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HIGHER ALKYL ESTER PRODUCTION

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This invention relates to the manufacture of alkyl esters of inorganic oxy-acids from alkenes having at least five carbon atoms per molecule. It deals with an improved method of reacting such alkenes and acids whereby esters are obtained more efficiently and economically than has hitherto been possible. The invention is especially concerned with a method of reaction using promoters which accelerate ester formation and result in higher yields of desirable products.

Although it has been known for some time that the higher alkenes can be converted to esters by reaction with inorganic oxy-acids such as sulfuric, pyrosulfuric, chlorosulfonic, phosphoric, pyrophosphoric and like acids, the yields of desirable esters from the process have been low in prior methods of operation as a result of extensive by-product formation. Polymerization, condensation and, when using sulfuric acid or the like, sulfonation are characteristic side reactions which lead to reduced yields of esters.

An important object of the present invention is to provide a process whereby the foregoing disadvantages of prior methods of reacting alkenes of five or more carbon atoms with inorganic oxy-acids may be minimized. Another object is to accelerate the reaction of such olefins and inorganic acids and to promote increased yields of desirable esters. Still another object is to obtain more complete conversion of higher alkenes to esters of strong polybasic inorganic acids. A further object is to promote the formation of mono-alkyl esters of such polybasic acids and reduce the production of poly-alkyl esters without sacrifice in total ester yield. Yet another object is to provide a process whereby esters containing a higher proportion of alkyl-2 esters are obtained from higher alkenes having the double bond at or near the end of the chain. It is also an object of the invention to provide a process whereby higher alkenes may be esterified with acids having a concentration from 2% to about 10% lower than the optimum under previous methods of operation. Still other objects and advantages of the new process will be apparent from the following description of the invention.

The invention is based upon the discovery that organic hydroxy compounds containing one or more aliphatic groups with more than four carbon atoms and which form oxonium compounds in a strong acid medium, or sulfuric acid esters of such hydroxy compounds when added in controlled amounts of only a few per cent based on

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the alkenes to be esterified, exert a remarkable accelerating effect on the esterification of higher alkenes by inorganic oxy-acids whereby increased yields of desirable alkyl esters are obtained compared with those resulting from the esterification in the absence of the accelerating compounds. Based upon this discovery, an improved method of esterifying alkenes of five or more carbon atoms per molecule with inorganic oxy-acids has been developed, an essential feature of which is that the reaction of the higher alkene and inorganic oxy-acid is carried out in the presence of from about 0.5% to 10% by weight, based on the weight of alkenes present, of an organic hydroxy compound having an aliphatic group of at least five carbon atoms in the molecule or sulfites of such hydroxy compounds.

For the purpose of making the new method of operation clear, it will be described in more detail in connection with the sulfation of higher alkenes, particularly those of more than ten carbon atoms. However, as previously indicated, the invention is not limited to this preferred modification but is applicable not only to the production of other sulfate esters of five or more carbon atoms per molecule but also to the manufacture of phosphoric acid esters and esters of other strong inorganic oxy-acids when using the same alkenes.

In sulfating the higher alkenes (i. e. those containing five or more carbon atoms) with sulfuric acid of a concentration of, say, 90% or more (depending on the molecular weight of the initial alkene) and thus converting the alkenes into sulfuric acid esters—namely, acid esters (mono-alkyl sulfates) and neutral esters (dialkyl sulfates)—certain undesirable by-products are formed, such as polymerization and condensation products and alkyl sulfonic acids. The extent to which these by-products are formed can vary rather considerably, according to the conditions under which the reaction takes place, such as concentration of acid, temperature and reaction time. Since the higher sulfuric alkyl esters and in particular those with more than 10 carbon atoms are especially suitable for the preparation of sulfuric acid ester salts which have good surface-active properties and are of great value for application as detergents, wetting agents, etc., the sulfating reaction should be directed as much as possible to the formation of mono-alkyl sulfates, which will yield the required ester salts after neutralization with basic substances. The dialkyl sulfates which are like-

wise formed during the sulfation can also be utilized for the preparation of the ester salts in question, for which purpose they are saponified in a known manner by treatment with basic substances at elevated temperatures, thereby forming ester salts and higher alcohols.

The above-mentioned formation of by-products during the sulfation is naturally highly undesirable, since it results in a loss of alkenes. By reducing the concentration of the sulfuric acid used for the sulfation, polymerization and similar undesirable subsidiary reactions can admittedly be counteracted up to a point, but there is a certain minimum limit for the concentration which varies according to the other sulfation conditions, and which usually lies above about 95% for alkenes with more than ten carbon atoms. If a lower concentration of sulfuric acid is used, a very sharp drop takes place in the percentage of alkene converted into the desired mono-alkyl sulfate. For this reason, it has been customary up to now to carry out the sulfation of alkenes with more than ten carbon atoms with sulfuric acid of a higher concentration than 95%—usually about 97%—in order to obtain proper conversions.

