

## UNITED STATES PATENT OFFICE

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## CATALYTIC OXIDATION OF ALKYL SUBSTITUTED AROMATIC COMPOUNDS

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This invention relates to oxidation of alkyl-substituted aromatic compounds and, more particularly to the production of aromatic acids by oxidation of alkyl-substituted aromatic hydrocarbons.

It is an object of the present invention to provide a process for the controlled oxidation of alkyl-substituted aromatic compounds, particularly toluene, xylene and the substituted benzenes.

It is a further and more specific object of the present invention to provide a new and improved process for the production, from alkyl-substituted aromatic compounds, of aromatic acids without rupture of the aromatic ring, and more particularly to obtain benzoic acid from toluene, toluic and phthalic acids from xylene, and benzene mono- or polycarboxylic acids and alkyl-substituted derivatives from the corresponding alkyl-substituted benzenes.

Other objects and advantages of the present invention will be apparent by reference to the following specification.

I have found that oxidation without ring cleavage of alkyl-substituted aromatic compounds with production in good yield of the corresponding acids can be accomplished by subjecting the said compounds to oxidation in the liquid phase by means of an oxygen-containing gas, for example oxygen or air or air enriched with oxygen.

In this manner it is possible to oxidize hydrocarbons, such as toluene, xylene and other alkyl-substituted benzenes with production of benzoic, toluic and phthalic acids or other benzene mono- or polycarboxylic acids and alkyl-substituted derivatives thereof. Similarly alkyl-substituted aromatic compounds which contain substituents, in addition to alkyl groups may also be oxidized according to this invention, such for example as alkyl-substituted aromatic compounds containing  $\text{NO}_2$ , halogen, and carboxyl groups. While my process may be carried out at various temperatures ranging upward from about 100° C. to about 320° C., generally speaking the use of temperatures in the more restricted range of 130—250° C., tends, other conditions remaining the same, to give less of partial oxidation products, less loss of carbon to oxides of carbon, and a higher proportion of acids.

I have further discovered three factors which, all taken together, produce the optimum result but which, nevertheless, individually contribute to an improved result as will appear hereinafter. Each of these factors, or methods, facilitate oxidation at low temperatures, improved results are obtained when any two of them are employed and

the best results are secured when all three methods are used simultaneously.

As one of the three factors previously mentioned, I have found that the yields of acid produced according to my invention may be considerably increased by carrying on the oxidation in the presence of an oxidation catalyst, such, specifically as the solid polyvalent metals having an atomic weight between about 50 and about 200.

10 For example, I may use such metals in the finely divided metallic state or as organic and inorganic salts or oxides including such specific metals as cerium, cobalt, copper, manganese, and uranium, with or without inorganic acids such as nitric, phosphoric and hydrochloric acids or mixtures of any two or more of these substances. As specific catalysts under the above description there may be employed vanadium, cerium and cobalt chlorides, manganese acetate alone or together with barium acetate, barium or cobalt permanganate, sodium cobalt nitrite or mixtures of two or more of such compounds. In addition to the oxidation catalysts, promoters such as the alkali and alkaline earth metals may also be employed, if desired, such, for example as the barium, magnesium and potassium acetates, butyrates, propionates, and the like.

I have also found that enhanced yields of aromatic acids are obtained if the oxidation is carried on in the presence of a solvent for the hydrocarbons. Various liquids substantially inert to the oxidation and capable of dissolving the hydrocarbons such as carbon tetrachloride and benzene can be used, but I prefer to use as solvent an organic acid, such as acetic, propionic, butyric, trimethyl acetic and isobutyric, such aromatic acids as phenyl acetic, and such hydroxy acids or derivatives as methoxy acetic, and the like. Varying proportions of these acids, based upon the weight per cent. present in the solution being oxidized, may be utilized, such as from 1 to 99 per cent. by weight although I prefer to utilize about 10 to 50 per cent. Within these indicated ranges I have found that the solvents effect a considerable increase in the yield of aromatic acid obtained by oxidation of the hydrocarbon.

