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PROCESS FOR PRODUCING ALIPHATIC CARBOXYLIC ACIDS AND AROMATIC CARBOXYLIC ACIDS

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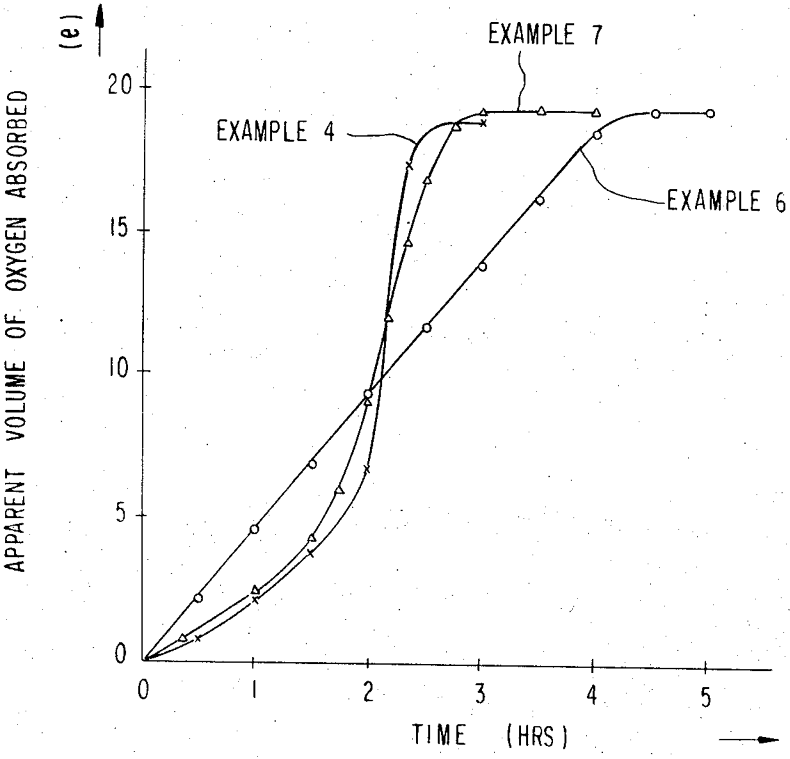

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PROCESS FOR PRODUCING ALIPHATIC CARBOXYLIC ACIDS AND AROMATIC CARBOXYLIC ACIDS

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U.S. Cl. 260—524 R **10 Claims**

ABSTRACT OF THE DISCLOSURE

A process for the simultaneous production of an aliphatic carboxylic acid and an aromatic carboxylic acid in a high yield by oxidizing an aliphatic secondary alcohol and an alkyl-substituted aromatic hydrocarbon in the liquid phase in an amount of from 0.05 to 1.0 times the weight of said aliphatic secondary alcohol at a temperature of from 100 to 160° C. and at a partial pressure of oxygen of lower than 3 kg./sq. cm. in the presence of a cobalt compound.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a process for producing simultaneously an aliphatic carboxylic acid and an aromatic carboxylic acid by oxidizing simultaneously an aliphatic secondary alcohol and an alkyl-substituted aromatic hydrocarbon in the liquid phase with an oxygen-containing gas.

(2) Description of the prior art

It is generally difficult to prepare a carboxylic acid by the oxidative decomposition of an aliphatic secondary alcohol and. thus the so-called nitric acid oxidation method has been employed for the purpose. However, in modifying the method using molecular oxygen, quite severe conditions are required and just as the conventional method results in a low yield.

Also, a method for preparing acetic acid involving the liquid-phase oxidation of the acetic acid ester of the sec-butanol with oxygen instead of the direct oxidation of the alcohol is disclosed in Japanese patent publication No. 9,173/66. This method also requires severe conditions such as a temperature of 190° C. and a pressure of 80 atms.

On the other hand, when an aromatic hydrocarbon contains two or more oxidizable alkyl groups, one of the alkyl groups can be oxidized comparatively readily to a carboxyl group, while the monocarboxylic acid thus formed is essentially resistant to further oxidation into the di- or polycarboxylic acid.

