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PREPARATION OF SULFONES

Milton Crowther, Warren Lee Beaumont, and John Calvin Kesler, Salisbury, N.C., assignors to Proctor Chemical Company, Inc., Salisbury, N.C., a corporation of North Carolina

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This invention relates to the preparation of sulfones and is particularly concerned with new improvements in processes for oxidation of sulfides and sulfoxides to sulfones that will have improved color and odor.

FIELD OF INVENTION

Sulfones may conveniently be prepared by oxidation of sulfides or sulfoxides using sufficient oxidizing reagent to carry the oxidation through to the corresponding sulfone. Various improvements in this general type of procedure have been described in the literature and in patents, for example, see U.S. Patents 3,005,852; 3,006,926 and 3,006,963, which relate to the use of certain catalysts to promote the reaction between the sulfide or sulfoxide and the oxidizing reagent.

For the most part, the published literature on the subject indicates that the oxidation of sulfides to sulfones in aqueous media with hydrogen peroxide or other comparable oxidizing reagents should be carried out under acid conditions, e.g., see "Chemical Abstracts," 49, 15724 (1955), and "Journal Organic Chemistry," 19, 1486 (1954). In any event, procedures known heretofore for the preparation of sulfones by the general oxidation reaction as just described have produced sulfone containing products which have a strong, disagreeable odor and which are colored yellow or brown. Such odor and color characteristics are, however, undesirable or detrimental to various uses of the sulfones. Thus, the use of 2,2'-dihydroxyethyl sulfone in the finishing of cellulose fabrics is adversely effected by color in the sulfone since the use of such treating material causes the finished fabric to develop considerable discoloration.

OBJECTS

A principal object of this invention is the provision of new methods for the preparation of sulfones by the oxidation of sulfides or sulfoxides. Further objects include:

(1) New and improved methods for the oxidation of sulfides or sulfoxides with hydrogen peroxide which make it possible to obtain sulfones which are substantially colorless and have a mild odor.

(2) The provision of new methods for the preparation of 2,2'-dihydroxyethyl sulfone from thiodiglycol by oxidation with hydrogen peroxide to produce aqueous solutions of the sulfone which have excellent color and odor properties and which may be used in the treatment of cellulosic fabrics to obtain treated, finished fabrics which are substantially free of discoloration due to treatment by the sulfone.

(3) The provision of new and improved aqueous solutions comprising alkyl or hydroxyalkyl sulfones of improved stability and excellent color and odor characteristics.

(4) The elimination of adverse color and odor formation in procedures for preparation of sulfones by oxidation of the corresponding sulfides or sulfoxides.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

GENERAL DESCRIPTION

These objects are accomplished according to the present invention by carrying out the reaction of an organic sulfide or sulfoxide with an oxidizing agent, specifically hydrogen peroxide, in the requisite proportions to oxidize the sulfur containing compound to a sulfone in the presence of a weakly alkaline salt at a pH between 7.0 and 9.3. The weakly alkaline salt should be the salt of a strong base and a weak acid having a dissociation constant such that the salt will not create a pH in an aqueous medium in excess of 9.3 regardless of the concentration of the salt in the aqueous medium. Typical examples of such salts are sodium tetraborate and sodium bicarbonate, but other salts of comparable alkaline reaction may be employed.

Although it has been known heretofore that the general process of oxidizing sulfides or sulfoxides to sulfones may be carried out at various pH ranges from about 1 to 10 to 11, the success of the present invention is due primarily to the discovery that critical improvements in color and odor characteristics of the resulting products can be attained by conducting the oxidation reaction at a pH between 7.0 and 9.3 and in the presence of a weakly alkaline salt as just described. The technical reason for these results is uncertain, but it appears that acid conditions promote the formation of the color and odor forming bodies in the resulting sulfone products and that the presence of the weakly alkaline salts tend to suppress acid formation and concurrent formation of color and odor bodies. If no acid, base or salt is added to the reaction medium, considerable strong acid is produced as a byproduct during the oxidation. Most of this acid is produced during the conversion of the sulfoxide to the sulfone with very little acid being formed during the oxidation of sulfide to sulfoxide. In any event, it has been discovered that a lighter colored product is produced if no acid is added to the reaction medium and that critically improved results are obtained if a weakly alkaline salt is added to the reaction mixture in such quantities that pH of the reaction remains within the range 7.0 to 9.3 during the entire oxidation.

EXAMPLES

A further understanding of the new procedures and resulting products of this invention may be had by reference to the following examples of actual operations conducted in accordance with the invention. In these examples and throughout the rest of the specification and claims, all parts and percentages are by weight unless otherwise specified.

