A PROCESS FOR THE CATALYTIC EPOXIDATION OF UNSATURATED COMPOUNDS USING HYDROGEN PEROXIDE

The present invention relates to a process for the catalytic epoxidation of unsaturated nitriles or fatty acid esters in a two-phase system using hydrogen peroxide, according to the double phase technique with an organic cationium salt as a phase transfer catalyst. The reaction is performed at a pH of 2 or less in the presence of an oxidation catalyst system comprising a component containing the element tungsten and a component containing the element phosphorus.
A PROCESS FOR THE CATALYTIC EPOXIDATION OF UNSATURATED COMPOUNDS USING HYDROGEN PEROXIDE

The present invention relates to a process for the catalytic epoxidation of unsaturated nitriles or fatty acid esters in a two-phase system using hydrogen peroxide.

Epoxides are valuable intermediates in organic synthesis, and the products obtained from them can be used in a variety of applications. The epoxidised nitriles or fatty acid esters may be used as intermediates in further reactions to produce e.g. nonionic surfactants. Further, the functional groups may be transformed to other functional groups, e.g. amido groups.

A number of processes have been used to obtain epoxides. The methods all require a source of active oxygen, which could be $O_2(g)$, chlorine water or hydrogen peroxide. The use of oxygen has not been successful for the production of higher epoxides, and the use of chlorine water (the chlorohydrin process) has the disadvantage that one mole of salt is obtained per mole epoxide that is formed, and this salt must be disposed of. Hydrogen peroxide has been used both indirectly, as in processes utilising hydroperoxides or peracids, as well as such, as in the Venturello method. The use of hydroperoxides and peracids suffers from the disadvantage that alcohols and carboxylic acids respectively are formed as by-products and must be removed from the epoxides.

The Venturello method for epoxidation of olefins is described in GB-A-2055821. A two-phase technique with onium salts is used, where the organic phase contains the olefin and the aqueous phase contains the hydrogen peroxide. The organic phase may comprise only the reacting olefin, used in suitable excess, or it may comprise the reacting olefin dissolved in a suitable organic solvent. The reaction is performed in the presence of a catalytic system comprising a first catalytic component containing tungsten, molybdenum or vanadium and a second catalyst component which is a
derivative of phosphorous or arsenic. The preferred amount of catalyst is 0.005 to 0.2 moles of metal or of total metals belonging to the first catalyst component per 1 mole of hydrogen peroxide. The preferred pH-interval is 2-6.

Surprisingly it has been found that when a catalytic epoxidation of unsaturated compounds by reaction with hydrogen peroxide according to the double phase technique with an organic onium salt as a phase transfer catalyst and in the presence of an oxidation catalyst system comprising a component containing the element tungsten and a component containing the element phosphorus, as is disclosed in GB-A-2055821, is performed at a pH of 2 or less, preferably from 0.4-2, the reaction is much faster when it is performed with an unsaturated nitrile or fatty acid ester than with an olefin. Furthermore, the epoxide is still obtained in a good yield. An amount of 0.005-0.02 mole of tungsten per mole of hydrogen peroxide is sufficient to obtain a yield of epoxidised product around 80%.

For example, when oleonitrile is epoxidised at 70°C and at a pH of 1.3-1.7 according to the present invention, 0.012 mole of tungsten per mole of hydrogen peroxide was sufficient to obtain a yield of 82% within 70 minutes, whereas for 1-decene at the same temperature and at a pH of 0.4-1.8 in the presence of about the same amount of tungsten, a yield of 83% of epoxydecane was obtained within 145 minutes. Also for the epoxidation of oleic acid methyl ester using similar reaction conditions, the reaction time was shorter than for the epoxidation of 1-decene. A yield of 86.8% of epoxidised ester was obtained after 95 minutes.

When 1-decene was epoxidised at a pH of 2.5-3.5 the time was even longer to obtain the same yield. Although the amount of catalyst was higher (0.0248 mole of tungsten per mole of hydrogen peroxide), 285 minutes were required.

Further, the unsaturated nitrile or fatty acid ester does not have to be present in excess or in a solvent, which is a great advantage when it comes to working up the reaction
mixture. Accordingly, there are both environmental and economical benefits connected with this improved process.

