

[54] METHOD OF INHIBITING SULFONE  
FORMATION IN SULFONATIONS

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[57] ABSTRACT

Process for sulfonating a sulfonatable material with  
sulfur trioxide using an inorganic sulfite to inhibit sul-  
fone formation.

14 Claims, No Drawings

## METHOD OF INHIBITING SULFONE FORMATION IN SULFONATIONS

### BACKGROUND OF THE INVENTION

This invention is directed to the sulfonation of sulfonatable materials. More particularly this invention is concerned with an improved method sulfonating a sulfonatable material wherein the sulfone formation is decreased to an acceptable level.

The term "sulfonation", and its derivative terms throughout this disclosure are intended to include reactions in which sulfonation is the end of the process as well as reactions in which sulfation characterizes the end product.

Various sulfonic acids and sulfonates and in particular aromatic sulfonic acids are manufactured in large quantities as intermediates in the synthesis of phenolic compounds and as intermediates in the synthesis of other organic chemical compounds. The aromatic sulfonic acids are also useful as catalysts for such type reactions as polymerization, esterifications, alkylations, hydrolysis, condensations, and the like; as detergents and emulsifying agents. Some uses require that the sulfonic acid be of high quality. For example, a very high grade of para-toluene sulfonic acid is desired in the manufacture of para-cresol, an intermediate in the manufacture of 2,6-di-tertiary-butylcresol, a well-known antioxidant. In the past, aromatic hydrocarbons such as benzene and naphthalene, toluene, xylene and other lower alkyl substituted benzenes as well as the alkyl substituted benzenes having long alkyl chains such as keryl benzene and the like have been sulfonated to the corresponding monosulfonic acids by reacting the hydrocarbon in the liquid phase with a sulfonating agent such as sulfuric acid or oleum.

These procedures had a number of serious disadvantages. Formation of water during reaction resulted in incomplete reactions and the presence of residual sulfuric acid in the product. Moreover, whenever the hydrocarbon structure was such as to permit formation of isomers, an isomeric mixture was obtained. In the case of toluene, for instance, although the para-isomer was usually predominant, high proportions of meta toluene-sulfonic acid were produced.

More recently, direct sulfonation with sulfur trioxide was proposed. Theoretically such practice would be expected to overcome most of such difficulties. However, sulfonation of benzene and such other aromatic hydrocarbons as the lower alkyl substituted benzenes having 1 to 4 carbon atoms in the alkyl groups with sulfur trioxide, as with the use of oleums, is accompanied by the objectionable formation of large quantities of aromatic sulfones.

The formation of aromatic sulfones is objectionable since the sulfones represent the consumption of a sizeable portion of the aromatic hydrocarbon reactant. Furthermore, in the synthesis of phenols, the formation of phenyl sulfone, tolyl sulfone, xylyl sulfone and naphthyl sulfones not only consumes two moles of the aromatic hydrocarbon per mole of sulfone formed, but the sulfone does not react with caustic to form a phenate. The presence of sulfones is thus undesirable during the synthesis of various derivatives of the sulfonic acid.

In a liquid phase sulfonation of aromatic hydrocarbons with sulfur trioxide, the quantity of sulfones formed has been reported to be as high as 30 percent,

that is, the amount of sulfone formed represents the consumption of 30 percent of the aromatic hydrocarbon raw material. This is especially true in the sulfonation of benzene and toluene with sulfur trioxide for the sulfone formation can go as high as 30 percent and about 25 percent respectively. In the sulfonation of xylene, the sulfone formation is not quite as high, attaining a maximum of about 8 to 10 percent.

Various methods have been proposed for the reduction of objectionable formation of sulfones in the reaction of an aromatic hydrocarbon with sulfur trioxide. It has been proposed, for example, to carry out the sulfonation reaction in the presence of a solvent such as chloroform or liquid sulfur dioxide. It has also been proposed to use a sulfur trioxide complex such as a complex with trioxane as a sulfonating agent. It has been proposed that various sulfone inhibitors be employed. As sulfone inhibitors, there have been suggested alkali metal and alkaline earth metal sulfates, sodium sulfate apparently being the preferred inhibitor of this class. It has also been proposed that alkali metal and alkaline earth metal sulfonates be employed as the sulfone inhibitor. As sulfone inhibitors it has also been proposed to use lower saturated alkyl acids, especially those containing 2 to 8 carbon atoms.