Example 1

Into an opened stainless steel kettle equipped for cooling with a refrigerated salt solution, there were charged 1698 parts of commercial grade thiodiglycol. Over a period of about 5 hours, 1325 parts of 35% hydrogen

peroxide were added at a rate such that the temperature of the reaction remained at 80° C. There was produced an aqueous solution having a pH of 3.75 containing approximately 67% 2,2'-dihydroxyethyl sulfoxide. Approximately 2851 parts of the solution were recovered.

Example 2

Into a reaction vessel equipped with stirrer, thermometer, heating mantle, reflux condenser and a valve controlled fluid inlet tube there were charge 245 parts of the solution of Example 1 and 15 parts of water. The reflux condenser of the reaction vessel was fitted with a modified trap suitable for collecting distillate. There were then added to the vessel 13.9 parts of borax and this mixture was stirred until the borax was completely dissolved. When tested with a glass electrode pH meter, the pH of the solution was found to be 9.2.

The contents of the vessel were heated to 104° C. and then, after heating had been discontinued, 114 parts of 35% hydrogen peroxide were added slowly over a period of about 30 minutes. The pH of the reaction solution at this point was found to be 8.0 and a test for unreacted hydrogen peroxide was negative. Ninety parts of distillate were collected and there remained in the reaction vessel 298 parts of sulfone solution. This solution was colorless and had a very faint bland odor.

Example 3

Into the vessel as described in Example 2, there were charged 245.5 parts of the solution of Example 1 and 15 parts of water, and then 6.95 parts of borax were dissolved in the solution. Over a period of 24 minutes, 114.2 parts of 35% hydrogen peroxide were added dropwise to the contents of the reaction vessel which were maintained at a gentle reflux temperature of 105° C. Eight minutes after the last of the peroxide had been added, the contents of the vessel were cooled to about 20° C. A test with starch solution and potassium iodide showed that no free hydrogen peroxide remained. The pH of the reaction mixture was found to be 7.7 and the product was colorless and practically odorless.

Example 4

The procedure of Example 3 was repeated with the exception that only 3.48 parts of borax were added to the sulfoxide solution before oxidation with the hydrogen peroxide. At the completion of the reaction, i.e., at the end of 32 minutes, and after the reaction solution had been cooled to about 20° C., a peroxide test indicated the presence of unreacted peroxide and the pH was found to be 5.0. The solution was again heated to reflux and held for one hour, at the end of which the test for peroxide indicated none was present. At this point, the pH solution was found to be 2.5. The resulting product had a yellow color and a strong odor.

Example 5

To a reaction vessel equipped with stirrer, thermometer, reflux condenser, external cooling device and valve controlled fluid charging line, there were charged 610 parts of thiodiglycol. Then, 428 parts of 35% hydrogen peroxide solution were added streamwise over a period of 28 minutes. This caused the temperature of the reaction mixture to rise from 26° to 81° C. A cooled sample of the reaction solution was found to possess a pH of 6.1. While the solution was maintained at a temperature of 80° C. by external cooling, 523 parts of 35% hydrogen peroxide containing 40.3 parts of borax dissolved therein, were added streamwise over a period of 1 hour and 26 minutes. External heating was then applied to maintain the contents of the vessel at 80° C. for an additional 48 minutes. The resulting reaction solution was then cooled to room temperature and tested for presence of free peroxide and pH. The test for peroxide was negative and the pH was found to be 8.0. The solution was colorless and practically odorless.

Example 6

Into the equipment described in Example 5, there were charged 610 parts of thiodiglycol and 40.3 parts of borax. While this mixture was agitated, 932.5 parts of 35% hydrogen peroxide were added dropwise, starting at a temperature of 26° C. and allowing exotherm to raise the temperature to 60° C. At this temperature, moderate cooling was applied to retain the temperature at 60° C. throughout the balance of the hydrogen peroxide addition which was spread over a period of about 1½ hours. After all of the peroxide had been added, the charge was maintained at 60° C. for 3 more hours, at which point a test for peroxide was negative and the pH was found to be 8.3. The resulting solution was colorless and had a very faint odor.

Example 7

In reaction equipment as described in Example 2, there were charged 245.5 parts of thiodiglycol and 6.15 parts of sodium bicarbonate. The charge was heated to gentle reflux (105° C.) and 114.2 parts of 35% hydrogen peroxide were added at a rate sufficient to maintain gentle reflux without application of heat. This consumed 25 minutes. By external heating, the charge was maintained for 2 additional hours at general reflux, after which time a test for peroxide indicated no free peroxide in the reaction solution. The pH was found to be 9.1. The resulting sulfone solution had a very pale yellow tint and possessed a very faint bland odor.

