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PROCESS FOR PREPARING SULFONYL
DIBENZOIC ACIDS AND DERIVATIVES
THEREOF

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This invention relates to a process for preparing sulfonyl dibenzoic acid including monocarboxydiphenyl sulfone and various isomers, homologs and derivatives thereof. The term "sulfonyl dibenzoic acid" clearly covers the principal products of interest in this specification and is intended to cover in a broader sense all products prepared in accordance with this invention by the oxidation of compounds set forth below in the table. Sometimes the term "sulfonyl mono- or dibenzoic acid" is used in this same sense.

This application is a continuation-in-part of my application Serial No. 143,594 filed February 10, 1950 now Patent No. 2,614,120, which describes inter alia, some of the uses of p,p'-sulfonyl dibenzoic acid, its isomers and homologs.

Sulfonyl dibenzoic acid is a known compound, cf. Meyer, *Annalen der Chemie*, 433,336 (1923); the para isomer melts at 370° C. The methyl and ethyl diesters of this dibasic organic acid are also known and have melting points of 194° C. and 158° C. respectively.

The usual methods for oxidizing sulfonyl derivatives of alkylated aromatic compounds employ relatively expensive oxidizing agents such as permanganates, dichromates, etc. Oxidation can also be brought about by preparing a chlorinated derivative of the corresponding sulfonyl derivative of an alkylated aromatic compound and proceeding in accordance with a complicated and expensive operating procedure. Moreover, the products produced by these methods are very difficult to separate from the oxidizing agent or, in the case of the chlorination procedure, from compounds of a lower state of oxidation. The process of the instant invention provides an inexpensive, smooth reliable means for producing p,p'-sulfonyl dibenzoic acid, isomers, homologs and derivatives thereof. Another advantage lies in the fact that only the alkyl portion of the isomer, homolog or derivative of diphenyl sulfone is attacked and affected by the oxidation so that no ring cleavage occurs. This is not always the case where such prior art chemical oxidants as referred to above are employed.

I have discovered an improved process for the preparation of various isomers, homologs and derivatives of sulfonyl mono- or dibenzoic acid which, briefly stated, comprises oxidizing the corresponding isomer, homolog or derivative of diphenyl sulfone in the presence of a cobalt of manganese catalyst in a solvent which is substantially inert to oxidation and which contains an aldehyde as an activator or oxidation promoter, at a temperature of from about 80°

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to about 110° C. Some aspects of this process are similar to certain aspects of processes disclosed in the prior art such as in Loder's U. S. Patent No. 2,245,528 issued June 10, 1941, which is applicable to the oxidation of non-homologous alkyl-substituted aromatic compounds by a process which is not the same as that of the instant invention. As exemplary of the prior art, this Loder patent describes the oxidation of hydrocarbons such as toluene so as to produce an acid such as benzoic acid. The process is said to be carried out at various temperatures ranging upward from about 100° C. to about 320° C.; generally speaking, it is said that 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 acid. There are three factors which are discussed in detail in the operation of Loder's process. The first is the oxidation catalyst which is defined specifically as a solid polyvalent metal having an atomic weight between about 50 and about 200 which includes cobalt, manganese, vanadium, nickel (although not specifically mentioned), cobalt chloride, manganese acetate, sodium cobalt nitrite, etc. Another factor in the process of this patent is the employment of a promoter such as the alkali and alkaline earth metals, e. g. potassium acetate, etc. Another factor is the employment of a solvent for the hydrocarbon which is being oxidized, examples of which include carbon tetrachloride, benzene, but preferably an organic acid such as acetic acid. A further factor of the Loder process is said to involve the employment of one or more "initiators" which term is employed to designate substances capable of initiating the attack on the hydrocarbon which may not otherwise readily react with molecular oxygen under preferred lower temperature conditions which are described as temperatures when operating at 200° C. or below. Such "initiators" include organic peroxy compounds, aldehydes, ketones, ethers, olefins, and, it is said "any organic compound which tends to form peroxide bodies under the reaction conditions." It is further stated that the constant maintenance of a concentration of initiator is important in the conduct of the reaction and that such initiators are desirably kept within the range of about 0.1 to about 10 percent based upon the weight of the hydrocarbon being treated; however, as much as 50 percent of the initiator may be employed without deleterious effect ac-

cording to the patentee. It is said further that elevated pressures can be employed up to about 100 atmospheres although pressures in the range of from about 10 to 50 atmospheres are preferred. In the examples presented by Loder, initiators such as methyl ethyl ketone and diethyl ketone are employed in some of the examples whereas in other examples no initiator whatsoever is employed. The principal product obtained in the examples is benzoic acid; however, such products are indicated to be rather complex mixtures of oxidation products. For example, the oxidation of mixed xylenes in an acetic acid medium containing diethyl ketone as an oxidation initiator, and a mixed cobalt acetate-manganese acetate catalyst, gave about 50.3 percent yield of toluic acid, 2 percent yield of phthalic acids, 1.5 percent yield of toluyl alcohols, 8 percent yield of toluyl esters and 5.7 percent yield of toluic aldehydes. It is apparent that the processes known to the prior art such as described in the Loder patent are not satisfactory for preparing good yields of aromatic carboxylic acids and make no suggestion of preparing sulfonyl dibenzoic acid, isomers, homologs or derivatives thereof.

Henke et al., U. S. 2,276,774 patented March 17, 1942 (same assignee as in the Loder patent) refers to the Loder patent which has just been discussed as providing a method whereby alkyl-substituted aromatic compounds in a suitable solvent are oxidized in the liquid phase by means of an oxygen-containing gas in the presence of a cobalt catalyst at high temperatures. The Henke et al. patent provides a means for carrying out this process in an improved apparatus whereby the oxidation is conducted in a vessel composed of a chromium-bearing steel and in the presence of an acetic acid soluble lead salt of a lower aliphatic acid. In accordance with the improved process of Henke et al., temperatures of from about 150° C. to about 250° C. can be employed in the oxidation of toluene to form benzoic acid.

