CONTINUOUS PRODUCTION OF DIKETENE

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References Cited
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FOREIGN PATENTS OR APPLICATIONS
702,913 1/1954 Great Britain......................... 260/343.9

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ABSTRACT

The continuous production of diketene by dimerizing ketene in diketene containing ketene as a solvent using specific temperature conditions and concentrations.

Diketene prepared by the process is a starting material for the production of acetoacetic esters, dyes, solvents and pesticides.

8 Claims, No Drawings
CONTINUOUS PRODUCTION OF DIKETENE

The invention relates to a process for the continuous production of diketene by dimerization of ketene in a solvent consisting of diketene containing ketene using specific temperature conditions and concentrations.

Various methods are known for manufacturing diketene by dimerizing ketene, for example in contact with a metallic surface (U.S. Pat. No. 1,998,404) or in the presence of butylactone (German Pat. No. 1,240,847) or acetone (UK Pat. Nos. 410,394 or 550,486) as a solvent. The most economical methods are those in which the end product itself is used as the solvent (German Pat. Nos. 1,043,323, 700,218 and 832,440), particularly as the separation and recovery of the solvent are dispensed with. It is convenient to recycle the diketene, to load it with ketene in an absorber and then to carry out the dimerization in a reactor at a temperature of from −5°C to +50°C and a specific residence time. A large reaction space, for example a dimerization chamber, makes possible the necessary dimerization period. It is a disadvantage of all methods that the rate of reaction and consequently the necessary residence time is of low initial concentration of ketene or a low temperature, while at high concentrations of ketene or high temperature (30°C to 50°C) the formation of tar increases.

Some of the effluent crude diketene is continuously withdrawn while the remainder is returned to the absorber (German Pat. No. 1,015,429, UK Pat. No. 702,913). In spite of this being a more advantageous embodiment of the process it is still not satisfactory.

The object of this invention is a process for continuous producing diketene in a simple and economical manner in better space-time yields and purity and in some cases with better yields.

We have found that diketene is advantageously obtained continuously by dimerization of ketene in diketene by carrying out the dimerization in a first stage at a temperature of less than 40°C and with an initial concentration of more than 3 percent by weight of ketene in the dimerization mixture, then in a second stage at a temperature of from 40°C to 55°C with a concentration of from 3 to 1.2 percent by weight of ketene and in a third stage at a temperature of more than 55°C with a concentration of less than 1.2 percent by weight of ketene (percentages with reference to diketene), the recycle diketene having a content of at least 0.5 percent by weight of ketene.

The reaction may be represented by the following formulae:

\[ \text{CH}_2=\text{C}=\text{O} \rightarrow \text{H}_2\text{O}+\text{CH}_2\text{O} \]

\[ \text{C}=\text{O} \]

The process is based on the observation that optimum results are achieved not by a single factor such as a specific dimerization temperature or residence time but by a combination of factors of which a specific concentration of ketene in the recycle diketene is the most significant. In the dimerization, which is carried out in three successive stages at different temperatures, the ketene concentration is correlated with the temperature. The larger the amount of ketene in the diketene stream which has been dimerized, the higher has to be the dimerization temperature. Another essential feature of the invention is that a specific minimum content of ketene has to be present in the diketene cycle, in particular at the points where the diketene is returned and mixed with fresh ketene. As compared with prior art methods, the process according to the invention gives diketene in a simple and economical manner in better space-time yields and purity and in some cases in better yields. In particular the formation of dehydroacetic acid and higher polymers which occur as tarry residues is substantially avoided and the reliability of operation thus improved. Separation of the diketene from the reaction mixture is simpler. Short residence times, for example from four to thirty minutes, are generally sufficient for the dimerization and also smaller, less expensive reactors, for example in the form of coiled tubes, may be used instead of dimerization chambers. These advantageous results even in coiled tubes are surprising having regard to German Pat. No. 1,015,429 (column 4, lines 1 to 34); Tube lengths are not excessive; for example for converting from 400 to 600 kilograms per hour of ketene into diketene, tube lengths of from 150 to 300 meters and internal tube diameters of from 10 to 20 cm are adequate as dimensions of the dimerization chamber. In the process of the invention, a turbulent flow of the reaction mixture, for example having a Reynolds number of more than 100,000, can be set up in the dimerization without the yields of end product being impaired, and this was not to be expected from the prior art (German Pat. No. 1,015,429). Special requirements, for example the use of copper or copper alloys in parts of the plant (German Pat. No. 628,321, page 3, lines 18 to 27) do not exist.

