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METHOD OF PRODUCING SULFONATED ALKANES

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This invention relates to a process for the manufacture of alkane sulfonic acids utilizing an alkane carboxylic acid as the starting material. More specifically, the invention concerns a method for sulfonating a carboxylic acid selected from the alkane mono- and dicarboxylic acids to thereby introduce a sulfo group on the carbon atom alpha to each of the carboxyl groups, decarboxylating the intermediate sulfonic acid and recovering the resulting alkane sulfonic acid from the reaction product.

In one of its embodiments the present invention relates to a process for producing a sulfonated alkane which comprises reacting an alkane carboxylic acid containing at least 4 carbon atoms and not more than two carboxyl groups per molecule with a sulfonating agent at a sulfonating reaction temperature, reacting the resulting sulfonated carboxylic acid with one equivalent of an alkaline base per equivalent of sulfo radicals in said acid to thereby form the salt derivatives of only the sulfo radicals in said acid and thereafter heating said salt at a temperature of from about 100° to about 350° C. to form said sulfonated alkane.

A more specific embodiment of the invention concerns the above process whereby a fatty acid is sulfonated in the presence of an inert solvent for the fatty acid with a sulfonating agent comprising sulfur trioxide at a sulfonation temperature at which the product and the organic material within the reaction zone are stable.

One of the outstanding advantages of the method of sulfonation herein provided is the fact that a sulfonic acid product is capable of being produced in which the position of the entering sulfo radicals is definitely known, as distinguished from sulfonation processes heretofore utilized involving the sulfonation of aliphatic hydrocarbons wherein the positions of the entering sulfo radicals are not definitely determinable, except by analysis of the resulting product and in most instances a mixture of various sulfonic acid position isomers is obtained which is difficult to analyze to determine the proportions of various isomers in the mixture. In the present method of sulfonation, an alkane carboxylic or fatty acid is utilized as the starting material, at least one of the carboxyl groups invariably occupying a terminal carbon atom of the aliphatic chain. Upon sulfonation in accordance with the process of the present invention, all of the entering sulfo radicals attach themselves to carbon atoms alpha to the carboxyl groups and when the resulting sulfonated carboxylic acid is decarboxylated, the sulfo group appears on the carbon atom initially in the alpha position relative to the carboxyl group of the starting material. As a consequence of the above factors and since the type of carboxylic acid starting material is predetermined, the structure of the final product and the position of the sulfo radicals may be predetermined. Thus, for example when a fatty acid containing a terminal carboxyl group is employed in the reaction, since the sulfo group introduced by way of the sulfonation reaction becomes attached to the carbon atom alpha to the carboxyl group, it thus becomes possible to predict with reasonable accuracy the composition of the product, which

will invariably contain the sulfo group in the new terminal position after the intermediate sulfonated carboxylic acid is decarboxylated. The position the sulfo group takes upon sulfonation becomes of importance in the manufacture of surface active agents because of the desirability of employing alkane sulfonic acids in which the hydrophobic hydrocarbon radical is at one end of the molecule and the hydrophilic sulfonate group is at the other end of the molecule. By means of the present invention, this result can be realized with accuracy.