Some of the advantages of the process of the instant invention as compared to that described by Loder and similar prior art are the employment of lower temperatures, operation at atmospheric pressure with consequently less complex apparatus, and greatly reduced corrosion of the apparatus employed. This latter point is quite important since it would appear that a process such as described by Loder can be more advantageously performed in accordance with the Henke et al. improvement of U. S. 2,276,774 in order to reduce the corrosion of the apparatus being employed.

In comparing the instant process with the prior art of the type described in Loder U. S. 2,245,528, it is believed worth while pointing out that many of the compounds disclosed in such prior art as subject to oxidation by such processes cannot actually be oxidized in accordance therewith. Thus, many of the compounds disclosed by Loder are incapable of operation under the conditions described, for example, o-nitrotoluene, tetrachloro-para-xylene and o-chlorotoluene. Other compounds disclosed by Loder such as alkyl-substituted aromatics may be inhibitors for the oxidation process described, for example, the aromatic amines, hydroquinone derivatives, and substituted phenols.

As indicated above, the temperature conditions described by Loder are greater than 100° C. and preferably from 130° to 250° C. The examples

given indicate that 130° is probably the actual minimum temperature and that temperatures in excess of this figure are to be preferably employed. In contrast, the instant invention most advantageously employs temperatures in the range of 90° to 100° C. with a maximum at about 120° C. since higher temperatures bring about deactivation of the catalyst as pointed out hereinafter. The present invention can also employ temperatures down to as low as 50° C. Temperatures of 130° and higher are inoperable in accordance with the process of the instant invention. The lower temperature employable in accordance with the instant invention results in lower cost of operation, lower corrosion effects in the apparatus employed, etc. As pointed out above, Loder refers to the employment of numerous types of initiators and indicates in a broad generality that such initiators can be continuously added to the reaction mixture. However, the addition of aldehyde as an initiator is not specifically covered by any of the working examples nor is the continuous addition of any specific initiator referred to anywhere in Loder's disclosure.

In regard to the catalysts employed by both Loder and similar prior art as well as by the process of the instant invention, it can be noted that King et al., Ind. Eng. Chem. 21, 1227-31 (1929) disclose the treatment of liquid ethyl benzene with molecular oxygen using manganous acetate and cerium oxide as catalysts to effect oxidation.

As indicated previously, the concept of initiators in the prior art such as Loder is extremely broad. Apparently any organic compound which tends to form peroxide bodies under the reaction conditions can be considered an initiator. This would include gasolines, various oils, lubricating oil, vegetable oil, etc. In regard to such materials being initiators, it is worth while noting that I have found that air contaminated with lubricating oil often quenches rather than initiates many liquid phase oxidations of this type.

The oxidation catalyst activators of the instant invention, e. g. the lower aliphatic unsubstituted aldehydes, are essential to the oxidation reaction in accordance with the instant invention and must be present in a certain concentration in the reaction mixture at all times; otherwise, oxidation will cease. Thus, these activators are not initiators in the sense that they start the reaction but are essential to the continued course of the reaction. The "activation" of the oxidation catalyst is a term employed in describing the present invention which describes a change in the effectiveness of the catalyst and corresponds to a color change of the catalyst solution as when a cobalt catalyst solution changes from a pink color to a dark green color. When, for example, the dark green color is present, oxidation of the aldehyde activator is taking place concurrently with the oxidation of the substituted diphenyl sulfone in accordance with the instant invention. The catalyst mixture may accordingly be "initiated" in the sense employed by the prior art illustrated by Loder by the presence of the aldehyde and the catalyst may be activated. But unless the activator is present at all times thereafter, the catalyst will deactivate, i. e., turn from green to pink and the oxidation will cease. Other initiators such as disclosed in the Loder Patent 2,245,528 have not been found to function as activators in the process of the instant invention.

Accordingly, the concept of an activator as de-

scribed in this invention is quite different from the prior art concept of the initiator in which a peroxide-forming material is initially added after which the partially oxidized hydrocarbons may thereafter act as oxygen carriers capable of attacking other hydrocarbon molecules, as alleged by the prior art. Although initiators may improve the reaction results, they are not essential in the completion of the reactions of the type described by the prior art as indicated by the fact that in many instances initiators are eliminated altogether. Initiators such as ketones which are employed by the prior art will not function as activators in accordance with the instant process.

In conducting several experiments, it has been found that p,p'-ditolyl sulfone cannot be oxidized without the employment of an aldehyde activator in accordance with other requirements of the process of the instant invention.

The following four experiments employ processes which are based on variations of suggestions contained in the prior art and illustrate the necessity for employing an activator and adhering to other limitations of temperature, etc. as required by the process of the instant invention:

A. Thirty grams of p,p'-ditolylsulfone, 150 cc. of butyric acid and a catalyst composed of 3 grams of cobaltous acetate tetrahydrate, 1 gram of lead acetate and 1 gram of manganous acetate were charged to a turbo-mixer constructed of Pyrex glass and stainless steel. The solution was rapidly agitated for ten hours at 125° C. while a stream of oxygen of about 1 to 1.5 cubic feet per hour was bubbled through it. The blades of the turbo-mixer served to break up the oxygen stream into small bubbles and cause intimate contact of the oxygen with the reaction medium. At the end of the ten hours, the reaction mixture was cooled and discharged. No solid material was found to be present, and hence no sulfonyl dibenzoic acid was formed inasmuch as this dicarboxylic acid is insoluble in either hot or cold butyric or acetic acids.