The temperature is not critical for performing the reaction, but 50-80°C is a convenient temperature interval. The activated oxidation catalyst is formed in a first step by reaction between hydrogen peroxide, a component that contains tungsten and a component that contains phosphorus. The tungsten is preferably added as an acid or neutral compound, such as e.g. H₂WO₄, and the phosphorus is preferably added as H₃PO₄. An onium salt is added as a phase transfer catalyst. Examples of onium salts are quaternary ammonium and phosphonium salts. Most preferably a quaternary ammonium salt is used. The optimal choice of the onium salt will depend on the unsaturated reactant to be epoxidised.

When all the components of the catalyst have been mixed, the catalyst is formed by heating the mixture 15-30 minutes at 50-60°C. It is not necessary to isolate the catalyst, and the unsaturated compound to be epoxidised and the remaining hydrogen peroxide may be added directly to the catalyst. Before the addition of the major part of the hydrogen peroxide the temperature is raised to 70-80°C. The concentration of the hydrogen peroxide added is preferably not higher than 30%, most preferably around 15%, since higher concentrations cause more by-products to be formed. These lower concentrations are also preferable for safety reasons. When it comes to the less reactive unsaturated compounds, all catalyst components as well as the unsaturated starting material and all remaining hydrogen peroxide could be mixed at once at room temperature, and then heated together to the reaction temperature. It is important to follow the formation of epoxide closely, since the yield of epoxide reaches a maximum and thereafter will decline if the reaction mixture is further heated and stirred.

More specific examples of unsaturated nitriles and fatty acid esters that may be epoxidised according to this invention are oleonitrile, oleic acid methyl ester and
nitriles and esters derived from unsaturated acids such as
tall oil acid, linoleic acid, erucic acid and fish-oil acids.
The following examples are illustrative of the
present invention and should not be considered as limiting
thereof.

Comparative example 1

6.8 mmole H₂WO₄, 4.3 mmole H₃PO₄ (85%), 504 mmole
H₂O₂ (30%), 50 g deionised water, 4 mmole di(hydrogenated
tallow) dimethyl ammonium chloride (Querton 442; 75% in
isopropyl alcohol) and 500 mmole 1-decene were mixed at room
temperature. The mixture was vigorously stirred and heated.
After 40 minutes the temperature was 67°C, and the pH was
0.4. The temperature was kept between 68-78°C, and the
epoxidation was followed by a titration procedure that is
described in Analytical Chemistry 36 (1964) p667. Before each
titration the stirrer was stopped, and a sample was taken
from the organic phase. After 145 minutes total reaction time
the yield of 1,2-epoxydecane had reached 83%, and the phases
were separated. The pH had continuously changed during the
reaction from 0.4 to 1.8.

A comparative test was performed to show the effect
of pH on the reaction rate.

Comparative example 2

12.5 mmole Na₃WO₄·2H₂O, 15.4 mmole NaH₂PO₄, 50 g
deionised water, 5.0 mmole H₂SO₄ (97%), 13.0 mmole
H₃PO₄ (85%), 5.0 mmole di(hydrogenated tallow) dimethyl
ammonium chloride (Querton 442; 75% in isopropyl alcohol),
504 mmole H₂O₂ (30%) and 500 mmole 1-decene were mixed at
room temperature. The mixture was vigorously stirred and
heated. After 25 minutes the temperature was 68°C, and the pH
was 2.5. The temperature was kept between 68-75°C, and the
epoxidation was followed by the above-mentioned titration
procedure. Before each titration the stirrer was stopped, and
a sample was taken from the organic phase. After 285 minutes
total reaction time the yield of 1,2-epoxydecane had reached
82%, and the phases were separated. The pH had continuously
changed during the reaction, and at the end it was 3.5.
From these tests it is obvious that the pH of the reaction mixture is very important for the reaction rate. When the epoxidation reaction is performed at a pH between 0.4 and 1.8 the reaction rate is much higher than when the reaction is performed at a pH between 2.5-3.5, although only about half the amount of tungsten is used in the first case.