The starting material utilized in the present process is an aliphatic carboxylic acid, preferably a fatty acid containing at least 4 carbon atoms per molecule and not more than two carboxyl groups per molecule. The acid starting material may be a member of the mono- or dibasic, straight chain or n-alkanoic series or a branched chain isomer thereof, generally limited to members of this series containing up to about 24 carbon atoms per molecule, because of the operating or processing difficulties encountered with the high melting point members of higher molecular weight which also tend to react as paraffinic hydrocarbons as the molecular weight increases. Thus, typical fatty acids of the above general character include n-butyric acid, isobutyric acid, n-valeric acid, isovaleric acid, caproic acid, heptoic acid, caprylic acid, nonylic acid, capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, arachidic acid, docosanoic acid, and lignoceric acid including both the normal or straight chain isomers of the above aliphatic acids as well as the branched chain isomers thereof. Unsaturated fatty acids such as oleic acid, linoleic acid, eleostearic acid, etc. may be employed as initial starting materials if the latter acids are pretreated prior to their use in the present process with hydrogen in order to saturate the olefinic and dienic double bonds present within the structure of these unsaturated fatty acids. This may suitably be effected by contacting the unsaturated fatty acid in the presence of hydrogen with a suitable hydrogenation catalyst such as nickel deposited upon alumina or silica at temperatures of from about 30° to about 150° C. The fatty acids may be recovered from normally abundant animal, vegetable or mineral sources, for example by hydrolysis of the glyceride esters occurring in fats and distillation of the crude mixture of fatty acids if a starting material of a particular molecular weight is desired in the process.

The alkane carboxylic acid is sulfonated in accordance with the present process by contacting the same with a relatively concentrated sulfonating agent for the particular reaction conditions selected for the charging stock, the latter depending upon the stability of the carboxylic acid in the presence of the sulfonating agent, which at certain temperatures has the ability to oxidize and/or condense the charging stock into the dark-colored by-products and chars. The preferred sulfonating agents utilizable herein are those containing free sulfur trioxide, either the 100% sulfur trioxide reagent itself or an oleum comprising free sulfur trioxide dissolved in 100% sulfuric acid. The latter oleums are supplied as articles of commerce containing up to about 75% free sulfur trioxide. Sulfur trioxide itself exists in three physical modifications, the so-called "alpha" form which is a solid, asbestos-like material melting at about 62° C., generally considered to be a sulfur trioxide polymer, the so-called "beta" form which is also a polymeric, solid form of sulfur trioxide at normal temperatures, melting at about 33° C., and the so-called "gamma" form which is a normally liquid modification of sulfur trioxide at room temperatures, melting at about 17° C. and generally being the preferred form of the reagent utilizable herein. Still another form of sulfonating agent found to be effective in sulfonating the present fatty acid starting materials to introduce a sulfo

radical on the carbon atom alpha to the carboxyl group thereof are the halosulfonic acids, such as chlorosulfonic acid and bromosulfonic acid which exist at normal temperatures in liquid form and may be supplied directly to the sulfonation reactor as such or in admixture with a suitable solvent therefor.

A particularly desirable method of effecting the present sulfonation reaction comprises mixing the carboxylic acid charging stock with an inert solvent therefor which is not only stable in the presence of the sulfonating agent but furthermore does not react therewith to contaminate the reaction mixture with side-reaction products. Preferably, the inert solvent for the carboxylic acid starting material is an organic compound of relatively low boiling point which may be separated from the reaction mixture following completion of the sulfonation reaction by distillation therefrom. A particularly desirable class of inert solvents are those which boil at or near the desired sulfonation temperature, such that the solvent vaporizes as the heat of reaction raises the temperature above the level desired for the sulfonation reaction, thereby dissipating the heat of the sulfonation reaction by evaporative cooling. Thus, the sulfonation reactor may have an attached reflux condenser which liquefies the vaporized diluent and returns it to the sulfonation reactor as the sulfonation proceeds. Typical classes of organic compounds which have the above properties, making them particularly suitable at liquefiable diluents in the present process are the paraffinic and cycloparaffinic hydrocarbons which have no tertiary hydrogen, and their halogenated derivatives, such as liquid n-butane, n-pentane, n-hexane, cyclopentane, cyclohexane, etc. carbon tetrachloride, dichlorodifluoromethane, ethylene difluoride, ethylene dichloride, ethylene dibromide, carbon tetrabromide, isopropylchloride, and other saturated hydrocarbons and halogen-substituted saturated hydrocarbons, which boil preferably below about 100° C. Still another type of liquid solvent utilizable in the process is the inorganic liquid solvent typified by sulfur dioxide, which boils at or near the desired sulfonation temperature.