B. The same reaction mixture as employed in experiment A was charged to an oxidation column fabricated from a Pyrex glass pipe, one inch in internal diameter and four feet long, with fittings of either glass or stainless steel. The lower end of the column had an oxygen inlet for dispersing the oxygen in small bubbles through the column while the upper end of the column was equipped with a condenser system for returning condensable vapors to the column. The column was heated with an external winding of Nichrome ribbon. The mixture of experiment A was charged to the column and heated to 145° C. for twelve hours in contact with oxygen. At the end of this time, the reaction mixture was cooled and withdrawn from the column. No sulfonyl dibenzoic acid was found to be formed.

C. The same equipment as was used in experiment A was employed here. Thirty grams of p,p'-ditolylsulfone, 3 grams of cobaltous acetate tetrahydrate, 1 gram of manganous acetate, and 1 gram of lead acetate were dissolved in 150 cc. of glacial acetic acid and this mixture was contacted with oxygen for ten hours at 100° C. No sulfonyl dibenzoic acid was found to be formed.

D. Fifteen grams of p,p'-ditolylsulfone, 3 grams of cobalt stearate and 150 grams of acetic acid were charged to the oxidation column described in experiment B and heated to 140° C. under 55 to 58 pounds per square inch gauge pressure of oxygen. Molecular oxygen was bubbled through

the solution for two hours and forty minutes. No trace of sulfonyl dibenzoic acid was found to be formed during this time.

E. Compare Examples 4 and 5 below as to the minimum catalyst required in accordance with the process of the instant invention.

Without wishing to be bound by any theory of operation for the instant process, it appears that the process of the present invention is a new and distinct oxidation process, particularly compared with certain prior art processes which have been discussed hereinabove. That is, prior art processes have, in many instances, been based on peroxygen oxidation, which type of process is dependent for its effectiveness on a high peracid or peroxygen content. Such prior art processes employ relatively low catalyst concentrations and "initiator" concentrations, together with relatively high temperatures. Such prior art type processes cause a more complex reaction mixture to be formed than produced in accordance with the instant invention.

By employing higher catalyst concentrations, substantial amounts of aldehyde, relatively low temperatures, and other factors described in this specification, the process of the present invention permits considerably milder and more specific oxidation, with the beneficial result of higher conversion and yield than heretofore obtainable. In other words, since, by the process of the present invention it is possible to employ temperatures below 100° C., there is less breakdown of oxidation intermediates into carbon dioxide and by-products by the process of the instant invention than in the prior art processes necessitating the use of higher temperatures. These considerations clearly indicate that a new and improved process has been described in accordance with the description in this specification, especially since the products obtained are not isomeric or homologous to those of the most closely related prior art processes.

An application of David C. Hull filed December 16, 1949, which was copending with my parent application and which has since issued as Patent 2,588,388, dated March 11, 1952, discloses the oxidation of alkyl-substituted cyclohexanes using aldehyde-activated catalysts. Another application by Hull, Serial No. 247,718, filed September 21, 1951, which is copending with my parent application and the instant application, discloses the catalytic oxidation of certain substituted aromatic compounds at relatively low temperatures in the liquid phase to obtain aromatic acids, aromatic ketones and various other oxidation products; this application relates more particularly to the oxidation by means of an aldehyde-activated metal catalyst of substituted aromatic compounds in which the substituent terminates in an alkyl radical under such reaction conditions that the cleavage of the aromatic ring is avoided. However, the compounds of the instant application are not isomeric or homologous with those of the Hull application.

It is clear from a perusal of the prior art that no disclosure is made of the oxidation of compounds containing a multiplicity of benzene rings substituted with lower alkyl radicals and linked together with a divalent inorganic radical such as the sulfonyl group ($-\text{SO}_2-$); see the table below for compounds which can be oxidized in accordance with the process of the instant invention.

The present invention has for its principal object to provide a process for the economical and

efficient conversion of p,p'-ditolyl sulfone to form p,p'-sulfonyl dibenzoic acid. A further object is to provide a process whereby this compound can be directly prepared by the oxidation of p,p'-ditolyl sulfone without the decomposition of the molecular structure by cleavage at the junctures of the sulfonyl group with the benzene nuclei. A still further object is to provide a process whereby such an oxidation can be carried out in a single step. Another object is to provide a process for the direct oxidation of p,p'-ditolyl sulfone to form p,p'-sulfonyl dibenzoic acid in high yields at relatively low temperatures at either ordinary atmospheric or superatmospheric pressure conditions. Other objects are apparent elsewhere herein and include the preceding objects as applicable to isomers, homologs and derivatives of p,p'-sulfonyl dibenzoic acid.

These objects can be accomplished by the following invention which, in its broader aspects, comprises first preparing a solution of a cobalt or manganese salt of an organic acid in a solvent such as an aliphatic acid, e. g. acetic acid, treating the solution with an oxygen-containing gas and simultaneously adding an aldehyde such as acetaldehyde, thereby to bring the cobalt or manganese catalyst into a highly active state, and thereafter feeding the p,p'-ditolyl sulfone, isomer, homolog or derivative thereof together with an excess of oxygen, into the catalyst solution while maintaining the catalyst in the solution in an active state by continuously adding aldehyde. It will be observed, as will be apparent from the description set forth hereinafter in detail, that a relatively large amount of aldehyde is generally used, say of the order of about twice or more of the amount of ditolyl sulfone being oxidized although theoretically as little as twice the molecularly equivalent amount could be employed. Also relatively high catalyst concentrations and acid solvent concentrations are usually employed. In accordance with the invention, the original ditolyl sulfone in such a solution is directly converted at a relatively low temperature within the range of 50° C. to 120° C. and at atmospheric pressure to the sulfonyl dibenzoic acid corresponding thereto. The product is obtained in substantial yields at temperatures of from about 80° C. to about 110° C.

