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[54] PROCESS FOR THE PRODUCTION OF ARYL CARBOXYLIC ACIDS

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[58] **Field of Search** .....204/78, 80; 260/524 M

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[57] **ABSTRACT**

Aryl carboxylic acids are produced from alkyl substituted aryl compounds or partially oxidized alkyl substituted aryl compounds in an electrolytic cell with a lead containing anode and using chromium in an ionized state in mineral acid as a carrier for electrons. The process is particularly useful in the oxidation of p-toluic acid to terephthalic acid and of tetra-alkyl benzene to tetracarboxylic acids. Both terephthalic acid and tetracarboxylic acids are useful in the production of polyester resins. Trimetallic acid used in making trimellitate plasticizers for polyvinyl chloride resins may also be produced by this process.

6 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF ARYL CARBOXYLIC ACIDS

The present invention relates to the oxidation of alkyl substituted aryl compounds and partially oxidized alkyl substituted aryl compounds to form aryl carboxylic acids. More particularly it relates to such oxidations carried out in an electrolytic cell.

An outstanding advantage of the process of this invention is the unique simplicity of the process. In converting a suitable aromatic feed stock to an aryl carboxylic acid, this process consumes only water and electrical energy. In contrast to the processes of the prior art no special organic solvents are required, no additional acidifying agents are needed, and substantially no oxidant is consumed. The necessary inventory of oxidant is minimized and no separate oxidant regeneration process is employed.

The process of this invention for the preparation of aryl carboxylic acids from the corresponding alkyl substituted aryl compounds and partially oxidized alkyl substituted aryl compounds comprises charging to an electrolytic cell having a cathode and a lead-containing anode a feed stock selected from the group which consists of an alkyl substituted aryl compound, a partially-oxidized alkyl substituted aryl compound and a mixture of an alkyl substituted aryl compound and a partially-oxidized alkyl substituted aryl compound and chromium in solution in a strong mineral acid and passing through said cell a direct electrical current whereby said feed stock is oxidized to a corresponding aryl carboxylic acid by said chromium in an ionized electron-accepting state accepting electrons from said feed stock, carrying them to said anode, discharging them at said anode and there being regenerated to an electron-accepting state.

Alkyl substituted aryl compounds useful as a feed stock in the process of this invention may contain one aromatic nucleus or may be polynuclear; e.g., benzene, naphthalene, anthracene, phenanthrene, diphenyl, triphenyl, and the like, having aliphatic substituents. The chain length of the aliphatic substituents is not critical. Alkyl groups having as many as eight to ten carbon atoms in the chain may be used. However, for economy, ease of product, purification, and handling considerations it is preferable to limit alkyl group chain lengths to six carbon atoms or less. Still more preferred are aryl compounds with aliphatic substituents having a chain length of four carbon atoms or fewer. Examples of typical preferred alkyl substituted aryl compounds include methylbenzene, ethylbenzene, n-propylbenzene, i-propylbenzene, n-butylbenzene, s-butylbenzene, cyclohexylbenzene, dimethylbenzene, diethylbenzene, di-n-propylbenzene, di-i-propylbenzene, di-n-butylbenzene, di-s-butylbenzene, trimethylbenzene, triethylbenzene, tri-n-propylbenzene, tri-i-propylbenzene, tri-n-butylbenzene, tri-s-butylbenzene, ethyltoluene, ethyl-n-propyltoluene,ethyl-i-propyltoluene, ethyl-s-butyltoluene, diethyltoluene, diethyl-n-propyltoluene, diethyl-i-propyltoluene, diethyl-s-butyltoluene, triethyltoluene, triethyl-n-propyltoluene, triethyl-i-propyltoluene, triethyl-s-butyltoluene, n-propylethylbenzene, i-propylethylbenzene, n-butylethylbenzene, s-butylethylbenzene, dimethylethylbenzene, di-n-propylethylbenzene, di-i-propylethylbenzene, di-n-butylethylbenzene, di-s-butylethylbenzene, trimethylethylbenzene, tetraethylbenzene, tri-n-propylethylbenzene, tri-s-butylethylbenzene, i-propyl-n-propylbenzene, n-butyl-n-propylbenzene, s-butyl-n-propylbenzene, dimethyl-n-propylbenzene, di-i-propyl-n-propylbenzene, di-n-butyl-n-propylbenzene, di-s-butyl-n-propylbenzene, trimethyl-n-propylbenzene, triethyl-n-propylbenzene, tri-n-propylbenzene, tri-i-propylbenzene, tri-n-butyl-n-propylbenzene, tri-s-butyl-n-propylbenzene, n-butyl-i-propylbenzene, s-butyl-i-propylbenzene, dimethyl-i-propylbenzene, diethyl-i-propylbenzene, di-i-propylbenzene, tri-i-propylethylbenzene, tri-n-butylethylbenzene, di-n-propyl-i-propylbenzene, di-s-butyl-i-propylbenzene, tri-methyl-i-propylbenzene, triethyl-i-propylbenzene, tri-i-propyl-benzene, tri-n-butyl-i-propylbenzene, i-butyl-n-butylbenzene, dimethyl-i-butylbenzene, diethyl-i-butylbenzene, di-n-propyl-i-butylbenzene, di-i-propyl-i-butylbenzene, di-n-butyl-i-butyl-benzene, di-s-butyl-i-butylbenzene, trimethyl-i-butylbenzene, triethyl-i-butylbenzene, tri-n-propyl-i-butylbenzene, tri-i-propyl-i-butylbenzene, dimethyl-s-butylbenzene, diethyl-s-butylbenzene, di-n-propyl-s-butylbenzene, di-i-propyl-s-butyl-benzene, di-n-butyl-s-butylbenzene, trimethyl-s-butylbenzene, triethyl-s-butylbenzene, tri-n-propyl-s-butylbenzene, tri-i-propyl-s-butylbenzene, tri-n-butyl-s-butylbenzene, and correspondingly (or higher) substituted polynuclear materials; also alpha-methyl naphthalene, beta-methyl naphthalene and other higher substituted polynuclear materials. Alkyl substituted aryl compounds are also useful as a feed stock in mixtures of two or more alkyl substituted aryl compounds giving as a product a mixture of two or more of the corresponding aryl carboxylic acids.

