Hydroxylation of olefins.

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The file contains technical information submitted after the application was filed and not included in this specification.

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Description

This invention relates to the hydroxylation of olefins. In particular, it relates to a procedure for reacting an olefin, e.g. ethylene and propylene, with an organic hydroperoxide oxidant in the presence of a specific catalyst composition to produce the corresponding glycol.

It is well known from the technical literature including patents, that olefins can be effectively oxidized with osmium oxide compounds, particularly osmium tetroxide, to their corresponding diols when the reaction is carried out with catalytic amounts of osmium tetroxide and a stoichiometric amount of a strong co-oxidizing agent.

More specifically, Japanese Patent Application No. Sho 54—145604, published November 14, 1979, is directed to a process for hydroxylating olefins in the presence of OsO₄, a quaternary ammonium salt co-catalyst, such as tetra ethyl ammonium bromide, and a peroxide, including organo peroxides and H₂O₂ as the oxidant. Selectivities to glycol of from about 4.5 to about 66% are disclosed. It is to be noted, however, that the critical component of the co-catalyst as implied in this patent is the quaternary ammonium cation rather than the particular identity of the anion, since the anion can be any of halogen, hydroxy, nitrate, perchlorate, sulfate, methane sulfonate, trifluoromethane sulfonate, and tetra fluoro borate ions, while the cation must always be quaternary ammonium. In contrast, the present invention recognizes that it is the identity of the anion which is critical, the critical anion being a halogen.

U.S. Patent No. 4,414,385 discloses the use of hydrogen peroxide and a catalytically active oxide, such as osmium tetroxide, dissolved in an essentially anhydrous, non-alcoholic, inert, preferably organic, solvent, to convert, by oxidation, unsaturated organic compounds to useful oxygenated products such as glycols, phenols, aldehydes, ketones, quinones and organic acids. The formation of glycols is achieved by conducting the reaction at temperatures of between several degrees below 0°C and 21°C. Such low reaction temperatures drastically, and disadvantageously, reduce the reaction rate to commercially unacceptable levels. At temperatures greater than 21°C, the formation of aldehydes, ketones, and acids is favored.

U.S. Patent No. 2,773,101 discloses a method for recovering an osmium containing catalyst such as osmium tetroxide, by converting it to the non-volatile osmium dioxide form, distilling the hydroxylation product, re-oxidizing the osmium dioxide to the volatile osmium tetroxide, and then recovering the same by distillation. Suitable oxidizing agents used to oxidize olefins, and re-oxidize the osmium dioxide, include inorganic peroxides such as hydrogen peroxide, sodium peroxide, barium peroxide; organic peroxides, such as t-butyl peroxide or hydroperoxide, benzoyl peroxide; as well as other well known oxidizing agents such as oxygen, perchlorates, nitric acid, and chlorine water. As with other methods of the prior art, the above process yields undesirable by-products (see col. 1 line 55) thus reducing the selectivity of the process.

U.S. Patent No. 4,049,724 describes the preparation of glycols from alkenes and from unsaturated alcohols in an aqueous system using osmium tetroxide and specifying stable and water-soluble aliphatic hydroperoxides, such as tert-butyl hydroperoxide, while a critical pH of 8 to 12 is maintained by a suitable combination of alkaline metal buffering compounds. The preparation of propylene glycol utilizing tert-butyl hydroperoxide is exemplified in the patent at a selectivity based on the hydroperoxide of 45 percent.

See also, K. B. Sharpless in JACS, March 31, 1976, pp. 1986—7 which discloses that whereas alkaline solutions of hydrogen peroxide decomposed violently in the presence of OsO₄ solutions of t-butyl hydroperoxide in the presence of base (tetraethylammonium hydroxide gave yields superior to that obtained with sodium or potassium hydroxide) and OsO₄ were stable and provided good yields of vicinal diols from a variety of olefins.

Recently, U.S. Patent No. 4,203,926 discloses the heterogeneous catalysis of ethylene and propylene to the corresponding glycol in a process in which ethylbenzene hydroperoxide is reacted with the olefin in a two-phase liquid (organic-aqueous) reaction system in the presence of osmium tetroxide and cesium, rubidium or potassium hydroxide. This two-phase system requires organic soluble hydroperoxides and appears specific for ethylbenzene hydroperoxide.

None of the above references discloses the halogen ion containing co-catalysts of the present invention.

According to the present invention there is provided a process for hydroxylating olefins which comprises reacting at least one olefinic compound having at least one ethylenic unsaturation with water and at least one organic hydroperoxide in the presence of a catalyst composition comprising osmium tetroxide or another osmium compound which converts to osmium tetroxide under the reaction conditions, and a co-catalyst, under conditions and in a manner sufficient to convert at least one of said ethylenic unsaturation to its corresponding diol, characterised in that the co-catalyst is selected from at least one of the group consisting of alkali metal halide, alkaline earth metal halide, hydrogen halide, quaternary hydrocarbyl phosphonium halide, halogen, and transition metal halide said transition metal being selected from the group consisting of Fe, Co, Ni, Cu, V, Cr, Mn, Sc, Ti, Mo, Ru, Rh, Pd and W.

