preparing butyric acid and more particularly to a method of preparing butyric acid by the hydrogenation of diketene with the aid of a suitable hydrogenation catalyst. The invention provides a novel, valuable and more economical method of preparing butyric acid, the uses of which are, of course, well known.

I have found that diketene may be reduced under certain temperatures and pressures to produce high yields of butyric acid. The reaction is carried out in the presence of a hydrogenation catalyst at super atmospheric pressures preferably by employing a low temperature reduction followed by a more or less continued reduction at considerably higher temperatures and usually at the same or higher pressures.

The course of the reduction can be represented as follows:



Diketene can be assumed to have any one, or all three, of the commonly suggested structures; acetyl ketene, (shown above), betacrotonolactone, and/or vinyl aceto-beta-lactone. The mechanism of the reaction would be represented in each case as suggested above where beta-hydroxy butyro lactone is formed as an intermediate. The reduction of diketene is highly exothermic and unless the temperature of the initial reaction, which forms beta-hydroxy butyro lactone, is carefully controlled, the diketene will decompose with explosive violence. As indicated by the dotted line in the above formula, on continued hydrogenation, the beta-lactone breaks at the beta carbon oxygen bond rather than at the carbonyl carbon to oxygen bond as might be expected.

It is, accordingly, an object of the invention to provide a new process of preparing butyric acid which is valuable and economical. Another object of the invention is the production of butyric acid by the reduction of diketene whereby a high yield of acid is obtained. Still another object of the invention is a continuous process of preparing butyric acid by the catalytic reduction of diketene under conditions preventing explosive

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decomposition of the diketene. Other objects will become apparent hereinafter.

In accordance with one feature of the invention, butyric acid may be prepared by a batch process by hydrogenating diketene, in a suitable apparatus adaptable for hydrogenation processes, which is preferably equipped with a heat exchanger, by conducting the initial reaction stage at a relatively low temperature of the order of 25 to 90° C. and a pressure of the order of 300 to 1200 pounds per square inch. As stated previously, the initial reaction is highly exothermic and adequate heat transfer should be supplied to prevent decomposition of the diketene with explosive violence. It is also desirable to control the rate of reaction by employing one or more diluents for the reaction. Inert diluents such as dioxane, hydrocarbon fractions and cyclohexane may be advantageously employed. Preferably, however, I employ beta-hydroxy butyro lactone as a diluent for the initial reduction, i. e. the reduction of diketene to beta-hydroxy butyro lactone. In a continuous process, as explained more fully in the following paragraphs, the lactone diluent may be supplied to the initial reduction by continuously recycling a portion of the lactone, as formed by that reduction, to the diketene being introduced into the reduction chamber. When the initial reaction, which is very rapid, has been substantially completed, the second phase of the reduction is commenced and completed preferably by raising the temperature to the order of 130 to 200° C. and by raising the hydrogen pressure up to 150 atmospheres. Higher pressures and temperatures than these may be employed in the second reaction stage although they appear to give no substantial advantage to the process.

In accordance with another feature of the invention, the process may be conducted continuously by passing the liquid mixture of diketene, and the diluent through a series of enclosed fixed catalyst beds contained in associated pressure chambers, each of which can be maintained at proper temperatures and pressures. Those through which the liquid first passes are maintained within the proper initial temperature and pressure ranges to produce the intermediate compound and those subsequent to this point being maintained at the higher temperatures and pressures as above specified. The final product can be conducted directly to a still or other device and the product separated therein.

If the continuous process employs beta-hydroxy butyro lactone as the diluent for the initial re-

duction, the lactone may be continuously obtained from the initial reaction by retaining, recycling or otherwise maintaining a portion of the intermediate (lactone) product in the reduction chamber system and combining it with the diketene entering the reduction chamber system. Another and major portion of the lactone product is at the same time conducted to a second associated reduction chamber system and there reduced, in accordance with the invention, to butyric acid. The use of beta-hydroxy butyro lactone as a diluent simplifies the purification of the final product since no extraneous diluents have to be separated from the product.

While the present invention may be carried out in any suitable apparatus, for a better understanding of my process and particularly the preferred continuous operation to be described in Examples VII and VIII, an apparatus arrangement is now described.

Reference is made to the attached drawing from a part of the present application which drawing is a side elevation view somewhat in the nature of a flow sheet showing one apparatus arrangement suitable for more or less continuous operation.

As shown in the drawing, there is provided an autoclave which may be a standard commercial unit provided with a stirrer and other usual equipment. However, in particular this autoclave should be provided with adequate temperature control means 13 and 14 for reasons which will be apparent from the description which follows. Such temperature control means may comprise for example either external jackets, internal cooling coils, or various combinations of such or other means.

