United States Patent

Ellis et al.

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[54] **PROCESS FOR PRODUCING ORGANIC ACIDS**

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[52] **U.S. Cl.** .....**260/533 R,** 260/413

[51] **Int. Cl.** **C07c 51/00,** C07c 51/32

[58] **Field of Search** .....260/533 R, 413

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

An improvement in a process for converting an unsaturated, acyclic hydrocarbon to a carboxylic acid in which the unsaturated, acyclic hydrocarbon is reacted with oxygen containing a small amount of ozone at a low temperature to obtain an intermediate product in a first stage and the intermediate product is oxidized in a second stage with molecular oxygen at a higher temperature to obtain the desired carboxylic acid, which involves employing a solvent mixture comprising a major amount of a carboxylic acid solvent having a boiling point as high or higher than the highest boiling point of a carboxylic acid formed during the reaction and a minor amount of lower carboxylic acid solvent or a lower alcohol solvent, whereby fogging during the first stage of the process is reduced.

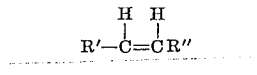
14 Claims, No Drawings

PROCESS FOR PRODUCING ORGANIC ACIDS

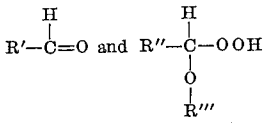
This invention relates to a process for converting an unsaturated, acyclic hydrocarbon to an organic carboxylic acid by using ozone an oxygen. More specifically, this invention relates to an improvement in the process wherein an unsaturated, acyclic hydrocarbon is subjected to ozonolysis in a first stage while the same is dissolved in a solvent mixture containing a minor amount of a lower organic carboxylic acid solvent or a lower alcohol solvent.

Unsaturated, acyclic hydrocarbons that can be used herein as charge can include straight or branched chain olefins, terminal as well as internal, having from five to 12 carbon atoms, preferably from six to 10 carbon atoms. Specific examples of olefins that can be used are pentene-1, octene-1, octene-1,2, dodecene-3, decene-5, 3-methylpentene-1, 3-ethyldecene-3, etc.

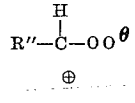
The ozonolysis procedure used in the first step follows the conventional outline. Thus, for example, a stream of gas containing molecular oxygen, such as oxygen itself and from about 0.5 to about 6, or even higher, but preferably about 2 to about 3 per cent, by weight of ozone relative to oxygen is passed continuously through the olefin charge dissolved in a unique solvent mixture, to be defined hereinafter, at such a rate so that the exit stream will be substantially free of ozone, continuing until some ozone is found in the exit gas, at which time the ozonolysis reaction will have terminated. Since ozonolysis is substantially instantaneous, the time of contact depends upon obtaining suitable contact between ozone and unreacted olefin. The temperature can be from about −20° C. to about 35° C., preferably about 10° C. to about 20° C., and while pressure as high as about 50 pounds per square inch gauge can be employed, atmospheric pressure is preferred. As a result of ozonolysis, cleavage of the olefinic double bond occurs to form aldehydes and hydroperoxides. Thus, the olefin



for example, R′ and R″ being alkyl substituents, is believed to be converted to



wherein R‴ represents an alkyl group in the case of an alcohol solvent and an acyl group in the case of an acid solvent. The hydroperoxide is believed to result from the addition reaction of the intermediate Zwitterion



with a component of the solvent mixture used herein.

The aldehydes and hydroperoxides so produced are then subjected to oxidation in a second stage with a gas containing molecular oxygen, preferably air. Any effective method which insures contact between the aldehyde and the hydroperoxide and oxygen can be used. In a preferred embodiment air is continuously passed through the ozonolysis product and this is preferably continued until there is no noticeable reduction in oxygen content of the exit stream. The amount of oxygen stoichiometrically needed, relative to the ozonolysis product, defined as consisting essentially of aldehydes and hydroperoxides, on a molar basis must be at least about 0.5:1, but in general from about 5:1 to about 100:1, is used. Temperatures of about 70° C. to about 150° C., preferably about 80° C. to about 110° C., can be used. Pressures as high as about 100 pounds per square inch gauge can be employed, but in general atmospheric pressure is preferred. A reaction time of about 0.5 to about two hours will generally suffice. As a result of the oxidation step it is believed the aldehydes are oxidized and the hydroperoxides are rearranged to the corresponding organic carboxylic acids. Recovery of the organic carboxylic acids from the reaction mixture can be effected in any desired manner, but in general fractional distillation is preferred.

