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PRODUCTION OF HEXAHYDROTEREPHTHALIC ACID

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The present invention relates to a catalytic process for the hydrogenation of terephthalic acid to hexahydroterephthalic acid.

The hydrogenation of the aromatic ring of esters of terephthalic acid has been previously described. In a typical prior art process, esters of terephthalic acid are hydrogenated to esters of hexahydroterephthalic acid in good yield by conducting the hydrogenation in the molten state at an elevated temperature and pressure in the presence of a metal hydrogenation catalyst. Although the prior art discloses that the metal hydrogenation catalyst may comprise nickel, platinum or palladium or compounds of these metals, the preferred catalyst is said to be a nickel catalyst, such as Raney nickel or nickel-kieselguhr.

Although the aforesaid prior art process provides an attractive means of manufacturing esters of hexahydroterephthalic acid, the free acid is often the product ultimately desired. Hexahydroterephthalic acid can, of course, be obtained by saponifying the esters which are produced by the prior art processes but this adds an additional step which imposes additional cost. It would obviously be much more convenient to prepare the acid directly by the hydrogenation of terephthalic acid but a practical process for such direct hydrogenation has not heretofore been proposed.

There is apparently good reason why the art has not heretofore proposed a suitable process for the hydrogenation of terephthalic acid, because we have found that this acid cannot be hydrogenated satisfactorily by the techniques used for the hydrogenation of its esters. We have found for one thing that satisfactory hydrogenation of terephthalic acid requires the presence of an inert liquid medium in which terephthalic acid is at least partially soluble under reaction conditions and, secondly, we have found that terephthalic acid is selective to the influence of certain catalysts. It has been found, for instance, that the acid does not hydrogenate satisfactorily in the presence of a nickel catalyst, which is the preferred catalyst for the hydrogenation of terephthalic esters. Similarly, we have found that only low yields of hexahydroterephthalic acid can be obtained in the presence of platinum, rhodium and other known hydrogenation catalysts. However, we have made the discovery that through the selective use of a palladium or ruthenium catalyst, one can hydrogenate terephthalic acid under moderate conditions to provide almost quantitative yields of the desired product, hexahydroterephthalic acid.

In accordance with our discovery, the present invention provides a process for the hydrogenation of terephthalic acid to hexahydroterephthalic acid which comprises subjecting terephthalic acid to the action of hydrogen at an elevated temperature and pressure in the presence of a catalyst selected from the group consisting of palladium and ruthenium and in the presence of an

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inert liquid medium in which terephthalic acid is at least partially soluble under reaction conditions.

The process is illustrated by the following examples. Parts and percentages in the examples and elsewhere in this specification are by weight unless otherwise specified.

Example 1

Terephthalic acid in the amount of 55 parts was placed in a stainless steel rocking type autoclave along with 5.5 parts of a commercial 5% palladium-on-activated charcoal catalyst and 200 parts of water. The air in the autoclave was displaced with nitrogen, the nitrogen with hydrogen and the autoclave was then pressured to 5,000 p.s.i.g. with hydrogen. The autoclave was next vented to 2,500 p.s.i.g. and, while agitating the reaction mixture, the temperature was raised over a period of 75 minutes to a temperature of 180° C. and held there for 35 minutes. The autoclave was then cooled and the hydrogen released. The product was taken up in aqueous sodium hydroxide, filtered, and the clear, colorless solution diluted with water to a total weight of about 1,600 parts. [Ultraviolet analysis indicated complete reduction of the aromatic nucleus. Titrimetric analysis indicated that the yield of hexahydroterephthalic acid was 98.5%.] Next, the solution was reacted dropwise with stirring to pH 2 with concentrated hydrochloric acid to give an odorless, colorless suspension. Since the strong characteristic odor of hexahydrobenzoic acid was completely lacking, mono-decarboxylation during hydrogenation did not occur. The product was cooled to about 5° C., collected on a sintered funnel, washed four times with cold water and dried in a vacuum oven at 50° C. to give 29.6 parts (51.8%) of colorless microcrystals, M.P. 306–308° C., undepressed on admixture with an authentic specimen of trans-hexahydroterephthalic acid. The filtrate and washings were combined and extracted ten times with ¼ volume of ether. The combined extracts were dried over anhydrous sodium sulfate and stripped to give 23.6 parts (41.3%) of colorless crystals, M.P. 173–174° C., undepressed on admixture with authentic cis-hexahydroterephthalic acid, bringing the in-the-barrel yield of cis and trans acids to 93.1%. More exhaustive extraction of the cis isomer would probably have increased the yield.