A new class of sulfone inhibitors for the sulfonation of sulfonatable materials has now been discovered. This new class of sulfone inhibitors is the inorganic sulfites.

### BRIEF DESCRIPTION OF THE INVENTION

The process of this invention for sulfonating a sulfonatable material includes reacting a sulfonatable material which contains a replaceable hydrogen atom with sulfur trioxide, and using an inorganic sulfite in an amount effective to reduce sulfone formation. The process is most conveniently carried out in the liquid phase, and in the presence of a diluent for the reactive sulfur trioxide.

The sulfite inhibitors of the invention have produced sulfonic acids which contain amounts of sulfones similar to the amounts obtained when using known sulfone inhibitors such as acetic acid, but have obtained such results by using much smaller quantities than are normally used under similar conditions. The amount of the sulfite normally used is much less than that generally used for other known inhibitors, and therefore the efficiency of the sulfite is many times greater than that of the known sulfone inhibitors. The use of the sulfite is advantageous also since the sulfites are insoluble and are easily separated from the reaction mixture.

In addition, when an aromatic sulfonic acid (e.g., benzene sulfonic acid and toluene sulfonic acid) is to be converted to a phenol by fusion, it is not even necessary to remove for example the sodium sulfite. Any sodium sulfite used in the sulfonation process may be carried through such a fusion since it will be present in much larger quantities in the sodium phenate fusion product due to the fusion reaction. Of course, it may be desirable to separate and recover the sodium sulfite before fusion.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Organic compounds within the broad class of sulfonatable organic materials include such compounds as the phenols and alkyl phenols, alcohols of both the ali-

phatic and alicyclic series, aromatic hydrocarbons such as the various benzene derivatives containing a nuclear-displaceable hydrogen atom which may be occupied by a sulfo radical and the polycyclic aromatic hydrocarbons containing naphthyl, phenanthryl and anthryl nuclei; olefinic hydrocarbons, such as octene, decene, etc.; and cycloolefins or their alkyl derivatives, such as cyclohexene and ethylcyclohexene; heterocyclic compounds such as thiophene, pyridine and the like; ethers and esters, such as phenylmethyl ether and the fatty acid glycerides, respectively. The latter class also includes such compounds as the glyceride monoester of oleic acid, etc.; acids, such as benzoic acid and the aliphatic acids, particularly those containing an olefinic linkage such as oleic acid and other compounds containing a replaceable hydrogen atom. It is, of course, recognized that various derivatives of the above classes of compounds containing non-interfering substituents, such as halogen, nitro, amino, keto, carboxyl, etc. groups are also suitable sulfonatable compounds, and the term "sulfonatable hydrocarbon" is intended to include them.

The preferred sulfonatable compounds are the aromatic hydrocarbons, and more preferred are the monoaromatic hydrocarbons such as benzene and its alkyl derivatives with the length of the alkyl group being up to about 28 carbon atoms.

Suitable preferred aromatic hydrocarbons include benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, keryl benzene, dodecyl benzene,  $\alpha$ -methylnaphthalene, ethylbenzene, cumene, mesitylene, durene, p-cymene, butylbenzene, o-diethylbenzene, m-diethylbenzene, p-diethylbenzene, isoamylbenzene, isohexylbenzene, pentaethylbenzene, pentamethylbenzene; 1, 2, 3, 4- tetraethylenebenzene; 1,2,3,5-tetramethylbenzene; 1,2,4-tri-ethylbenzene; 1,2,3-trimethylbenzene; m-butyl-toluene; p-butyltoluene; 3,5-diethyltoluene; o-ethyltoluene; p-ethyltoluene; m-propyltoluene; 4-ethyl-m-xylene;  $\alpha$ -dimethylnaphthalene; b-ethylnaphthalene; 2,3-dimethylantracene; 9-ethylantracene; 2-methylantracene; 9-methylantracene; 9,10-dimethylphenanthrene; and 3-methylphenanthrene. The most preferred sulfonatable compound is toluene. Preferably, the sulfonatable material is sulfonated to its corresponding monosulfonic acid.