By carrying out the sulfation of the alkenes in the presence of the accelerating substances used in accordance with the invention, the sulfating reaction is much more complete, with the result that higher yields of sulfuric acid esters are obtained than would be the case when operating without the addition of these substances, but otherwise under the same conditions in respect of temperature, time of reaction, concentration of acid, and ratio of the two reaction components.

Among the organic hydroxy compounds which have been found to be particularly useful accelerators of esterification according to the invention are the aliphatic monohydroxy and polyhydroxy alcohols of at least five carbon atoms per molecule. As a rule, those hydroxyl-containing compounds in which the —OH group is in the terminal position or near the end of an aliphatic chain of at least five carbon atoms have been found to be rather more active than those compounds in which the said group is situated nearer to the center of the molecule.

A group of compounds found to be particularly active comprises the alkanols containing more than six carbon atoms, especially the primary or secondary alkanols of 7 to 20 carbon atoms having the hydroxyl group in the 1- or 2-position. Examples of compounds belonging to this group are heptanol-1, heptanol-2, heptanol-3, heptanol-4, octanol-1, octanol-2, nonanol-1, nonanol-2, decanol-1, decanol-2, dodecanol-1, dodecanol-2, pentadecanol-2, stearyl alcohol, etc. Methyl isobutyl carbinol is another example of the alcohols which may be used.

Another group of hydroxy compounds which can be used as promoters in the process of the invention are the cycloaliphatic alcohols such as cyclohexanol, the mono- and di-methylcyclohexanols, the hydrogenation product of isophorone, etc. Among the polyhydroxy alcohols which may be used are, for instance, hexylene glycol, the pentane- and hexane-triols, etc. The hydroxy compounds used may be substituted by halogen atoms or organic groups such as keto or carboxyl or ester groups and the like. Instead of the alcohols themselves, the sulfurous acid esters thereof, particularly the dialkyl sulfites such as dioctyl sulfite, didecyl sulfite, distearyl sulfite, ethyl dodecyl sulfite, etc., can be used.

The accelerators of esterification used in accordance with the invention can be added in the form of simple compounds; if desired, however, mixtures can be used containing various active hydroxy compounds and/or sulfites thereof, with or without other substances which in themselves are inactive. Thus, for example, there can be employed advantageously primary alcohols obtained by Oxo synthesis, starting with higher alkenes or alkene polymers (e. g. tri-isobutene) and consisting of mixtures of various isomers; or the so-called polymers which are obtained as by-products in the conversion of the sulfation products of higher alkenes into ester salts, and which contain higher secondary alcohols.

The accelerating hydroxy compound or sulfurous ester used should be added in an amount between about 0.5% and 10% by weight based on the alkenes being esterified. Smaller amounts are less effective and larger amounts give no appreciable further increase in yield and may be undesirable. As a general rule, amounts between about 2% and about 6% by weight of the alkene are preferred.

The process of the invention can be carried out under the usual conditions for esterification of alkenes which vary with the particular inorganic oxy-acid and alkene or mixture of alkenes being used. With oxy-acids of sulfur such as sulfuric acid, pyrosulfuric acid, chlorosulfonic acid and the like, it is desirable to use low temperatures of the order of about -10°C. to $+25^{\circ}\text{C.}$, as a rule. The oxy-acids of phosphorus such as phosphoric and pyrophosphoric acids, for example, usually require higher temperatures of reaction but, as a general rule, temperatures of 50°C. or lower are preferred. The acid is preferably used at a concentration of between 85% and about 95% and may be used in amounts of 0.5 to 4 moles or more per mole of olefin treated. Short contact times of the order of about 5 to 50 seconds are most preferable as a rule, but, depending upon the type of reactor and the method of operation which are adopted, longer times, for example, about 5 to 30 minutes or more, can be satisfactorily employed.

Although the process can thus be carried out under the usual reaction conditions for sulfation, an important advantage of the process according to the invention is that good yields of sulfuric acid alkyl esters are obtained when using sulfuric acid of a lower concentration than has been customary up to now for the sulfation of alkenes. The possibility of working with sulfuric acid of a lower concentration than usual, generally 2% to 5% lower than the optimum in the absence of a hydroxylic promoter, not only has the advantage that the formation of polymerization products during the sulfation process is reduced, but also that when the excess sulfuric acid is recovered, it does not have to be concentrated as much in order to be suitable for re-use in the process.

