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OXIDATION OF XYLENE AND TOLUIC ACID MIXTURES TO PHTHALIC ACIDS

Walter R. Haefele, Oakland, George W. Hearne, Lafayette, and Seaver A. Ballard, Orinda, Calif., assignors to Shell Development Company, Emeryville, Calif., a corporation of Delaware

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This invention relates to a process for the production of aromatic carboxylic acids and it more particularly relates to a process for the production of phthalic acids, especially terephthalic and isophthalic acids.

It has been known for many years that phthalic acids can be produced by oxidation of xylenes with agents such as chromic acid, permanganate and nitric acid. Thus, terephthalic acid has been found among the products formed by oxidation of p-xylene with MnO_2 and sulfuric acid, and isophthalic acid has been produced by oxidation of m-xylene with $K_2Cr_2O_7$ and dilute sulfuric acid. Such processes, however, while of theoretical and possibly even laboratory interest, have not been applicable to commercial-scale production of isophthalic acid and terephthalic acid because of the complexity of the products and the undue expense of the processes. It also is known that xylenes can be oxidized by treatment in the liquid phase to produce toluic acids. In U. S. 2,245,528 to Loder, there is described such a process wherein air is bubbled through mixed xylenes in the presence of acetic acid, cobalt and manganese acetates as catalyst, and methyl ethyl ketone as an "initiator". The product was chiefly toluic acid (50.3% yield). Toluyl esters were obtained in 8.1% yield, toluic aldehydes in 5.7% yield, phthalic acids in 2.0% yield, and toluyl alcohols in 1.5% yield. Our experiments have largely confirmed the teachings of the Loder patent in that we have found that, while oxidation of xylenes according to the general process described in the Loder patent appears to afford a useful process for the production of toluic acids, it appears to be wholly unsatisfactory as a method for conversion of xylenes predominantly to phthalic acids instead of to toluic acids.

The conversion of the toluic acids, produced, for example, according to the disclosures of Loder, to the corresponding phthalic acids by a subsequent oxidation is one that is fraught with difficulty, particularly from the standpoint of obtaining adequate conversion of the toluic acid to desired phthalic acid. This appears to be due to the fact, which has been shown by our work as well as by that of others, that the toluic acids are quite refractory to oxidation of the methyl group. A recent patent, U. S. 2,479,067, to Gresham, discloses a process in which p-toluic acid is oxidized to terephthalic acid in the liquid state in the presence of lead acetate as catalyst, acetic acid as solvent and propionaldehyde and methyl ethyl ketone as initiators. The highest conversion demonstrated in the patent is 21.3% of the applied p-toluic acid to terephthalic acid. This figure, considered with the yield of toluic acids disclosed by the Loder patent, indicates a likely maximum conversion of xylene to phthalic acid in the order of 10% when operating by the two-step process that is provided by the successive use of the methods of the above patents to Gresham and to Loder.

An object of the present invention is to provide a method for the conversion, via oxidation, of xylenes to the corresponding phthalic acids that is capable of

providing higher percentage conversions of xylene to phthalic acid than heretofore obtained. Another object is a method for the direct catalytic oxidation in a single step and with improved conversions, of xylenes to phthalic acids. A method whereby the oxidation of xylene by treatment with molecular oxygen in the presence of an oxidation catalyst can be so directed that a phthalic acid, rather than a toluic acid, is obtained as the principal product, also is an object of the invention. A method whereby temperatures below 150° C. and as low as 100° C. can be used during the oxidation is a still further object. Other objects will appear hereinafter.

It has been discovered in accordance with the present invention that when a mixture comprising a xylene and a toluic acid in certain critical proportions is subjected to intimate contact with an oxygen-containing gas in the presence of an oxidation catalyst and, preferably, a solvent, and a xylene is added to the mixture at such a rate that these proportions are maintained, while the aeration with the molecular-containing gas is continued, the added xylene is converted in high yields and conversions directly to the corresponding phthalic acid or acids. The process of the invention is effective for the direct conversion of xylenes to phthalic acids under conditions at which toluic acids, when treated in the absence of xylene, appear either to be inert to oxidation or to form the corresponding phthalic acid in only negligible yields and conversions, and at which the xylenes when treated alone are converted to toluic acids as the major if not the only products. A xylene, when added to the actively oxidizing medium containing the suitable proportions of xylene and toluic acid, appears to be selectively oxidized directly to the corresponding phthalic acid. Contrary to expectations, only negligible, if any, accumulation of further amounts of toluic acid in the reaction mixture generally occurs during the oxidation of such added xylene.

