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OXIDATION OF AROMATIC COMPOUNDS CONTAINING OXYGENATED SIDE CHAINS

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11 Claims. (Cl. 260—524)

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This invention relates to the oxidation of organic compounds, more particularly to the oxidation of partially oxidized alkyl aromatic hydrocarbons to produce aromatic carboxylic acids. The oxidation of partially oxidized derivatives of alkyl aromatic hydrocarbons to produce aromatic carboxylic acids having the carboxyl carbon atom or atoms directly attached to a nuclear carbon atom presents the organic chemist with a delicate problem of control if high yields of the desired acids are to be obtained. If the conditions under which the oxidation is conducted are too severe, considerable losses of the charging stock are sustained by reason of ring rupture of the aromatic nuclei. If the conditions under which the oxidation is conducted are not sufficiently severe, large proportions of the charging stock are converted to oxidation products which are intermediate between the charging stock and the desired carboxylic acids.

It is an object of this invention to provide a method by which partially oxidized alkyl aromatic hydrocarbons characterized by an oxidation level intermediate between the alkyl aromatic hydrocarbons and aromatic carboxylic acids may be converted to aromatic carboxylic acids having the carboxyl atom or atoms directly attached to nuclear carbon atoms in approximately theoretical yields.

It has now been found that partially oxidized derivatives of alkyl aromatic hydrocarbons, especially those having at least one hydrogen atom attached to the alpha carbon atom of an alkyl group, may be oxidized to produce aromatic carboxylic acids and aromatic carboxylic acid salts having the carboxyl carbon atom or atoms directly attached to a nuclear carbon atom by contacting the partially oxidized alkyl aromatic hydrocarbon with sulfur and an aqueous solution of a basic material selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides at a temperature above about 550° F. The sulfur may be introduced into the reaction mixture as such or in the form of a water-soluble polysulfide or certain other inorganic sulfur compounds which, in the presence of the reactants and under the reaction conditions, yield elemental sulfur. Such other sulfur compounds are more particularly described hereinafter.

The invention may be understood upon consideration of the following examples of the oxidation of toluic acids to phthalic acids which are provided to illustrate the character of the reactions which produce the desired aromatic carboxylic acids and their derivatives, but which are not intended in and of themselves to mark out the limits of the invention.

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Example 1

This run was conducted in a stainless steel bomb having a capacity of 2.5 liters. The bomb was fitted with a pressure gauge, a thermowell, a bursting disc, a bleeding line and valve, and a shaker. The bomb was charged with a mixture of toluic acid isomers, elemental sulfur, and aqueous sodium hydroxide. The toluic acids were prepared by air oxidation of mixed xylenes and separated from the reaction product mixture by distillation. The mol ratio of toluic acid to sulfur to sodium hydroxide charged to the bomb was 1:4:1. After charging, the bomb was sealed and heated to a temperature of 600° F. The bomb was then rocked for a period of 1½ hours. During the heating and rocking the pressure in the bomb rose to a maximum value of 2200 p. s. i. g. The bomb was then cooled, depressured, opened, and its contents were removed. The reaction product mixture consisted of an aqueous slurry of sodium phthalate and phthalic acid, hydrogen sulfide, and sulfur in the form of sodium polysulfide. The slurry was refluxed to boil out hydrogen sulfide and to precipitate excess sulfur. Sufficient aqueous caustic was added to bring the pH of the mixture to a value of seven. The resulting solution was filtered and hydrochloric acid was added to the filtrate in amount sufficient to precipitate substantially all of the phthalic acids from the filtrate. During the reaction 87% of the toluic acid charged was converted to phthalic acids. The yield of phthalic acids obtained was equivalent to 115.2 weight per cent of the toluic acids charged.

Example 2

In this example the reaction was conducted in a continuous manner in a reaction system consisting of a reactor section of 40 ft. of stainless steel tubing wound as a coil and immersed in a molten metal bath. The inside diameter of the tubing was $\frac{5}{16}$ inch. The partially oxidized alkyl aromatic hydrocarbon material constituting the feed was the sodium hydroxide extract of the reaction product obtained during air oxidation of mixed xylenes containing 80% by volume of meta- and paraxylenes. This feed mixture together with sulfur in the form of sodium polysulfide was pumped into the coil. From the coil