As a further feature of the invention I have found that, especially when operating at the lower temperatures, say 200° or below, the yields and efficiency of the process may be even further improved by carrying on the oxidation, whether with or without the solvents referred to, in the presence of one or more "initiators," which term I employ herein to designate substances capable of initiating attack on the hydrocarbon molecule which

may itself not readily react with molecular oxygen under my preferred low temperature conditions. For example, there may be employed organic peroxides such as benzoyl peroxide; inorganic peroxides; peracids, such as peracetic and perbenzoic acids; the aldehydes, such as acetaldehyde, propionaldehyde, and isobutyraldehyde; ketones, such as acetone, methyl ethyl ketone, diethyl ketone, and cyclohexanone; ethers, such as diisopropyl, diethyl and diethyl ethers; olefines such as cyclohexene and octylene, and, in fact, any organic compound which tends to form peroxide bodies under the reaction conditions.

The initiator may be added to the reactants at the start or continuously during the oxidation or both; or, if preferred the oxidation may be begun at a temperature and pressure at which partial oxidation products, capable of being oxidized to or acting as oxygen carriers are formed, and the partially oxidized hydrocarbons thus produced may thereafter act as oxygen carriers capable of attacking other hydrocarbon molecules at the relatively low temperatures which I have generally outlined and will hereinafter more specifically describe. The constant maintenance of a concentration of initiator is important, however, and therefore, in general, I deliberately add the initiator to the reactants as described hereinafter. The oxygen carrier is thus able to initiate the oxidation which then may become at least partially self-sustaining at temperatures very much lower than otherwise possible.

The proportions of initiators which are desirable according to this invention range from about 0.1 to 10 per cent, based upon the weight of the hydrocarbon being treated. I do not wish to be restricted to these proportions, however, for I have found that as much as 50 per cent initiator may be utilized without deleterious effect upon progress of the oxidation and at the same time as low as 0.05 per cent initiator may be employed with an increased efficiency and yield of aromatic acid. Although primarily applicable to ketones such as acetone, dimethyl or methyl ethyl ketones, or cyclohexanone, or mixtures thereof, these ranges describe satisfactorily the amounts of other initiators which are suitable according to my invention.

While the process is operable at ordinary pressures I prefer to use elevated pressures ranging upwards from about 2 atmospheres to about 100 atmospheres. Although pressures in the neighborhood of from 10 to 50 atmospheres are preferred, higher pressures, for example as high as 1000 atmospheres, may be used. The minimum pressure is that required to permit effecting the reaction in the liquid phase, by which is meant that the hydrocarbon is preferably oxidized in the liquid or dissolved state. Pressures in excess of this minimum may be used, however, since pressure has been found to favor the reaction rate.

Having described separately some of the features of my invention, the following examples will illustrate how these features may be combined for oxidation of alkyl-substituted aromatic compounds generally.

*Example 1.*—A mixture containing 276 grams toluene, 276 grams acetic acid, 0.23 grams cobalt acetate, 0.23 grams manganese acetate and 4.3 grams methyl ethyl ketone was charged into a tantalum lined converter of 1200 cc. capacity, provided with suitably valved gas outlet and inlet lines at top and bottom, respectively. The

mixture was heated to 190° C., under a pressure of 50 atmospheres and air was bubbled through the mixture for 3½ hours at the rate of 200 liters per hour, the pressure being maintained at 50 atmospheres and the temperature at 185–200° C. The exit gas was directed through a condenser, and traps cooled by dry ice. Solid benzoic acid was removed from the oxidation products and recovered by cooling the final product to crystallize the benzoic acid. The total weight of benzoic acid recovered was 126.9 grams. An additional 45.8 grams of benzoic acid was recovered from the filtrate after stripping off the acetic acid and unconverted toluene. 123.2 grams of unused toluene was recovered. The conversion and yield were 47.2% and 85.2% respectively. The residue obtained after recovery of benzoic and acetic acids consisted of benzaldehyde and tar.