It has further been found that the sulfuric acid esters obtained by the present process have a higher alkyl-2 sulfate content than the products obtained by the normal sulfation process. This is of great practical importance in view of the fact that the ester salts obtained from the 2-sulfates have better properties—inter alia a better detergent effect and lesser hygroscopicity—than the corresponding ester salts in which the sulfate group is situated nearer to the center of the molecule.

The process according to the invention can be applied to the preparation of sulfuric acid or

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other inorganic oxy-acid esters starting either with pure alkenes or with hydrocarbon mixtures containing alkenes, such as the products or fractions thereof, obtained by cracking hydrocarbons. Products from cracking paraffin wax or other paraffinous hydrocarbon material, and predominantly consisting of alpha-alkenes, are especially advantageous starting materials. Alkenes of 5 to 25 carbon atoms are preferred.

Although the process can be effected batchwise or intermittently, it is preferably carried out in the continuous manner, the alkene, sulfuric or other strong polybasic inorganic acid and the hydroxy compound used as accelerating agent being passed in intimate contact with each other through a reaction space kept at the desired temperature; any unconverted portion of the alkene can then be recirculated. The accelerating agents may be removed from the esterification product, for example by extraction, before the latter is worked up further.

The examples below illustrate the beneficial effect achieved by using the hydroxyl compounds of five or more carbon atoms according to the invention.

Example I

Pure dodecene-1, to which 1.8% by weight of decanol-1 had been added, was brought into intimate contact with sulfuric acid of 95.0% in a film reactor of the type described in the "Chemisch Weekblad," 37, 1940, pages 579-580. The molecular ratio of sulfuric acid to alkene was about 3, the temperature being kept at about 20° C. and the residence time of the mixture in the reactor being about 20 seconds. It was found from the analysis of the resulting sulfation product that the alkyl sulfuric acid yield was 39.4 mol per cent and the dialkyl sulfate yield was 28.5 mol per cent, corresponding to a total yield of 53.7 mol per cent, calculated as ester salt.

When the quantity of decanol-1 added was increased to 5.7%, the alkyl sulfuric acid yield rose to 65 mol per cent, while the dialkyl sulfate yield amounted to 27.0 mol per cent, corresponding to a total yield of 78.5 mol per cent, calculated as ester salt. The content of 2-sulfate in the alkyl sulfuric acid was about 61%.

When the reaction was carried out under the same reaction conditions but without the addition of decanol-1, the alkyl sulfuric acid and dialkyl sulfate yields amounted only to 5.3 and 0 mol per cent, respectively.

Similar results were obtained when the decanol-1 was replaced by an approximately equal quantity of dioctyl sulfite.

Example II

The sulfation of dodecene-1 was carried out under the same conditions as in Example I, but this time in the presence of 10.1% (calculated on the dodecene) of an alcohol-containing polymer separated as a non-aqueous layer after the neutralization and saponification step in the preparation of sulfuric acid ester salts from a cracked fraction containing C₁₀-C₁₈ alkenes. The alkyl sulfuric acid and dialkyl sulfate yields were 45.7 mol per cent and 39.1 mol per cent, respectively, corresponding to a total yield of 65.3 mol per cent, calculated as ester salt. The alkyl sulfuric acid had a 2-sulfate content of about 75%.

Example III

After the addition of about 6% by weight of dodecanol-1, a C₁₀-C₁₈ fraction (containing about 75% alkenes) of a cracked distillate obtained by

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cracking paraffin wax was sulfated in a film reactor with sulfuric acid of 92.0%, the molecular ratio of sulfuric acid to alkenes being about 4.2; the temperature was kept at 0° C.-5° C. and the residence time was about 20 seconds. The yield of sodium alkyl sulfate, obtained after alkaline saponification of the sulfation product, was 53%. The film reactor used here consisted of two concentric cylinders, the outer one of which was cooled externally. The reaction components passed through the annular space and were thoroughly mixed by the rapid rotation of the inner cylinder.

When this test was repeated without the addition of dodecanol-1, a total yield of only 2 mol per cent, calculated as ester salt, was obtained.

Good results are also obtained when using concentrated phosphoric acid as the inorganic acid instead of sulfuric acid.

It will thus be seen that the invention offers many advantages over prior methods of esterifying higher olefins with strong polybasic inorganic acids. In addition to increasing the yield of esters and promoting the formation of more valuable alkyl-2 esters from olefins having the double bond near the end of the chain, the hydroxyl compounds of five or more carbon atoms and corresponding sulfites used in the new process accelerate the esterification reaction and make it feasible to use acids of lower concentration. The process is capable of other variations not only in regard to the hydroxyl compounds and their sulfurous acid esters which may be used as promoters but also in respect to the olefins which may be esterified and the strong inorganic polybasic acids which may be employed as reactants. It will accordingly be understood that the invention is not restricted to the details of operation disclosed by way of illustration nor by any theory proposed in explanation of the improved results which are obtained.