Accordingly, a method wherein a monocarboxylic acid is converted into the methyl ester and then the methyl ester is oxidized, a method wherein an aromatic hydrocarbon is oxidized under severe conditions in the presence of a catalyst containing bromine, and a method wherein an aromatic hydrocarbon is oxidized in the presence of a small proportion of an oxidation accelerator have been proposed.

For example, Japanese patent publication No. 9,654/66 (U.S. patent application Ser. No. 314,498, filed Oct. 7, 1963), a method employing an oxidation accelerator, teaches a method of adding sec-butanol to the reaction system in a small amount in comparison with the amount of lower fatty acid employed as solvent. However, when this method is applied to the oxidation of p-xylene, the yield of terephthalic acid thus obtained is low as only 77.6% and yet necessitates a partial pressure of oxygen as high as from 7.03 to 70.3 kg./sq. cm., making the method economically unprofitable and unsafe. It has been found by experimentation that, in the reaction according to the above patent, the sec-butanol added to the reaction system is consumed during the process thereof.

Therefore, it is an object of the present invention to provide an industrially profitable process for producing simultaneously an industrial and useful aliphatic carboxylic acid and an aromatic carboxylic acid by oxidizing a secondary alcohol and an alkyl-substituted aromatic hydrocarbon with an oxygen-containing gas in the presence of a cobalt compound.

SUMMARY OF THE INVENTION

Accordingly, the process of this invention for producing an aliphatic carboxylic acid comprises oxidizing an aliphatic secondary alcohol with an oxygen-containing gas and procedures an aliphatic carboxylic acid with a high yield under very mild conditions. More precisely, the process of this invention comprises contacting an aliphatic secondary alcohol and an alkyl-substituted aromatic hydrocarbon, in an amount of from 0.5 to 1.0 times by weight based on the weight of the aliphatic secondary alcohol, with an oxygen-containing gas in the presence of a cobalt-compound. Further, the alkyl-substituted aromatic hydrocarbon is converted into an aromatic carboxylic acid simultaneously in high yield.

The merits of the process of the present invention are as follows:

(1) By oxidizing an aliphatic secondary alcohol and an alkyl-substituted aromatic hydrocarbon simultaneously, the oxidation reaction can be conducted under very mild conditions, conditions so mild that oxidation of each component separately is difficult to accomplish, and industrially useful aliphatic carboxylic acids such as acetic acid and propionic acid and aromatic carboxylic acids such as benzoic acid, terephthalic acid, isophthalic acid, and phthalic acid can be obtained with high yields.

(2) The carboxylic acids produced are obtained in such purity that further purification procedures are almost unnecessary.

(3) Production of an aliphatic carboxylic acid and an aromatic carboxylic acid simultaneously is economically profitable.

(4) Because the oxidation reaction of the present invention is conducted under mild conditions, the reaction conditions can be controlled readily and the reaction can be carried out quite safely.

DETAILED DESCRIPTION OF THE INVENTION

Examples of suitable aliphatic secondary alcohols employed in the process of this invention are isopropanol, sec-butanol, sec-pentanol, and the like. Examples of suitable alkyl-substituted aromatic hydrocarbons used in the present invention are toluene, ethylbenzene, cumene, o-xylene, m-xylene, p-xylene, o-ethyltoluene, m-ethyltoluene, p-ethyltoluene, o-cymene, m-cymene, p-cymene, o-diisopropylbenzene, m-diisopropylbenzene, p-diisopropylbenzene, mesitylene, and other polyalkylbenzenes. Furthermore, as a matter of course, such alkyl-substituted aromatic carboxylic acid, as o-, m-, and p-toluic acids and their ester derivatives can be used in the present invention.