Autoclave 1 is connected by conduit 3 to autoclave 2 which may be a similar construction to the first-mentioned autoclave. Autoclave 1 is also connected through a pump 5 to a storage tank 6 or other source of the feed material, diketene. Both autoclaves 1 and 2 are provided with connections 15 and 16 to a source 4 of hydrogen.

Referring now in particular to autoclave 2, exit conduit 9 is provided for the removal of the butyric acid from autoclave 2 through suitable condenser means 7. Condenser means 7 is connected with a means 8 for the condensed acid liquid. Receiver 8, which preferably is also a gas and liquid separator is connected through blower 10 and conduits 11 and 16 back with autoclave 2 in order that unconsumed hydrogenating medium may be circulated back to the autoclave.

While not shown, in accordance with usual commercial practice, the equipment may be provided with various flow meters, temperature recording devices and the like for facilitating the operation of the apparatus.

Various hydrogenation catalysts, such as Raney nickel, platinum black, copper chromite and nickel on Kieselguhr, may be employed in the process, but metallic catalysts of the Raney nickel type are preferred. The Raney nickel catalyst is prepared as shown in U. S. Patents 1,628,190 and 1,915,473 by a method of leaching out aluminum from a nickel-aluminum alloy with sodium hydroxide.

The invention is further described in the following examples:

Example I

A rocking autoclave is charged with 100 grams of diketene, 100 grams of dioxane as the diluent and 2 grams of Raney nickel. The temperature of the autoclave was controlled and initial reaction was carried out at 50 to 60° C. at 1200 pounds per square inch of hydrogen and was very rapid. When the reduction had slowed down, the temperature was raised to 160° C. and the hydrogenation completed in three hours. Distillation of the reaction mixture gave 8 grams of a butyraldehyde-water azeotrope and 84 grams of butyric acid, B. P. $_{730}$ 163° C.

Example II

100 grams of diketene, 100 grams of dioxane and 2 grams of Raney nickel were charged into a small autoclave. The initial pressure was maintained at 40 atmospheres of hydrogen and the autoclave was gradually heated up to 200° C. over a period of 3 hours. Distillation of the products of the reaction gave 87 grams of butyric acid.

Example III

300 grams of crude diketene, prepared by the polymerization of ketene in diketene at 40 to 50° C., 300 cc. of dioxane, and 5 grams of Raney nickel were placed in a rocker type autoclave. The autoclave was charged to 100 atmospheres and the temperature was gradually raised to 160° C. over a period of three hours. Distillation gave 278 grams of butyric acid.

Example IV

100 grams of diketene with 2 grams of Raney nickel and 100 grams of beta-hydroxy butyro lactone as a diluent for the reaction were charged into a rocking autoclave. Reduction of the diketene was commenced at 60 to 70° C. at a hydrogen pressure of 800 pounds per square inch. After the reduction had slowed down, the temperature was raised to 150° C. and maintained there for 3 hours. The reaction products were filtered and distilled to give 174 grams of butyric acid.

I have found that relatively high yields of butyric acid are obtained from this process. When employing Raney nickel catalyst, usually the yield is over 80% of the theoretical yield.

The reaction is operable with other catalysts, although as seen in the following example, the yield of acid may not be as high as when employing Raney nickel.

Example V

100 grams of diketene with 5 grams of copper chromite catalyst and 100 grams of dioxane as a diluent for the reaction were charged to the rocking autoclave. The initial reduction began at 60° C. and 600 pounds per square inch. Over a period of 6 hours the temperature was gradually increased to 250° C. and the pressure to 1500 pounds per square inch. Distillation at atmospheric pressure gave 10 grams of butyraldehyde, 12 grams of butyric acid and a solid residue consisting mainly of dehydroacetic acid.

Example VI

Butyric acid was produced by the process as described in Example IV except copper chromite was employed as the catalyst. The yield was considerably less than when employing Raney nickel catalyst. Approximately 34 grams of butyric acid were obtained.

Example VII

Diketene is reduced to butyric acid continuously by hydrogenating in two stages in two associated autoclaves while maintaining the nec-

essary temperatures and pressure. Referring to the drawing, autoclave 1 is charged with beta butyro lactone and Raney nickel catalyst and heated at 60–80° C.; autoclave 2 is charged with butyric acid and Raney nickel catalyst and heated to 160–180° C. Hydrogen gas is added to the system at 300 p. s. i. Diketene is added continuously to autoclave 1 by a piston pump 5 from the storage tank 6. Beta butyro lactone overflows from autoclave 1 through the liquid seal 3 into autoclave 2. Butyric acid is removed continuously by recirculating the gas in autoclave 2 with a blower 10, condensing out the liquid at 7, and separating gas and liquid at 8. In a typical run using two five gallon autoclaves and three per cent Raney nickel 1000 pounds of diketene gave 950 pounds of butyric acid.