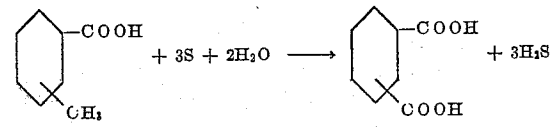
the reaction product entered a surge chamber consisting of a 2.4 liter stainless steel bomb held at an intermediate temperature to avoid further reaction and still maintain the reaction products in solution. A back pressure of nitrogen was maintained on this surge vessel to control operating pressures. Gases were bled from the surge vessel through a pressure regulator as required to maintain the pressure within tolerable limits. Upon completion of the run the products in the surge vessel were bled under pressure to a flash chamber from which most of the hydrogen sulfide formed during the reaction escaped overhead and in which the liquid products collected. The liquid products were then drained from the flash chamber and phthalic acids were recovered in the manner described in Example 1. The ratio of toluic acids to sulfur to sodium sulfide introduced into the coil was 1:6.2:3.3. The reaction time, as determined by dividing the reactor volume by feed rate of the reactants, was ½ hour. The reaction temperature was 605° F. and the maximum pressure observed during the reaction period was 2150 p. s. i. g. Phthalic acids were recovered from the reaction product mixture in amount equal to 83% by weight of the toluic acids charged.

Example 3

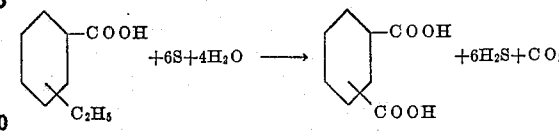
120 gm. of acetophenone (1.0 mol), 80 gm. of sulfur, and a solution of 40 gm. of NaOH in 200 cc. of water were charged to a 2.5 liter bomb. The bomb was sealed and heated to 480° F., at which temperature shaking was begun. The pressure in the bomb rose from 300 p. s. i. to 1300 p. s. i. as the temperature rose from 480° F. to 585° F. over a period of 50 minutes. The bomb was cooled, opened, and the products were removed. There was a large amount of heavy black oil that did not dissolve in the aqueous alkaline solution. It was separated, dried, and found to weigh 108 gm. The aqueous solution was acidified to pH 5.0 and the resulting precipitate of yellow sulfur filtered off. Filtrate was strongly acidified with HCl while hot and a large voluminous precipitate was obtained. The mixture was cooled, filtered, and the filter cake washed twice with water and dried. 19 gm. of white needle-like crystals having a neutral equivalent of 110 were recovered. After sublimation this material had an M. P. of 120° C. and an N. E.=122. (N. E. benzoic acid=122.)

The oxidation of the toluic acids and acetophenone as conducted in the foregoing examples illustrate the manner in which partial oxidation products derived from alkyl aromatic hydrocarbons may be oxidized to aromatic carboxylic acids having the carboxyl carbon atom directly attached to a nuclear carbon atom. Other partial oxidation products derived from alkyl aromatic hydrocarbons such as aromatic alcohols, aromatic ketones, aromatic aldehydes, alkyl aromatic alcohols, alkyl aromatic ketones, alkyl aromatic aldehydes, and alkyl aromatic carboxylic acids may be oxidized to aromatic carboxylic acids by the method illustrated in the examples. Where the alkyl aromatic alcohol, aldehyde or ketone is a product of the partial oxidation of an alkyl aromatic hydrocarbon having at least one hydrogen atom attached to two or more alpha carbon atoms of alkyl groups, aromatic polycarboxylic acids are produced during the reaction.

When a toluic acid is oxidized pursuant to the process of the invention, the reaction appears to be as follows:

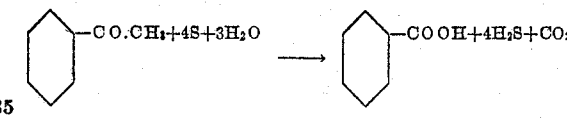


Where a higher alkyl benzoic acid is oxidized pursuant to the invention, the reaction product mixture contains carbon dioxide produced by the oxidation of the alkyl carbon atoms other than the alpha carbon atom in the manner illustrated by the following equation for the oxidation of ethylbenzoic acid:

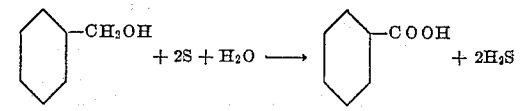


In the oxidation of higher alkyl benzoic acids all of the carbon atoms, except the alpha carbon atom, are converted to carbon dioxide and the oxidation of the alpha carbon atom produces a phthalic acid. Larger amounts of sulfur and water are required in the oxidation of such higher alkyl benzoic acids.

Where acetophenone is oxidized by the process of the invention, the reaction appears to proceed as follows:



Where benzyl alcohol is oxidized by the process of the invention, the reaction appears to proceed as follows:



While the above equations indicate only the presence of sulfur and water and their consumption during the oxidation of the charging stocks, it has been found necessary to have substantial amounts of a basic material such as an alkali metal hydroxide or an alkaline earth metal hydroxide present in the reaction mixture. The role of the basic material in the reaction has not been definitely established, but it appears to function as a solvent for both the charging stock and the sulfur, and intermediate reactions may occur in which the basic material participates without being consumed. When it is attempted to oxidize the partially oxidized alkyl aromatic hydrocarbon derivatives described above in the absence of a basic material, the reaction proceeds as if water were not present, producing stilbene and thiophene derivatives. Toluic acid, water and sodium hydroxide do not react at all under the conditions of the above examples in the absence of sulfur.