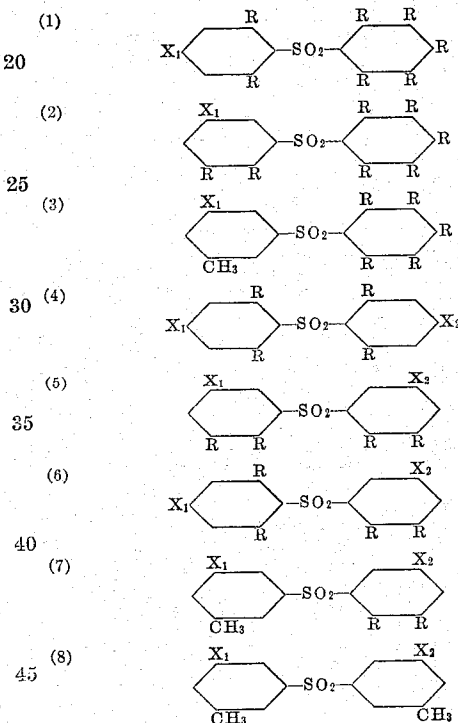
Suitable forms of apparatus which can be employed or modified for the carrying out of the process of my invention are illustrated in patents issued to D. C. Hull, 2,287,803, and 2,353,157, and 2,588,388, etc., British Patent No. 623,836, etc.

In accordance with my invention in more specific terms, I have found that a sulfonyl mono or dibenzoic acid (including certain alkyl, aryl, alkoxy, aryloxy and carboxy derivatives thereof as explained below) can be prepared by a process which comprises reacting at a temperature of from about 80° C. to about 110° C., a substituted diphenyl sulfone having one of the formulas presented in Table I set forth hereinbelow with a gas containing oxygen in a solvent containing from about 1 percent to about 12 percent by weight of the solvent of a catalyst which is maintained in an activated condition during the course of the reaction by the introduction of an aldehyde into the catalyst solution, the solvent being selected from the group consisting of lower alkanolic acids containing from 1 to 6 carbon atoms, dioxane, lower aliphatic ketones and aliphatic and aromatic hydrocarbons containing from 2 to 12 carbon atoms, the catalyst being

selected from the group consisting of cobalt and manganese salts (including hydrates of such salts), such salts being ordinarily derived from an organic acid selected from those consisting of the fatty acids and the resin acids, the aldehyde being employed in an amount which is at least molecularly equivalent to the moles of sulfonyl mono or dibenzoic acid compound which is formed, as explained further below.

The term substituted diphenyl sulfone as referred to in this specification includes compounds which can be represented by the formulas set forth in the following table:

TABLE
Formulas of oxidizable substituted
diphenyl sulfones



wherein X₁ and X₂ each represents an oxidizable radical of the group consisting of primary and secondary alkyl radicals containing from 1 to 4 carbon atoms and each R represents a member of the group consisting of a hydrogen atom, a chlorine atom, a bromine atom, an alkyl radical containing from 1 to 8 carbon atoms, an alkoxy radical containing from 1 to 8 carbon atoms, an aryl radical of the benzene series containing from 6 to 9 carbon atoms, an aryloxy radical of the benzene series containing from 6 to 9 carbon atoms, a carboxy radical and an acyloxy radical containing from 1 to 8 carbon atoms.

In regard to the preferred aspect of this invention, compounds of Formula 4 illustrated in the table above wherein the R substituents are hydrogen atoms can be oxidized so as to convert X₁ and X₂ into carboxy radicals. Thus, the oxidation of p,p'-ditolyl sulfone to form p,p'-sulfonyl dibenzoic acid is a principal object of my invention. This product can then be employed in the manufacture of valuable linear polyesters.

The p,p'-ditolyl sulfone which can be employed as the starting material in accordance with this invention has been prepared either by reacting toluene with sulfuric acid by the method of Meyer, Ann. 433, 327 (1923) or Fouque and

La Croix, Bull. Soc. Chim. 33, 180 (1923) or by reacting toluene with p-toluene sulfonyl chloride by the well known Friedel-Crafts synthesis employing aluminum chloride as a catalyst. The other compounds coming within the scope of the formula set forth in the table can be similarly prepared. Thus, the xylyl-tolyl sulfone employed as a starting material in Example 8 was prepared by the Friedel-Crafts synthesis employing p-xylene and p-toluene sulfonyl chloride. The crude sulfones prepared by these methods can be purified by vacuum distillation, crystallization from ethanol or acetic acid, etc. The oxidation process of this invention can then be carried out using the pure material or crude materials can also be employed. Of course, if the process of this invention is carried out in a continuous manner as described hereinbelow, where impurities may build up in the reaction mixture, a rather pure starting material is advantageously employed.

In regard to the formulae set forth in the table, the X radicals oxidized in accordance with the process of this invention can consist of both straight-chain and branched chain alkyl groups, provided that there is at least one hydrogen atom linked to the carbon atom adjacent to the benzene ring nucleus. Thus, X can be methyl, ethyl, isopropyl, propyl, secondary butyl, butyl, etc. For reasons not entirely understood, tertiary butyl groups have been found to be resistant to oxidation in accordance with the process of this invention, although some oxidation appears to occur to a limited extent. Theoretical considerations indicate that one step in the oxidation reaction of the process of this invention probably consists in the removal of a hydrogen atom from the carbon linked directly to the aromatic nucleus with the formation of a free radical. When an alkyl group is in an ortho position to the sulfone group, little or no oxidation is effected by the process of the instant invention. Where two alkyl groups are attached to a single benzene nucleus, no oxidation to any significant extent takes place insofar as either of these alkyl groups are concerned if they are ortho in position to each other. However, two alkyl groups attached to a single benzene nucleus will be oxidized if they are in meta relationship to each other and meta to the sulfone group although the oxidation of the first of the two alkyl groups will hinder the oxidation of the second alkyl group to a certain extent resulting in its oxidation taking place more slowly. Chloro and bromo substitution of the aromatic nucleus can be permitted without interfering with the oxidation of an X group provided that a halogen atom is not ortho to an X group which is to be oxidized. In a similar manner, the nucleus may be substituted with phenyl, carboxy, alkoxy, aryloxy or acyloxy groups such as methoxy, ethoxy, acetoxy, p-chlorophenyl, etc. Moreover, there seems to be no reason to suppose that the compounds of the type covered by the formulae in the table would not be subject to the process of this invention if they contained substituents such as aromatic nuclei and other related nuclei, e. g. naphthylene, bi-phenyl, pyrene, etc.