The present invention is conducted by reacting at least one olefin with water and at least one organic hydroperoxide in the presence of a specifically defined catalyst composition under conditions and in a manner sufficient to hydroxylate said olefin.
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1. Olefinic compound

The olefinic compound which can be hydroxylated in accordance with this invention possesses at least one ethylenic unsaturation and typically has from 2 to 20 carbon atoms, including mono-olefinic compounds, diolefinic or polyolefinic compounds, both conjugated and non-conjugated, substituted, (e.g., with C₆ to C₁₄ aryl) and C₁ to C₁₅ alkyl) and unsubstituted aliphatic and alicyclic olefins, hydroxy-substituted olefinic compounds, olefinically unsaturated aliphatic carboxylic acids and anhydrides, such as oleic acid, 1, 2, 3, 6-tetrahydrophthalic anhydride and the like. Illustrative olefins include ethylene, propylene, butylene, pentenes, normal hexenes, the octenes, cyclohexene butadiene, styrene, vinyl cyclohexene, and the like.

The preferred olefinic compounds for this process are the C₂ to C₄ lower olefins, i.e. ethylene, propylene and butylene or allyl alcohol, and ethylene and propylene are particularly preferred. Mixtures of any of the above noted olefinic compounds can also be employed.

2. Catalyst composition

(a) Osmium tetroxide

The catalyst, osmium tetroxide (as hereinafter defined), is used in catalytic quantities, i.e., effective to convert at least one ethylenic unsaturation to its corresponding diol. It has been found that from 0.01 to 10 millimoles (mmol) of the catalyst per 100 ml of the total reaction mixture is suitable; however, it is preferred to carry out the reaction with from 0.03 to 0.1 mmol of catalyst per 100 ml of the reaction mixture. The amount of catalyst can also be related to the amount of osmium metal that is used. Thus, from 5 to 1,000 ppm, preferably from 25 to 800 ppm osmium can be used, based on the total liquid contents of the reaction vessel. The order of addition of catalyst is not critical to obtain high selectivities to glycols, since osmium does not catalyze the decomposition of the hydroperoxide in the olefin's absence.

Osmium tetroxide is readily soluble in an organic polar solvent and can be dissolved in a said solvent for addition to the reactor.

(b) Co-catalyst

The co-catalyst which is employed in conjunction with OsO₄ contains halogen. The co-catalyst increases the rate and/or selectivity of the hydroxylation reaction and provides for the regeneration of the catalytic state of osmium. The co-catalyst is defined herein to be selected from the group consisting of alkali metal (e.g., Li, Na, K, Rb, Cs, and Fr) and alkali earth metal (e.g., Be, Mg, Ca, Sr, Ba, Ra) halides, hydrogen halides, quaternary hydrocarbyl phosphonium halides, halogens and transition metal halides and mixtures of any of the above classes of co-catalysts as well as mixtures of any co-catalysts within each class.

More specifically, representative examples of alkali and alkali earth metal halide co-catalysts (referred to herein as Group 1 co-catalysts) include lithium bromide, sodium bromide, potassium chloride, sodium iodide, potassium iodide, cesium chloride, magnesium chloride, calcium bromide, and barium fluoride and mixtures thereof.

The preferred Group 1 co-catalysts include sodium iodide, potassium iodide, and sodium bromide. Representative examples of suitable hydrogen halides (referred to herein as Group 2 co-catalysts) include hydrogen: iodide, chloride, fluoride, and bromide and mixtures thereof, preferably hydrogen iodide, and hydrogen bromide.

Representative examples of suitable quaternary hydrocarbyl phosphonium halides (referred to herein as Group 3 co-catalysts) includes those represented by the structural formula:

\[(R)₄ P⁺ X⁻\] (I)

wherein X is a halogen, i.e., F, Cl, Br or I and each R is a hydrocarbyl group independently selected from the group consisting of substituted and unsubstituted: alkyl, typically alkyl having from 1 to 30 carbons, preferably from 1 to 20 carbons, and most preferably from 1 to 10 (e.g., 1-5) carbons; aryl, preferably aryl having from 6 to 14 carbons, and most preferably from 6 to 10 carbons; aralkyl and alkaryl, typically aralkyl and alkaryl wherein the alkyl and aryl portions thereof are as defined immediately above respectively. The substituents on the hydrocarbyl group R may be one or more of hydroxy; halide; ether groups, typically groups represented by the structural formulae: \(--O–R_r, --R–O–R\) (wherein R₁ and R₂ are independently selected from alkyl, typically about C₁ to about C₁₀ alkyl, preferably C₁ to C₆ alkyl, and most preferably C₁ to C₂ alkyl); and ester groups, typically ester groups represented by the structural formulae:

\[O\] \[O\] \[O\] \[O\] \[O\]
\[\text{C–O–}R_r\] \[\text{O–C–}R_r\] \[\text{R}_2\text{O–C–}R_r\] \[\text{R}_2\text{–O–C–}R_r\] \[\text{R}_2\text{–O–C–}R_r\]

wherein R₁ and R₂ are as defined above. Preferably R is tetraalkyl or tetra aryl as defined above.
Representative examples of Group 3 co-catalysts include tetramethyl phosphonium bromide, tetrapropyl phosphonium fluoride, tetraethyl phosphonium chloride, tetradechl phosphonium iodide, tetraphenyl phosphonium chloride, dimethyl diethyl phosphonium bromide, methytriethyl phosphonium chloride, tetrabutyl phosphonium iodide, phenyltrimethyl phosphonium chloride, diphenyl diethyl phosphonium bromide, tetra 2-(methoxy) ethyl phosphonium chloride, tetra 4-(propoxy methyl) phenyl phosphonium bromide, di 3-(methoxy carbonyl) propyl-diethyl phosphonium iodide, di 4-(ethyl carbonyloxy) butyl-dimethyl phosphonium chloride, tetra 5-(ethoxy carbonyl) penty phosphonium bromide, tetra 4-hydroxy butyl phosphonium chloride, tetra 3-chloro propyl phosphonium bromide, and mixtures thereof.