The materials which may be oxidized to aromatic carboxylic acids having the carboxyl carbon atom or atoms directly attached to nuclear carbon atoms include, in addition to the materials specifically exemplified above, various intermediately oxidized materials produced by partial oxidation or other alkyl and polyalkyl benzenes and alkyl and polyakyl naphthalenes without limitation as to the number or length of the alkyl side-chains. The alkyl aromatic hydrocarbons themselves may be converted to aromatic carboxylic acids by the

process of the invention, but the yields are very much lower than those obtained when a partially oxidized charging stock is treated. It is believed that the reaction proceeds more readily with the partially oxidized derivatives of alkyl aromatic hydrocarbons because they are substantially more soluble in water and in aqueous alkaline solutions than are the hydrocarbons themselves. Indications are that higher yields of aromatic carboxylic acids may be obtained from the hydrocarbons if the reaction mixture is subjected to extremely violent agitation during the reaction period.

It has been observed that the tertiary butyl group is more resistant to the reaction of this invention than other alkyl configurations and that partial oxidation products derived from alkyl aromatic hydrocarbons in which the alpha carbon atom of an alkyl side-chain is attached to at least one hydrogen atom are more rapidly and completely responsive to the reaction of the invention than those having a quaternary alpha carbon atom in the alkyl side-chain.

Sulfur can be introduced into the reaction mixture as such, or in the form of a water-soluble polysulfide, as shown in the above examples, or in the form of a sulfur compound which is convertible to sulfur under the conditions of the reaction. For example, hydrogen sulfide and sulfur dioxide may be introduced into the reaction mixture in lieu of sulfur and an identical reaction is obtained. Sulfur dioxide or a water-soluble sulfite may be employed in the reaction mixture as the primary source of sulfur for the oxidation. When these materials are used, a small amount of elemental sulfur, not usually exceeding about 6% of the amount which would be required if elemental sulfur were to be used as the sole oxidizing agent, may be introduced into the reaction mixture. This small amount of sulfur initiates the oxidation reaction and some hydrogen sulfide is formed. The hydrogen sulfide then reacts with sulfur dioxide to produce more sulfur and the reaction continues in this manner. The sulfur may also be introduced into the reaction mixture in the form of thionic acids and their salts, or sodium thiosulfate may be employed as the source of sulfur. These materials decompose under the conditions of the reaction to produce sulfate, sulfite, and sulfur, and the sulfite and sulfur are consumed in the oxidation reaction. In general, any inorganic sulfur compound containing at least one sulfur atom which is at a valence level below plus 6 and above minus 2 may be introduced into the reaction mixture as the primary source of sulfur and where such materials are used a small amount of elemental sulfur is desirably but not necessarily introduced into the reaction mixture to act as a catalyst or initiator.

While sulfur acts as the oxidizing agent in the reaction, the oxygen necessary to form the carboxyl groups of the acidic reaction product is supplied by water; consequently, water must be present in the reaction mixture. It is desirably present in amounts greatly exceeding the amount theoretically required to supply the necessary oxygen.

The proportions of the reactants which are desirably present in the reaction mixture, except for the basic material, may be determined from a balanced equation for the oxidation reaction in which sulfur acts as the oxidizing agent and water supplies the oxygen to the carboxyl groups which are formed. Where complete oxidation of

the charge stock is desired, that is, where it is desired to convert each alkyl side-chain or partially oxidized alkyl side-chain to a carboxyl group directly attached to a nuclear carbon atom, it is preferred to employ a small excess of sulfur over the amount theoretically required to effect the oxidation. An excess of the order of 10% by weight is ordinarily suitable.

The basic materials suitable for use in the process of this invention include, in addition to the sodium hydroxide illustrated above, the other alkali metal hydroxides, especially potassium hydroxide, and the alkaline earth metal hydroxides, especially magnesium hydroxide, calcium hydroxide and barium hydroxide; also, their salts with weak inorganic acids as carbonates, bicarbonates, sulfides, and sulfites. The amount of the basic material which is present in the reaction mixture may be varied over a considerable range. At least sufficient basic material to react with all of the carboxyl groups formed in the course of the reaction to form the metal salts of the acids should be present. The basic material is preferably present somewhat in excess of this amount; larger amounts of basic material, for example, five to six times the amount necessary to neutralize the carboxylic acids formed, have been employed with good effect. The basic material may be entirely in solution in water or it may be employed in the form of a dispersion or slurry. The moderately soluble alkline earth metal hydroxides are suitably introduced into the reactor in the form of an aqueous slurry.