In order to assist in the recovery, by distillation, of the product carboxylic acids from the reaction product at the end of the second stage, we intend to use a solvent mixture containing a major amount of an organic carboxylic acid solvent having a boiling point as high, or higher, than the highest boiling point of the organic carboxylic acids produced herein. This is so because the organic carboxylic acids produced can then be distilled from the reaction mixture, leaving behind the high-boiling organic carboxylic acid solvent which can then be recycled for reuse in a subsequent oxidation process. If an organic carboxylic acid, such as acetic acid, having a boiling point lower than the organic carboxylic acids produced were used, recovery of the product organic carboxylic acids could not begin until all said lower-boiling carboxylic acid is first distilled therefrom. Moreover, near the end of the distillation period, recovery of the last of the desired organic carboxylic acid product from any small amount of heavier by-products that might be present would be difficult without the addition of a chaser thereto.

Unfortunately, we have found that the use of the defined high-boiling organic acid solvent in the ozonolysis procedure employed in the first step results in a potentially hazardous fog. These conditions could give rise to explosive mixtures. We have found that such fogs can be substantially reduced by adding a minor amount of a lower organic carboxylic acid solvent or a lower alcohol solvent to the defined high-boiling carboxylic acid solvent. Of course, during the distillation recovery period such added organic carboxylic acid or lower alcohol could come off prior to the desired organic carboxylic acid product and reused, but since the amounts used are small no significant increase in operating expense would be entailed thereby.

The organic carboxylic acid solvent having a boiling point as high, or higher, than the organic carboxylic acids produced herein, can be defined as having from five to 10 carbon atoms, preferably from six to nine carbon atoms. Specific examples of such organic carboxylic acids are alkanoic acids such as hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, 2-methylhexanoic acid, 3-methyloctanoic acid,

etc. The lower organic carboxylic acid solvents that are added to the organic carboxylic acid solvent are the alkanoic acids formic acid, acetic acid and propionic acid, while the alcohols are the alkanols, methanol, ethanol, normal propanol and isopropanol. The amount of higher boiling carboxylic acid solvent used, based on the total reaction mixture, can be from about 50 to about 95 per cent by weight, preferably from about 65 to about 85 per cent by weight. The amount of lower carboxylic acid solvent added to the higher boiling point carboxylic acid solvent, based on the total reaction mixture, can be from about 1 to about 10 per cent by weight, preferably from about 2 to about 5 per cent by weight, while the amount of lower alcohol solvent can be from about 5 to 15 per cent by weight, preferably from about 7 to 10 per cent by weight.

The process defined herein can further be illustrated by the following.

EXAMPLE I

Thirty grams of an internal olefin mixture containing 91 per cent by weight of decene-5 was dissolved in 70 grams of pelargonic acid and oxidized at 20° to 25° C. and atmospheric pressure by passing oxygen containing from 2 to 3 per cent by weight of ozone through the mixture at the rate of 1 liter per minute over a period of about 2 hours. During the ozonization a heavy fog was observed in the vapor phase. After the ozone take-up was completed the mixture was heated to 120° while oxygen was passed therethrough at the rate of 1 liter per minute over a period of 2 hours. During the heat-up period the temperature increased to about 170° C. for a short time in a violent reaction. The temperature subsequently returned to 120° C. The product obtained was found to contain mainly pentanoic acids.

EXAMPLE II

The experiment of EXAMPLE I was repeated, except that 5 grams of propionic acid was added to the reaction mixture prior to ozonization. Only a slight amount of fog was noted, and the temperature during oxidation rose to only 150° C.

EXAMPLE III

The experiment of EXAMPLE I was again repeated, except that four grams of acetic acid was added to the reaction mixture prior to ozonization. Only a slight amount of fog was noted, and the temperature during the subsequent oxidation step rose to only 140° C.

EXAMPLE IV

When the experiment of EXAMPLE I was repeated, but with 4 grams of formic acid also present initially, only traces of fog were noted and the temperature during oxidation rose to only 140° C.