The inert liquid diluent is preferably maintained within the reaction zone in sufficient quantity to provide a diluent to charging stock volume ratio of about 0.5 to 1 to about 10 to 1, and as heretofore indicated, one of the preferred means of maintaining the initial diluent to charging stock ratio is to permit the vapors of diluent vaporized during the sulfonation reaction to escape from the reactor into a reflux condenser which liquefies the diluent and returns it in its liquid state to the reaction zone. Of the above types of compounds utilizable as diluents the aliphatic hydrocarbons, and particularly the low molecular weight members thereof, are preferred in the present process, since they are readily soluble with the charging stock and to the required degree with the sulfonating agent.

When utilizing sulfur trioxide in its free form as the sulfonating agent, it is generally preferred to supply the reagent to the sulfonation zone in the form of its vapor carried into the reactor in admixture with an inert carrier gas which may be passed through a bulk supply of sulfur trioxide in order to carry a portion of the sulfur trioxide in vaporized form from the bulk supply zone into the sulfonation reactor. It has been found that by reducing the concentration of sulfur trioxide in the sulfonating agent (in effect, diluting the highly retactive reagent), the sulfonation reaction is more readily controlled, with the production of fewer by-product impurities such as oxidation products, charred or cracked materials and highly colored impurities generally undesirable in the final product. Inert gaseous materials utilizable as the sulfur trioxide carrier gas include air, nitrogen, carbon monoxide, carbon dioxide, sulfur dioxide, dehydrated flue gas or a low molecular weight paraffinic hydrocarbon such as methane, propane, butane, mixtures thereof, or the material utilized as the inert diluent, hereinabove specified. Suitable proportions of sulfur trioxide in admixture with the inert carrier gas are, for example, from 0.5 to about 25% by volume of sulfur trioxide in the mixture of gases.

The sulfonation reaction is desirably effected at temperatures of from about —10° to about 30° C. or higher, unless such higher temperatures cause undue charring of the carboxylic acid starting material. Another factor which determines the preferred reaction temperature is the viscosity of the reaction mixture which increases as the reaction temperature is reduced and the molecular weight of the charging stock is increased. A particularly desirable range of reaction temperatures for most charging stocks is from about 0° to about 10° C., and it is found that the inert liquid diluent, particularly if it is a compound of relatively low molecular weight, reduces the viscosity of the reaction mixture and permits free mixing of the sulfonating agent with the charging stock without the development of local high temperature zones within the reaction mixture. Suitable pressures for the sulfonation reaction are determined primarily by the boiling point of the charging stock and the diluent utilized, the pressure desirably being sufficient to maintain both in substantially liquid phase condition during the course of the reaction. Thus, pressures from atmospheric to about 100 p. s. i. are found to be particularly suitable. The proportion of sulfonating agent to carboxylic acid starting material charged into the sulfonation reactor will depend upon the type of sulfonating agent utilized, and particularly upon the concentration of sulfur trioxide in the sulfonating agent. When utilizing a sulfuric acid oleum containing from 30 to about 75% free sulfur trioxide, the proportion of sulfonating agent to charging stock, calculated on the basis of the number of mols of free sulfur trioxide (not combined with water) per mol of carboxylic acid will be from about 0.9 to 1 to about 1.5 to 1, although the molar ratio, calculated on the basis of total sulfur trioxide (combined and free), will be somewhat greater, since the sulfuric acid merely acts as a carrier for the free sulfur trioxide which is the active component of the sulfonating agent. When utilizing free sulfur trioxide itself, not combined with sulfuric acid in the form of an oleum, the molar ratio of sulfonating agent to charging stock required to effect complete monosulfonation is generally within the range of from about 1.0 to about 1.3 mols of sulfur trioxide per mol of carboxylic acid.