A temperature range which can be advantageously employed in carrying out the process of this invention is preferably from about 80° C. to about 105°-110° C. Temperatures as high as 120° C. and as low as 50° C. can also be employed. Temperatures higher than 120° C. usually bring

about deactivation of the catalyst as noted by a color change even through aldehyde is present, e. g. a change from dark green back to a pink color in the case of the employment of a cobalt catalyst. At temperatures lower than 50° C., peroxidic intermediates may build up to disadvantageous levels of concentration. The preferred range of temperatures employable in accordance with the instant process which can be most advantageously employed are temperatures between 90° C. and 100° C., e. g. 95° C.

The gas containing oxygen employed to effect the oxidation can advantageously be pure oxygen or a mixture of oxygen with other gases which do not deleteriously affect the course of the oxidation reaction, e. g. nitrogen, carbon dioxide, inert gases such as argon, etc. Thus, air can be advantageously employed as the gas-containing oxygen. Similarly, gases containing ozone can be employed. Pressure can be employed in the process of this invention, if desired, to effect a more intimate contact of the reactants with oxygen and to prevent to a large extent excessive loss of aldehyde from the effluent gas stream. However, the employment of pressure is entirely unnecessary. As to pressure, while it is usually advantageous to operate at atmospheric pressure, pressures can be employed below atmospheric or as high as 2 to 10 atmospheres or more. It will of course be understood that the temperature and pressure can vary according to the requirements of the particular material undergoing oxidation, the rate of feed of the several reactants and with other variables, the control of which, in the light of the teachings herein, is within the skill of the trained chemist or chemical engineer familiar with the art.

Various solvents can be employed in carrying out the process of this invention including lower alkanolic acids (containing as many as six or more carbon atoms) such as acetic, propionic, butyric, etc., or other inert solvents which include dioxane, lower aliphatic ketones such as acetone, methyl ethyl ketone, etc., and aliphatic and aromatic hydrocarbons containing from 2 to 12 carbon atoms, e. g. benzene, pentane, cyclohexane, xylene, etc. and various other inert solvents, e. g. triethyl phosphate, etc. The preferred solvent is a substantially anhydrous lower alkanolic acid or mixture of such acids; however, a somewhat dilute acid can be employed. In general, it has been found that, in use, more satisfactory yields of the desired products are obtained if the acid concentration in the solvent is maintained during the course of the reaction at about 85% or more.

The catalysts which can be advantageously employed are cobalt and manganese salts which are soluble in the solvent employed. According to the prior art, numerous other metals can be employed as equivalent catalysts such as iron, nickel, copper, vanadium, and other salts. We have found that cobalt salts are most advantageous and that manganese salts can be advantageously employed but result in lower rates of oxidation than the corresponding cobalt compounds. Most advantageously cobalt acetate or cobalt butyrate can be employed. Other cobalt salts which can be advantageously employed include cobalt naphthenate, cobalt resinate and cobalt stearate. The equivalent salts of manganese can also be employed. The catalyst most advantageously employed is the tetrahydrate of cobaltous acetate which has the formula $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$. Advantageously the con-

centration of cobalt catalyst based on the original quantity of solvent present can be from 1 percent to about 12 percent by weight thereof. The most advantageous concentration of the catalyst depends to a considerable extent upon the purity of the substituted diphenyl sulfone employed as a starting material. The same range of concentrations can also be employed in regard to the manganese catalyst. The concentration of both cobalt or manganese catalyst can be higher or lower if desired although lower concentrations do not give satisfactory yields of the oxidation products. In regard to the employment of other catalysts besides manganese and cobalt salts, we have found that vanadium stearate did not catalyze the reaction in accordance with the process of this invention and that nickel acetate gave only a trace of sulfonyl dibenzoic acid after 10 hours of operation in a manner similar to that set forth below in Example 2. As compared to certain of the prior art processes where the catalyst concentration is of the order of 0.1 percent, the catalyst concentrations employed in accordance with the instant invention are advantageously well in excess of 1 percent. Although it is preferred to dissolve the catalyst in an anhydrous acid as the solvent, a somewhat diluted acid can be employed as mentioned above.

The aldehyde which is introduced into the catalyst solution serves as an activator of the catalyst and is essential to the maintenance of the course of the reaction to produce the desired sulfonyl dibenzoic acid, isomer, homolog or other derivative thereof. In order to oxidize the corresponding substituted diphenyl sulfones, the aldehyde activator is advantageously added to the catalyst solution before any of the substituted diphenyl sulfone is added. The aldehyde serves as an activator and oxidation will not take place without the continuous presence of aldehyde in the reaction mixture. If the aldehyde ever becomes completely oxidized and no more is introduced into the reaction mixture, the oxidation ceases. Thus, the aldehyde does not act as an initiator in the sense of the prior art as discussed hereinbefore, but it acts as an activator or co-oxidant. The fact that oxidation is taking place can be noted by a change of color of the catalyst solution in most cases; for example, the cobalt acetate catalyst changes from a pink color in solution to a dark green color and the manganous acetate catalyst changes to a sepia brown color. As pointed out, it is generally quite advantageous to activate the catalyst solution by introducing aldehyde and oxygen into the solution prior to admitting the derivative of diphenyl sulfone into the reaction mixture. It has been found that no activators other than aldehydes function in the reaction of the instant process. Neither ketones nor toluene (a peroxide-forming material) have been found to function in the reaction. It is preferred to employ lower unsubstituted aliphatic aldehydes as the activators in accordance with this invention. However, benzaldehyde, anisaldehyde, enanthaldehyde, etc. can also be employed as activators. Other aldehydes can also be employed such as acrolein, crotonaldehyde, etc.