Example 2

The procedure of Example 1 was repeated with the exception that the autoclave was charged with 100 parts of terephthalic acid and 10 parts of catalyst, the reaction pressure was 3,000 p.s.i.g., the temperature 200° C., and the reaction time 2 hours. Analysis of the product showed that the yield of mixed cis and trans-hexahydroterephthalic acids was greater than 83.5% at a terephthalic acid conversion of 100%.

Example 3

The procedure of Example 2 was repeated with the exception that the reaction pressure was 5,000, the reaction temperature 180° C., and the reaction time 35 minutes. The yield of hexahydroterephthalic acid (a mixture of cis and trans isomers) was greater than 93% at a terephthalic acid conversion of 100%.

Example 4

The procedure of Example 2 was repeated with the exception that the reaction pressure was 5,000 p.s.i.g. and the reaction temperature 160° C. The yield of hexahydroterephthalic acid (a mixture of cis and trans isomers) was approximately 92% at 100% conversion of terephthalic acid.

Example 5

The procedure of Example 2 was followed with the exception that the reaction pressure was 5,000 p.s.i.g., the reaction temperature 250° C., and the reaction time 30 minutes. The yield of hexahydroterephthalic acid (a mixture of cis and trans isomers) was approximately 92% at 100% conversion of terephthalic acid.

Example 6

The procedure of Example 2 was followed with the exception that the reaction pressure was 5,000 p.s.i.g., the reaction temperature 195° C., and the reaction time two hours. The yield of hexahydroterephthalic acid (a mixture of cis and trans isomers) was approximately 98.5% at 100% conversion of terephthalic acid.

Example 7

One hundred parts of terephthalic acid was placed in a stainless steel rocking type autoclave with two parts of a commercial 20-64 mesh 5% palladium-on-silica gel catalyst and 200 parts of water. The autoclave was flushed twice with nitrogen and twice with hydrogen and pressured to 3,000 p.s.i.g. with hydrogen. Starting at this pressure the autoclave was heated to 240° C. over the course of 1½ hours. When the temperature reached 240° C. the pressure was raised to 5,000 p.s.i.g. and was maintained at 5,000±200 p.s.i.g. for 1.8 hours. Work-up and analysis of the product showed that 100% of the terephthalic acid had been converted and the yield of mixed cis and trans-hexahydroterephthalic acids was greater than 92.5%.

Example 8

Following the procedure of Example 2, 75 parts of terephthalic acid was hydrogenated at 140° C. and 5,000 p.s.i.g. in the presence of 300 parts of water and 10 parts of a powdered 1.25% ruthenium-on-activated charcoal catalyst for 9 hours. The yield of hexahydroterephthalic acid (mixture of trans and cis isomers) was approximately 98% at 100% conversion of terephthalic acid. Essentially the same results were obtained in a repetition of this example in which the temperature was raised to 200° C. and the reaction time decreased to 4½ hours.

To illustrate the selectivity of palladium and ruthenium catalysts in this invention, comparable experiments were carried out using Raney nickel, nickel-on-kieselguhr, platinum-on-charcoal and rhodium-on-charcoal, respectively, as catalysts. With Raney nickel at a reaction pressure of 6,000 p.s.i.g. and a reaction temperature of 160° C., only about 10% of the terephthalic acid was converted after a period of eight hours. Using 5% nickel-on-kieselguhr at a reaction pressure of 5,000 p.s.i.g. and a reaction temperature of 200° C., there was no detectable yield at the end of six hours. In the presence of a 5% platinum-on-activated charcoal catalyst at a reaction temperature of 270° C. and a reaction pressure of 6,000 p.s.i.g., hydrogenation for 6 hours resulted in a conversion of terephthalic acid of only 62% and a yield of hexahydroterephthalic acid of only 70%. At less drastic reaction conditions in the presence of the same platinum catalyst, the conversion and yield were considerably lower. Carrying out the reaction in the presence of a 5% rhodium-on-activated charcoal catalyst at 300° C. and 5,000 p.s.i.g. for 4½ hours gave a conversion of 100% but a yield of only 38%. At less drastic conditions, the yield was even lower.