I claim as my invention:

1. In a process of esterifying an olefin having at least five carbon atoms per molecule with a strong polybasic inorganic oxy-acid, the improvement which comprises esterifying said olefin by reaction with said acid in the presence of about 0.5% to 10% by weight of said olefin of an organic compound of the group consisting of hydroxyl compounds having an aliphatic group containing at least five carbon atoms and sulfite esters of said hydroxyl compounds.

2. In a process of esterifying an olefin having at least five carbon atoms per molecule with a strong polybasic inorganic ortho oxy-acid, the improvement which comprises esterifying said olefin by reaction with said acid in the presence of about 0.5% to 10% by weight of said olefin of an organic compound of the group consisting of hydroxyl compounds having an aliphatic group containing at least five carbon atoms and sulfite esters of said hydroxyl compounds.

3. In a process of producing a secondary alkyl ester of an inorganic acid by reacting an alkene having at least five carbon atoms per molecule with a strong polybasic inorganic oxy-acid of the group consisting of the ortho oxy-acids of sulfur and phosphorus, the improvement which comprises esterifying said alkene with said acid in the presence of about 0.5% to 10% by weight of said alkene of an aliphatic hydroxyl compound having at least five carbon atoms per molecule.

4. A process of sulfating an alkene of 5 to 25 carbon atoms per molecule which comprises reacting said alkene with sulfuric acid in the pres-

ence of about 0.5% to 10% by weight of said alkene of an organic hydroxyl compound having an aliphatic group of at least five carbon atoms in the molecule.

5. A process of sulfating an alkene of 12 to 22 carbon atoms per molecule which comprises reacting said alkene with concentrated sulfuric acid in the presence of about 0.5% to about 10% by weight, based upon said alkene, of a hydroxyl-substituted aliphatic hydrocarbon of at least seven carbon atoms.

6. In a process of esterifying an alkene of 5 to 25 carbon atoms per molecule which comprises reacting said alkene with a strong polybasic ortho inorganic oxy-acid of sulfur, the improvement which comprises esterifying said alkene with said acid in the presence of about 0.5% to about 10% by weight, based upon said alkene, of an aliphatic alcohol of 7 to 25 carbon atoms per molecule.

7. In a process of reacting an alkene of at least five carbon atoms per molecule with sulfuric acid to produce an alkyl sulfate, the improvement which comprises adding to the reaction mixture about 0.5% to 10% by weight of said alkene of a saturated aliphatic alcohol having 7 to 20 carbon atoms per molecule of the formula



wherein R represents a member of the group consisting of hydrogen and the methyl radical and R' represents an alkyl radical.

8. A process of sulfating an alkene of 5 to 25 carbon atoms per molecule which comprises reacting said alkene with sulfuric acid in the presence of about 0.5% to 10% by weight of said alkene of a saturated aliphatic primary alcohol having 7 to 20 carbon atoms per molecule.

9. A process of sulfating an alkene of 5 to 25 carbon atoms per molecule which comprises reacting said alkene with sulfuric acid in the presence of about 0.5% to 10% by weight of said

alkene of an aliphatic saturated monohydroxy secondary alcohol having 7 to 20 carbon atoms per molecule.

10. A process of sulfating an alkene of 12 to 22 carbon atoms per molecule which comprises reacting said alkene with concentrated sulfuric acid in the presence of about 0.5% to about 10% by weight, based upon said alkene, of decanol.

11. A process of sulfating an alkene of 5 to 25 carbon atoms per molecule which comprises reacting said alkene with sulfuric acid in the presence of about 0.5% to 10% by weight of said alkene of an ester of an aliphatic alcohol of at least five carbon atoms per molecule and sulfuric acid.

12. A process of sulfating an alkene of 5 to 25 carbon atoms per molecule which comprises reacting said alkene with sulfuric acid in the presence of about 0.5% to 10% by weight of said alkene of a dialkyl sulfite having an alkyl group of at least seven carbon atoms.

13. A process of sulfating an alkene in accordance with claim 4 wherein the reaction is carried out with sulfuric acid having a concentration of 85% to about 95%.

14. In a process of producing alkyl sulfate salts by sulfating a mixture of alkenes of 12 to 18 carbon atoms predominating in terminally unsaturated alkenes and neutralizing the alkyl acid sulfates produced with a base, the improvement which comprises carrying out said sulfation in the presence of about 0.5% to 10% by weight of an organic hydroxyl compound having an aliphatic group of at least five carbon atoms in the molecule whereby the formation of alkyl-2 sulfate esters is promoted.

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