Example 1

0.68 mmoles \( \text{H}_2\text{WO}_4 \) was dissolved in 12.3 mmoles \( \text{H}_2\text{O}_2 \) (30%). The mixture was heated to 60°C and kept there for 15 minutes. After this time a yellow turbid solution had been formed, and the solution was then chilled to ca 35°C. 0.2 mmoles \( \text{H}_3\text{PO}_4 \) (40%) and 0.38 mmoles di(hydrogenated tallow) dimethyl ammonium chloride (Querton 442; 75% in isopropyl alcohol) were added, and the solution was stirred for one minute. Then 29.3 g of rapeseed fatty acid methyl ester containing 100.0 mmols of double bonds was added and the mixture was heated to 70°C. At this temperature 97.0 mmoles \( \text{H}_2\text{O}_2 \) (30%) was added dropwise during 30 minutes. The reaction was very exothermic, and the temperature was kept between 70-80°C during the addition. After the addition was complete, the reaction mixture was kept at 70°C for 65 minutes, and then the phases were separated. During the reaction, the pH varied between ca 1 at the start of the reaction to ca 2 at the end. The yield of epoxidised ester was 86.8%.

Example 2

7.76 mmols \( \text{H}_2\text{WO}_4 \) and 60.4 mmols \( \text{H}_2\text{O}_2 \) (30%) were mixed and stirred at 60°C for 15 minutes. Then 2.3 mmols \( \text{H}_3\text{PO}_4 \) (40%) and 4.0 mmols dicoco dimethyl ammonium chloride (Arquad 2C-75) were added. The solution was chilled to room temperature, and 150.4 g oleonitrile with an iodine number of 96 containing 570.6 mmols double bonds was added at that temperature. The mixture was heated to 70°C, and 582.0 mmols \( \text{H}_2\text{O}_2 \) (15%) was added dropwise with stirring during ca 30 minutes. The temperature was kept between 66-75°C during the addition. At the start of \( \text{H}_2\text{O}_2 \) addition the pH was 1.3, and when all \( \text{H}_2\text{O}_2 \) had been added the pH had risen to 1.7. After
the addition was complete, the reaction mixture was kept at 75°C for 40 minutes. The yield of epoxidised nitrile was 82%.

From these examples it is obvious that the unsaturated nitriles and fatty acid esters are epoxidised much faster than the olefin used as a comparison.
CLAIMS

1. A process for the catalytic epoxidation of unsaturated nitriles or fatty acid esters by reaction with hydrogen peroxide according to the double phase technique with an organic onium salt as a phase transfer catalyst and in the presence of an oxidation catalytic system comprising a catalyst component containing the element tungsten and a catalyst component containing the element phosphorus, characterised in that the pH in the aqueous phase is 2 or less during the epoxidation reaction.

2. A process according to claim 1, where the total amount of tungsten used in the reaction is 0.005-0.02 moles per mole of hydrogen peroxide.

3. A process according to claims 1-2, where the total amount of hydrogen peroxide added is 1-1.2 moles per mole of nitrile or fatty acid ester.

4. A process according to claims 1-3, where the unsaturated fatty acid ester is selected from the group comprising oleic acid methyl ester, and esters derived from tall oil acid, linoleic acid, erucic acid and fish-oil acids.

5. A process according to claims 1-3, where the unsaturated nitrile is selected from the group comprising oleonitrile, nitriles derived from tall oil acid, linoleic acid, erucic acid and fish-oil acids.

6. A process according to claims 1-4, where the epoxidation reaction is conducted at a temperature of 50-80°C.

7. A process according to claims 1-5, where the epoxidation reaction is conducted at a pH of 0.4-2.

8. A process according to claims 1-6, where the onium salt is a quaternary ammonium salt.

9. A process according to claims 1-6, where the activated oxidation catalyst is formed in the reactor in a first step by performing a reaction between hydrogen peroxide, a component that contains tungsten and a component that contains phosphorus, followed by the addition of the
onium salt and the unsaturated compound, and whereupon the remaining hydrogen peroxide is added.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C07D 301/12
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 0606976 A1 (BP CHEMICALS LIMITED), 20 July 1994 (20.07.94), see part. page 3, lines 21-26 and lines 41-42, example 1 and claims 9-13</td>
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Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents

**A** document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search: 9 November 2000

Date of mailing of the international search report: 16 - 11 - 2000

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