The active component of the sulfonating agent utilized in the present process which produces the sulfate or sulfonic acid derivatives of the sulfonatable organic compound charged to the process is sulfur trioxide in any of its various physical modifications. This reagent has become commercially available in three forms: the so-called "alpha" form which is a solid asbestos-like material melting at 62°C and generally considered to be sulfur trioxide polymer; the "beta" form, believed to be a polymeric sulfur trioxide which is solid at normal temperatures and melts at about 33°C; and the "gamma" form which is normally a liquid physical modification of the sulfur trioxide at room temperature which melts at 17°C. Any of the above physical modifications of sulfur trioxide may be utilized in the present process. There can also be employed as the source of sulfur trioxide, oleum having an SO<sub>3</sub> content of 20 percent and above, up to and including 100% SO<sub>3</sub> with no sulfuric acid being present.

The preferred sulfur trioxide is the "gamma" form in the liquid phase and is commercially available as "Sul-

fan" and "Stabilized Sulfur Trioxide". Preferably, a sufficient amount of sulfonating agent is used to supply from about 0.9 to about 1.25 moles of SO<sub>3</sub> per mole of sulfonatable material. Most preferably a sufficient amount of sulfonating agent is used to supply from about 1.00 to about 1.10 moles of SO<sub>3</sub> per mole of sulfonatable material. Of course, large excesses of either the sulfonating agent or the sulfonatable material can be employed, when desired.

The inorganic sulfites which are suitable in this invention encompass all inorganic sulfites. The preferred sulfites are the alkali metal sulfites and the alkaline earth metal sulfites of which the alkali metal sulfites are the most preferred. Some preferred sulfites are the sulfites of sodium, potassium, magnesium, calcium, cadmium, strontium, lithium, cesium, barium, and beryllium. The most preferred inorganic sulfite to be used in our process is sodium sulfite.

The sulfite is employed in the process in an amount which is sufficient to inhibit or reduce the formation of sulfones in the reaction. For instance, the inorganic sulfites are so effective in inhibiting sulfone formation that a substantial reduction in sulfone formation can be achieved by merely passing the sulfonating agent, such as SO<sub>3</sub>, and/or a diluent, such as SO<sub>2</sub>, over a bed of solid inorganic sulfite; separating inorganic sulfite, if any and if desired, from the sulfonating agent and/or diluent by decantation; and then contacting the sulfonating agent and/or diluent with the remaining ingredients (the sulfonatable material, and any remaining sulfonating material and/or diluent). Usually amounts of about 20 percent by weight based on the sulfonatable material are more than sufficient for effective sulfone inhibition. Of course, larger amounts of the sulfite can be present in the reaction, since the maximum amount of sulfite is primarily dependent upon practical considerations such as economics and equipment capacities. Preferably the amount of inorganic sulfite is between 0.01 percent by weight and about 10 percent by weight based upon the weight of the sulfonatable material. The most preferred range of sulfite is between about 2 and about 4 percent by weight based upon the sulfonatable material.

The diluent, when present, is any material which is non-reactive (not reactive in any manner which will harm the reaction or the product) and should dissolve at least one of the reactants. Preferred diluents are sulfur dioxide (gas or liquid), ethylene tetrachloride, air, nitrogen, argon, benzene sulfonic acid, nitroparaffins such as nitroethane and nitropropane, and chloroform, and the various "Freons" such as trichloromonofluoromethane, dichlorodifluoromethane, monochlorotrifluoromethane, monobromotrifluoromethane, monochlorodifluoromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, trichloromonofluoroethane, and trichlorotrifluoroethane. The most preferred diluent is liquid sulfur dioxide.