In accordance with the first stage of the process of this invention in the ultimate production of an alkane sulfonic acid or sulfonate salt, the sulfonic acid derivative of the carboxylic acid formed in the preceding sulfonation reaction, generally a polybasic acid (depending upon whether monosulfonation or polysulfonation has taken place) at least one of the acid groups being a sulfo radical and one or two of the other acid groups a carboxyl group of the carboxylic acid starting material, is converted to its partial-salt by reaction with a suitable neutralizing agent selected from the inorganic hydroxides, carboxylates, oxides, carbonates, and bicarbonates. The conversion of the polybasic acid in which one and not more than two of the acid radicals are sulfo groups and one and not more than two of the other acid groups is a carboxyl group to a partial salt derivative thereof is accomplished by reacting each mol of the sulfonated carboxylic acid with one equivalent of base per equivalent of sulfo groups, the base preferentially reacting with the more acidic sulfo radicals rather than with the carboxyl groups present in the intermediate sulfonated carboxylic acid. Prior to the neutralization reaction, the sulfonated carboxylic acid may be separated from the reaction mixture in order to eliminate the excess sulfonating agent therefrom and thus reduce the quantity of neutralizing base required to convert the sulfonated material to its partial-salt. Such separation may generally be effected by adding sufficient water to the sulfonation reaction

mixture to form the monohydrate of the sulfuric acid remaining within the sulfonation mixture, the latter sulfuric acid mono-hydrate being relatively immiscible with the sulfonic acid so that it separates therefrom as a distinct phase, particularly in the presence of an inert solvent of the type previously described. During the half-neutralization which is generally accomplished by adding an aqueous solution or suspension of the neutralizing agent to the sulfonic acid (or vice versa), it is desirable to remove from the aqueous mixture the heat of the neutralization reaction to thereby prevent overheating of the reaction mixture. In order to control the temperature occasioned by neutralization of the sulfonated carboxylic acid, the sulfonation diluent present in the reaction mixture may be retained therein and permitted to reflux as the neutralizing agent is added to the sulfonic acid. Typical neutralizing agents for the production of the partial-salts are such compounds as sodium hydroxide, potassium hydroxide, lithium hydroxide, the corresponding carbonates and bicarbonates, as well as other materials having an alkaline reaction in aqueous solution or suspension.

The partial-salt produced by neutralizing the mono- or disulfonic acid groups introduced into the carboxylic acid in the prior sulfonation step may be recovered therefrom by evaporating the resulting aqueous solution to dryness and extracting from the dried residue the organic partial-salt with a suitable solvent in which the inorganic portion of the residue is insoluble. Thus, if desired, the entire sulfonation reaction mixture, including the excess sulfonating agent, may be reacted with sufficient alkaline base to neutralize only the sulfo groups present in the sulfonated carboxylic acid without separating the sulfonic acid from the excess sulfonating agent. A mixture of inorganic salts of the neutralizing agent and sulfonating agent are thereby obtained in admixture with the partial-salt of the sulfonated carboxylic acid. The term "partial-salt," as specified herein, is intended to indicate the salts of only the neutralized sulfo radicals present in the sulfonated carboxylic acid; that is, the salts formed by reacting an equivalent of a base with an equivalent of the sulfo groups present in the sulfonated carboxylic acid. If desired, the resultant mixture may be subjected to the next, succeeding stage of the present process, wherein the partial-salt is decarboxylated to form the alkane sulfonate, without prior separation of the inorganic salts from the partial-salt of the organic material. However, if the final product is desired in a purified form, free of inorganic salts of the sulfonating agent, the partial-salt of the desired sulfonic acid is preferably extracted from the inorganic material, as indicated above, with such extractive solvents as ethyl alcohol, propyl alcohol, isopropyl alcohol, acetone, methylethyl ketone, ethyl acetate, etc., leaving a residue of the inorganic sulfate, the carboxylic acid sulfonated salt being recovered from the solvent by evaporation of the solvent from the solution. Alternatively, this extraction may be carried out after the decarboxylation step described below.