*Example 2.*—A mixture containing 425.0 grams ethyl benzene, 63.1 grams acetic acid, and 0.05 grams cobalt acetate was charged into a tantalum-lined converter of 1200 cc. capacity, provided with suitably valved outlet and inlet lines at top and bottom, respectively. The mixture was heated to 168–178° C. for 1½ hours under a pressure of 50 atmospheres. Air was bubbled through the mixture for 1½ hours at the rate of 225 liters per hour, the pressure being maintained at 50 atmospheres and the temperature at 168–178° C. The exit gas was directed through a condenser, and traps cooled by dry ice.

Solid benzoic acid was removed from the oxidation product and recovered by cooling the final products to crystallize the benzoic acid. The total weight of benzoic acid recovered was 24.1 grams. In addition, there was separated from the final product 2.8 grams phenyl ethyl ester, 1.1 grams phenyl ethanol, and 53.6 grams acetophenone. 122.2 grams of unreacted ethyl benzene was recovered. The conversion and yield to benzoic acid were, respectively, 18.2% and 25.6%. The conversion and yield to acetophenone were, respectively, 41.4% and 58%.

*Example 3.*—Into a tantalum-lined converter, such as described in Examples 1 and 2, was charged 236.0 grams of mixed xylenes, 130.6 grams acetic acid, 3.7 grams diethyl ketone, 0.185 grams cobalt acetate and 0.185 grams manganese acetate. This mixture was heated to 187–202° C. under a pressure of 50 atmospheres and air was bubbled through the mixture at this temperature and pressure for 2 hours at the rate of 250 liters per hour.

By distillation under atmospheric and reduced pressures, the reaction products were separated to give 75.7 grams of unreacted xylenes, and 50.3% yield of toluic acids, 2.0% yield of phthalic acids, 1.5% yield of toluyl alcohols, 8.1% yield of toluyl esters and 5.7% yield of toluic aldehydes.

*Example 4.*—Into a converter such as described in Examples 1 and 2 there was charged a mixture containing 400 grams isopropyl benzene, 4 grams water and 0.4 gram cobalt acetate. This mixture was heated at a temperature of 170–229° C. under a pressure of 30 atmospheres and air was bubbled through this mixture for 2 hours at the rate of 250 liters per hour. At the expiration of this time the reaction products were separated by distillation to give 45 grams benzoic acid, and 230 grams cumene. The remaining material was of a tarry nature. The yield of benzoic acid was about 35%.

Although specific disclosure has been made in the examples of methods for carrying on my in-

vention in a batch process, it should be understood that this invention may also be practiced in a continuous manner. Thus, after completion of the benzoic acid or other acid production, such as shown in the specific examples, the materials capable of being converted to the desired acid, plus the catalyst, solvent, and initiator may be recovered and recycled to the reaction zone together with further quantities of aromatic hydrocarbon. In a continuous process it will also be found desirable to make such additions of catalyst, solvent, and initiator as will maintain the reaction rate and yield of acid at the desired high degree.

While the process as described in the examples involves passage of the oxidizing gas through a body of liquid, it will be understood that other means of assuring the desired liquid-gas contact may be employed, as, for example, passage of liquid and gas co-current or counter-current through a tube or tower, which may be supplied with plates, packing or other devices for enhancing contact.

I claim:

1. A method of oxidizing aromatic compounds containing alkyl substituents which comprises subjecting such compounds to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst and a solvent for the aromatic compound which is substantially inert to the oxidation.

2. A method of oxidizing aromatic compounds containing alkyl substituents which comprises subjecting such compounds to oxidation by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions and a solvent for the aromatic compound which is substantially inert to the oxidation at a temperature in the range of 100°-320° C. and at a pressure in the range of 2 to 1000 atmospheres and separating the corresponding aromatic acid from the reaction mixture.