The ratio of aldehyde to substituted diphenyl sulfone which is most advantageously present in the reaction medium in order to effect oxidation has not been determined exactly and may depend upon such factors as the rate of oxygen throughput, the concentration of the substituted diphenyl sulfone in the solvent, purity of the

sulfone, and so on. Successful operation using the same materials, conditions and equipment as in Example 2 below has been carried out employing only 9 cc. of acetaldehyde to produce 16 grams of p,p'-sulfonyl dibenzoic acid from an original charge of 15 grams of p,p'-ditolylsulfone in five hours whereby the mole ratio of aldehyde to sulfone oxidized to the diacid was about three. This mole ratio can be as low as 2 which represents one mole of aldehyde required for each mole equivalent of a methyl group oxidized. Thus, it is advantageous to employ at least as many moles of the aldehyde as the number of mole equivalents of the X substituents on the substituted diphenyl sulfone (see the table) which is being oxidized. Advantageously, three moles and as many as ten moles of aldehyde can be employed for each mole of ditolyl sulfone being oxidized.

When it is desired to repress or minimize the formation of monobasic acid during the preparation of a dibasic acid, it is advantageous to maintain during the course of the reaction the amount of substituted diphenyl sulfone containing two X substituents (see Formulas 4 through 8 above) at a concentration not substantially greater than 15 grams per 100 cc. of the catalyst solution.

Once the catalyst solution has been prepared it is advantageously brought into a highly active or "activated" condition as described above by simultaneously feeding in an aliphatic aldehyde and oxygen or an oxygen-containing gas at such a rate and at such a temperature as to cause the catalyst to become and remain active, a condition usually initially indicated by a change in color of the original solution. The oxygen feed can be advantageously regulated to provide a slight excess of oxygen over and above that required for the oxidation reaction, such excess being indicated by the presence of a few percent of oxygen in the gaseous effluent from the process. It will, of course, be understood that such matters as feed rates of aldehyde and oxygen, temperatures and the like, in general, are advantageously determined for each particular catalyst with reference to the compound to be oxidized. In the case of a cobalt catalyst and acetic acid, the original solution, which is pink, changes to green upon activation, indicating that the cobalt ions have changed from a lower to a higher state of valence, that is, from the cobaltous to the cobaltic state and that the solution is in the desired catalytically active condition.

While in some cases the catalyst solutions can become active merely upon the introduction of the aldehydes and blowing with air or oxygen at moderately low temperatures, it is generally advantageous to heat the solution to a temperature of at least 50-60° C. in order to initiate catalyst activity. More advantageously, the temperature employed in initiating catalyst activity is that at which the reaction is to be conducted. In view of the fact that the oxidation reactions here involved are exothermic in character, it may be necessary to continuously cool the reaction mixture in order to keep the temperature within the desired limits, to prevent excessive loss of reactants by evaporation, etc.

The reaction can be advantageously conducted in accordance with the procedure described hereinabove. The catalyst can be suspended in the solvent and the mixture heated to about 90° to about 100° C. whereupon a mixture of oxygen and aldehyde vapors can then be passed into the mixture with good agitation until the catalyst

is activated. A solution of a substituted diphenyl sulfone, see the table, e. g. p,p'-ditolyl sulfone, can then be slowly added while the introduction of aldehyde and oxygen is continued. The aldehyde becomes oxidized to the acid and keeps the catalyst in an active state. At the same time the X-groups of the substituted diphenyl sulfone are oxidized to carboxyl groups. The corresponding sulfonyl dibenzoic acid separates from the reaction mixture as fine crystals. This product can be further purified by dissolving in alkali, filtering and precipitating with dilute HCl. Other purification procedures can also be employed.

The following examples will serve to further illustrate my invention:

Example 1.—100 cc. of acetic acid and 7 grams of cobalt acetate were mixed and heated to 90° to 95° C. Oxygen was bubbled into the solution through a dispersion plate and 25 grams of acetaldehyde was pumped in during a period of 1 hour. The color of the solution changed from pink to dark green showing that the catalyst (cobalt acetate) had been activated. A solution of 30 grams of p,p'-ditolyl sulfone in acetic acid was then added dropwise over a period of 12–14 hours. During this time, oxygen was continuously bubbled into the solution and a total of 70–80 grams of acetaldehyde was added. The aldehyde feed was then stopped and the reaction mixture was filtered. A cake of p,p'-sulfonyl dibenzoic acid was obtained. It was washed with water followed by dilute HCl and then more water. The yield was 36 grams of p,p'-sulfonyl dibenzoic acid which is a 96 percent yield. It titrated to give an equivalent weight of 154; the calculated weight was 153. The product can be further purified by dissolving it in aqueous alkali and precipitating with dilute HCl or H₂SO₄. Similar results can be obtained employing acetaldehyde as the promoter or activator, and manganese acetate as the catalyst to oxidize m,m'-ditolyl sulfone to form m,m'-sulfonyl dibenzoic acid. Similarly, other sulfonyl dibenzoic acid derivatives can be prepared such as p,m'-sulfonyl dibenzoic acid, etc.