Preferred Group 3 co-catalysts include: tetra alkyl and tetra aryl phosphonium halides such as tetra ethyl phosphonium chloride, and bromide.

Representative examples of halogen co-catalysts (referred to herein as Group 4 co-catalysts) include F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> preferably I<sub>2</sub>.

Transition metal halides (referred to herein as Group 5 co-catalysts) typically are salts having a cation of a transition and a halide anion.

Representative examples of such transition metals include those with the highest stable oxidation state such as Fe, Co, Ni, Cu, V, Cr, Mn, Sc, Ti, Mo, Ru, Rh, Pd, and W.

The preferred transition metals include Cu, Fe, Ni, Co, and Mn.

Representative examples of Group 5 co-catalysts include FeF<sub>2</sub>, FeCl<sub>2</sub>, FeBr<sub>2</sub>, FeF<sub>3</sub>, FeCl<sub>3</sub>, FeBr<sub>3</sub>, FeI<sub>2</sub>, FeI<sub>3</sub>, CoCl<sub>2</sub>, CoF<sub>2</sub>, CoF<sub>3</sub>, NiF<sub>2</sub>, NiF<sub>3</sub>, NiCl<sub>2</sub>, CuF<sub>2</sub>, CuF<sub>3</sub>, Cu<sub>2</sub>FeCl<sub>3</sub>, CuCl<sub>2</sub>, CuF<sub>2</sub>, V<sub>2</sub>Cl<sub>6</sub>, V<sub>2</sub>F<sub>10</sub>, V<sub>2</sub>F<sub>12</sub>, V<sub>2</sub>F<sub>14</sub>, V<sub>2</sub>Cl<sub>6</sub>, V<sub>2</sub>Br<sub>6</sub>, V<sub>2</sub>Cl<sub>6</sub>, V<sub>2</sub>F<sub>6</sub>, CrF<sub>2</sub>, CrF<sub>3</sub>, CrF<sub>5</sub>, CrF<sub>6</sub>, CrCl<sub>3</sub>, CrCl<sub>4</sub>, CrBr<sub>3</sub>, CrBr<sub>4</sub>, CrCl<sub>4</sub>, MoOCl<sub>4</sub>, MoCl<sub>5</sub>, MoF<sub>3</sub>, MoF<sub>5</sub>, MoCl<sub>3</sub>, MoCl<sub>5</sub>, MoBr<sub>3</sub>, MoBr<sub>5</sub>, MoF<sub>3</sub>, MoF<sub>5</sub>, RuF<sub>3</sub>, RuCl<sub>3</sub>, RuF<sub>3</sub>, RuCl<sub>3</sub>, RuCl<sub>5</sub>, RuBr<sub>3</sub>, RhF<sub>3</sub>, RhCl<sub>3</sub>, RhF<sub>3</sub>, RhCl<sub>3</sub>, PdF<sub>3</sub>, PdCl<sub>3</sub>, PdBr<sub>3</sub>, PdI<sub>3</sub>, WCl<sub>6</sub>, WbR<sub>3</sub>, WC<sub>6</sub>, WB<sub>6</sub>, and WI<sub>6</sub>.

'Preferred Group 5 co-catalysts include WCl<sub>6</sub>.'

It is recommended for best results that the most preferred valence of the transition metals of Group 5 co-catalysts as initially employed be that which represents the highest stable oxidation state thereof. While this is not critical, it avoids the need in some instances to oxidize the transition metal in-situ so that it can be reduced.

The co-catalyst(s) is employed in amount effective to increase the rate and/or selectivity of the hydroxylation reaction. Thus, while any effective amount of co-catalyst can be employed, such effective amounts typically will vary from 5 to 100,000 ppm, preferably from 50 to 10,000 ppm, and most preferably from 100 to 1000 ppm, by weight based on the total weight of the liquid contents of the reaction vessel.

Alternatively, the amount of co-catalyst can be expressed as a molar ratio between the molar amount of halide species in the co-catalyst to the molar amount of osmium metal in the OsO<sub>4</sub>. Accordingly, such molar ratios typically will vary from 2:1 to 100:1, preferably from 2:1 to 50:1, and most preferably from 2:1 to 25:1.

(3) Inert polar solvents

While the hydroxylation reaction can be conducted in a heterogeneous system, the preferred mode for conducting the hydroxylation reaction is in a liquid reaction mixture, preferably provided as a homogeneous or substantially homogeneous medium and preferably but optionally by using an inert, preferably polar organic solvent to dissolve where possible the catalyst composition and reactants. The solvent is entirely optional, however, and when present functions primarily to achieve even dispersal of heat in the reaction mixture. Partial immiscibility of the solvent with water is acceptable although not preferred. By inert solvent is meant one which does not undergo oxidation during the course of the reaction.

Representative inert solvents include organic polar solvents which can be an aliphatic or aromatic alcohol having from one to ten carbon atoms, an aliphatic or aromatic ketone having from three to ten carbon atoms, an aliphatic or allylic ether having from two to ten carbon atoms, a N,N-dialkyl amide having from three to ten carbon atoms, an aliphatic or aromatic sulfoxide having from two to fourteen carbon atoms and an aliphatic or aromatic sulfone having from two to fourteen carbon atoms.