Partially oxidized alkyl substituted aryl compounds useful as a feed stock in the process of this invention are partial oxidation products wherein the aliphatic substituents are converted to intermediate oxygenated derivatives such as alcohols, aldehydes, ketones, peroxide type compounds, carboxy acids having at least one substituted group on the aromatic nucleus capable of being oxidized to a carboxyl group, etc. Partially oxidized alkyl substituted aryl compounds are useful as a feed stock in mixtures of two or more of such partially oxidized feed stocks. Said mixtures may additionally contain one or more alkyl substituted aryl compounds and be useful as feed stocks in the process of the present invention.

Illustrative examples of said partially oxidized feed stocks include, but are not limited to, aromatic compounds having non-oxidizable substituent groups besides at least one oxidizable methyl group such as m-toluic acid; p-toluic acid, m-methyl toluate and p-methyl toluate; hydroxymethyl-substituted aromatic compounds such as benzyl alcohol, m- and p-hydroxymethyl toluenes, and tolyl carbinols; aldehyde-substituted aromatic compounds such as benzaldehyde, m- and p-tolualdehydes, isophthaloaldehyde, terephthaloaldehyde, m- and p-carboxy benzaldehyde and esters thereof; and those hydroxymethyl-substituted and aldehyde substituted aromatic compounds containing other non-oxidizable substituent groups. "Non-oxidizable substituents" consist of those groups which are not oxidized to carboxyl groups under the reaction conditions employed in this invention, such as

a halogen atom, carboxyl group, carboalkoxy group, a cyano group and a nitro group. Other examples of suitable feed stocks for the present process are dimethyl biphenyl, methyl acetylphenones, and the like.

The feed stock for the process of this invention may be a mixture of isomeric materials or such a mixture containing lower or higher homologues. It may also contain some saturated aliphatic hydrocarbon materials of similar boiling ranges. Mixtures of materials may be converted to the corresponding mixtures of aromatic carboxylic acids, which acids may then be separated, e.g., by physical means such as distillation, or by a combination of chemical and physical means such as esterification followed by fractionation.

A preferred feed stock has the formula

$$R_mAr(COOH)_n$$

wherein Ar is an aryl group, R is selected from the group which consists of an alkyl group, an aldehyde group, a carbinol group and a ketone group, m is a number from 1 to 4, n is a number from 0 to 3, $m+n$ is a number from 1 to 4 and when m is a number greater than 1 the R's need not be the same group.

