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IN SITU EPOXIDATION OF OLEIC ACID USING FORMIC ACID

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The present invention relates to a method of epoxidizing higher fatty acids containing an ethylenic linkage, and particularly those fatty acids obtained from fatty oils which contain oleic acid. The epoxidation is performed with hydrogen peroxide and formic acid in presence of an organic solvent and at a relatively high temperature. A similar method of epoxidation but applied particularly to esters of unsaturated higher fatty acids is disclosed in our co-pending application Serial No. 367,752 filed July 13, 1953.

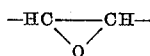
Heretofore, in the principal method of epoxidizing unsaturated fatty acids, such as oleic acid, a prepared peracetic acid solution has been employed as the peroxidizing reagent. Such solutions are generally equilibrium mixtures of hydrogen peroxide and peracetic acid with substantial amount of free peroxide present. Under the reaction conditions employed for such epoxidation, substantially only the peracid fraction of the equilibrium mixture is utilized. There is little or no further formation of peracid from the free peroxide present and this free peroxide is unused; this is extremely wasteful, as much as 20% of the available active oxygen remaining unutilized. Accordingly, reaction techniques, wherein hydrogen peroxide and lower aliphatic acids are caused to react upon the unsaturated fatty acid, have long been sought, for direct epoxidation reactions. Such techniques are standard for hydroxylation reactions with hydrogen peroxide.

Despite the recognized attraction of such an epoxidation procedure, little progress has been made in its fulfillment because of the extreme difficulty of setting up reaction conditions favorable to the required peracid formation from the peroxide and lower aliphatic acid, which simultaneously would not destroy the desired end product, the formed epoxy derivative. It is to be noted that the very same conditions favoring peracid formation from aliphatic acid and hydrogen peroxide, notably high molar ratios of aliphatic acid to H_2O_2 , high temperatures, high acidity, long reaction times, are known to be deleterious to the survival of any epoxy compound.

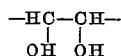
Epoxy fatty acids containing oleic acid find application as valuable intermediates in making lubricants, lubricant additives, stabilizers, plasticizers, resins, textile oils, etc.

The process described herein has the further advantage of producing as co-product only small amounts of a relatively cleavage resistant formoxy derivative.

In epoxidation reactions, therefore, the desirable end product is one containing the group:



the so-called oxirane group in preference to a hydroxylated precursor of a product of the following structure:



or a so-called glycol.

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It is an object of the present invention to provide a process for manufacturing epoxidized higher fatty acids by the employment of hydrogen peroxide and formic acid.

It is also an object of the invention to prepare such epoxidized higher fatty acids in extremely short periods of time.

It is a further object of the invention to prepare such epoxidized higher fatty acids without the necessity of employing a prepared performic acid.

It is a further object to provide a process for epoxidation wherein there is economic usage of the oxidizing agent.

It is a further object to provide a safe controllable epoxidation reaction.

In the broad aspect of the invention an ethylenic unsaturated higher fatty acid, that is to say, an acid containing from 16 to 22 carbon atoms, that is an acid obtained from a fatty oil, is reacted, at temperatures between about 50° C. and 100° C. with hydrogen peroxide and formic acid, in the presence of an organic solvent for the acid, for a period of time of from 1 hour to 5 hours.

The reaction is performed in the presence of a solvent, such as benzene, hexane, and the like, and is continued for a period of time of from about one-half hour to about 5 hours, when the epoxidation will be found to be complete.

The amount of formic acid per mole of ethylenic unsaturation should be from 0.25 mole to 1 mole. As the source of oxygen, the hydrogen peroxide should be present in approximately molar quantities for each ethylenic linkage present in the product to be epoxidized. A slight excess will generally be employed.

The following examples are given merely as illustrative of the invention and not as limitative of the conditions, as the broad ranges have been stated above.

Example 1

100 g. of a commercial fatty acid containing 90% oleic acid together with other unsaturated fatty acids (iodine number 92, equivalent to 0.362 mole of ethylenic unsaturation) were weighed into a three-neck flask equipped with a reflux condenser, thermometer and mechanical stirrer. 100 g. of hexane, and 9.15 g. of formic acid 91% (0.181 mole) were added and the mixture warmed to 60° C. Then 27.06 g. of 50% H_2O_2 (0.398 mole) were slowly added over a 40 minute period. The temperature was maintained between 60 to 65° C. for an additional 2½ hours. The reaction mixture was poured into a separatory funnel and the aqueous layer drawn off. The oil layer was washed with warm water until free of formic acid. The solvent and traces of water were removed in a vacuum stripping column at 60 to 70° C. at a pressure of 5 to 10 millimeters of mercury. The crystallized product obtained was analyzed and found to contain:

Percent oxirane oxygen	4.42 (theoretical—5.5%)
Iodine number	5.7
Acid number	183

Example 2

100 g. of a commercial soybean oil fatty acid containing about 26% oleic acid together with other unsaturated fatty acids (iodine number 120, equivalent to 0.472 mole of ethylenic unsaturation) were weighed into a three-neck flask equipped with a reflux condenser, thermometer and mechanical stirrer. 100 g. of benzene and 12.4 g. of formic acid 91% (0.245 mole) were added and the mixture warmed to between 60 to 65° C. Then 36.8 g. of 50% H_2O_2 (0.54 mole) were slowly added over 1 hour period. The temperature was then main-

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tained between 60 to 65° C. for an additional 4 hours. The reaction mixture was poured into a separatory funnel and the aqueous layer drawn off. The oil layer was washed with warm water until free of acetic acid. The solvent and traces of water were removed in a vacuum stripping column at 60 to 70° C. at a pressure of 5 to 10 millimeters of mercury. The crystallized product obtained was analyzed and found to contain:

Percent oxirane oxygen----- 4.96 (theoretical—7.04%)
 Iodine number----- 5.5
 Acid number----- 175

What is claimed is:

1. The method of epoxidizing an ethylenic unsaturated higher fatty acid containing oleic acid which comprises adding to said acid an inert organic solvent and formic acid, warming the mixture to approximately 50° C. to 80° C., then adding aqueous hydrogen peroxide and maintaining the reaction mixture at substantially 50° C. to 80° C. for not more than about 5 hours, said formic acid being present to the extent of 0.25 to 1.0 mole per mole of ethylenic unsaturation to be epoxidized, and said aqueous hydrogen peroxide being present in an amount to provide approximately 1 mole of hydrogen peroxide per mole of ethylenic unsaturation to be epoxidized.

2. The method of epoxidizing oleic acid which comprises adding to said acid an inert organic solvent and formic acid, warming the mixture to approximately 50° C. to 80° C., then adding aqueous hydrogen peroxide

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and maintaining the reaction mixture at substantially 50° C. to 80° C. for not more than about 5 hours, said formic acid being present to the extent of 0.25 to 1.0 mole per mole of ethylenic unsaturation to be epoxidized, and said aqueous hydrogen peroxide being present in an amount to provide approximately 1 mole of hydrogen peroxide per mole of ethylenic unsaturation to be epoxidized.

3. The method of epoxidizing an ethylenic unsaturated higher fatty acid containing oleic acid which comprises warming a mixture of said acid, an inert organic solvent, aqueous hydrogen peroxide and formic acid, for not more than five hours, in the temperature range substantially 50° C. to 80° C., said formic acid being present to the extent of 0.25 to 1.0 mole per mole of ethylenic unsaturation to be epoxidized, and said aqueous hydrogen peroxide being present in an amount to provide approximately one mole of hydrogen peroxide per mole of ethylenic unsaturation to be epoxidized.

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