METHOD FOR THE PREPARATION OF α,β-UNSATURATED CARBOXYLIC ACIDS

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Filed: Sept. 24, 1973

Appl. No.: 399,705

Foreign Application Priority Data
Sept. 27, 1972 Germany .............................. 2247312

U.S. Cl. ........................................ 260/533 A; 260/497 R
Int. Cl. ......................................... C07C 51/14
Field of Search .................................. 260/533 A

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ABSTRACT
An improved method for the oxycarbonylation of olefins to form α,β-unsaturated carboxylic acids, which method employs a catalyst system consisting essentially of certain combinations of compounds of metals of the fourth to seventh sub-groups of the Periodic System with compounds of copper, zinc, cerium, tin, iron, cobalt, and nickel.

6 Claims, No Drawings
METHOD FOR THE PREPARATION OF \(\alpha,\beta\)-UNSATURATED CARBOXYLIC ACIDS

The present invention relates to a process for the preparation of \(\alpha,\beta\)-unsaturated carboxylic acids by the oxidative carboxylation of olefins in the presence of catalyst systems consisting essentially of certain combinations of compounds of metals of the fourth to seventh sub-groups of the Periodic System with compounds of copper, zinc, cerium, tin, iron, cobalt, and nickel.

The preparation of unsaturated carboxylic acids by the reaction of olefins with carbon monoxide and oxygen, i.e., by so-called oxycarbonylation, in the presence of a platinum metal as a catalyst is known in the art. Among the platinum metals, palladium takes a preferred position. By the joint use of a compound of a metal with a higher oxidation potential than the platinum metal employed, for example by the use of a catalyst system comprising palladium chloride and copper chloride, one obtains, e.g., in the oxycarbonylation of ethylene in glacial acetic acid as a solvent, acryl acid in good yield in addition to \(\beta\)-acetoxy propionic acid. The latter-mentioned acid can easily be cleaved thermally into acrylic acid and acetic acid.

Fenton and Olivier have discussed the oxycarbonylation of olefins in the presence of catalysts comprising a platinum metal in a comprehensive article in CHEM-TECH, 220 – 225, (April, 1972). The aforementioned catalyst systems have the disadvantage of the high cost of the platinum metals, of difficult working up procedures, and of the sensitivity of the catalyst to catalyst poisons.

Several of the catalyst systems according to the present invention are superior to catalysts comprising a platinum metal, particularly from the point of view of the rate with which the oxycarbonylation of an olefin occurs.

Copending U.S. Pat. application Ser. No. 382,378, filed July 25, 1973, describes and claims a process for the preparation of \(\alpha,\beta\)-unsaturated carboxylic acids from olefins, carbon monoxide, and oxygen in a non-aqueous liquid medium in the presence of a catalyst. Exemplary olefins which can be oxycarbonylated to form unsaturated carboxylic acids are ethylene, propylene, butylene, isobutylene, pentene-2, hexene-1, and butadiene. The heart of the invention in this process is the use of a catalyst system comprising at least one compound selected from the group consisting of (a) compounds of aluminum, boron, or of the alkaline earth metals and (b) compounds of elements of the fourth to seventh subgroups of the Periodic System, said compounds being soluble in the liquid reaction medium.

The present invention concerns an improvement in this earlier process in which the oxycarbonylation of olefins is carried out in the presence of a catalyst which, on the one hand, comprises a compound of one of the elements of the fourth to seventh subgroups of the Periodic System and, on the other hand, of at least one compound of copper, tin, cerium, iron, cobalt, nickel, or zinc.

Copending U.S. Pat. application Ser. No. 372,695 filed June 22, 1973 describes and claims the oxycarbonylation of ethylene and propylene in the presence of a catalyst system comprising rhenium, a metal in the seventh sub-group of the Periodic System, with, as a co-catalyst, a compound or compounds of lithium, copper, iron, manganese, and of metals in the second to sixth main and sub-groups of the Periodic System, which latter encompass tin, cerium, and zinc. Thus, catalyst systems comprising a compound of rhenium in combination with compounds of copper, iron, tin, cerium, and zinc are outside the scope of the present invention.

The reaction conditions employed in the process described in the aforementioned application Ser. No. 382,378, incorporated herein by reference, are also necessary and sufficient for carrying out the improvement according to the present invention. That is, the reaction takes place in a substantially non-aqueous liquid medium, suitably at an elevated temperature up to 300°C. (although some catalysts are active at room temperature), and preferably at a temperature between 80°C. and 200°C.