In the process of the present invention, by varying the feed ratios of the alkyl-substituted aromatic hydrocarbons to the aliphatic secondary alcohol, the ratio of the aromatic carboxylic acid to the aliphatic carboxylic acid produced can be varied as desired. A preferred feed ratio of the alkyl-substituted aromatic hydrocarbon to the aliphatic secondary alcohol is from 0.05 to 1 by weight. If the feed ratio is higher than 1, the yield of the aromatic carboxylic acid is reduced and also the yield of the aliphatic carboxylic acid is extremely reduced. Conversely, if the feed ratio is lower than 0.05, the reaction proceeds with difficulty.

In the process of the present invention, the presence of the alkyl-substituted aromatic hydrocarbon has an important role in the oxidation of the aliphatic secondary alcohol because when the alkyl-substituted aromatic hydrocarbon is absent in the reaction system, the oxidation of the secondary alcohol scarcely proceeds as shown in Comparison Example 1, given hereinafter. However, the material to be profitably oxidized in the presence of the alkyl-substituted aromatic hydrocarbon is the hereinbefore described aliphatic secondary alcohol. If the secondary alcohol is supplied to the reaction system as an aliphatic acid ester thereof, an aliphatic carboxylic acid is not obtained or is obtained in an extremely low yield and the yield of the aromatic carboxylic acid is low correspondingly. This is illustrated in Comparison Example 2 given hereinafter.

The process of the present invention can be conducted effectively without using a solvent but it is preferably conducted using the aliphatic carboxylic acid, which is one of the products of the process of this invention, as the solvent.

In the process of this invention, a cobalt compound is employed as catalyst. The cobalt compounds which are preferably used are those cobalt compounds which are soluble in the reaction liquid, such as cobalt acetate, cobalt tolylate, cobalt naphthenate, and the like. Other cobalt compounds can also be employed where desired.

The reaction of the present invention is carried out at normal pressures or under raised pressure. Also, the process of the present invention can be practiced at an oxygen partial pressure in a range from 0.01 to 30 kg./sq. cm. The process of the present invention can be carried out with a sufficiently high rate of reaction even at low oxygen partial pressures, which facilitates the control of the reaction conditions and provides a high degree of safety. On considering these points, a preferred oxygen partial pressure in the process of this invention is less than 3 kg./sq. cm. Although the reaction of the present invention proceeds with a high yield even at an oxygen partial pressure higher than 3 kg./sq. cm., when the oxygen partial pressure becomes higher than 3 kg./sq. cm., a mild reaction in the beginning is followed by a violent reaction, which makes the removal of reaction heat and the control of reaction temperature more difficult. Also, in such case, side reaction can occur. Moreover, with the employment of a high oxygen partial pressure the control of the composition of the vapour phase in the reaction system outside of the explosive range is difficult, which increases the danger of explosion together with the occurrence of the violent reaction. On the other hand, while the lower limit of the oxygen partial pressure is not critical, it is preferably higher than 0.01 kg./sq. cm. A most preferred partial pressure is from 0.1 to 3 kg./sq. cm.

The reaction temperature in the process of this invention can range from 100° C. to 160° C. If the temperature is lower than 100° C., the reaction proceeds slowly, which makes the process industrially unprofitable. Whereas, if the reaction temperature is higher than 160° C., side reactions can occur to reduce the yield of carboxylic acids as well as reduce the quality of the products.

Thus, the most preferred combination of reaction temperatures and oxygen partial pressures is from 100 to 160° C. in reaction temperature and lower than 3 kg./sq. cm. in oxygen partial pressure. Under these conditions, the absorption rate of oxygen is essentially constant during the entire reaction time and also the reaction proceeds with a sufficiently high rate of reaction.

As a result, in the process of this invention, the removal of the heat of reaction and the control of the reaction temperature can be quite easily conducted, the desired carboxylic acids can be obtained in a high yield using a comparatively small reactor, and also the process can be operated safely.

As an oxygen-containing gas employed in the process of this invention, there can be used a highly enriched oxygen gas or a gas mixture of oxygen and an inert gas, such as nitrogen or carbon dioxide. In general, air is most suitably use. Air enriched with oxygen can be used where desired.