The following examples further illustrate the process carried out with the preferred catalyst, a cobalt salt. As can be seen from Examples 4 and 5, it appears that the minimum concentration of cobaltous acetate tetrahydrate is about 1 per cent based on the acetic acid solvent in order to prepare any substantial amount of dicarboxylic acid by the process of this invention. Example 3 illustrates that air can be employed as the oxidant if desired, while Example 6 shows that butyraldehyde can be used in conjunction with butyric acid to effect the oxidation process.

Example 2.—In a turbo-mixer constructed of Pyrex glass and stainless steel, 15 grams of p,p'-ditolylsulfone, 3 grams of cobalt acetate tetrahydrate and 150 cc. of acetic acid were contacted with molecular oxygen for five hours at 95° C. Acetaldehyde vapor was admitted along with a stream of oxygen and during the time of reaction, a total of 20 cc. of liquid aldehyde was employed. The p,p'-sulfonyl dibenzoic acid recovered amounted to 18.1 grams with a neutralization equivalent of 155. The theoretical yield is 18.65 grams and the calculated neutralization equivalent for the pure acid is 153.

Example 3.—An experiment similar to that of Example 2, was carried out using the same initial charge material but air as the oxidant at 95° C. for eight hours. During this time a total

of 15 cc. of acetaldehyde was introduced as an activator. A total of 16 grams of p,p'-sulfonyl dibenzoic acid was recovered having a neutralization equivalent of 159.

Example 4.—With the same equipment as in Example 2, 15 grams of p,p'-ditolylsulfone, 150 cc. of acetic acid and 0.75 gram of cobaltous acetate tetrahydrate (a solution of 0.5% by weight of the catalyst in the acetic acid solvent) were contacted with oxygen for six hours at 95° C. The total aldehyde used was 38 cc. No p,p'-sulfonyl dibenzoic acid was formed at this low catalyst concentration.

Example 5.—With the same equipment as in Example 2, 15 grams of p,p'-ditolylsulfone, 150 cc. of acetic acid and 1.5 grams of cobaltous acetate tetrahydrate were contacted with oxygen for nine hours at 95° C. A total of 13 cc. of acetaldehyde was employed as an activator. A crude product essentially comprising p,p'-sulfonyl dibenzoic acid of neutralization equivalent 167.3 was separated from the reaction mixture. The yield was 17.1 grams.

Example 6.—In a turbo-mixer as described in Example 2, 3 grams of cobaltous acetate tetrahydrate, 150 grams of butyric acid, and 15 grams of p,p'-ditolylsulfone were reacted with gaseous oxygen over a period of 7.5 hours at a temperature of 100° to 120° C. During this time a total of 48 cc. of butyraldehyde was added. The p,p'-sulfonyl dibenzoic acid recovered amounted to 9 grams.

The following example demonstrates that manganous acetate is a suitable catalyst for this oxidation.

Example 7.—In a turbo-mixer as described in Example 2, 6 grams of manganous acetate, 15 grams of p,p'-ditolylsulfone, and 150 cc. of acetic acid were contacted with oxygen over a period of 12.5 hours during which time 36 cc. of acetaldehyde was added in small increments. Approximately 30 percent of the p,p'-ditolylsulfone was converted to p,p'-sulfonyl dibenzoic acid.

The example listed below shows the oxidation of o,p-xylyl-p-tolylsulfone to a dicarboxylic acid.

Example 8.—A mixture of 15 grams of o,p-xylyl-p-tolylsulfone, 150 cc. of acetic acid and 3 grams of cobalt acetate was charged to the turbo-mixer described in Example 2 and contacted with oxygen for seven hours at 95° C. During this time 27 cc. of acetaldehyde was added to the reaction mixture. The batch was then cooled and filtered, and the solid material washed with two 200 cc. portions of hot acetic acid. Finally the precipitate was dried at 120° C. to give 14 grams of 5-carboxy-2-methylphenyl-4-carboxyphenylsulfone of neutralization equivalent 156. Theoretical yield of this dibasic acid was 18.5 having a calculated neutralization equivalent of 160.

The following example illustrates an advantageous process which shows that continuous operation of the oxidation process can be carried out. An apparatus such as described by Bowden et al. British Patent 623,836, May 24, 1949, can be advantageously employed in operating according to this continuous process.

Example 9.—In a turbo-mixer such as described in Example 2, 150 cc. of acetic acid, 3 grams of cobaltous acetate tetrahydrate and 15 grams of p,p'-ditolylsulfone were contacted with air at 95° C. in the presence of acetaldehyde. The air rate was approximately 2 cubic feet per hour. At hourly intervals after the first two hours of operation, 3 gram increments of ditolylsulfone

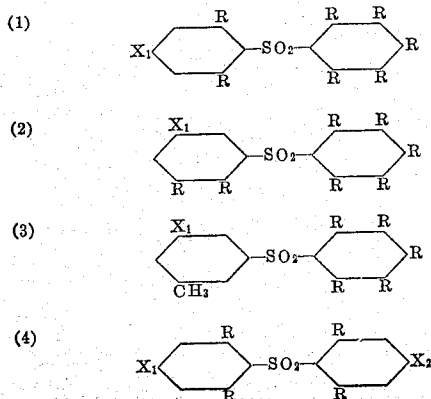
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were added to the reaction mixture. At the end of 16 hours, 14 such additions had been made to give a total of 57 grams of ditolylsulfone added. At this time 71.5 percent of the ditolylsulfone was converted to p,p'-sulfonyl dibenzoic acid and a total of 55 cc. of acetaldehyde had been added to the reaction mixture. However, about a third of this aldehyde was carried out of the reaction mixture with the effluent gas stream. Approximately 25 percent of the reaction mixture was removed and filtered hot. The filtrate, containing soluble ditolylsulfone and soluble p-tolyl-p-carboxyphenylsulfone, and dissolved catalyst, was returned to the reaction mixture. The residue was washed once with acetic acid and dried at 110° C. to give an unpurified dicarboxylic acid of neutralization equivalent 169. The reaction was continued in the manner already described until approximately the equivalent of 60 grams of charged ditolylsulfone was present in the reaction mixture, when another 25 percent of the reaction mixture was withdrawn and the acidic residue recovered. The process can thus be operated in a continuous fashion as outlined above providing a little acetic acid is removed from the reactor from time to time, and any catalyst which is lost from the reactor by the separation operation is replenished.