Examples of suitable polar solvents include methanol, ethanol, propanol, butanol, hexanol, decanol, t-butyl alcohol, benzyl alcohol, acetone, methylthethyl ketone, methylybutyl ketone, acetonophenone, ethylene glycol, propylene glycol, diethylene glycol, tetraethylene glycol, dimethyl formamide, diethyl formamide, dimethyl acetic acid dimethyl 1,3-sulfoxide, diethyl sulfoxide, di-n butyl sulfoxide, diphenyl sulfoxide, dibenzyl sulfoxide, dimethyl sulfoxide, di-n sulfoxide dibenzyl sulfoxide, diphenyl sulfoxide, acetonitrile, pyridine, dioxane, tetrahydrofuran, tetrahydropyran dioxyone, and the like, and mixtures thereof. Preferred solvents are those which are completely miscible with water such as acetonitrile, dioxane, acetone, diethyl ether, primary alcohols such as methanol, ethanol, and isobutanol and tertiary alcohols such as tertiary butanol.

The solvent may be a hydroxylation product and the most preferred solvent(s) is the hydroxylated olefin which possesses at least one glycol functionality or mixtures of the product glycol and the product alcohol derived from the organoalkylohydroperoxide.

For example, when ethylene is hydroxylated using t-butyl hydroperoxide, the most preferred solvent is
ethylene glycol, t-butyl alcohol, or a mixture of ethylene glycol and t-butyl alcohol, the latter being formed in situ from t-butyl hydroperoxide. The former (product glycol) avoids solvent separation process steps and the latter is economical since the ethylene glycol and t-butyl alcohol are both saleable products which have to be separated anyway. In either instance, an additional solvent separation step is avoided.

The inert solvent is preferably employed in amounts sufficient to achieve a homogeneous or substantially homogeneous solution with respect to at least the olefin and catalyst composition. Typically, such amounts can vary from 0 to 98 percent, preferably from 30 to 98 percent, and most preferably from 50 to 80 percent, by weight, based on the total weight of the reaction mixture.

(4) Organic hydroperoxide
The oxidant for the hydroxylation reaction is at least one organic hydroperoxide conventionally employed for such reactions.

Conventional organo-hydroperoxides include those having the formula:

\[ R''\text{OOH} \]

wherein \( R'' \), which may be substituted or unsubstituted is: alkyl, typically \( \text{C}_1 \) to \( \text{C}_{20} \), preferably \( \text{C}_3 \) to \( \text{C}_{10} \), most preferably \( \text{C}_3 \) to \( \text{C}_6 \) alkyl; aryl, typically \( \text{C}_6 \) to \( \text{C}_{14} \), preferably \( \text{C}_8 \) to \( \text{C}_{10} \), most preferably \( \text{C}_8 \) aryl; aralkyl, wherein the aryl and alkyl groups thereof are as defined immediately above; cyclo-alkyl, typically \( \text{C}_5 \) to \( \text{C}_{20} \), preferably \( \text{C}_7 \) to \( \text{C}_{10} \), most preferably \( \text{C}_7 \) cycloalkyl; as well as oxacyclics having 1 to 5 oxygens and preferably 3 to 20 carbons, and azacyclics having 1 to 5 nitrogens and preferably 3 to 20 carbons; and wherein the substituents of said \( R'' \) group include halogen, hydroxyl, ester and other groups.

Representative examples of suitable organo-hydroperoxides include ethyl benzene hydroperoxide, t-butyl hydroperoxide, 1-alkyl hydroperoxides, cumene hydroperoxide, 2-methyl-2-hydroperoxy-methyl propionate, 2-methyl-2-hydroperoxy propanoic acid, pyrrolyl-hydroperoxide, furan hydroperoxide, 2-butylhydroperoxide, cyclohexyl hydroperoxide, 1-phenylethyl hydroperoxide and mixtures thereof.

The most preferred organo-hydroperoxides include t-butyl hydroperoxide, ethyl benzyl hydroperoxide, cumene hydroperoxide and t-amyl hydroperoxide. Frequently these hydroperoxides are made by the molecular oxygen oxidation of the corresponding hydrocarbon which also produces an alcohol as a by-product. For example, when isobutane is oxidized with molecular oxygen there is produced tertiary butyl hydroperoxide and tertiary butyl alcohol. It is not necessary to separate the alcohol from the hydroperoxide since the alcohol can function as a diluent or solvent.

The amount of organo-hydroperoxide employed for hydroxylation of the olefin can be employed, it is preferred that such effective amounts constitute a ratio of moles of ethylene unsaturation in the olefin to moles of organo-hydroperoxide of from 0.5:1 to 100:1, preferably 1:1 to 20:1 and most preferably 2:1 to 10:1. The organo-hydroperoxide is preferably employed as an aqueous solution comprising from 25 to 80%, preferably from 30 to 80%, and most preferably from 30 to 75%, by weight, hydroperoxide, based on the weight of the aqueous hydroperoxide solution, although it can be added in anhydrous form.