In the process of the present invention, the aliphatic carboxylic acid can be separated from the aromatic carboxylic acid produced by conventional means, such as filtration, distillation and the like after the reaction is completed. The carboxylic acids, thus prepared, have high purity.

Furthermore, the residues left after separating the carboxylic acids from the reaction product mixture can be adjusted to the proper composition and used again in the oxidation reaction.

Thus, by repeatedly using the unreacted materials or partially oxidized products, the yields of the desired products can be improved further.

The process of this invention can be conducted as a batch system or continuously.

The present invention is illustrated below by reference to examples and the attached drawing. The examples are merely illustrative and are not to be interpreted as limiting. Various modifications are possible within the scope of the invention. In the examples, all percents are percents by weight unless otherwise indicated.

Reference is made to the attached drawing. The attached drawing is a graph showing the apparent volume of oxygen absorbed (1) during the course of the reaction proceeding according to the process of this invention. The curves labeled Example 4, Example 6 and Example 7 show the apparent volumes of oxygen absorbed at specific time periods during the course of the reaction performed in these examples.

EXAMPLE 1

In a flask equipped with a stirrer, a thermometer, an inlet for oxygen gas, and a reflux condenser were charged 42.5 g. of p-xylene, 59.3 g. of sec-butanol, 288 g. of acetic acid, and 9.96 g. of cobalt acetate tetrahydrate. The flask was immersed in an oil bath at 100° C., an oxygen-containing gas was passed into the system in a rate of 5 liters/hr. while stirring the system. After the passing of the oxygen gas was started, absorption of oxygen occurred immediately and the absorption was finished after 25 hours, when the amount of oxygen absorbed was 52 liters.

After cooling the reaction mixture, a solid product thus formed was separated by filtration, washed with acetic acid and further washed with ether to provide 61.0 g. of a pure white powder of terephthalic acid with a yield of 91.8%. Also, from the filtrate was recovered 2.5 g. of p-toluic acid. By analyzing the reaction product liquid, the entire acetic acid content in the liqued was confirmed to be 328.8 g. Furthermore, the conversion of sec-butanol was 61.3% and the selectivity for acetic acid was 68%.

COMPARISON EXAMPLE 1

The same procedure as in Example 1 was followed with the exception that p-xylene was not added. No absorption of oxygen was observed even after 8 hours.

COMPARISON EXAMPLE 2

The same procedure as in Example 1 was followed with the exception that 92.9 g. of the sec-butyl acetate was used instead of the alcohol and the amount of acetic acid was changed to 240 g. After 32 hours, the absorption of oxygen was stopped. Using the procedures of Example 1, 53 g. of terephthalic acid was obtained. The sec-butyl acetate yield was 15% and no acetic acid was obtained.

EXAMPLE 2

In a flask as in Example 1 were charged 42.5 g. of p-xylene, 118.6 g. of sec-butanol, 240 g. of acetic acid and 7.1 g. of anhydrous cobalt acetate. The flask was immersed in an oil bath at 100° C., and oxygen gas was passed into the system at a rate of 5 liters/hour with stirring. The absorption of oxygen was completed after 51 hours and using the procedures of Example 1, 60.5 g. of a white powder of terephthalic acid were obtained in a yield of 91%. Also, the amount of acetic acid in the reaction product liquid was 335.9 g. The conversion of sec-butanol was 67.0% and the selectivity for acetic acid was 70.5%.

EXAMPLE 3

In a 300 ml. stirring-type autoclave were charged 8.6 g. of p-xylene, 16.0 of sec-butanol, 10.4 g. of acetic acid, 6.0 g. of cobalt naphthenate, and 50 ml. of benzene and then the system was heated to 130° C., with stirring, under an oxygen pressure of 30 kg./sq. cm. After 10 hours, the autoclave was cooled and the reaction product was filtered to provide 9.7 g. of terephthalic acid with a yield of 79%. The conversion of sec-butanol was 80% and the selectivity for acetic acid was 58%. From the filtrate was recovered 1.3 g. of p-touic acid.