The chemical equation for an oxycarbonylation reaction, e.g. for the oxycarbonylation of ethylene,

\[
\ce{H_2C=CH_2 + CO + 1/2 O_2 -> H_3C=CH-COOH}
\]

does not show that the formation of the \(\alpha,\beta\)-unsaturated carboxylic acid is favored by the use of pressure. The use of pressure is also indicated if only for the maintenance of liquid phase conditions. For this reason the reaction is carried out under pressure, advantageously under a pressure of from 1 to 200 atmospheres, even when the oxycarbonylation of olefins in the presence of the catalyst according to the present invention takes place at normal pressure.

The process can be carried out discontinuously or continuously.

Oxygen is preferably introduced so that the oxygen content of the gases being removed remains under the explosion concentration, i.e., less than about 10 volume percent, and preferably less than about 3 volume percent. The excess gas, principally comprising olefin and carbon monoxide, can be reintroduced into the liquid reaction medium. The addition of an inert gas, for example nitrogen, is suitable for the avoidance of explosive gas mixtures.

The amount of catalyst to be employed can vary over wide limits, depending on the specific activity of the catalyst and of the other reaction conditions, and can, in general, be between 0.01 to 5 percent by weight of the liquid medium. Within the catalyst, the mol ratio of the metal from the fourth to seventh subgroups of the Periodic System to the metal or metals used therewith may vary broadly between 100:1 and 1:100 since the components exert an almost equivalent catalytic effect.

It is known in the art, for example from the work of Fenton and Olivier mentioned earlier herein, to carry out oxycarbonylation in a non-aqueous medium and to hinder undesirable side reactions, which can take place under the influence of water formed during the course of the reaction, by adding agents binding water to the reaction medium. Among these, the anhydrides and chlorides of carboxylic acids can be mentioned as most important. Preferably, the anhydride or chloride of that carboxylic acid which is present as the liquid reaction medium is used. However, molecular sieves comprising aluminum silicates may also be used to bind water produced by side reactions.

The reaction medium and the catalyst components are so adapted to each other that at least a catalytically active quantity of the metal compounds can pass into solution. Due to the fundamentally strong polar nature of the metal compounds, strongly polar anhydrous liquids particularly come into consideration. Preferably,
aliphatic carboxylic acids such as acetic acid, propionic acid, or crotonic acid are employed. Other suitable organic liquids are formamide, mono- and dimethyl formamide, acetamide, N-substituted acetamides, acetone, methyl ethyl ketone, cyclohexanone, dimethyl carbonate, methyl formate, diethyl oxalate, of which the less polar liquids are used primarily in admixture with more strongly polar liquids, particularly when the metal compounds are particularly strongly polar. Certain organic liquids, such as acetyl acetone, dimethyl formamide, dimethyl sulfoxide, or hexamethyl phosphoramide themselves exert a complexing action and can detrimentally affect the course of the reaction, for which reason their suitability must be carefully checked in each individual case.

The liquid reaction medium is advantageously selected that it can be easily separated — in particular by distillation — from the α,β-unsaturated carboxylic acid formed. Therefore, low-boiling liquids are preferably used for the production of high-boiling carboxylic acids, and vice versa. However, the acid which is to be produced can itself be used as reaction medium, thereby avoiding all problems as to separation, i.e., acryl acid for the oxycarboxylation of ethylene, or methacrylic acid for the oxycarboxylation of propylene.

The metal compounds used as catalyst should, as mentioned above, be at least of limited solubility in the reaction medium. However, they can also pass into solution by chemical reaction; for instance metal oxides or hydroxides which pass into the corresponding acetates in acetic acid can be employed. It is sufficient for a catalytically active quantity of the metal compounds to pass in solution at the reaction temperature, possibly merely in the presence of all other reactants, while the solubility at room temperature in the pure organic liquid may be any desired. If the active catalyst is not present in dissolved form in the reaction mixture, it must at least form from the dissolved components.