The amount of diluent when employed in the process is usually at least 2 parts by weight per part of sulfur trioxide. The maximum amount of diluent is primarily determined by such practical considerations as economics and equipment capacities. Generally amounts of about 20 parts by weight of diluent per part of sulfur trioxide are more than sufficient for satisfactory results. Preferably the amount of diluent is between about 4 parts and about 10 parts per 1 part of sulfur trioxide

with the most preferred quantity being about 6 parts by weight per 1 part of sulfur trioxide.

The process can be carried out in either the vapor or liquid phase, and preferably in the liquid phase.

The sequence of adding the various ingredients does not seem to be especially critical. For example, as long as sufficient inorganic sulfite is used before substantial sulfonation occurs, there will be considerable reduction in the formation of sulfones. For instance, when a diluent such as sulfur dioxide is employed, the sulfite can be utilized by merely passing sulfur dioxide gas or liquid over a solid bed of the sulfite.

It has, however, been found that improved results with regard to the inhibiting of sulfones is obtained when the inorganic sulfite is admixed with at least a portion of the diluent and then contacting the mixture of sulfite and diluent with the remaining ingredients (the sulfonatable material, the sulfur trioxide and any remaining diluent). It is therefore preferred that the inorganic sulfite be added to the process in this manner.

When the sulfite is employed in this manner, products are obtained which contain a lower level of sulfone formation as compared to when the sulfite is utilized by other methods.

The temperature used in carrying out the reaction can vary over a wide range, and preferably is chosen so as to maintain the reactants in the liquid phase. Usually temperatures between about  $-30^{\circ}\text{C}$  and about  $+30^{\circ}\text{C}$  are employed. The preferred temperature range is between about  $-10^{\circ}\text{C}$  and about  $+20^{\circ}\text{C}$ .

The reaction is virtually instantaneous and for all practical purposes its rate depends primarily on the rate of contacting the reactants with each other, which in turn is dependent on the maximum temperature deemed desirable. The more rapidly the reactants are contacted with each other, the more heat (of reaction) per unit time must be removed from the system. In a system of a given cooling capacity there is therefore a limit to the rate at which the reactants may be mixed without exceeding temperature limits. Also, as the permissible temperature is increased, the time required for mixing a given amount of reactants may be decreased.

Ordinarily atmospheric pressure is employed in the process. It is, of course, understood that higher or lower pressures can be employed when desired.

The process of this invention and its advantages are illustrated in the following non-limiting examples in which all parts are by weight unless the contrary is stated.

#### EXAMPLE 1

To a mixture of 3.3 parts of sodium sulfite slurried in 150 parts of liquid  $\text{SO}_2$  are simultaneously added over a period of 0.5 hours with agitation 83 parts of toluene and 76 parts of liquid  $\text{SO}_3$  dissolved in 300 parts of liquid  $\text{SO}_2$ . The temperature is maintained between  $20^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$ , throughout the addition of the toluene and  $\text{SO}_3$ . The temperature is then raised to  $45^{\circ}\text{--}65^{\circ}\text{C}$  to free the product of  $\text{SO}_2$  by evaporation. The temperature is maintained at  $45^{\circ}\text{--}65^{\circ}\text{C}$  for about 15–30 minutes to expel residual sulfur dioxide.

The sulfone content of the sulfonic acid so prepared is obtained by the following conventional procedure:

50 grams of the sulfonic acid dissolved in 200 ml.  $\text{H}_2\text{O}$  is neutralized to pH 8 with 50% NaOH, cooled and

extracted with three 75 ml. portions of diethyl ether. The combined ether extracts, after being washed with 50 ml. of cool  $\text{H}_2\text{O}$ , are transferred to a tared flask for removal of ether and subsequent weighing of the sulfone. The flask and contents are brought to constant weight in an oven at a temperature exceeding the boiling point of the respective hydrocarbon and water before final weighing.