It has been found in accordance with the invention that xylenes, when added to a reaction mixture in which a xylene and a toluic acid are concurrently undergoing treatment with oxygen-containing gas in the presence of a suitable catalyst and in which the toluic acid is present in excess, on a weight basis, up to about three times the weight of xylene, and the rate of addition of xylene is carefully regulated so that the ratio of toluic acid to xylene in said mixture is maintained within said range during the oxidation of the added xylene, the added xylene is converted in excellent conversion directly to the corresponding phthalic acid rather than to the toluic acid heretofore obtained as the oxidation product of xylenes. In accordance with the invention, xylene and toluic acid are concurrently contacted in liquid phase with oxygen-containing gas in the presence of a catalyst while additional xylene is added to the reaction mixture at such a rate that the weight ratio between the toluic acid and xylene in the mixture is maintained during the subsequent oxidation treatment within the critical range of from about 1:1 to about 3:1. The phthalic acid, which ordinarily separates from the liquid mixture as a heavy crystalline precipitate, can be continuously removed, as by filtration or equivalent means, and the remaining liquid, containing xylene and toluic acid, returned to the reaction vessel. The best results are obtained when the weight ratio between the toluic acid and the xylene in the mixture is maintained throughout the oxidation of the added xylene within the range of from about 65:35 to about 50:50. In the preferred practice of the invention, there is withdrawn from the reaction mixture during the oxidation, either continuously or intermittently, a small fraction of the entire mixture, e. g., between about 0.5% and about 15% per

hour, which is either discarded or from which xylene and toluic acid are separated in substantially pure form prior to their return to the reaction mixture, the small off-take of reaction mixture apart from or in addition to the withdrawal of phthalic acid produced by the oxidation reaction serving to prevent the accumulation of possibly inhibitory substances that might interfere with the oxidation.

The process of the invention is of particular value for the oxidation of meta-xylene and of para-xylene to isophthalic acid and terephthalic acid, respectively. The meta-xylene and the para-xylene in substantially the pure state can be oxidized singly to the corresponding phthalic acids according to the process of the invention. Mixtures of meta-xylene and para-xylene can be oxidized to mixtures of isophthalic and terephthalic acid, or mixed xylenes, containing any two or three of the three isomeric xylenes can be oxidized to phthalic acids according to the process of the invention. Ortho-xylene contained in such mixtures will be converted, although usually in somewhat lower conversions, to phthalic acid.

As the oxidation catalyst there can be used catalysts that heretofore have been employed for accelerating the oxidation of xylenes in liquid phase to toluic acids, such as the solid polyvalent metals having atomic weights between about 50 and 200. The catalyst may comprise the metal per se, suspended in finely divided condition in the reaction mixture or carried on a supporting material, or the metal may be in the form of an inorganic or organic compound thereof, such as an oxide, a salt, or a chelate complex of the metal with an organic compound. Illustrative of such metals are manganese, cobalt, nickel, vanadium, copper, cerium, and molybdenum. As compounds thereof there can be employed oxides, the salts of such metals and strong mineral acids, such as the chlorides, nitrates or sulfates, or organic compounds such as the acetates, salicylates, butyrates, toluates, chelate complexes with diketones, such as cobalt isovalerylacetonate, and the like. A single metal or compound of a metal may be used as the catalyst, or a mixed catalyst can be employed. Specific illustrative catalysts are cobalt acetate, cobalt p-toluate, manganese naphthenate, cobalt acetylacetonate, mixed manganese-lead-cobalt acetates, etc. Only small amounts of the catalyst need be employed, a generally suitable range being from about 0.01 to about 5% of the reaction mixture.