A feed stock of xylenes and partially oxidized xylenes, such as toluic acids, aldehydes and ketones, is particularly useful in the production of terephthalic acid by the process of this invention. The ortho are meta phthalic acids thus produced may be isomerized to the terephthalic acid by known methods. The oxidation of p-toluic acid to terephthalic acid, which is a difficult oxidation by conventional methods, is readily accomplished by the process of this invention. Although feed stocks useful herein may be soluble in the solvent for the electron carrier, the oxidation of the feed stock takes place without the necessity for the feed stock being soluble in the solvent for the electron carrier. Preferred feed stocks are substantially insoluble in the solvent for the electron carrier.

The size, shape and dimensions of the electrolytic cell as well as the materials from which it is fabricated are not critical except that the anode must be of lead or of a lead-bearing composition such as an alloy of lead with tin, silver, antimony or other suitable metals. Since a strong mineral acid is used in the cell, it is preferable that the surfaces of the cell exposed to the mineral acid be resistant to attack by the acid in order to obtain longer cell service life and minimize maintenance requirements. A cell with both a lead cathode and a lead anode has been found satisfactory. A carbon cathode is also acceptable. A platinum-plated steel cathode may also be used in the present process.

Similarly the form of the anode is not critical. A cylinder of lead sheet, a lead grid or a lead-containing sheet or grid can be fitted within, or a suitable lead-containing coating placed upon, an inert containing vessel of the cell and will serve as an effective anode in the process of this invention.

In selecting a containing vessel of a material other than lead it is necessary only that the vessel be inert to electrolytic action. A typical inert containing vessel is a vessel of ceramic or glass. Likewise, a container of any of the available plastics which are chemically resistant to strong mineral acids, inert to electrolytic action, and capable of maintaining their structural integrity under the operating conditions selected may be used in the process of this invention as the containing vessel.

The current density of the cell is not critical so long as there is sufficient driving force so that an electron carrier after accepting electrons from the feed stock will discharge electrons at the anode. In general, operation at higher current densities will be more economical.

Chromium dissolved in a strong mineral acid is the electron carrier which accomplishes the oxidation of the feed stock. Although the oxidation state of the chromium during the course of the feed stock oxidation is not known at all times, it is postulated that upon accepting electrons from the feed stock the oxidation state of the chromium is +3 and after discharge of electrons at the anode the oxidation state of the chromium is +6. Preferred strong mineral acids are sulfuric acid and phosphoric acid. In still more preferred embodiments sulfuric acid is found to give very good results. The acid concentration is not critical so long as the chromium remains in solution during the course of the electrolytic oxidation process. An acid concentration of from about 40 percent to about 60 percent is preferred to be certain that the chromium remains in solution.

During the process of this invention some hydrogen gas is produced. Although the process may be conducted at elevated or reduced pressures, the most convenient procedure for facilitating the venting of this gas is to conduct the process at ambient atmospheric pressure.

The process of this invention may be conducted at a range of temperatures from about room temperature to about the boiling temperature of the cell contents. The cell contents comprise the feed stock, the electron carrier and the solvent for the electron carrier. The boiling temperature or boiling point of the cell contents is defined as the temperature at which, under process operating conditions, the liquid cell contents are transformed into a vapor. Where such vaporization takes place over a range of temperatures, the boiling point or temperature, as used herein, is the lowest temperature in the range. The oxidation takes place at a higher rate as the temperature is increased above room temperature. A temperature above about 60° C is preferred and a temperature above about 70°C is more preferred. Particularly where a high molecular weight feed stock is used, a temperature above about 80°C is still more preferred. The maximum temperature at which the process is conducted is determined by the boiling point of the cell contents under process operating conditions in order to avoid excessive loss of cell contents by evaporation. In a preferred embodiment the process is conducted at a temperature no higher than about 10°C below the boiling point of the cell contents and in a more preferred embodiment no higher than about 20°C below the boiling point of the cell contents.

The following examples more specifically illustrate some of the preferred embodiments of the process of this invention.

EXAMPLE 1

This example illustrates the preparation of terephthalic acid from p-toluic acid by the process of this invention. Using an electrolytic cell comprising a

vertically mounted cylindrical lead cup, 7.0 cm. inside diameter and 20 cm. high acting as anode with a concentric lead rod 0.63 cm. outside diameter reaching to 3.2 cm. from the bottom of the cup and serving as the cathode, there are charged into the cup, 500 ml. of electrolyte comprised of 0.6 molar chromic sulfate [$Cr_2(SO_4)_3$] in 50% aqueous sulfuric acid and 0.1 mole [13.6g]of p-toluic acid. The solution is heated to 115°C and 1.79 Faradays of electricity is passed through the cell by applying 4 volts D.C. between the anode and cathode during a period of 4 hours. The slurry is stirred by hand. The product is then cooled and filtered. The filter cake is washed with water, dried and weighed [12.0 g]. Analysis shows that it contains 0.0381 mole of unreacted p-toluic acid and 0.04105 mole of terephthalic acid. This represents 41 percent conversion of the charged p-toluic acid to terephthalic acid in a yield of 66 percent of theory.