(5) Water
It is believed that the hydroxylation of the olefin occurs according to the following reaction (using ethylene and t-butyl hydroperoxide as illustrative reactants):

\[
\text{H}_2\text{C}==\text{CH}_2+(\text{CH}_3)_2\text{COOH}+\text{H}_2\text{O}→\text{H}_2\text{C}=\text{CH}_2+(\text{CH}_3)_2\text{COH}
\]

\[
\text{OH} \quad \text{OH}
\]

From this it is seen that the water is preferably present in at least a stoichiometric amount based on the amount of olefin ethylenic unsaturation to be hydroxylated. The source of this water may vary. Water can be added separately, preferably as the solvent for the organo-hydroperoxide. Consequently, water is preferably provided to, and/or is present in the initial reaction mixture in at least a stoichiometric molar ratio with the molar amount of ethylenic unsaturation of the olefin to be hydroxylated. Such ratios preferably also are present in the reaction mixture at any given time after start-up. According, water is typically present in the reaction mixture at molar ratios of water to olefin ethylenic unsaturation to be hydroxylated in the reaction mixture of from 1:1 to 100:1 (e.g. 1:1 to 10:1), preferably from 1:1 to 50:1 (e.g. 1:1 to 10:1), and most preferably from 1:1 to 20:1 (e.g. 1:5:1). Such molar ratios typically can be achieved by controlling the amount of water in the reaction mixture to be from 10 to 90 percent, preferably from 15 to 85 percent, and most preferably from 20 to 60 percent, by weight, based on the total weight of the reaction mixture. Preferably the amount of water employed is less than that which will cause separation of the reaction mixture into an aqueous phase and organic phase although this is not a critical condition.

(6) Reaction conditions
Since the preferred olefins to be hydroxylated, e.g., ethylene and propylene, are gases, the olefin is
incorporated into the reaction system by pressuring the reactor with olefin. Although the magnitude of the pressure is not critical, it determines the amount of the olefin that is present in the reaction liquid and therefore affects the rate of the reaction. It is believed that a pressure between 5 and 1,000 psig (0.0345 and 6.89 MPa g) is useful for ethylene, and a pressure of between 5 and 1500 psig (0.0345 and 10.34 MPa g) is useful for propylene. However it is generally suitable to operate within the pressure ranges of typically between 50 and 500 psig (0.345 and 3.45 MPa g), preferably between 50 and 200 psig (0.345 and 1.38 MPa g), (e.g. 50 to 150 psig, i.e. 0.345 to 1.034 MPa g) for ethylene, and a pressure typically between 10 and 500 psig (0.689 and 3.45 MPa g), preferably 50 and 200 psig (0.345 and 1.38 MPa g) for propylene, to provide a suitable reaction rate without requiring high pressure equipment. The reaction is preferably carried out with olefin in excess of stoichiometry (i.e., greater than 2 moles of olefinic unsaturation to be hydroxylated per mole of hydroperoxide) to substantially completely react all of the hydroperoxide in the reaction mixture, and more preferably, at least about a 25% excess of stoichiometry of the olefin. It is advantageous to carry out reaction in the liquid phase; therefore sufficient pressure is employed to maintain the reactant in the liquid phase, at least to the extent that some olefin is in the liquid phase. For liquid reactants, atmospheric pressure is suitable.

In practice, the osmium tetroxide or precursor thereof is readily charged into the reaction vessel as a solution in the polar solvent, e.g., t-butanol, along with the co-catalyst, inert polar solvent, hydroperoxide and water prior to pressuring the vessel with olefin. It is useful also to heat up the contents of the vessel prior to introduction of the olefin.

The hydroxylation reaction is carried out at a moderate temperature. At higher temperatures the reaction rate increases substantially but this can occur at a significant reduction in selectivity to the glycol. At very low temperatures, the selectivity to glycol is excellent but the reaction rate is slow. Within these constraints, it has been found that a moderate reaction temperature range of from 0 to 200°C (e.g., 25 to 200°C) is desirable, preferably from 0 to 100°C, and optimally from 25 to 100°C (e.g., 25 to 50°C).

The pH of the reaction mixture during the hydroxylation reaction while not critical preferably will not be allowed to drop below about 4; preferably not below 6. Likewise, the pH of the reaction preferably will not be allowed to exceed about 12, although the process can still be conducted at pH's as high as 14. Accordingly, the pH of the reaction mixture typically will be maintained between 4 and 12, preferably between 6 and 12, and most preferably between 7 and 12. The pH of the reaction mixture can be controlled by any suitable means such as by the use of conventional buffers or base where desired.

The hydroxylation reaction can be carried out as a batch reaction, or as a continuous reaction. In the batch reaction, all the necessary components are placed in a reaction vessel and the reaction is allowed to proceed, preferably for 1/2 to 2 hours for substantially complete reaction of the hydroperoxide. The reaction can be carried out in a continuous manner by metering the reaction components into an agitated tank reactor, or a series of tank reactors, pressurized with the olefin and removing the reaction product mixture at an appropriate rate to maintain the reactor liquid level.

The reaction product mixture including inerts and by-products (after the removal of unreacted gaseous olefin) includes the diols, e.g., ethylene or propylene glycol, the polar solvent, the alcohol decomposition residue of the hydroperoxide, an osmium compound, the co-catalyst and water but most important is preferably a single phase mixture. Recovery of the product, e.g., ethylene glycol, is easily accomplished by fractional distillation.

A particularly preferred embodiment of the process according to the invention comprises admixing to form a liquid reaction mixture, at least one olefinic compound having at least one ethylenic unsaturation, at least one organic hydroperoxide, water in at least a stoichiometric molar ratio with the moles of ethylenic unsaturation to be hydroxylated, and the catalyst composition, under conditions and in a manner sufficient to convert at least one of said ethylenic unsaturation to its corresponding diol hydroxylation product.