The ketene used for the process according to the invention may be pure or in the form of crude material such as is obtained after dissociation of acetic acid, addition of ammonia and cooling, for example to 10°C. This crude ketene may contain impurities such as methane, carbon dioxide, carbon monoxide, ethylene, propene, butadiene, butyne, hydrogen and particularly water vapor, acetic acid vapor and acetic anhydride vapor, for example in a composition of 80.5 percent by volume of ketene, 2.5 percent by volume of acetic acid, 16.5 percent by volume of gaseous impurities (inert gas) and possibly 0.5 percent by weight of salts, for example ammonium phosphate.

Dimerization may be carried out as follows: the ketene is mixed with diketene in an absorber, preferably countercurrent, and the mixture is then dimerized in three stages in a reactor. After the dimerization, some of the dimerization mixture, preferably from 2 to 7 percent by weight of the mixture, is withdrawn and the remainder of the mixture is returned to the absorber. In the diketene loop, atmospheric pressure or a pressure of 1 to 4 atmospheres gauge and a flow velocity of from 0.2 to 1 meter per second are set up as a rule, and the flow may be laminar or, for reasons of economy, turbulent.

In the absorber, the ketene entering at the lower end impinges on diketene having a content of at least 0.5 percent, preferably from 0.5 to 1.2 percent, by weight of ketene (with reference to diketene, regarded as 100 percent) entering at the top of the absorber. Mixing generally takes place at a temperature of less than 40°C, preferably at from −5°C to +30°C. The rise in temperature during mixing, in which as a rule 12 percent of the total conversion takes place, is generally
A packed column, for example having a length of 3 to 7 meters and a diameter of 40 to 100 cm, may be used advantageously as the absorber for converting 400 to 600 kg of ketene per hour into diketene using Pall rings of aluminum (25 mm × 25 mm × 0.7 mm) or of stainless steel as packing. Liquid-ring pumps or plate columns are also suitable as absorbers. An outlet is provided at the top of the absorber for the withdrawal of offgas which consists as a rule of 70 to 95 percent by weight of inert gas (mainly carbon monoxide, ethylene and methane) and from 5 to 30 percent by weight of ketene. The ketene component in the offgas can be collected in an attached container with an appropriate solvent, for example acetic acid. As a rule 94 percent by weight of the ketene supplied is absorbed, while 6 percent by weight passes into the offgas and is further processed into other products.

After the mixing and upon entry into the first dimerization stage, the mixture has a content of more than 3 percent, preferably from 3 to 7 percent, by weight of ketene with reference to diketene. It passes via a pump from the absorber to the reactor. Any conveying pump, in particular a rotary pump, may be used. The reactor for the dimerization may be any of the reactors suitable for reactions with liquid mixtures, for example stirred kettles, cascades of stirred kettles, plate columns and preferably coiled tubes. A preferred reactor for the process according to the invention is a coiled tube having an internal diameter of 10 to 20 cm and a length of 120 to 240 meters, i.e. having a reaction space of about 1 to 7.5 m³. It generally consists of fifteen to thirty straight members. The coiled tube has three stages having different temperatures. The first stage has a temperature of not more than 40°C, preferably from 30° to 40°C, the second stage of from 40° to 55°C, preferably from 45° to 52°C and the third stage a temperature of more than 55°C, preferably of 60° to 70°C. As regards dimerization space and length of tube, the individual stages are such that in each stage a specific amount of the ketene in the inflowing mixture is dimerized. This can easily be achieved by preliminary experiment. The mixture in the first stage has an initial concentration of more than 3 percent, in the second stage a concentration of 3 to 1.2, preferably 2.1 to 1.5 percent, and in the third stage a concentration of less than 1.2 percent, preferably from less than 1.2 to 0.5 percent, by weight of ketene with reference to diketene. The residence times in the case of a coiled tube are generally from 0.7 minute to six minutes in the first stage and from one minute to ten minutes in the second and third stages. Inert gases are advantageously separated, for example in a cyclone separator, at the outlet from the third stage. The mixture is conveniently passed upwardly through the coiled tube. If the mixture were to be passed downwardly through the reactor, the gas bubbles would migrate upwardly countercurrent to the liquid and would be braked thereby. Gas-filled cavities of varying size would form and cause an undefined decrease in the volume of the reactor, the residence time would be shortened and therefore a large portion of the ketene would escape in the absorber.

After three dimerization stages, the reaction mixture is advantageously cooled to the abovementioned temperature in the absorber, for example in a plate cooler, and fed into the absorber. Some of the mixture is as a rule withdrawn between the dimerization and the cooling means, passed through a holding means where the remainder of the ketene in the mixture is dimerized and then supplied to further processing, for example into acetoacetic esters, or purified by distillation.

Diketene prepared by the process according to the invention is a valuable starting material for the manufacture of acetoacetic esters and dyes, solvents and pesticides. Reference is made to the said Patents and Ullmann Encyclopädie der technischen Chemie, volume 9, pages 541 et seq. as regards the use of diketene.