Suitable metal compounds are, for instance, the chlorides, bromides, chlorates, nitrates, carbonates, cyanides, hydroxides, oxides, formates, acetates, benzoates, phthalates, picrates, acetyl acetones, etc. Salts free of water of crystallization are preferred in principle. The carbonyl and complexing agents of the complexes can also be used provided that the complexes are not more stable than the catalytically active complexes. Organometallic compounds can also be used in many cases, although they are not preferred because of their high price. It may be advantageous to contact the metal compounds for a prolonged time with the reaction medium and possibly heat them before the start of the reaction. Once the active complexes have been formed, the catalysts will not be modified for a prolonged time. It has even been observed that the activity and selectivity increase further upon prolonged operation. Nevertheless it is advantageous to replace the catalyst now and then or continuously because of the unavoidable entrance of impurities.

Although by combining compounds of metals of the fourth to seventh sub-groups of the Periodic System with compounds of the aforementioned metals (i.e., copper, zinc, cerium, tin, iron, cobalt, and nickel), catalyst systems are obtained which preferably lead to the formation of an α,β-unsaturated carboxylic acid, side reactions can usually not be completely hindered. For example acetoxy carboxylic acids may be formed when the process is carried out in acetic acid or the two isomeric unsaturated carboxylic acids may be formed in the oxycarboxylation of propylene. Further, the catalysts of the invention promote direct oxidation of olefins to the corresponding glycol which then, if one operates in a carboxylic acid reaction medium, is completely or in part converted to the corresponding ester. The concurrent reactions which occur in the presence of particularly chosen catalysts, namely the oxycarboxylation of ethylene or propylene to an α,β-unsaturated carboxylic acid on the one hand, and the direct oxidation of the olefin to the corresponding glycol on the other hand, can result in the formation of glycol monosters or glycol diesters of the unsaturated carboxylic acid first formed, i.e., to a result which can be highly desirable.

In the oxycarboxylation of ethylene, a catalyst system comprising manganese-III-acetate and copper-II-chloride has proved particularly useful. Operation under a pressure between 80 and 100 atmospheres and in a temperature region between 100°C. and 150°C. permits the oxycarboxylation to proceed smoothly and with a high yield. In addition to acetoxypropionic acid, acrylic acid is formed by the reaction in high yield, as is described more in detail in Example 1 herein. The acetoxypropionic acid can be converted to acetic acid and acrylic acid by pyrolysis.

Although no detailed theory of the mechanism of the catalytic process can yet be formulated, nevertheless one can proceed from the viewpoint that the metal compounds to be combined with one another according to the invention form multinuclear complexes having olefin molecules, carboxyl groups, and oxygen as ligands. Surprisingly, it has proved that those catalysts which comprise a cyanide or a halide, particularly a chloride or a bromide, are particularly active. If the aforementioned theoretical considerations concerning the formation of multi-nuclear complexes as intermediate products are accurate, then the aforementioned halides may likewise be ligands of the postulated complexes. In order to make the formation of such particularly active complexes possible, at least one of the metal compounds forming part of the catalyst system can be introduced as a halide and/or the halide or the cyanide of a different metal can be introduced into the reaction mixture.

All of the combinations of compounds of metals of the fourth to seventh sub-groups of the Periodic System, on the one hand, with compounds of copper, zinc, cerium, tin, iron, cobalt, and nickel, on the other hand, have the common property that they favorably influence catalytically the formation of α,β-unsaturated carboxylic acids by the oxycarboxylation of an olefin. Different combinations show considerable differences from the point of view of their selectivity and in their striking catalytic activity influencing space time yield. Thus, whereas in the oxycarboxylation of ethylene, acrylic acid and — if the reaction is carried out in acetic acid — β-acetoxypropionic acid are primarily formed, the corresponding reaction of propylene can lead to the formation of the two isomers, methacrylic acid and crotonic acid, or to the corresponding addition compounds of these acids with the carboxylic acid employed as the reaction medium. Mention has already been made of the case with which these addition compounds, for example the acetoxy carboxylic acids, can be cleaved, for example into acetic acid and the corresponding α,β-unsaturated carboxylic acid.
Of the unsaturated acids often concurrently formed during the oxycarbonylation of propylene, that is methacrylic acid and crotonic acid, the former acid is at the present time known to be of the greatest technical significance. Nevertheless, a new method for the simple manufacture of crotonic acid or of its derivatives, particularly of its esters, also leads to technically interesting products.

A better understanding of the present invention and of its many advantages will be had by referring to the following specific examples, given by way of illustration.