The following examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. All parts and percentages in the examples as well as in the remainder of the specification are by weight unless otherwise specified.

In the following examples unless otherwise specified selectivity, conversion and yield are calculated as follows:

\[
\text{% selectivity} = \frac{\text{moles of glycol}}{\text{moles of oxygenated product}} \times 100
\]

\[
\text{% conversion} = \frac{\text{moles of product}}{\text{moles of hydroperoxide charged}} \times 100
\]

\[
\% \text{ yield} = \% \text{ conversion} \times \text{selectivity}
\]

Furthermore, all product analysis is conducted by gas chromatography.
Example I

Into a 300 ml titanium autoclave is charged 0.023 g of osmium tetroxide as a 0.5 weight percent solution thereof in t-butanol, 0.50 g sodium bromide, 54.9 methanol and 11.1 g of t-butyl hydroperoxide as a 70% by weight solution thereof in water (designated herein as "70%/H_2O"). The solution is warmed to 40°C and then ethylene (200 psig 1.38 MPag) is added. After stirring for 20 minutes, the product solution is analyzed by gas chromatography and indicates the production of 2.72 g of ethylene glycol which is a 99% selectivity and 54.9% yield based on the tertiary butyl hydroperoxide charged.

Example II

Into a 300 ml titanium autoclave is charged 0.050 g of osmium tetroxide (0.5%/t-butanol solution), 1.09 g sodium bromide, 46.0 g water, and 15.1 g of tertiary butyl hydroperoxide (70%/H_2O). To this solution is added 31.0 g of propylene and the reaction mixture is stirred at 25°C for two hours. Propylene glycol (4.0 g) is produced in an amount which corresponds to a 86% selectivity and 48.0% yield.

Example III

Into a 300 ml titanium autoclave is charged 0.026 g of osmium tetroxide (0.5%/t-butanol solution), a 0.25 g sodium iodide, 66.6 g of methanol and 15.6 g of tertiary butyl hydroperoxide (70%/H_2O). The solution is warmed to 40°C with stirring and ethylene (400 psig 2.76 MPag) is added. After stirring for thirty minutes, the reaction is cooled. Ethylene glycol (3.92 g) is produced in an amount indicating a selectivity of 99% and yield of 54.5%.

Example IV

Into a 300 ml titanium autoclave is charged 0.04 g OsO_4, 7.2 g t-butyl hydroperoxide (70%/H_2O), 0.50 g sodium bromide, 42.6 g t-butanol, and 3.0 g water. The contents are warmed to 40°C and propylene (32.0 g) is added. The reaction is stirred at this temperature for thirty minutes. Propylene glycol (2.80 g) is produced in an amount corresponding to selectivity of 77% and a yield of 65.7%.

Example V

A similar run to Example IV using sodium iodide in place of sodium bromide gave comparable yield of propylene glycol.

Example VI

Into a 300 ml titanium autoclave is charged 5 g of a 0.4 weight% solution of OsO_4 in water (0.1 mmole OsO_4), 20 g t-butyl alcohol, 0.31 g WCl_6 and 5.0 g 1-octene. To the resulting reaction mixture under continuous stirring is added slowly 3.0 g of a solution of t-butyl hydroperoxide in water (70%/H_2O) over a period of 15 minutes. The temperature of the reaction mixture varies between 27 and 47°C. The reaction mixture is stirred for an additional 30 minutes at the aforementioned temperature range. The selectivity to 1, 2-octane diol is 44% and the conversion is 100%.

Claims

1. A process for hydroxylating olefins which comprises reacting at least one olefinic compound having at least one ethylenic unsaturation with water and at least one organic hydroperoxide in the presence of a catalyst composition comprising osmium tetroxide or another osmium compound which converts to osmium tetroxide under the reaction conditions, and a co-catalyst, under conditions and in a manner sufficient to convert at least one of said ethylenic unsaturation to its corresponding diole, characterised in that the co-catalyst is selected from at least one of the group consisting of alkali metal halide, alkaline earth metal halide, hydrogen halide, quaternary hydrocarbyl phosphonium halide, halogen, and transition metal halide said transition metal being selected from the group consisting of Fe, Co, Ni, Cu V, Cr, Mn, Sc, Ti, Mo, Ru, Rh, Pd and W.

2. The process according to claim 1 in which the olefinic compound has 2 to 20 carbon atoms.

3. The process according to claim 1 or 2 wherein the catalyst composition possesses a molar ratio of halide species in the co-catalyst to osmium metal in the OsO_4 or precursor thereof of from 2:1 to 100:1.

4. The process according to claim 1, 2 or 3 wherein the transition metal is selected from the group consisting of Cu, Fe, Ni, Co, and Mn.

5. The process according to claim 1, 2 or 3 wherein the co-catalyst is a quaternary hydrocarbyl phosphonium halide of the structural formula:

(R)_n P(X)^+ X^-

wherein X is Cl, F, Br or I and each R is independently selected from alkyl, aryl, aralkyl and alkyalkyl groups which may be unsubstituted or substituted with one or more substituents selected from hydroxy, halide, other groups and ester groups.

