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LIQUID PHASE OXIDATION

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8 Claims. (Cl. 260—524)

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This invention relates to liquid phase oxidation of alkyl substituted aromatic compounds in the presence of metallic catalysts. More specifically the invention relates to a method of promoting the catalytic oxidation by conducting it in the presence of certain substances which provide free radicals.

The liquid phase oxidation of alkylbenzenes, for example xylene, in the presence of metal oxide or metal salt catalysts is well known to the art. These oxidations have been quite useful in the preparation of partially oxidized products, for example toluic acid, but only very small proportions of the dibasic acids have heretofore been prepared, especially when p-dialkylbenzenes are oxidized.

The primary purpose of this invention is to provide an improved method whereby substantial yields of acids may be prepared by the oxidation of alkylbenzenes. A further purpose of this invention is to provide a new and more practicable method of preparing both monobasic and dibasic acids by the oxidation of dialkylbenzenes with gaseous oxygen. A still further purpose is to increase the yield of terephthalic acid in the oxidation of p-xylene.

Liquid phase oxidations of alkylbenzenes are conventionally conducted in closed retorts under pressure, if necessary, to confine the hydrocarbon at the temperature of reaction. Pressures from 50 to 1000 pounds per square inch are useful and temperatures of 100 to 250° C. have been used. It is also known that a wide variety of metal oxides and salts are very effective in accelerating the oxidation, for example cobalt oxide, vanadium oxide, lead oxide, barium oxide, iron oxide, manganese oxide, chromium oxide, copper oxide, nickel oxide, or the corresponding hydroxides or salts of the same metals or mixtures of them. Under conditions of oxidation the hydroxides, and most of the oxides are probably converted to salts of the alkyl carboyxlic acids, for example cobalt toluate, and the catalytic effect is achieved by the metal in this form. The oxidations are usually conducted by means of oxygen, air, oxygen enriched air, or any other mixture of oxygen and inert gas, in corrosion resistant reactors; for example nickel, stainless steel or glass-lined steel. When oxygen is used in high concentrations there is some explosion hazard; and therefore preferred use involves mixtures of oxygen and inert gases wherein the oxygen is less than fifty percent by volume.

The oxidation of alkylbenzenes can be practiced with any compound having a benzene nucleus and at least one alkyl substituent, for example toluene, o-xylene, m-xylene, p-xylene, mixed xylenes, ethylbenzene, the various isometric diethylbenzenes, and the hydrocarbons having one or more alkyl substituents, such as n-propyl, isopropyl and the different butyl radicals, as for example in cumene and cymene. Of particular importance are the dialkylbenzenes wherein the alkyl radicals may be the same or different and each radical has from one to four carbon atoms.

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It has been found that the chemical action is promoted by the presence of certain substances which yield free radicals under conditions of the reaction. Not all substances known to be productive of free radicals are effective in inducing the promotion effect, but the critical characteristics of promoters have not yet been definitely ascertained. Accordingly, predictions of the operativeness of various free radical substances are not possible. In accordance with this invention it has been found that substantial increases in yield of both monobasic and dibasic acids are obtained when the reaction is conducted in the presence of a small proportion of hexachlorethane. In the practice of this invention it has been found desirable to use from 0.05 to 2.0 percent by weight of hexachlorethane, based upon the weight of the alkylbenzenes charged.

It has been found that the reaction is autocatalytic and that sometimes a period of induction is required before rapid oxidation begins. The induction period is especially noticeable when a new reactor is used, or when an old reactor is used after not being used for a period of time or after use for a different reaction. It is believed that traces of product on the surface of previously used reactors catalyzes the reaction and eliminates, or minimizes, the usual period of induction. The addition of a small quantity of an oxidation product, for example monocarboxylic acid or a dicarboxylic acid corresponding to the alkylbenzene being oxidized, is beneficial. In the oxidation of p-xylene to terephthalic acid a small quantity of p-toluic acid may be used to reduce the length of the induction period.

Further details of the practice of this invention are set forth with respect to the following specific examples.