EXAMPLE 2

This example illustrates the preparation of terephthalic acid from p-toluic acid by the process of this invention using phosphoric acid as the solvent for electron carrier. The method of Example 1 is followed except that chromic phosphate $CrPO_4$ and 50 percent aqueous phosphoric acid are used. A portion of the p-toluic acid is oxidized to terephthalic acid.

EXAMPLE 3

This example illustrates the use of a different electrolytic cell in the preparation of terephthalic acid from p-toluic acid by the process of this invention.

The method of Example 1 is followed except that in place of the cylindrical lead cup a ceramic cup of slightly larger dimensions is used and a separate lead anode in the form of lead wire mesh is fitted inside the cup in a manner to provide a clearance between the anode and the cathode substantially the same as in Example 1. A portion of the p-toluic acid is oxidized to terephthalic acid. The composition of the containing vessel is not critical. In place of the ceramic cup, a glass vessel may be used with equivalent results.

EXAMPLE 4

This example illustrates the use of a different metallic cathode in the preparation of terephthalic acid from p-toluic acid by the process of this invention.

The method of Example 1 is followed except that in place of the concentric lead rod cathode a platinum plated steel cathode of substantially the same size and shape is used. A portion of p-toluic acid is oxidized to terephthalic acid. Other suitable metal or carbon cathodes can be used effectively in the process of this invention.

EXAMPLES 5 – 12

These examples illustrate the wide variety of aryl carboxy acids which may be produced by the process of this invention from alkyl substituted aryl compounds and partially oxidized alkyl substituted aryl compounds.

The method of Example 1 is followed using the feed stocks shown in the examples to give a measurable quantity of the corresponding acids.

Example	Feed Stock	Acid
5	benzaldehyde	benzoic acid
6	4-methyl-propiophenone	terephthalic acid
7	4,4'dimethyl bibenzyl	terephthalic acid
8	mixed xylenes	mixed phthalic acids
9	pseudo cumene	trimellitic acid
10	1,2,4,5-tetramethyl benzene	1,2,4,5-benzene tetracarboxylic acid
11	phenyl carbinol	benzoic acid
12	di-methyl naphthalene	2,6-naphthalene dicarboxylic acid

The utility of the aryl carboxy acids which may be made according to the process of this invention is well known. The isomerization of o-phthalic acid and m-phthalic acid to terephthalic acid is taught in U. S. Pat. Nos. 2,863,913, 2,863,914, 2,905,709, and 2,906,774. Benzoic acid and its salt, sodium benzoate, are most widely used as preservatives agents for foods, pharmaceutical preparations and cosmetics. The largest use of terephthalic acid is in the production of poly(ethylene terephthalate) film and fibers. O-phthalic and m-phthalic acids may be used in the production of phthalate ester plasticizers for polyvinyl chloride composition as well as for isomerization to terephthalic acid. Trimellitic acid likewise is used in the production of polyvinyl chloride plasticizers, particularly in wire and cable formulations. 1,2,4,5-Benzene tetracarboxylic acid and 2,6-naphthalene dicarboxylic acid are useful in the production of polyester resins.

We claim:

1. A process for the preparation of terephthalic acid which comprises heating an electrolytic cell having a lead-containing anode to a temperature above 70° C and charging to said cell para-toluic acid and chromium in solution in sulfuric acid and passing through said cell a direct electric current whereby said para-toluic acid is oxidized to terephthalic acid by said chromium in an ionized electron-accepting state accepting electrons from said para-toluic acid, carrying them to said anode, discharging them at said anode and there being regenerated to an electron-accepting state.

2. The process of claim 1 wherein the electrolytic cell has a lead-containing cathode.

3. The process of claim 1 wherein the electrolytic cell has a platinum plated steel cathode.

4. The process of claim 1 wherein the electrolytic cell has a carbon cathode.

5. The process of claim 1 wherein the lead-containing anode is a lead alloy grid.

6. The process of claim 1 wherein the lead-containing anode is a cylinder of lead mesh.

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