In the following examples, the following procedure was used. Acetic acid and acetic acid anhydride, in the amounts described below, were introduced together with the catalyst mixture into a 2-liter "Teflon"-coated autoclave equipped with heating apparatus. The autoclave was closed. The olefin was now introduced under pressure into the autoclave. Ethylene was introduced until a pressure of 40 atmospheres was reached. The propylene, because of its low liquefaction pressure of ten atmospheres or more must be introduced under pressure in several stages in order to saturate the reaction medium with this olefin. Then, carbon monoxide and oxygen were introduced under pressure and the reaction mixture was heated to 100°C. – 150°C.

At the end of the reaction, recognizable by the drop in pressure and — on discontinuance of heating — by the drop in the interior reactor temperature, the contents of the autoclave were worked up by distillation. In the oxycarbonylation of ethylene, the acrylic acid formed distilled over at a head temperature of 140°C. In the reaction of propylene, the crotonic acid and methacrylic acid were taken off under vacuum at a temperature between 80°C. and 100°C. The crotonic acid solidified in a cooled receiver (m.p. = 72°C.).

The reaction products formed were analyzed by known methods using gas chromatography, determination of the bromine number, and by taking the IR-spectrum and the magnetic resonance spectrum.

**EXAMPLE 1**

2.5 g of manganese-III-acetate and 2.5 g of copper-II-chloride were dissolved in 450 ml of glacial acetic acid to which were added 50 ml of acetic anhydride. Thereafter, 40 atmospheres of ethylene, 40 atmospheres of carbon monoxide, and 15 atmospheres of oxygen were introduced under pressure and the autoclave was heated to 140°C. Distillation gave:

- 23.5 g of acrylic acid
- 11.9 g of β-acetoxypropionic acid.

**EXAMPLE 2**

2.5 g of manganese-III-acetate and 2.5 g of copper-II-chloride were dissolved in 400 ml of glacial acetic acid and 50 ml of acetic anhydride with warming. After saturation with propylene, 80 atmospheres of carbon monoxide and 20 atmospheres of oxygen were introduced under pressure and the vessel was heated to 150°C. 14.95 grams of crotonic acid and 13.15 grams of β-acetoxy-n-butyric acid were formed.

**EXAMPLE 3**

2 g of manganese dioxide and 2 g of copper chloride were dissolved in 450 ml of acetic acid and 50 ml of acetic anhydride. The mixture was then saturated with propylene. 80 atmospheres of carbon monoxide and 20 atmospheres of oxygen were introduced under pressure and the reaction mixture was heated to 150°C. 1.2 g of crotonic acid and 0.3 g of methacrylic acid were formed.

**EXAMPLE 4**

The catalyst employed in Example 3 was again dissolved in 450 ml of glacial acetic acid and 50 ml of acetic anhydride and used as in Example 3. Working up gave 16.3 g of crotonic acid and 0.25 g of methacrylic acid.

**EXAMPLE 5**

The catalyst of Examples 3 and 4 was again dissolved in 450 ml of glacial acetic acid and 50 ml of acetic anhydride. Then, 40 atmospheres of ethylene, 40 atmospheres of carbon monoxide, and 20 atmospheres of oxygen were introduced under pressure and heated to 140°C. 33.25 g of acrylic acid were formed.

**EXAMPLE 6**

1.2 g of tungsten hexachloride and 5 g of copper-II-chloride were dissolved in 300 ml of glacial acetic acid and 25 ml of acetic anhydride. After saturation with propylene, 80 atmospheres of carbon monoxide and 20 atmospheres of oxygen were introduced under pressure and heated to 140°C. 14.2 g of crotonic acid and 0.5 g of methacrylic acid were produced.

**EXAMPLE 7**

A solution of 2 g of manganese-III-acetate, 2 g of copper acetate, and 5 g of potassium bromide in 490 ml of glacial acetic acid and 10 ml of acetic anhydride was saturated with propylene by the successive introduction thereinto of propylene at a pressure of 10 atmospheres. 80 atmospheres of carbon monoxide and 20 atmospheres of oxygen were then introduced under pressure into the solution. The reaction mixture was heated to 120°C. 20 minutes after this temperature was reached, heating was discontinued. Working up of the reactor contents after cooling gave:

- 34.5 g of crotonic acid
- 1.3 g of methacrylic acid
- 3.6 g of propylene glycol diacetate.