Decarboxylation of the partial-salt formed by neutralization of the sulfonated carboxylic acid is effected in accordance with the present process by heating the partial-salt to a temperature at which the free carboxyl group is split off from the remainder of the compound, generally at a temperature of from about 150° to about 350° C., the sulfonated carboxylic acid decarboxylating to form the volatile carbon dioxide. A residue of alkane sulfonate remains in the decarboxylation zone and if the latter is desired in the form of its sulfonic acid derivative, treatment of the sulfonate salt with a strong aqueous mineral acid, such as sulfuric acid converts the sulfonate to the sulfonic acid which may be extracted from the reaction mixture by contacting the acid solution with a solvent for the sulfonic acid, such as a light hydrocarbon fraction, diethylether or other water-insoluble, organic solvent.

The process herein described may likewise be used to convert alkane dicarboxylic acids to the corresponding mono-carboxylic-monosulfonic acids of one less carbon atom, or to the corresponding disulfonic acids of two less carbon atoms, by effecting mono- or disulfonation, respectively, at the α-carbon atoms of the carboxylic acids, neutralizing the sulfonic acids, and causing thermol decarboxylation of the carboxyl groups adjacent to sulfonic groups. Thus, succinic, glutaric, adipic, pimelic, suberic and sebacic acids, and their homologs, may be converted to α-carboxylic-ω-sulfonic acids of one carbon atom less, or to α,ω-disulfonic acids of two fewer carbon atoms, by the steps outlined.

This invention is further illustrated with respect to several of its specific embodiments in the following examples which, however, are not intended to limit the scope of the invention necessarily in accordance therewith.

Example I

Purified n-lauric acid formed by fractional distillation of coconut fatty acids is utilized as charging stock in the following sulfonation reaction.

One mol of the above prepared lauric acid is mixed with 5 volumes of n-butane solvent, the resulting mixture placed in a glass reaction vessel fitted with a thermometer well, a motor-driven stirrer, a reflux condenser containing Dry Ice and a gas-inlet tube through which a mixture of sulfur trioxide and butane vapors can be introduced into the reaction vessel. The mixture is cooled to −5° C. by immersing the reaction flask in a mixture of ice and salt. As the lauric acid-n-butane mixture is stirred, a stream of vaporized sulfur trioxide in n-butane vapor (formed by bubbling vaporized butane through liquid sulfur trioxide) and containing 6.5 volume percent sulfur trioxide is led into the n-butane solution of lauric acid. The heat of the sulfonation reaction causes the butane solution to boil, but the temperature is maintained substantially within the range of from about −2° to about 3° C. by evaporative cooling of the butane solution. The reflux condenser returns the vaporized butane to the reactor as liquefied solvent. Following the addition of 1.1 mols of sulfur trioxide to the butane-SO_3 mixture, the flow of the latter mixture is interrupted, 1 mol of sodium hydroxide, in the form of a 5% aqueous solution, is added to the stirred mixture in the sulfonation flask and stirring is continued for 30 minutes after addition of the caustic. Again, the heat of the neutralization reaction is dissipated from the flask by evaporation of the butane solvent from the solution. The aqueous phase resulting from the foregoing neutralization reaction is separated by decantation from the reaction mixture and transferred to a steam-heated evaporating dish for recovery of the sulfonated material. By analysis of the dried residue in the evaporating dish and on the basis of the total weight of dried salt recovered it is found that sulfonation of the lauric acid is substantially complete (98.5 to 99.5% of theoretical). Furthermore, extraction of the dried residue with diethylether failed to yield any substantial amounts of lauric acid, which would be present in the residue left after evaporation of the ether extract, if present in the residue.