Example 8

Into equipment as described in Example 1, there were charged 1463 parts of commercial thiodiglycol and, then, 1142 parts of 35% hydrogen peroxide solution were added streamwise over a period of six hours during which the temperature of the charge was allowed to rise from 22° to 70° C. A temperature rise above 70° C. was prevented by external cooling. After addition of the peroxide, the reaction mixture was allowed to stand for about 12 hours when it was withdrawn from the stainless steel reaction kettle and placed in a glass-lined reactor equipped with a water cooled jacket and glass coated stirrer.

With the charge heated to 100° C., 35% hydrogen peroxide solution was added streamwise until the reaction solution had reached a temperature of gentle reflux (106–107° C.). A this point, external cooling was applied to maintain general reflux conditions. Further hydrogen peroxide was added until a total of 1142 parts had been added over a period of 3 hours. The temperature of the reaction mixture was held at 103–105° C. for an additional 1 hour and 20 minutes, at which time a withdrawn sample indicated the presence of no free peroxide. The reaction mixture was strongly acidic and required 272 parts of 25% sodium hydroxide to raise the pH to 7.0. The reaction had a pronounced disagreeable odor and was deep yellow in color.

DISCUSSION OF DETAILS

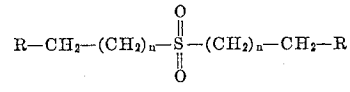
The amount of weakly alkaline salt used in the reaction mixtures in accordance with this invention may be varied and will depend to some extent upon the particular salt which is employed. The optimum concentration can be readily determined by a brief series of tests as indicated by Examples 2, 3 and 4 above. An excess of salt in the reaction mixture does not appear to have any adverse effect provided the salt is one that will not raise the pH of the reaction mixture above 9.3 regardless of the quantity added. At least sufficient quantities of the salt should be included in the reaction mixture, or be added in increments during the reaction, to maintain the solution at least above 7.0. Typically, between about 1 and 10 mols of the weakly alkaline salt will be added for each

100 mols of organic sulfide or sulfoxide used in the reaction.

Sodium tetraborate, typically in the form of borax, and sodium bicarbonate are particularly useful as the weakly alkaline salts for use in the new procedures. However, other weakly alkaline salts of strong bases and weak acids may be employed. Examples of other useful weakly alkaline salts are the alkali metal or alkaline earth metal salts of tetraboric acid, orthoboric acid, carbonic acid, acetic acid, glycine, silicic acid and the like. Preferably, the salt should be sufficiently soluble in water to completely dissolve in the amount used in accordance with the foregoing discussion. However, less soluble salts which dissolve as the reaction proceeds may be used.

Preferably, the salt is mixed in the required amount with the sulfide or sulfoxide before addition of the hydrogen peroxide. However, the salt may be incorporated in the reaction mixture in other suitable ways. Thus, the salt may be dissolved in the hydrogen peroxide solution which is added, preferably streamwise, to the sulfide or sulfoxide or the salt may be added separately in increments as the reaction proceeds at a rate required to maintain the pH of the reaction mixture above 7.0.

The reaction appears to be applicable to reduction of all organic sulfones from the corresponding sulfoxides or sulfides. However, the new procedures are uniquely suitable to the preparation of 2,2'-dihydroxyethyl sulfone having improved color and odor characteristics. The procedure is also especially applicable to the preparation of sulfones of the formula:



wherein R is a radical selected from the group consisting of hydrogen and hydroxyl, and *n* is an integer from 1 to 5, from the corresponding sulfide or sulfoxide, e.g., diethyl sulfide, dihexyl sulfoxide, methyl hexyl sulfide, 2-hydroxy ethyl hexyl sulfide and the like.

The reaction temperature may be varied bearing in mind that the use of lower temperatures extends the time for completion of the reaction while elevated temperatures complicate the equipment required to carry out the process. Most satisfactory results are obtained using a temperature below 125° C., typically between about 25° and 100° C.

Addition of the hydrogen peroxide to the sulfide or sulfoxide is recommended, such addition being in increments or streamwise to extend over a period of time permitting control of the temperature within the range indicated, typically between about ¼ and 6 hours. Other methods of mixing the reactants can, however, be utilized.

The oxidizing agent is typically 35% aqueous hydrogen peroxide, although other forms of hydrogen peroxide may be used, e.g., 5 to 60% aqueous hydrogen peroxide. The reaction may begin with addition of the hydrogen peroxide to undiluted sulfide or sulfoxide or with a solution or suspension of the reactant in water, e.g., 0.1 to 5 parts of water for each part of sulfide or sulfoxide.