**EXAMPLE 8**

The same procedure as in Example 7, using a catalyst system comprising 1 g of tantalum-V-chloride and 2 g of copper chloride, produced:

- 4.9 g of crotonic acid
- 1 g of methacrylic acid
- 15.2 g of β-acetoxy-n-butyric acid.

**EXAMPLE 9**

A catalyst comprising 2.5 g of manganese-III-acetate and 2.5 g of tin-II-chloride was treated according to Example 8. 3.5 g of crotonic acid and small amounts of methacrylic acid were obtained.

**EXAMPLE 10**

A catalyst system comprising 2.5 g of manganese-III-acetate and 2.5 of cerium-III-chloride, when employed according to the process of Example 9, gave: 4.7 g of crotonic acid, 1.4 g of β-acetoxy-n-butyric acid, and small amounts of methacrylic acid.

**EXAMPLE 11**

In 25 ml of glacial acetic acid, 3 g of acetylacetone, and 2.4 g of ferric chloride were dissolved while stirring.
and to this solution 1.1 ml of titanium tetrachloride were added. The precipitated orange-red complex of titanium and iron corresponds to the one published in Chem. Ber. Vol 37, pg. 589 (1904).

In an Teflon coated autoclave an additional 450 ml of glacial acetic acid and 50 ml of acetic anhydride were added to the above mentioned reaction mixture. Proceeding as in Example 7 the autoclave was charged with propylene, carbon monoxide and oxygen and heated to 160°C. The precipitated orange-red complex of titanium and iron was filtered off by centrifugation and washed with 20 ml of glacial acetic acid and 80 ml of acetic anhydride.

The reaction yielded
32.4 g of β-acetoxy-n-butyric acid (which correspond to 19.1 g of crotonic acid)
9.1 g of propylene glycol diacetate

EXAMPLE 12

The same procedure as in Example 11, using a catalyst comprising a solution of 2.0 of cerium-III-chloride and 2.0 g of chromium-III-chloride in 630 ml of glacial acetic acid and 70 ml of acetic anhydride, produced
1.5 g of crotonic acid
0.5 g of methacrylic acid
13 g of propylene glycol diacetate.

EXAMPLE 13

Proceeding according to example 12, 2 g of bis(triacetylacetonatotitanium-IV)hexachlorotitinate and 2 g of copper-III-chloride were used as catalyst. The reaction produced
3.7 g of crotonic acid
60 g of α-acetoxy-n-butyric acid (corresponding to 35.4 g of crotonic acid)
2.8 g of propylene glycol diacetate, and
a small amount of methacrylic acid.

EXAMPLE 14

The same procedure as in Example 12, using 2 g of manganese-III-acetate and 2 g of nickel-II-bromide as catalyst, yielded
3.0 g of crotonic acid
0.5 g of methacrylic acid, and
5.1 g of propylene glycol diacetate.

EXAMPLE 15

The reaction was carried out as described in Example 12 using a solution of 2 g of vanadium-V-oxy-tri-acetate, 2 g of copper-II-acetate, and 5 g of potassium chloride in 450 ml of glacial acetic acid and 50 ml of acetic anhydride as catalyst and reaction medium.

Methacrylic acid and crotonic acid were produced in a 1 to 3 ratio.

What is claimed is:
1. In the method for preparing α,β-unsaturated carboxylic acids by the oxidative carbonylation of ethylene or propylene with carbon monoxide and oxygen in a substantially non-aqueous reaction medium in the presence of a catalytic amount of a catalyst soluble in said non-aqueous medium, the improvement wherein said catalyst consists essentially of a compound of a metal of the fourth to seventh sub-groups of the Periodic System having an atomic weight between 47 and 185, and a compound of copper, zinc, cerium, tin, iron, cobalt, or nickel, said catalyst further essentially containing a halide, either of a said catalytic metal, of a non-catalytic metal, or of a mixture of a said catalytic metal and a non-catalytic metal.
2. A method as in claim 1 wherein the reaction is performed under a pressure above atmospheric pressure.
3. A method as in claim 1 wherein the reaction is performed at an elevated temperature.
4. A method as in claim 1 wherein the reaction is performed at a temperature between about 80°C. and about 200°C.
5. A method as in claim 1 wherein the reaction is performed under a pressure between about 80 atmospheres and about 120 atmospheres and at a temperature between about 100°C. and about 150°C.
6. A method as in claim 1 wherein said olefin is ethylene and said catalyst consists essentially of manganese-III-acetate and copper-III-chloride.