Example VIII

The apparatus used is that described in the drawing and in Example VII. Autoclave 1 is charged with equal volumes of cyclohexane and diketene with Raney nickel catalyst and is heated at 70° C. When the initial reduction is complete this charge is transferred to autoclave 2 and heated to 145° C. A second charge of Raney nickel is added to autoclave 1 and hydrogen gas is added to the system at 1200 p. s. i. A mixture of equal volumes of diketene and cyclohexane is added continuously to autoclave 1 by a piston pump 5 from the storage tank 6. Beta butyro lactone and cyclohexane overflow from autoclave 1 through the liquid seal 3 into autoclave 2. Butyric acid and cyclohexane are removed continuously by recirculating the gas into autoclave 2, condensing out the liquid at 7, and separating gas and liquid at 8. One thousand pounds of diketene gave 916 pounds of butyric acid.

From the foregoing examples showing more or less continuous operation, the second stage temperature used is preferably greater than 130° C. However, some reaction can be obtained by merely utilizing in the second stage a temperature higher than that used in the first stage. In other words some butyric acid can be obtained within the range between 90° C. to 130° C., although a temperature substantially above 130° C. is generally preferred.

In the process, the threshold pressure for the reduction at 120° C. to 160° C. may be regarded as approximately 300 lbs./sq. in. Therefore, if pressures above 300 lbs./sq. in. are initially used or attained, the same pressure may be used for both stages of the reduction.

I claim:

1. The process for preparing butyric acid which comprises hydrogenating diketene in a closed vessel at super atmospheric pressures and in the presence of a Raney nickel hydrogenation catalyst and an inert organic liquid diluent at a relatively low temperature within the range of 25 to 90° C. until the initial reaction subsides and continuing the hydrogenation at a relatively higher temperature within the range 130 to 200° C. until hydrogenation is substantially complete.

2. The process for preparing butyric acid which comprises initially hydrogenating 100 grams of diketene in the presence of 100 grams of dioxane and 2 grams of Raney nickel hydrogenation catalyst at a temperature within the range of 50 to 60° C. and 1200 pounds per square inch until the reaction indicates completion and then raising the temperature to 160° C. introducing additional hydrogen and completing a second stage of hydrogenation at this temperature and a similar pressure whereby butyric acid is formed.

3. The process for preparing butyric acid which comprises hydrogenating diketene in a closed vessel in the presence of a Raney nickel hydrogenation catalyst and an inert organic liquid diluent for the reaction, at a relatively low temperature within the range of 25 to 90° C. and at an initial hydrogen pressure within the range of 300 to 1200 pounds per square inch, and then continuing the hydrogenation at a relatively higher temperature within the range of 140 to 200° C. and a hydrogen pressure of 1200 pounds per square inch until the reduction is substantially complete.

4. The continuous process for preparing butyric acid for the continuous catalytic hydrogenation of diketene which comprises continuously adding diketene to a reduction chamber containing a Raney nickel hydrogenation catalyst and hydrogen under a pressure of 800 pounds per square inch and there reducing the diketene at a temperature in the range of 60 to 70° C. to produce continuously beta-hydroxy butyro lactone, continuously withdrawing a portion of this lactone and continuously diluting the diketene being added to the reduction chamber with said portion, continuously withdrawing a second portion of said lactone from the reduction chamber and subjecting it to a further catalytic reduction in another associated reduction chamber under a hydrogen pressure of 800 pounds per square inch at a temperature of 150° C. to produce butyric acid, the amount of the lactone and diketene present in the first reduction chamber being each in order of 100 grams and the catalyst being in the order of 2 grams.

5. A continuous type process for preparing butyric acid which comprises substantially continuously hydrogenating diketene in the presence of a substantial amount of an inert organic liquid diluent for said diketene, conducting said hydrogenation under elevated temperature and pressure conditions and in the presence of a Raney nickel hydrogenation catalyst to obtain a lactone, then substantially continuously subjecting the lactone hydrogenation products to a second hydrogenation conducted at a higher temperature than the first mentioned elevated temperature, substantially continuously withdrawing butyric acid and gases from the second hydrogenation, separating gases from the acid and returning at least a part of the separated gases to said second hydrogenation.

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