6. The process according to claim 1, 2 or 3 wherein the co-catalyst is one or more of sodium iodide,
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sodium bromide, potassium iodide, hydrogen iodide, hydrogen bromide, tetraethyl phosphonium chloride, tetraethyl phosphonium bromide and tungsten hexachloride.

7. The process according to any of the preceding claims, wherein the organic hydroperoxide is selected from the group consisting of t-butyl hydroperoxide, ethyl benzyl hydroperoxide, t-amyl hydroperoxide and cumene hydroperoxide.

8. The process according to any of the preceding claims, wherein the olefinic compound is ethylene, propylene or a mixture thereof.

9. A process according to any of the preceding claims, which comprises admixing to form a liquid reaction mixture, at least one olefinic compound having at least one ethylenic unsaturation, at least one organic hydroperoxide, water in at least a stoichiometric molar ratio with the moles of ethylenic unsaturation to be hydroxylated, and the catalyst composition, under conditions and in a manner sufficient to convert at least one of said ethylenic unsaturation to its corresponding diol hydroxylation product.

10. The process according to claim 9 wherein the liquid reaction mixture additionally comprises at least one inert organic solvent.

11. The process according to claim 10, in which the inert solvent is employed in an amount sufficient to achieve a homogeneous or substantially homogeneous solution.

12. The process according to claim 10 or 11, in which the inert solvent is present in an amount of 50 to 80 weight percent based on the total weight of the liquid reaction mixture.

13. The process according to claim 9, 10, 11 or 12 wherein the inert organic solvent is the hydroxylation product.

14. The process according to claim 9, 10, 11 or 12 wherein the inert organic solvent is a polar solvent.

15. The process according to any of the preceding claims, wherein the concentration of osmium is in the range of 5 ppm to 1000 ppm based on the total liquid contents.

16. The process according to any of the preceding claims, wherein the hydroxylation is carried out at a temperature in the range of 0°C to 200°C.

Patentansprüche

1. Verfahren zur Hydroxylierung von Olefine durch Umsetzung mindestens einer olefinischen Verbindung mit mindestens einer ethylenischen Doppelbindung mit Wasser und mindestens einem organischen Hydroperoxid in Gegenwart einer Katalysatorzusammensetzung, die Osmiumtetroxid oder eine andere Osmiumverbindung, welche unter den Reaktionsbedingungen in Osmiumtetroxid umgewandelt wird, und einen Cokatalysator enthält, unter Bedingungen und in einer Weise, die ausreicht, um mindestens eine der genannten ethylenischen Doppelbindungen in ihr entsprechendes Diol umzuwandeln, dadurch gekennzeichnet, daß der Cokatalysator ausgewählt ist aus mindestens einem aus der Gruppe bestehend aus Alkalimetallhalogenid, Erdalkalimetallhalogenid, Halogenwasserstoff, quaternäres Kohlenwasserstoffphosphoniumhalogenid, Halogen und Übergangsmetallhalogenid, wobei das Übergangsmetall ausgewählt ist aus der Gruppe bestehend aus Fe, Co, Ni, Cu, V, Cr, Mn, Sc, Ti, Mo, Ru, Rh, Pd und W.

2. Verfahren gemäß Anspruch 1, worin die olefinische Verbindung 2 bis 20 Kohlenstoffatome aufweist.

3. Verfahren gemäß Anspruch 1 oder 2, worin die Katalysatorzusammensetzung eine Molverhältnis von Halogenidart im Cokatalysator zum Osmiummetall im OsO₄ oder dessen Vorläufer von 2:1 bis 100:1 besitzt.

4. Verfahren gemäß Anspruch 1, 2 oder 3, worin das Übergangsmetall ausgewählt ist aus der Gruppe bestehend aus Cu, Fe, Ni, Co und Mn.

5. Verfahren gemäß Anspruch 1, 2 oder 3, worin der Cokatalysator ein quaternäres Kohlenwasserstoffphosphoniumhalogenid der Strukturformel:

\[(R)_lP^+X^-\]

ist, worin X Cl, F, Br oder I ist und jeder Rest R unabhängig voneinander ausgewählt ist aus Alkyl-, Aryl-, Aralkyl- und Alkarylgruppen, die nichtsubstituiert oder substituiert mit einem oder mehreren Substituenten ausgewählt aus Hydroxyl-, Halogenid-, Ethergruppen und Esterguppen sein können.

6. Verfahren gemäß Anspruch 1, 2 oder 3, worin der Cokatalysator einer oder mehrere aus Natrumiodid, Natriumbromid, Kaliumiodid, Jodwasserstoff, Bromwasserstoff, Tetraethylphosphoniumchlorid, Tetraethylphosphoniumbromid und Wolframhexachlorid ist.

7. Verfahren gemäß einem der vorstehenden Ansprüche, worin das organische Hydroperoxid ausgewählt ist aus der Gruppe bestehend aus t-Butylhydroperoxid, Ethylbenzylhydroperoxid, t-Amylhydroperoxid und Cumylhydroperoxid.

8. Verfahren gemäß einem der vorstehenden Ansprüche, worin die olefinische Verbindung Ethylen, Propylen oder ein Gemisch daraus ist.

9. Verfahren gemäß einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß man unter Bildung eines flüssigen Reaktionsgemisches mindestens eine olefinische Verbindung mit mindestens einer ethylenischen Doppelbindung, mindestens ein organisches Hydroperoxid, Wasser in einem mindestens stöchiometrischen Molverhältnis mit den Molen der zu hydroxylierenden ethylenischen Doppelbindungen
und die Katalysatorzusammensetzung unter Bedingungen und in einer Art und Weise vermischt, die ausreicht, um mindestens eine der genannten ethylenischen Doppelbindungen in ihr entsprechendes Diole als Hydroxylierungsprodukt umzuwandeln.