3. A method of oxidizing aromatic compounds containing alkyl substituents which comprises subjecting such compounds to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions and a solvent for the aromatic compound which is substantially inert to the oxidation at a temperature in the range of 100°-320° C. and at a pressure in the range of 2 to 1000 atmospheres and separating the corresponding aromatic acid from the reaction mixture.

4. A method of oxidizing aromatic compounds containing alkyl substituents which comprises subjecting such compounds to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions and a solvent for the aromatic compound which is substantially inert to the oxidation at a temperature in the range of 130°-250° C. and at a pressure in the range of 2 to 100 atmospheres and separating the corresponding aromatic acid from the reaction mixture.

5. A method of producing aromatic acids which comprises subjecting an alkyl substituted

aromatic compound to oxidation by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions and a solvent for the aromatic compound which is substantially inert to the oxidation at a temperature in the range of 100°-320° C. and at a pressure in the range of

10 2 to 1000 atmospheres and separating the corresponding aromatic acid from the reaction mixture.

6. A method of producing aromatic acids which comprises subjecting an alkyl substituted aromatic compound to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions and a solvent for the aromatic compound which is substantially inert to the oxidation at a temperature in the range of 100°-320° C. and at a pressure in the range of 2 to 1000 atmospheres and separating the corresponding aromatic acid from the reaction mixture.

7. A method of producing aromatic acids which comprises subjecting an alkyl substituted aromatic compound to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions and a solvent for the aromatic compound which is substantially inert to the oxidation at a temperature in the range of 130°-250° C. and at a pressure in the range of 2 to 1000 atmospheres and separating the corresponding aromatic acid from the reaction mixture.

8. A method of producing benzoic acid which comprises subjecting toluene to oxidation by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst and a solvent for the toluene which is substantially inert to the oxidation.

9. A method of producing benzoic acid which comprises subjecting toluene to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst and a solvent for the toluene which is substantially inert to the oxidation.

10. A method of producing benzoic acid which comprises subjecting toluene to oxidation by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions, and a solvent for the toluene which is substantially inert to the oxidation at a temperature in the range of 100°-320° C. and at a pressure in the range of 2 to 1000 atmospheres and separating the benzoic acid from the reaction mixture.

11. A method of producing benzoic acid which comprises subjecting toluene to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions, and a solvent for the toluene which is substantially inert to the oxidation at a temperature in the range of 100°-320° C. and at a pressure in the range of 2 to 1000 atmospheres,

and separating the benzoic acid from the reaction mixture.

12. A method of producing benzoic acid which comprises subjecting toluene to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions, and a solvent for the toluene which is substantially inert to the oxidation at a temperature in the range of 130°-250° C., and at a pressure in the range of 2 to 100 atmospheres, and separating the benzoic acid from the reaction mixture.

13. A method of producing benzoic acid which comprises subjecting toluene to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of a cobalt acetate catalyst, an acetic acid solvent, and an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions, at a temperature in the range of 100°-320° C., and at a pressure in the range of 2 to 100 atmospheres, and separating the benzoic acid from the reaction mixture.

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14. A method of producing benzoic acid which comprises subjecting toluene to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of a cobalt acetate catalyst, an acetic acid solvent, and an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions, at a temperature in the range of 130°-250° C., and at a pressure in the range of 2 to 1000 atmospheres, and separating the benzoic acid from the reaction mixture.

15. A method of producing benzoic acid which comprises subjecting toluene to oxidation in the liquid phase by means of a gas containing gaseous oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions, and a lower aliphatic acid solvent for the toluene at a temperature in the range of 130°-250° C., and at a pressure in the range of 2 to 100 atmospheres, and separating the benzoic acid from the reaction mixture.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 25, claim 13, for "2 to 100" read --2 to 1000--; and second column, line 10, claim 14, for "2 to 1000" read --2 to 100--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of July, A. D. 1941.

Henry Van Arsdale,  
Acting Commissioner of Patents.

(Seal)