As the examples have demonstrated, the hydrogenation of terephthalic acid can be carried out under variable reaction conditions to provide high yields of hexahydroterephthalic acid as a mixture of cis and trans isomers provided a palladium or ruthenium catalyst is employed and the reaction is carried out in an inert liquid medium in which terephthalic acid is at least partially soluble under reaction conditions.

While the reaction involved is specific to palladium

and ruthenium catalysts, the physical structure and composition of the catalyst can be widely varied without effect on the operability of the process. Most preferably, the catalyst is one in which metallic palladium or ruthenium is distributed on a support of high surface area. Catalysts of this description are well known to the art and include palladium-on-charcoal, palladium-on-silica, palladium-on-alumina, and palladium-on-rutile and the corresponding ruthenium catalysts. These supported catalysts are effective whether in the form of pellets or powder or otherwise. Unsupported catalysts are also useful as, for example, powdered palladium or ruthenium, although, as a general rule, the efficacy of the catalyst, on a terephthalic acid basis, is proportionate to the exposed surface area of palladium or ruthenium which explains the preference for supported catalysts.

The quantity of catalyst to be used in the invention varies widely. It has been found that rapid reactions and good yields are obtainable when the amount of palladium or ruthenium is as low as 0.003 part per 100 parts of terephthalic acid although, on a practical basis, it is desirable to employ at least about 0.025 part of palladium or ruthenium per 100 parts of terephthalic acid. There is, of course, no upper limit on the ratio of catalyst to terephthalic acid that can be used, this being entirely an economic consideration.

The conditions of temperature and pressure can also be varied widely in carrying out the invention but, in general, temperatures within the range of 150° to 300° C. are preferred with a temperature of 200° to 300° C. being most preferred as resulting in the most desirable reaction rates. There appears to be no upper limit on the pressure which can be employed in the invention but a minimum pressure of about 1,000 p.s.i.g. represents a practical lower pressure limit below which the speed of reaction is too slow to be practical. More preferably, it is desirable to conduct the process of the invention at a pressure of at least 3,000 p.s.i.g. in order to obtain optimum rate of reaction.

In selecting the reaction medium, there are many liquids which meet the requirements of being inert under the reaction conditions and possessing the ability to dissolve terephthalic acid at least partially. Water is by far the preferred inert liquid medium for economic considerations, but other liquids such as dimethyl sulfoxide, dimethyl formamide and hydrogenated esters of terephthalic acid are also useful.

The initial reaction mixture is prepared simply by charging terephthalic acid and the inert liquid medium to the reaction vessel either separately or in admixture with each other. In most cases, especially in continuous operation, it is desirable to feed to the reactor a slurry of terephthalic acid in the inert liquid medium and this consideration imposes the practical limitation of employing sufficient medium to form a flowable slurry. In general, this amount of inert liquid medium corresponds to about 2 to 5 times the weight of terephthalic acid employed. A greater amount of the inert liquid medium can, of course, be employed without detriment to the process but in order to avoid too dilute a reaction mixture it is preferred to have present not more than about 20 parts of the inert liquid medium per part of terephthalic acid.

Depending on the amount of inert liquid medium employed and on the temperature of the reaction, a variable quantity of terephthalic acid in the process will be dissolved during the reaction. By proper choice of the medium it is possible to conduct the reaction with substantially all of the terephthalic acid in solution although this is by no means essential and the reaction proceeds equally satisfactorily when only a portion of the terephthalic acid is dissolved.

What we claim and desire to protect by Letters Patent is:

1. A process for the production of hexahydrotereph-

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thalic acid which comprises subjecting terephthalic acid to the action of hydrogen at an elevated temperature within the range of 150-300° C. and at a pressure of at least 1000 p.s.i.g. in the presence of a palladium catalyst and in the presence of an inert liquid medium in which terephthalic acid is at least partially soluble under reaction conditions.

2. The process of claim 1 in which the inert liquid medium comprises water.

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