10. Verfahren gemäß Anspruch 9, worin das flüssige Reaktionsgemisch zusätzlich mindestens ein inertes organisches Lösungsmittel enthält.

11. Verfahren gemäß Anspruch 10, worin das inerte Lösungsmittel in einer Menge verwendet wird, die ausreicht, um eine homogene oder im wesentlichen homogene Lösung zu erhalten.


13. Verfahren gemäß Anspruch 9, 10, 11 oder 12, worin das inerte organische Lösungsmittel das Hydroxylierungsprodukt ist.

14. Verfahren gemäß Anspruch 9, 10, 11 oder 12, worin das inerte organische Lösungsmittel ein polares Lösungsmittel ist.

15. Verfahren gemäß einem der vorstehenden Ansprüche, worin die Konzentration von Osmium im Bereich von 5 ppm bis 1000 ppm, bezogen auf den gesamten flüssigen Gehalt, liegt.

16. Verfahren gemäß einem der vorstehenden Ansprüche, worin die Hydroxylierung bei einer Temperatur im Bereich von 0°C bis 200°C durchgeführt wird.

Revendications

1. Procédé d’hydroxylation d’œlèfines, qui consiste à faire réagir au moins un composé oléfinique ayant au moins une insération éthylénique avec de l’eau et au moins un hydroperoxyde organique en présence d’un catalyseur dont la composition comprend du tétraxyde d’osmium ou un autre composé d’osmium qui se transforme en tétraxyde d’osmium dans les conditions réactionnelles, et un cocatalyseur dans des conditions et d’une manière suffisantes pour convertir au moins une de la diète insération éthylénique en son diole correspondant, caractérisé en ce que le co-catalyseur ait au moins une substance choisie dans le groupe comprenant un halogénure de métal alcalin, un halogénure de métal alcalino-terreux, un halogénure d’hydrogène, un halogénure d’hydrocarborylphosphonium quaternaire, un halogène et un halogénure de métal de transition, ledit métal de transition étant choisi dans le groupe comprenant Fe, Co, Ni, Cu, V, Cr, Mn, Sc, Ti, Mo, Ru, Rh, Pd et W.

2. Procédé suivant la revendication 1, dans lequel le composé oléfinique comprend 2 à 20 atomes de carbone.

3. Procédé suivant la revendication 1 ou 2, dans lequel la composition du catalyseur a un rapport molaire de l’halogénure présent dans le co-catalyseur à l’osmium métallique présent dans OsO₄ ou son précurseur de 2:1 à 100:1.

4. Procédé suivant la revendication 1, 2, ou 3, dans lequel le métal de transition est choisi dans le groupe comprenant Cu, Fe, Ni, Co, et Mn.

5. Procédé suivant la revendication 1, 2, ou 3, dans lequel le co-catalyseur est un halogénure d’hydrocarborylphosphonium quaternaire de formule structurale:

$\text{(R)}_n\text{P}^+\text{X}^-$

6. Procédé suivant la revendication 1, 2 ou 3, dans lequel le co-catalyseur consiste en une ou plusieurs des substances telles que l’iodure de sodium, le bromure de sodium, l’iodure de potassium, l’iodure d’hydrogène, le bromure d’hydrogène, le chlorure de tétraéthylphosphonium, le bromure de tétraéthylphosphonium et l’hexachlorure de tungstène.


8. Procédé suivant l’une quelconque des revendications précédentes, suivant lequel le composé oléfinique est l’éthylène, le propylène ou leur mélange.

9. Procédé suivant l’une quelconque des revendications précédentes, qui consiste à mélanger, pour former un mélange réactionnel liquide, au moins un composé oléfinique ayant au moins une insération éthylénique, au moins un hydroperoxyde organique, de l’eau dans un rapport molaire au moins stoichiométrique avec les moles d’insération éthylénique à hydroxylie et la composition de catalyseur, dans des conditions et d’une manière suffisantes pour convertir au moins une de la diète insération éthylénique en son diole correspondant constituant le produit d’hydroxylation.

10. Procédé suivant la revendication 9, dans lequel le mélange réactionnel liquide comprend en outre au moins un solvant organique inerte.

11. Procédé suivant la revendication 10, dans lequel le solvant inerte est utilisé en une quantité suffisante pour obtenir une solution homogène ou pratiquement homogène.
12. Procédé suivant la revendication 10 ou 11, dans lequel le solvant inerte est présent en une quantité de 50 à 80% en poids sur la base du poids total du mélange réactionnel liquide.

13. Procédé suivant la revendication 9, 10, 11 ou 12, dans lequel le solvant organique inerte est le produit d’hydroxylation.

14. Procédé suivant la revendication 9, 10, 11 ou 12, dans lequel le solvant organique inerte est un solvant polaire.

15. Procédé suivant l’une quelconque des revendications précédentes, dans lequel la concentration de l’osmium se situe dans l’intervalle de 5 à 1000 ppm sur la base de la teneur totale en liquide.

16. Procédé suivant l’une quelconque des revendications précédentes, dans lequel l’hydroxylation est conduite à une température comprise dans l’intervalle de 0°C à 200°C.