The reaction should be conducted at temperatures above about 550° F. At lower temperatures the rate of reaction is slow, and at 500° F. no reaction appears to occur. The maximum temperature of reaction should be below the critical temperature of water in order that a liquid aqueous phase may be present in the reaction mixture. Preferably, the reaction is conducted at temperatures in the range about 500° F. to 675° F., 580° F. to 620° F. being optimum.

Pressure is a dependent variable in the reaction; it is usually in the range about 1000 to 3000 p. s. i. g. which insures the presence of a liquid aqueous phase. The pressure may be controlled during the reaction by bleeding off a portion of the gas formed during the reaction; this has the additional effect of reducing the partial pressure of hydrogen sulfide in the reactor.

The purification of the reaction products was generally described in Example 1 above. Variable percentages of sulfur are sometimes encountered in the reaction products. The amount of sulfur present does not ordinarily exceed 3% by weight of the product and appears to be a function of the amount of excess sulfur used for the oxidation and the care taken during the neutralization step. This sulfur is produced in part by acid decomposition of thiosulfate formed when sulfur is digested in alkaline solutions. Ordinarily, the thiosulfate is consumed during the oxidation unless large excesses of sulfur are employed. If it is not consumed it decomposes upon acidification of the products at elevated temperatures and at pH values below 3 to 4 to give free sulfur and sulfur dioxide. These factors may be controlled to minimize its formation and decomposition so that sulfur-free products are obtained. In the event that the product is contaminated with elemental sulfur, this impurity may be removed by redissolving the acids in caustic, filtering to remove the free sulfur, and reprecipitating the acids by the addition of a strong acid.

Hydrogen sulfide produced during the reaction may be recovered for re-use. It may be absorbed in aqueous sodium hydroxide which, under certain conditions, may be air blown to produce sodium polysulfide which is introduced into the reaction mixture.

I claim:

1. A process for producing aromatic carboxylic acids and salts of aromatic carboxylic acids having the carboxyl carbon atom directly attached to a nuclear carbon atom which comprises oxidizing an oxygen-containing product of the partial oxidation of an alkyl aromatic hydrocarbon by contacting said product with an aqueous mixture of a basic material selected from the group consisting of alkali metal hydroxides and their salts with weak inorganic acids, alkaline earth metal hydroxides and their salts with weak inorganic acids, and an inorganic sulfurous material containing sulfur atoms at a valence level below plus six and above minus 2 at a temperature above about 550° F.

2. A process for producing aromatic carboxylic acids and salts of aromatic carboxylic acids having the carboxyl carbon atom directly attached to a nuclear carbon atom which comprises oxidizing an oxygen-containing product of the partial oxidation of an alkyl aromatic hydrocarbon having at least one hydrogen atom attached to the alpha carbon of an alkyl group by contacting said product with an aqueous mixture of a basic material selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides and an inorganic sulfurous material containing sulfur atoms at a valence level below plus six and above minus 2 at a temperature above about 550° F.

3. The method as defined in claim 1, wherein the product of partial oxidation is an alkyl benzene carboxylic acid.

4. The method as defined in claim 1, wherein the product of partial oxidation of the alkyl aromatic hydrocarbon charged is an aromatic alcohol.

5. The method as defined in claim 1, wherein the product of partial oxidation of the alkyl aromatic hydrocarbon charged is an aromatic aldehyde.

6. The method as defined in claim 1, wherein the product of partial oxidation of the alkyl aromatic hydrocarbon charged is an aromatic ketone.

7. The method as defined in claim 1, wherein the inorganic sulfurous material comprises hydrogen sulfide and sulfur dioxide.

8. A process for producing aromatic polycarboxylic acids having the carboxyl carbon atom or atoms directly attached to a nuclear carbon atom which comprises contacting an alkyl aromatic carboxylic acid having at least one hydrogen attached to the alpha carbon atom of an alkyl group with an aqueous solution of an alkali metal hydroxide and a material selected from the group consisting of elemental sulfur, water-soluble polysulfides, mixtures of water-soluble sulfites and elemental sulfur, and mixtures of hydrogen sulfide and sulfur dioxide at a temperature above about 550° F.

9. The method as defined in claim 8, wherein the alkyl aromatic carboxylic acid is a toluic acid.

10. The method as defined in claim 8, wherein the alkyl aromatic carboxylic acid is a polyalkyl benzoic acid.

11. The method as defined in claim 8, wherein the alkyl aromatic carboxylic acid is an alkyl phthalic acid.

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