The temperature that is employed during the oxidation may range from about 100° C. up to about 300° C., or even higher, a preferred range being from about 100° C. up to about 225° C. It has been found in accordance with the invention that excellent conversions of the xylenes to the corresponding toluic acids can be realized at low temperatures, that is, at temperatures below 150° C. and down to about 100° C., at which the toluic acids have heretofore appeared to be highly refractory with respect to catalytic oxidation to the corresponding phthalic acids. The availability of these lower temperatures for the oxidation process is of particular advantage when the oxidation is conducted in the presence of an organic solvent, in that these lower temperatures permit the use of highly active catalysts, such as soluble salts of cobalt and of manganese, without the excessive attack upon the solvent that is likely to occur at the higher temperatures. As the oxygen-containing gas there can be employed air, oxygen-enriched air, "industrial" oxygen having an oxygen content of about 80% to 90% by volume, or even pure oxygen. The pressure, generally speaking, may be atmospheric or superatmospheric, e. g., up to 500 or more pounds per square inch. An advantage of employing the highly active catalysts referred to above is that their use permits the use of air as the oxidant gas and operation at substantially atmospheric pressures, even at the low temperature range of from about 100° C. to about 150° C., thereby avoiding the necessity for costly pressure equipment and the more expensive oxidant gases. As far as we know, the present invention affords the first instance in which a phthalic acid has been obtained directly in practical conversions by catalytic oxidation of either a xylene or a toluic acid under these advantageously mild conditions.

In carrying out the process of the invention, there may be included in the reaction mixture one or more organic solvents. So-called reaction initiators heretofore employed in the known processes for oxidation of toluic acids or of xylene may be added to the reaction mixture, such as any of the initiators disclosed in the above-mentioned patents to Loder and to Gresham. The advantages of the present invention are obtained, however, independently of the possible presence of organic solvents and of added reaction initiators. The absolute conversion of the xylene to a phthalic acid is higher when the process is conducted in the presence of a suitable solvent than when conducted under otherwise comparable conditions without a solvent. In each case, however, the conversion of the xylene to a phthalic acid is markedly higher when the oxidation of the xylene is conducted according to the process of this invention than when it is conducted by the corresponding process of the prior art.

Suitable solvents, if one is to be employed, include, among others, the halogen-substituted benzene, such as the chlorobenzenes, benzenoid hydrocarbons devoid of substituents that are prone to attack, such as benzene, diphenyl, and t-butylbenzene, halogen-substituted alkanes, such as carbon tetrachloride and s-trichloropropane, and carboxylic acids, such as benzoic acid, phenylacetic acid, or a lower saturated aliphatic carboxylic acid. Of the solvents that may be used, the chloro-substituted benzenes containing from one to two atoms of chlorine have been found to be outstanding for use in the process of the invention. When a solvent is employed, the solvent should not, as a rule, be used in an amount exceeding about 80% by weight of the reaction mixture, a preferred concentration of the solvent in the reaction mixture being from about 40% to about 80% by weight of the mixture.

The process of the invention is carried out by preparing a reaction mixture comprising as its essential components the xylene or mixture of xylenes, the toluic acid or mixture of toluic acids, and the catalyst, the weight ratio between the toluic acid and the xylene being within the range of from 75:25 to 50:50 and preferably between 65:35 and 50:50. While the oxygen-containing oxidant gas is intimately contacted with the mixture, as by bubbling through the mixture with agitation or by spraying or otherwise dispersing the mixture in an oxygen-containing atmosphere, the xylene or a mixture of xylenes is added either continuously or intermittently to the mixture at such a rate that the ratio of toluic acid to xylene is maintained within the desired range. The contents of xylene and of toluic acid in the mixture can be determined by withdrawing aliquots of the mixture and titrating or otherwise measuring the toluic acid content and by distilling off or otherwise separating the xylene in measured amount. As the oxidation progresses with addition of the xylene or mixture of xylenes to the reaction mixture, the phthalic acid that is produced generally separates out as a crystalline precipitate which, if not withdrawn, accumulates until it represents as much as 40% or even more of the entire reaction mixture. In a fully continuous operation, this precipitated phthalic acid will be taken out by filtration or equivalent means, as by intermittently or continuously withdrawing a portion of the reaction mixture from the reaction vessel, filtering the withdrawn portion and returning the filtrate to the vessel. It will be understood that, in such operations additional catalyst, solvent (if a solvent is being used), toluic acid, of xylene may be added to the reac-

tion vessel in such amounts that may be required to maintain the desired operating conditions in the reaction vessel.

The following examples will illustrate the various possible specific embodiments of the invention.