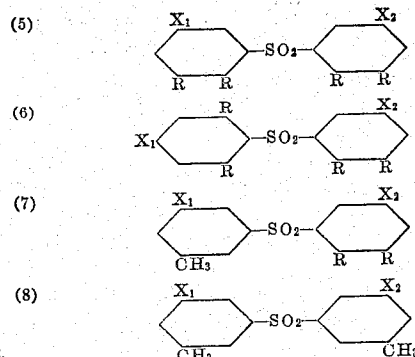
It is evident that the specific mode of carrying out the continuous process as well as the details of all the other working examples can be varied within the scope of the description hereinbefore elaborated upon, whereby any of the compounds listed in the table can be oxidized to form sulfonyl dibenzoic acid, isomers, homologs and derivatives thereof. In the claims, the term "a sulfonyl dibenzoic acid" is intended to include the isomers, homologs and derivatives of sulfonyl dibenzoic acid which can be prepared by the oxidation of the compounds listed in the table above. Elsewhere in this specification the term "sulfonyl mono- and dibenzoic acid" has been employed; this term is intended to be limited to the products obtained by the oxidation of compounds listed in the table. The term "sulfonyl monobenzoic acid" can be more accurately called mono-carboxydiphenyl sulfone. The term sulfonyl dibenzoic acid has sometimes been loosely employed in this specification in a manner which clearly includes both mono- and dibenzoic acid derivatives.

What I claim as my invention and desire to secure by Letters Patent of the United States is:

1. A process for preparing a carboxy substituted diphenyl sulfone which comprises reacting at a temperature of from about 80° C. to about 110° C. a substituted diphenyl sulfone selected from the group consisting of those compounds having the following formulas:



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wherein X₁ and X₂ each represents an oxidizable radical of the group consisting of primary and secondary alkyl radicals containing from 1 to 4 carbon atoms and each R represents a member of the group consisting of a hydrogen atom, an alkyl radical containing from 1 to 8 carbon atoms, and an aryl radical of the benzene series containing from 6 to 9 carbon atoms, with a gas containing oxygen in an inert solvent containing from about 1 percent to about 12 percent by weight of the solvent of a catalyst which is maintained in an activated condition during the course of the reaction by the introduction of an aldehyde into the catalyst solution, the catalyst being selected from the group consisting of cobalt and manganese salts of an organic acid.

2. A process as defined in claim 1 wherein the aldehyde is a lower aliphatic aldehyde.

3. A process as defined in claim 2 wherein the proportion of aldehyde added to the activated catalyst solution is at least equal to the number of mole equivalents of the X substituents on the substituted diphenyl sulfone being oxidized.

4. A process as defined in claim 3 wherein the substituted diphenyl sulfone contains two X substituents and the amount of this substituted diphenyl sulfone is maintained during the course of the reaction at a concentration not substantially greater than 15 grams per 100 cc. of the catalyst solution whereby the yield of monobasic acid is repressed.

5. A process as defined in claim 4 for preparing p,p'-sulfonyl dibenzoic acid wherein the substituted diphenyl sulfone employed is p,p'-ditolyl sulfone.

6. A process as defined in claim 4 for preparing p,m'-sulfonyl dibenzoic acid wherein the substituted diphenyl sulfone employed is p,m'-ditolyl sulfone.

7. A process as defined in claim 4 for preparing m,m'-sulfonyl dibenzoic acid wherein the substituted diphenyl sulfone employed is m,m'-ditolyl sulfone.

8. A process as defined in claim 1 for preparing 5-carboxy-2-methylphenyl-4-carboxyphenyl sulfone wherein the substituted diphenyl sulfone employed is o,p-xylyl-p-tolyl sulfone.

9. A process as defined in claim 1 for preparing p,p'-sulfonyl dibenzoic acid wherein the substituted diphenyl sulfone employed is p,p'-ditolyl sulfone.

10. A process as defined in claim 1 for preparing p,m'-sulfonyl dibenzoic acid wherein the substituted diphenyl sulfone employed is p,m'-ditolyl sulfone.

11. A process as defined in claim 1 for preparing m,m'-sulfonyl dibenzoic acid wherein the substituted diphenyl sulfone employed is m,m'-ditolyl sulfone.

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12. A process as defined in claim 1 for preparing 5-carboxy-2-methylphenyl-4-carboxyphenyl sulfone wherein the substituted diphenyl sulfone employed is o,p-xylyl-p-tolyl sulfone.

13. A process for preparing p,p'-sulfonyl dibenzoic acid which comprises reacting p,p'-ditolyl sulfone at a temperature of from about 80° C. to about 110° C. with a gas containing oxygen in a solvent selected from the group consisting of the lower alkanolic acids containing from about 1 percent to about 12 percent by weight of the solvent of a catalyst which is maintained in an activated condition during the course of the reaction by the introduction of a lower aliphatic aldehyde into the catalyst solution, the catalyst being selected from the group consisting of cobalt and manganese salts of an organic acid, there being added to the activated catalyst solution at least twice as many moles of the aldehyde as the number of moles of p,p'-ditolyl sulfone being oxidized.

14. A process as defined in claim 13 wherein

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the amount of p,p'-ditolyl sulfone is maintained during the course of the reaction at a concentration not substantially greater than 15 grams per 100 cc. of the catalyst solution.

15. A process as defined in claim 14 wherein the aldehyde is acetaldehyde, the catalyst is cobalt acetate and the solvent is acetic acid.

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