EXAMPLE V

Repeating the experiment of EXAMPLE I, but with 5 grams of methanol also present, fog was reduced slightly. When 10 grams of methanol was used only traces of fog was noted. In each case the temperature during oxidation rose to 130° C.

EXAMPLE VI

The experiment of EXAMPLE I was repeated, except that ten grams of normal propanol was also present in the initial reaction mixture. There was noted a slight decrease in fog, and the temperature during the oxidation was reduced to 120° C.

EXAMPLE VII

Thirty grams of a blend of internal olefins of a carbon range of C_6 to C_{10} was dissolved in 70 grams of pelargonic acid. The ozonization and oxidation were performed in the same manner as in EXAMPLE I. A heavy fog was observed and the temperature during the oxidation rose to 155° C.

EXAMPLE VIII

When the experiment of EXAMPLE VII was repeated, but with ten grams of formic acid also present initially, only a slight amount of fog was noted and the temperature during the oxidation step rose to no higher than 135° C.

EXAMPLE IX

Repeating the experiment of EXAMPLE VII, but with 10 grams of methanol present initially, only a slight amount of fog was noted, and the temperature rose to 120° C.

Obviously, many modifications and variations of the invention, as hereinabove set forth, can be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In a process for converting an unsaturated, acyclic hydrocarbon having from five to 12 carbon atoms to a carboxylic acid wherein the unsaturated, acyclic hydrocarbon in reacted with ozone at a low temperature of about −20° C. to about 35° C. to obtain an intermediate product in a first stage and the intermediate product is oxidized in a second stage with molecular oxygen at a higher temperature of about 70° C. to about 150° C. to obtain the desired carboxylic acid, the improvement which comprises carrying out the process in a solvent mixture comprising a major amount of an alkanoic acid solvent having from five to 10 carbon atoms and a boiling point as high or higher than the highest boiling point of a carboxylic acid formed during the reaction and a minor amount of a lower alkanoic acid solvent having from one to three carbon atoms or a lower alkanol solvent having from one to three carbon atoms.

2. The process of claim 1 wherein the hydrocarbon charge has from six to 10 carbon atoms, the reaction with ozone in the first stage is carried out at a temperature of about 10° C. to about 20° C., the oxidation in the second stage is carried out at a temperature of about 80° C. to about 110° C. and said higher boiling carboxylic acid solvent has from six to nine carbon atoms.

3. The process of claim 1 in which said higher boiling carboxylic acid solvent has from six to nine carbon atoms.

4. The process of claim 1 in which said higher boiling carboxylic acid solvent is pelargonic acid.

5. The process of claim 1 in which said lower carboxylic acid solvent is formic acid.

6. The process of claim 1 in which said lower carboxylic acid solvent is acetic acid.

7. The process of claim 1 in which said lower carboxylic acid solvent is propionic acid.

8. The process of claim 1 in which the lower alcohol solvent is ethanol or isopropanol.

9. The process of claim 1 in which the lower alcohol solvent is methanol.

10. The process of claim 1 in which the lower alcohol solvent is normal propanol.

11. The process of claim 1 in which the amount of said higher boiling carboxylic acid solvent is from about 50 to about 95 per cent by weight, based on the total reaction mixture, and the amount of said lower carboxylic acid solvent is from about 1 to about 10 per cent by weight based on the total reaction mixture.

12. The process of claim 1 in which the amount of said higher boiling carboxylic acid solvent is from about 65 to about 85 per cent by weight, based on the total reaction mixture, and the amount of said lower carboxylic acid solvent is from about 2 to about 5 per cent by weight based on the total reaction mixture.

13. The process of claim 1 in which the amount of said higher boiling carboxylic acid solvent is from about 50 to about 95 per cent by weight, based on the total reaction mixture, and the amount of said lower alcohol solvent is from about 5 to about 15 per cent by weight based on the total reaction mixture.

14. The process of claim 1 in which the amount of said higher boiling carboxylic acid solvent is from about 65 to about 85 per cent by weight, based on the total reaction mixture, and the amount of said lower alcohol solvent is from about 7 to about 10 per cent by weight based on the total reaction mixture.

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