Example I

This example is presented in order to illustrate the process of the invention and also to show the advantageously high conversion to terephthalic acid that is obtained by the conjoint oxidation of p-xylene and p-toluic acid compared to that resulting from the oxidative treatment of p-toluic acid as the only reactant. The apparatus that was used comprised a jacketed, vertically positioned glass tube having an inner diameter of 3.1 cm. and a length of 45 cm. Oxygen-containing gas was introduced into the reaction mixture through a sintered glass plate at the bottom of the tube. The gaseous effluent from the tube was passed from the upper end of the tube through a condenser equipped with a phase-separating head arranged for withdrawal of water from the system and return of organic condensate to the reactor. The temperature of the tube was maintained at the desired level by means of a vaporous heating medium that was passed through the jacket.

A solution of 0.131 mole of p-toluic acid in 0.51 mole of o-dichlorobenzene (20% by weight) containing 0.1% by weight of cobalt p-toluate was charged to the reactor and oxygen under atmospheric pressure was bubbled through the solution at 0.0033 mole per minute at 130° C. to 135° C. for 41 hours. Throughout this time there was no evidence of oxidation of the p-toluic acid to terephthalic acid. During the next 48 hours a total of 0.139 mole of p-xylene was added incrementally to the reaction vessel. No oxidation reaction was observed when about 0.057 mole of p-xylene had been added over a period of 66 hours (weight ratio p-toluic acid:p-xylene=about 75:25). Upon the further addition of p-xylene, oxidation reaction commenced. During the next 99 hours 0.296 mole of p-xylene was added in increments to the mixture at a rate such that the weight ratio of p-toluic acid to p-xylene in the mixture remained within the range of from about 75:25 to about 50:50. Terephthalic acid was produced continuously as a precipitate, building up in quantity until it constituted almost 40% by weight of the reaction mixture. The mixture then was separated by filtering off the terephthalic acid, washing the crystalline solid with hot ethanol, and steam distilling the combined alcohol extract and filtrate to separate p-xylene. There was obtained 0.155 mole of p-toluic acid, representing a net gain of only 0.024 mole over that initially charged, 0.245 mole of terephthalic acid, and 0.041 mole of p-xylene. The conversion of p-xylene to terephthalic acid, based on the amount of p-xylene charged after the commencement of the oxidation reactions, was 64.5%.

Example II

To the reactor described in Example I there was charged a solution containing 19% by weight of p-xylene and 24% by weight of p-toluic acid, and 0.1% by weight of cobalt p-toluate. When oxygen under atmospheric pressure was passed through the solution at 0.0033 mole per minute and at 130° C. to 135° C. oxidation commenced immediately. As the p-xylene in the mixture was consumed additional p-xylene was added in such amounts that the weight ratio of p-xylene to p-toluic acid in the solution remained within the range of from about 50:50 to about 75:25. Terephthalic acid was recovered according to the method illustrated in the preceding example in an amount corresponding to an approximately 65% conversion of p-xylene charged to terephthalic acid.

Example III

Example II was repeated using a solution containing

20% by weight each of m-toluic acid and m-xylene and 0.1% by weight of cobalt p-toluate in 0.41 mole of o-dichlorobenzene. As the oxidation continued, m-xylene was added to the reaction mixture in increments such that the weight ratio of m-toluic acid to m-xylene remained within the range of from about 50:50 to about 75:25. When a total of 0.755 mole of m-xylene had been supplied the run was discontinued and worked up according to the procedure described in Example I. There was recovered 0.47 mole of isophthalic acid, representing a 63% conversion of m-xylene to isophthalic acid.

The benefits of the present invention are most effectively realized when the oxidation of the xylene-toluic acid mixture is conducted in the presence of a solvent. The course of the oxidation reaction can be directed according to the invention to the formation of dicarboxylic acid when the oxidation is conducted in the absence of a solvent. In this case, the consumption of reactants is less; that is to say, there is a lower overall conversion of the reactants. The ratio of dibasic acid to monobasic acid in the products, however, is markedly increased by conducting the oxidation according to the present invention. These points are illustrated by the following example.