EXAMPLE 4

In a stirring-type stainless steel autoclave were charged 8.62 g. of p-xylene, 23.98 g. of sec-butanol, 52.23 g. of acetic acid, and 2.0 g. of cobalt acetate tetrahydrate. The autoclave was immersed in an oil bath at 120° C. and an oxygen-containing gas was introduced into the autoclave, with stirring to a pressure of 30 kg./sq. cm. Thereafter, the oxygen gas was supplied to the system so that the partial pressure of oxygen was maintained at 30 kg./sq. cm. After 3 hours, the absorption of oxygen was stopped. The absorption characteristics of oxygen of the example are shown by the curve labeled Example 4 in the accompanying drawing.

After cooling, the reaction product mixture, the solid product, thus formed, was separated by filtration, washed with acetic acid and dried to provide 12.68 g. of pure white powder of terephthalic acid. The amount of acetic acid in the reaction product liquid was 80.1 g. and the selectivity of acetic acid per the sec-butanol reacted was 82.1%.

EXAMPLE 5

In the reaction vessel as used in Example 4 were charged 17.24 g. of p-xylene, 31.97 g. of sec-butanol, 52.23 g. of acetic acid, and 2.00 g. of cobalt acetate and then the same procedure of Example 4 was conducted for 190 minutes. Terephthalic acid was obtained with a yield of 94.5%. The conversion of sec-butanol was 88.9% and the selectivity for acetic acid was 86.0%.

COMPARISON EXAMPLES 3 and 4

The same procedure as used in Example 4 was repeated using 17.24 g. of p-xylene, 52.23 g. of acetic acid, and 2.00 g. of cobalt acetate for Comparison Example 3 and using 17.24 g. of p-xylene, 7.99 g. of sec-butanol, 52.23 g. of acetic acid, and 2.00 g. of cobalt acetate for Comparison Example 4. The oxidation reaction was conducted for 180 minutes for Comparison Example 3 and for 210 minutes for Comparison Example 4. The yield for terephthalic acid was 30.2% in Comparison Example 3 and 66.6% in Comparison Example 4. Also in Comparison Example 4, the conversion of sec-butanol was 88.9% and the selectivity for acetic acid was 5.0%.

EXAMPLE 6

In a 200 ml. stirring-type autoclave equipped with an inlet for oxygen gas and a reflux condenser were charged 8.60 g. of p-xylene, 24.0 g. of sec-butanol, 52.2 g. of acetic acid, and 2.00 g. of cobalt acetate tetrahydrate and the autoclave was immersed in an oil bath maintained at temperature of 130° C. While stirring the system vigorously an oxygen gas was introduced into the autoclave so that the total pressure of the system was maintained at 2 kg./sq. cm. The gas in the autoclave was discharged through the reflux condenser at a rate of 3.5 liters/min. (at 25° C. and 1 atm.). After the oxygen gas introduction was begun, the absorption of oxygen occurred immediately. The apparent absorption rate of oxygen was 4.6 liters/hr. (at 25° C. and 1 atm.) almost throughout the process. This is shown by the curve labeled Example 6 in the accompanying drawing. After 5 hours, the product was cooled, recovered by filtration, washed thoroughly with acetic acid, and dried to provide 12.54 g. of pure white powder of terephthalic acid in a yield of 93.2%. The analytical results of the reaction product liquid showed that the conversion of sec-butanol was 85.4% and the selectivity for acetic acid was 81.8%.

EXAMPLE 7

The same procedure as Example 6 was repeated while the total pressure of the system was changed to 5 kg./sq. cm., the initial oxygen absorption rate was as low as 2.6 liters/hour and the rate was increased gradually up to 17.6 liters/hour. This is shown by the curve labeled Example 7 in the accompanying drawing. Using the procedures of Example 6, terephthalic acid was obtained in a yield of 92.5%. The conversion of sec-butanol was 88.3% and the selectivity for acetic acid was 75.8%.