Any suitable type of chemical process equipment may be used. A noteworthy feature of the new procedures is the lack of corrosiveness of the reaction mixtures permitting the reaction to be carried out in stainless steel equipment. This is in contrast to the need for use of glass lined or comparable corrosion resistant equipment in the acid type reaction principally utilized heretofore for the formation of sulfones by hydrogen peroxide oxidation.

The resulting sulfone may be separated from the reaction mixture by any known procedure such as distillation, solvent extraction or the like. For many uses, however, it will be found desirable to use the relatively concentrated aqueous solution of sulfone which is produced in some subsequent process. For example, an important use for the aqueous solutions of 2,2'-dihydroxyethyl sulfone which may be prepared in accordance with the invention is to treat cellulose fibers or fabrics in order to impart crease resistance and other desirable properties to the cellulosic materials. In such an application, the improved odor and color characteristics of the sulfone are of great advantage and make possible the preparation of finished textiles which are considerably less discolored than comparable fabrics treated with sulfone treating reagents available heretofore.

We claim:

1. A process for the preparation of 2,2'-dihydroxyethyl sulfone comprising:
   (A) reacting thiodiglycol with hydrogen peroxide in an aqueous medium in a proportion of about 2 mols of the peroxide for each mol of thiodiglycol,
   (B) providing in the aqueous reaction mixture a weakly alkaline salt in sufficient quantity to maintain the pH of the reaction mixture at between about 7.0 to 9.3 throughout the course of the reaction, and
   (B) recovering the resulting 2,2'-dihydroxyethyl sulfone.

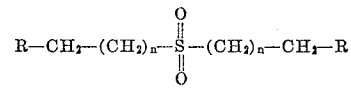
2. A process as claimed in claim 1 wherein said weakly alkaline salt is sodium tetraborate.

3. A process as claimed in claim 1 wherein said weakly alkaline salt is sodium bicarbonate.

4. A process as claimed in claim 1 wherein said weakly alkaline salt is provided in an amount between about 1 to 10 mols of the salt for each 100 mols of thiodiglycol.

5. In a process for the preparation of sulfone containing compounds by reacting a sulfone or sulfoxide with hydrogen peroxide, the improvement which makes possible the production of products having improved color comprising carrying out the reaction in the presence of a weakly alkaline salt which will not create a pH in excess of 9.3 regardless of concentration in the reaction medium, said salt being provided in sufficient quantity to maintain the reaction solution pH at greater than 7.0 throughout the course of the reaction.

6. In a process for the preparation of sulfones of the formula:



wherein R is a radical selected from the group consisting of hydrogen and hydroxyl, and *n* is an integer from 1 to 5 by reacting one mole of the corresponding sulfide with about two mols of hydrogen peroxide in an aqueous reaction medium, the improvement which comprises carrying out the reaction at a pH between 7.0 and 9.3 in the presence of an alkali metal salt of a weak acid dissolved in the reaction medium in a concentration of about 1 to 10 mols of the salt for each 100 mols of the sulfide.

7. A process as claimed in claim 1 wherein the weakly alkaline salt is mixed with the thiodiglycol.

8. A process as claimed in claim 1 wherein the weakly alkaline salt is mixed with the hydrogen peroxide which is added streamwise to the thiodiglycol.

9. A process for the preparation of 2,2'-dihydroxyethyl sulfone which is substantially odorless and colorless comprising:
   (A) providing an aqueous solution of hydrogen peroxide having dissolved therein sodium tetraborate in a concentration of about 1 to 10 mols for each 200 mols of hydrogen peroxide in the solution,
   (B) providing an aqueous solution of 2,2'-dihydroxyethyl sulfozide,
   (C) adding said hydrogen peroxide solution streamwise to said sulfoxide solution until about 1 mol of hydrogen peroxide has been added for each mol of sulfoxide,
   (D) maintaining the reaction medium at a temperature between about 25° and 100° C. during the reaction, and
   (E) recovering the resulting 2,2'-dihydroxyethyl sulfone.

10. A process for the preparation of 2,2'-dihydroxyethyl sulfone which is substantially odorless and colorless comprising:

(A) forming a mixture of sodium tetraborate and thiodiglycol containing the tetraborate in a proportion of 1 to 10 mols per 100 mols of thiodiglycol,

(B) adding hydrogen peroxide streamwise to said mixture until about 2 mols of hydrogen peroxide per mol of thiodiglycol have been added,

(C) maintaining the reaction medium at a temperature between about 25° and 125° C. during the hydrogen peroxide addition, and

(D) recovering the resulting 2,2'-dihydroxyethyl sulfone.

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