Example 1

A stainless-steel autoclave was provided with a mechanical agitator consisting of a three blade propeller type and an electric motor suitable for driving the propeller at 1,750 revolutions per minute. A gas inlet tube was so positioned so as to be immersed in the reaction mass at a point

just above the propeller. The autoclave was vented through a water cooled condenser and then through a valve to regulate the flow of exit gas. The condenser was provided with a means for separating the unreacted xylene and returning it to the autoclave. The temperature was maintained automatically by means of an electric heater and a thermocouple. The flow of gas through the autoclave was maintained by means of an air stream at a constant pressure and regulated by means of the valve in the vent line.

The autoclave was charged with 500 grams of p-xylene, 1.5 grams of cobaltous hydrate and 2.5 grams of p-toluic acid. The temperature was maintained at 160 to 170° C. for four hours, during which time the reactor was maintained at 200 pounds per square inch pressure, and air was provided at 15 cubic feet per hour. The analysis of the product showed a conversion of 10.3 percent to terephthalic acid.

Example 2

The procedure of the preceding example was duplicated, except that the autoclave was also charged with 1.0 gram of hexachlorethane. The yield of terephthalic acid was increased to 18.9 percent.

Example 3

Each of the two preceding examples were duplicated except that m-xylene was used in place of p-xylene. Without the use of hexachlorethane a yield of 4.2 percent of isophthalic acid was obtained; with the promoter a yield of 7.2 percent was obtained.

In copending application Serial No. 82,921, filed March 22, 1949 by William S. Emerson and Robert A. Heimsch, there are described and claimed methods of conducting the liquid phase oxidation in two stages of varying conditions of operation. The first stage of the reaction is conducted at lower temperatures and the second stage, after substantial oxidation has taken place, is conducted at higher temperatures. If desired the initial stage may be conducted with a substantially lower oxygen supply which is increased as the reaction approaches completion. These expedients may be used in addition to the hexachlorethane and further improvements in efficiency thereby obtained.

The invention is defined by the following claims.

We claim:

1. The catalytic liquid phase oxidation of dialkylbenzene to dicarboxylic acid, which comprises contacting a dialkylbenzene having from one to four carbon atoms in the alkyl groups, with an oxygen containing gas in the presence of an oxidation catalyst of the group consisting of metal oxides, metal salts, and mixtures thereof and hexachlorethane, at a temperature in excess of 140° C.

2. The catalytic liquid phase oxidation of dialkylbenzene to dicarboxylic acid, which comprises contacting a dialkylbenzene having from one to four carbon atoms in the alkyl groups, with an oxygen containing gas in the presence of an oxidation catalyst of the group consisting of metal oxides, metal salts, and mixtures thereof and hexachlorethane.

3. The catalytic liquid phase oxidation of dialkylbenzene to dicarboxylic acid, which comprises contacting a dialkylbenzene having from one to four carbon atoms in the alkyl groups, with an oxygen containing gas in the presence of an oxidation catalyst of the group consisting of metal oxides, metal salts, and mixtures thereof and hexachlorethane, at a temperature between 140° C. and 200° C.

4. The catalytic liquid phase oxidation of a xylene to a dicarboxylic acid, which comprises heating a xylene with an oxygen containing gas in the presence of a cobalt containing catalyst and from 0.05 to 2.0 percent by weight of hexachlorethane, at a temperature between 140° C. and 200° C.

5. The catalytic liquid phase oxidation of a xylene to a dicarboxylic acid, which comprises heating a xylene with an oxygen containing gas in the presence of an oxidation catalyst and from 0.05 to 2.0 percent by weight of hexachlorethane, at a temperature between 140 and 200° C.

6. A catalytic liquid phase oxidation of a xylene to a dicarboxylic acid, which comprises heating a xylene with an oxygen containing gas in the presence of a cobalt containing catalyst and hexachlorethane, at a temperature between 140 and 200° C.

7. The catalytic liquid phase oxidation of a xylene to a dicarboxylic acid, which comprises heating a xylene with an oxygen containing gas in the presence of a cobalt containing catalyst and from 0.05 to 2.0 percent by weight of hexachlorethane, at a temperature above 140° C.

8. The catalytic liquid phase oxidation of p-xylene to terephthalic acid, which comprises contacting p-xylene with air at a temperature of 140 to 200° C., in the presence of from 0.05 to 2.0 percent by weight of hexachlorethane and a cobalt containing catalyst.

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