The toluene sulfonic acid prepared by the method of this example contains 0.18 percent by weight of di-tolysulfone as determined by the above procedure.

#### EXAMPLE 2

Example 1 is repeated except that no sodium sulfite is present. The toluene sulfonic acid prepared by this method with no "inhibitor" contains more than 1.5 percent by weight di-tolysulfone as determined by the procedure set forth in Example 1.

#### EXAMPLE 3

Liquid  $\text{SO}_2$  is passed over a bed of solid sodium sulfite, and then the  $\text{SO}_2$  and any sodium sulfite are separated by decantation. To 150 parts of this liquid  $\text{SO}_2$  are simultaneously added over a period of 0.5 hours and with agitation 83 parts of toluene and 76 parts of liquid  $\text{SO}_3$  dissolved in 300 parts of liquid  $\text{SO}_2$ , which has not been exposed to a sulfite. The temperature is maintained between  $20^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$ , throughout the addition of the toluene and  $\text{SO}_3$ . The temperature is then raised to  $45^{\circ}\text{--}65^{\circ}\text{C}$  to free the product of  $\text{SO}_2$  by evaporation. The temperature is maintained at  $45^{\circ}\text{--}65^{\circ}\text{C}$  for about 15–30 minutes to expel residual sulfur dioxide.

The toluene sulfonic acid prepared by this method contains about 0.26 percent by weight of di-tolysulfone as determined by the procedure as set forth in Example 1.

What is claimed is:

1. A process of sulfonating a sulfonatable material selected from the group consisting of benzene and alkyl benzenes containing up to about 28 carbon atoms in the alkyl group and further containing a replaceable hydrogen atom which comprises reacting said sulfonatable material with sulfur trioxide in the presence of an alkali metal or alkaline earth metal sulfite in an amount effective to reduce sulfone formation.

2. The process of claim 1 wherein said alkali metal sulfite is sodium sulfite.

3. The process of claim 2 wherein said alkyl benzene is toluene.

4. The process of claim 3 wherein said process is conducted in the liquid phase.

5. The process of claim 4 wherein a diluent selected from the group consisting of sulfur dioxide, ethylene tetrachloride, benzene sulphonic acid, chloroform, nitroethane, nitropropane, trichloromonofluoromethane, dichlorodifluoromethane, monochlorotrifluoromethane, monobromotrifluoromethane, monochlorodifluoromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, trichloromonofluoroethane, and trichlorotrifluoroethane is present.

6. The process of claim 5 wherein said diluent is sulfur dioxide.

7. The process of claim 6 wherein the amount of sulfur dioxide is from 3 to about 20 parts by weight per part of sulfur trioxide.

8. The process of claim 2 wherein the sodium sulfite is present in an amount up to about 20 percent by weight of the sulfonatable material.

9. The process of claim 8 wherein the sodium sulfite is present in an amount of about 2 percent to about 4 percent by weight based upon the weight of sulfonatable material.

10. A process of sulfonating a sulfonatable material selected from the group consisting of benzene and alkyl benzenes containing up to about 28 carbon atoms in the alkyl group and further containing a replaceable hydrogen atom which comprises reacting said sulfonatable material with sulfur trioxide wherein the sulfone formation is reduced by passing either sulfur trioxide, a reaction diluent or mixtures thereof over a solid bed of an alkali metal or alkaline earth metal sulfite prior to the reaction of said sulfonatable material with sulfur

trioxide.

11. The process of claim 10 wherein said alkali metal sulfite is sodium sulfite.

12. The process of claim 11 wherein said alkyl benzene is toluene.

13. The process of claim 10 wherein a diluent selected from the group consisting of sulfur dioxide, ethylene tetrachloride, benzene sulphonic acid, chloroform, nitroethane, nitropropane, trichloromono-  
10 nofluoromethane, dichlorodifluoromethane, monochlorotrifluoromethane, monobromotrifluoromethane, monochlorodifluoromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, trichloromonofluoroethane, and trichlorotrifluoroethane is present.

14. The process of claim 13 wherein said diluent is sulfur dioxide.

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