Example IV

Mixed xylenes (approximate composition: 13% o-xylene, 48% m-xylene, 23% p-xylene, 3% ethylbenzene) containing 0.25% by weight of cobalt acetate tetrahydrate and 1% by weight of benzaldehyde as reaction initiator were charged to a stainless steel pressure vessel equipped with mechanical stirrer, gas-inlet, valved vapor outlet provided with a water cooled reflux column arranged for return of condensate to the vessel and accessory equipment including pumps for introducing air and xylene feed under pressure, thermometer and pressure gauge, and temperature-control means. In the first run, the mixed xylenes were oxidized by passing air under 600 pounds per square inch gauge through the pressure vessel at 175° C. at a rate of effluence from the pressure vessel of 3.5 to 3.7 liters (20° C., 1 atmosphere) per minute. When 1.3 moles of oxygen per mole of the mixed xylenes had been absorbed, the run was discontinued and the products were analyzed. It was found that 54% of the mixed xylenes had been converted to toluic acids and that 6.1% had been converted to phthalic acids.

In the second run, the pressure vessel was charged with 2.36 moles of mixed xylenes and 0.25% by weight of cobalt acetate tetrahydrate and 1% of benzaldehyde and the mixed xylenes were oxidized under the conditions used in the first run until the content of toluic acids in the mixture was about 84% by weight. By this time the absorption of oxygen by the mixture had virtually ceased as judged by the oxygen content of the effluent from the reactor. There then was added 0.2% by weight of cobalt acetate and introduction of mixed xylenes into the vessel was commenced. When the concentration of toluic acids in the reaction mixture had been reduced to between about 65% and 75% by dilution with the added mixed xylenes adsorption of oxygen commenced. Thereafter the rate of introduction of the mixed xylenes was so regulated that the weight ratio of toluic acids: xylenes in the mixture remained between about 50:50 and about 75:25 and the oxidation proceeded at a moderate rate (about 6% of the inlet gases being absorbed). When 2.20 moles of mixed xylenes had been thus introduced the run was terminated. The amount of oxygen absorbed was 1.1 moles per mole of mixed xylenes employed, slightly less than in the first run. The products were worked up as in Example I. The mixture was a heavy slurry of crystalline phthalic acids in the unreacted xylenes and the toluic acids. There were recovered 1.89 moles of toluic acid, of which about 1.8 moles is accounted for by the toluic acids formed during the oxidation of the original charge of xylenes, and .60 mole of

phthalic acids, which represents a 27% conversion of the subsequently added xylenes to phthalic acids.

Although in the foregoing examples the runs were conducted in a semi-continuous manner, it will be appreciated that a fully continuous method of operation can be employed, in which a portion of the reaction mixture is withdrawn, continuously or intermittently, phthalic acid is separated therefrom, and unconsumed xylene and toluic acid are returned, and fresh feed is supplied to the reactor at such rates or in such amounts that the ratio of toluic acid to xylene in the reaction mixture is maintained within the essential ranges that form a part of this invention.

This application is a continuation-in-part of application Serial No. 85,714, filed April 5, 1949, now abandoned.

We claim as our invention:

1. In a process for the production of a phthalic acid wherein a liquid mixture containing xylene and toluic acid is oxidized at about 100° C. to 275° C. in the presence of an oxidation catalyst by intimate contact of the mixture with an oxygen-containing gas, the improvement which comprises adding such amounts of xylene to said mixture during the oxidation that the weight ratio of toluic acid to xylene in the mixture is maintained below 75:25 but above about 50:50.

2. In a process for the production of a phthalic acid wherein a liquid mixture containing a xylene and the corresponding toluic acid is oxidized at about 100° C. to 275° C. in the presence of an oxidation catalyst by intimate contact of the mixture with a dispersed oxygen-containing gas, the improvement which comprises adding such amounts of said xylene to said mixture during the oxidation that the weight ratio of the toluic acid to the xylene in the mixture is maintained below 75:25 but above about 50:50.

3. The improvement as defined in claim 2 wherein the liquid mixture being subjected to oxidation contains an inert organic solvent.

4. The improvement as defined in claim 3 wherein the solvent is o-dichlorobenzene.

5. The improvement as defined by claim 2 wherein the xylene is m-xylene.

6. In a process for the production of terephthalic acid and wherein a liquid mixture containing p-xylene and p-toluic acid is oxidized at about 100° C. to 200° C. in the presence of a cobalt salt oxidation catalyst by intimate contact of the mixture with dispersed air, the improvement which comprises adding such amounts of p-xylene to said mixture during the oxidation that the weight ratio of the toluic acid to the xylene in the mixture is maintained at from about 65:35 to about 50:50.

7. The improvement as defined by claim 6 wherein the liquid mixture being subjected to oxidation contains o-dichlorobenzene as an inert solvent.

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