EXAMPLE 8

The same procedure of Example 6 was followed with the exception that air was employed instead of oxygen gas, the total pressure in the system was maintained at 10 kg./sq. cm., and the gas in the autoclave was discharged at a rate of 30.2 liters/hour. The apparent absorption rate of oxygen was 4.3 liters/hour throughout the whole reaction period. Analysis of the discharged gas showed that the content of oxygen was 8–9% by volume.

After conducting the reaction for 5 hours, the reaction product was worked up as in Example 6. The yield of terephthalic acid thus obtained was 93.1%, the conversion of sec-butanol was 84.8%, and the selectivity for acetic acid was 80.7%.

One g. of the terephthalic acid thus prepared was dissolved in 25 ml. of 14% aqueous ammonia. The optical density of the solution was measured at a wave length of 380 mμ and a cell length of 5 cm. The optical density thus measured was 0.143.

EXAMPLE 9

The same procedure of Example 8 was followed with the exception that 31.1 g. of acetic acid was employed instead of 52.2 g. The apparent absorption rate of oxygen was 5.9 liters/hour throughout the entire reaction period. The oxygen content in the discharged gas was 5–8% by volume. After conducting the reaction for 5 hours, the reaction product was worked up as in Example 6, and the terephthalic acid was obtained in a yield of 94.3%. The conversion of sec-butanol was 84.5% and the selectivity for acetic acid was 85.8%.

EXAMPLE 10

The same procedure of Example 8 was followed with the exception that the amount of sec-butanol and acetic acid were changed to 16.0 g. and 31.1 g. respectively. The apparent absorption rate of oxygen was 6.2 liters/hour and the oxygen content in the discharged gas was 4–7% by volume. After conducting the reaction for 5 hour and the oxygen content in the discharged gas was terephthalic acid was obtained in a yield of 95.2%. The conversion of sec-butanol was 88.9% and the selectivity for acetic acid was 82.2%.

What is claimed is:

1. A process for the preparation of an aliphatic carboxylic acid and an aromatic carboxylic acid which com-

prises contacting a reaction mixture of an aliphatic secondary alcohol and an alkyl-substituted aromatic hydrocarbon with a gas selected from the group consisting of oxygen and oxygen-containing gases in the presence of a cobalt compound as a catalyst, said alkyl-substituted aromatic hydrocarbon being present in the reaction mixture in a ratio by weight of from 0.05:1 to 1:1 to the aliphatic secondary alcohol.

2. The process of claim **1** wherein said aliphatic secondary alcohol is selected from the group consisting of iso-propanol, sec-butanol, and sec-pentanol.

3. The process of claim **1** wherein said alkyl-substituted aromatic hydrocarbon is p-xylene, and said aliphatic secondary alcohol is sec-butanol.

4. The process of claim **1** wherein said cobalt compound is selected from the group consisting of cobalt acetate, cobalt naphthenate or cobalt tolylate.

5. The process of claim **1** wherein the gas is selected from the group consisting of mixtures of nitrogen and oxygen, mixtures of carbon dioxide and oxygen, air, and air enriched with oxygen.

6. The process of claim **1** wherein the process is conducted at a temperature of from 100° C. to 160° C. and wherein the gas is used in an amount such that the oxygen partial pressure ranges from 0.01 to 30 kg./sq. cm.

7. The process of claim **1**, wherein the process is conducted at a temperature of from 100° C. to 160° C. and wherein the gas is used in an amount such that the oxygen partial pressure is lower than 3 kg./sq. cm.

8. The process of claim **1** wherein the process is carried out in the presence of an aliphatic carboxylic acid as a solvent.

9. The process of claim **8** wherein the solvent is the same as the aliphatic carboxylic acid produced in the process.

10. A process for the production of acetic acid and terephthalic acid which comprises contacting a reaction mixture of sec-butanol and p-xylene with a gas selected from the group consisting of oxygen and oxygen-containing gases in the presence of a cobalt compound, said p-xylene being present in the reaction mixture in a weight ratio of from 0.05:1 to 1:1 to the sec-butanol.

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