The following Example illustrate the invention. The parts given in the following Example are parts by weight.

**EXAMPLE**

A crude ketene gas (85 percent by weight of ketene and 15 percent by weight of inert gas consisting of 50 percent by weight of carbon monoxide, 25 percent by weight of ethylene, 20 percent by weight of methane and 5 percent by weight of carbon dioxide) with 646 parts per hour of ketene is passed into an absorber at a pressure of 1.2 atmospheres. The absorber is a packed column (two sections each 2.50 meters in length) having a cross-section of the empty tube of 0.28 m². The packing is Pall rings of aluminum (25 mm × 25 mm × 0.7 mm). 609 parts of ketene per hour is absorbed and 37 parts per hour leave together with inert gas and are further processed into acetic anhydride. 24,100 parts per hour of diketene still containing 226 parts per hour of ketene dissolved therein is fed into the top of the column for the absorption of this ketene. Since 83 parts per hour of ketene dimerizes during mixing, 752 parts per hour of ketene (consisting of 226 parts per hour of ketene from the previous circulation and 609 parts per hour of fresh ketene) pass from the absorber through a pump to the reactor.

The reactor is a coiled tube (22 straight portions and appropriate bends each having a length of 770 cm) having an internal diameter of 15 cm, a length of 170 meters and cooling water jackets. Flow in the reactor is turbulent (Reynolds number = 100,000). A bleed tube is provided downstream of the reactor for withdrawal of end product. The mixture is passed upwardly through the reactor and is kept at 38°C in the first stage (length of tube 50 meters), at 50°C in the second stage (50 meters) and at 65°C in the third stage. It has the abovementioned concentration of ketene which declines 2.3 percent in the first stage, in the second stage it has a concentration of from 2.3 to 1.2 percent and in the third stage of from less than 1.2 to 0.8%, by weight with reference to diketene. A total of 526 parts of ketene per hour is reacted. The residence times are two, two and three minutes in the sequence of stages. The remaining 226 parts of ketene per hour remains physically dissolved in the diketene. Some of this solution (609 parts per hour) is withdrawn beyond the coiled tube ahead of the cooling means and the ketene constituent is dimerized in an after-reactor. The main portion (23,500 parts per hour) is cooled to 30°C in a plate cooler, returned to the absorber and again mixed with ketene therein. A cyclone separator is located at the outlet from the coiled tube and 10 parts per hour of inert gas is separated therein. 5 parts of acetic acid, 42 parts of residue and 562 parts of diketene per hour (equivalent to 92 percent of the theoretical yield and 94 percent of the theoretical conversion, with reference to ketene fed in) are obtained from the 609 parts per hour of ketene absorbed in the
diketene. The space-time yield is 187 parts per m$^3$ per hour.

We claim:

1. A process for the continuous manufacture of diketene by dimerization of ketene in diketene as a solvent wherein dimerization is carried out in a first stage at a temperature of not more than 40°C and with an initial concentration of more than 3 percent by weight of ketene with reference to diketene in the dimerization mixture, then in a second stage at a temperature of from 40°C to 55°C with a concentration of from 3 to 1.2 percent by weight of ketene and in a third stage at a temperature of more than 55°C with a concentration of less than 1.2 percent by weight of ketene with reference to diketene in the dimerization mixture, and the recycle diketene has a content of at least 0.5 percent by weight of ketene with reference to diketene.

2. A process as set forth in claim 1 wherein dimerization is carried out in a coiled tube having an internal diameter of from 10 to 20 cm and a length of from 120 to 240 meters.

3. A process as set forth in claim 1 wherein dimerization is carried out in the first dimerization stage with from 3 to 7 percent by weight of ketene with reference to diketene.

4. A process as set forth in claim 1 wherein dimerization is carried out in the second dimerization stage with from 2.1 to 1.5 percent by weight of ketene with reference to diketene.

5. A process as set forth in claim 1 wherein dimerization in the third stage is carried out with from 1.2 to 0.5 percent by weight of ketene with reference to diketene.

6. A process as set forth in claim 1 wherein dimerization in the first stage is carried out at a temperature of from 30°C to 40°C.

7. A process as set forth in claim 1 wherein dimerization in the second dimerization stage is carried out at a temperature of from 45°C to 52°C.

8. A process as set forth in claim 1 wherein dimerization in the third dimerization stage is carried out at a temperature of from 60°C to 70°C.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,865,846
DATED : February 11, 1975
INVENTOR(S) GERHARD SCHULZ, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading, insert--[30] January 16, 1970 Germany
P 20 01 815.9--

Signed and Sealed this
eighteenth Day of May 1976

[SEAL]

Attest:

RUTH C. MASON
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