The dried salt recovered by evaporating the neutralized sulfonation product is heated to a temperature of 265° C. for 3 hours, to remove the carboxyl group from the lauric-acid sodium sulfonate half-salt. On the basis of the neutralization equivalent of the recovered material, its molecular weight determined by the cryoscopic method and a spectographic analysis of the product, the decarboxylated sulfonate is found to consist of essentially pure undecane sodium sulfonate. Comparison of the product and its derivatives with the corresponding compounds prepared from synthetic 1-undecane-sulfonic acid indicates that the sulfonic acid radical of the product occupies the terminal position in the undecane chain and that, therefore, the sulfonation occurring in the first step of the process placed the sulfo radical on the carbon atom alpha to the carboxyl group.

Example II

Purified stearic acid which on analysis corresponds to the formula: $C_{17}H_{35}COOH$ is utilized as charging stock in the following process for the production of heptadecane sulfonate.

One mol of the above stearic acid is dissolved in 5 volumes of dichloromethane in the apparatus described in Example I and sulfonated at a temperature of 0° C. by the dropwise addition of 65% oleum to the sulfonation mixture, utilizing 1.4 mols of free sulfur trioxide as the above oleum (170 grams). The reaction mixture is stirred for a period of one hour following the dropwise addition of oleum to the stearic acid during a period of 3 hours. The mixture is then neutralized by titration with 5% aqueous potassium hydroxide to an end-point at pH=7.0, corresponding to the neutralization of the excess sulfuric acid and the sulfonic acid, but not of the carboxylic acid. The temperature was controlled by allowing the methylene dichloride to reflux during the neutralization.

The potassium half-salt of the sulfonated stearic acid is recovered in the same manner as indicated in Example I and the dried salt decarboxylated by heating to a temperature of 250° C. for 3 hours. The recovered product when acidified with sulfuric acid and the organic material extracted with diethylether consists of heptadecane sulfonic acid containing the sulfo group on a terminal carbon atom.

I claim as my invention:

1. A method for converting an alkane carboxylic acid containing from 4 to about 24 carbon atoms per molecule and not more than two carboxylic acid groups per molecule to a sulfonated alkane which comprises sulfonating said carboxylic acid, converting the resulting sulfonated carboxylic acid to its sulfonate partial-salt free of carboxylate salts by neutralizing only the sulfo radicals of the last-named acid and thereafter heating said salt at a temperature of from about 100° to about 350° C. to form said sulfonated alkane.

2. The process of claim 1 further characterized in that said carboxylic acid contains from 8 to about 24 carbon atoms.

3. The process of claim 1 further characterized in that said sulfonation reaction is effected with a sulfonating agent comprising sulfur trioxide.

4. The process of claim 3 further characterized in that said sulfonating agent is oleum.

5. The process of claim 1 further characterized in that the sulfonation is effected in the presence of an inert diluent selected from the group consisting of sulfur dioxide, a paraffinic hydrocarbon and the halogenated analogues thereof.

6. The process of claim 1 further characterized in that said carboxylic acid is sulfonated at a temperature of from about −5° to about 30° C.

7. The process of claim 3 further characterized in that said sulfonating agent is a mixture of sulfur trioxide and an inert gas.

8. The process of claim 1 further characterized in that the partial-salt formed by neutralizing the intermediate sulfonic acid derivative of the carboxylic acid is separated from the reaction mixture prior to said heating thereof.

9. The process of claim 1 further characterized in that said carboxylic acid is a fatty acid.

10. The process of claim 9 further characterized in that said fatty acid is a saturated acid.

11. A process for producing a sulfonated alkane which comprises sulfonating an alkane carboxylic acid containing from 4 to about 24 carbon atoms and not more than two carboxyl groups per molecule, reacting the resulting sulfonated carboxylic acid with one equivalent of an alkali metal hydroxide per equivalent of sulfo radicals in said acid to thereby form the salt derivative of only the sulfo radicals in said acid, and thereafter heating said salt at a temperature of from about 120° to about 350° C. to form said sulfonated alkane.

12. The process of claim 11 further characterized in that said carboxylic acid is a dicarboxylic acid and said sulfonated alkane is the disulfo-derivative of an alkane having two fewer carbon atoms per molecule than said carboxylic acid.

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