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Solvent-free selective epoxidation of fatty esters over a tungsten-based catalyst

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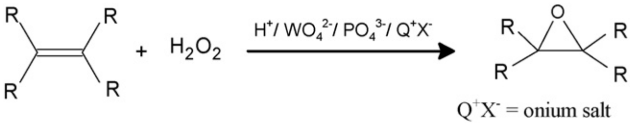
ABSTRACT

A solvent-free, rather complete and selective *cis* epoxidation of methyl oleate (MO) using a tungsten-containing catalyst called “Tetrakis”. High epoxide yields have been obtained by adjusting the reaction parameters (reaction time, temperature, gas phase, oxidant molar ratio and concentration). The highest selectivities are the result of a synergetic effect of hydrogen peroxide and air (or oxygen) used as oxidizing agents that decreases the MO dimerization and then favour the complete conversion of MO into its epoxide.

1. Introduction

In the general context of vegetable oil valorisation, fatty epoxides are an important class of chemicals that can be used as intermediates and in the near future in the manufacture of bio-fuel additives. During the last few years, H_2O_2-based catalytic epoxidation has received much attention from an economic and environmental point of view [1,2] and soluble transition metal-based catalysts have been developed for this oxidation with aqueous H_2O_2. In the literature, a first set of experiments has been done over molybdenum catalyst starting from crude or purified vegetable oils [3] and using H_2O_2 as oxidant; leading to a low yield of an epoxides mixture [3]. From pure unsaturated esters or acids, this yield has been improved when using similar catalysts but was still lower than 60% [3]. In order to increase the selectivity of the epoxide formation; the synthesis of tungsten-containing catalysts called “Tetrakis” and developed by Venturello et al. [4] has been studied. Tungsten-based catalysts including polyoxometalates (POM) show a high epoxides selectivity [5–14]. The two-component association of phosphotungstic anions, under acidic conditions, represents a valuable catalytic system for the epoxidation of these olefins with dilute hydrogen peroxide using a phase-transfer catalysis process (reaction 1) [15].



(1)

Water-soluble alkaline tungstates and phosphoric acid, preferably used in a 1/2 molar ratio, are particularly well suited for the purpose. This peroxo complex was found to be remarkably effective in stoichiometric as well as in catalytic biphasic oxidation of alkenes with H_2O_2 and was postulated to be the active oxygen transfer agent for alkene epoxidation [4].

The two-phase epoxidation of alkenes with hydrogen peroxide in the presence of $PW_{12}O_{40}{}^{3-}$ was suggested to proceed through the formation of an active peroxo POM in the aqueous phase from the interaction of the Keggin heteropolyanion with hydrogen peroxide [17]. Using the phase-transfer catalyst, Q^+ ($[(C_8H_{17})_3NCH_3]_3{}^+$), the peroxo POM is almost fully transferred into the organic phase. The reaction takes place preferentially in the organic phase via the oxygen atom transferred from the peroxo POM to the substrate [16]. Epoxidation of the pure fatty acids with the peroxophosphotungstate in a solvent (CH_2Cl_2) is possible leading to an epoxide yield of 84% [17].

The crude vegetable oils epoxidation has been rather little studied [18]. In that case, the epoxidized products could be very diversified because of the possibility of mono-, di-, or tri-epoxides according to the origin of oilseed [19]. Epoxidized crude vegetable oils such as soybean oil were produced using peracid (formic acid) formed in situ in the presence of a heavy metal complexing agent. An epoxidized oil was then obtained with oxirane number close to 6.9 and iodine number around 2.8 [19].

To resume, the olefin epoxidation requires the use of an organic solvent (often a chlorinated one) to obtain a good epoxide yield. The epoxidation of fatty esters or fatty acids also requires an organic solvent and more drastic reaction conditions, thus the epoxide yields are generally lower because there is by-products formation.

During this study, we tried to increase, in solvent free conditions, the epoxide yield starting from the fatty ester using

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a so-called “Tetrakis” phase-transfer catalyst. Complementary experiments on the epoxidation of other fatty unsaturated esters as well as crude vegetable oil are also presented.

2. Experimental

2.1. Catalyst preparation

The “Tetrakis” ($[(C_8H_{17})_3NCH_3]_3^+ [PO_4[W(O)(O_2)_2]_4]^{3-}$) catalyst was prepared according to Venturello et al. [4] and analysed by IR for the confirmation of its structure. In a typical procedure a suspension of 5 g of tungstic acid (Fluka) in 14 mL of H_2O_2 35% (w/v) (Acros Organics) was stirred and heated at 333 K until a colorless solution was obtained. After filtration and cooling the solution at room temperature; 1.24 mL of H_3PO_4 40% (w/v) (85%, w/v Prolabo) were added further diluted with 60 mL of distilled water. To the resultant solution, 4.18 g of methyltrioctylammonium chloride (Fluka) in 80 mL of dichloromethane (Carlo Erba) was added drop wise (2 min) under strong stirring. And the mixture was stirred about 15 min. After the decantation, the organic phase was dried over $MgSO_4$ (SDS) and gently evaporated on a rotary evaporator under reduce pressure at 308–313 K bath to obtain a slightly yellow syrup.

2.2. Epoxidation procedure

In a double wall reactor (with internal diameter of 16 mm) the catalyst “Tetrakis” (0.094 mmol) and MO (99% Aldrich, 3.37 mmol) were introduced under strong agitation. When a temperature of 313 K was reached, H_2O_2 35% (w/v) (330 μL) was added. After 30 min of reaction, 25 mL of water (room temperature) were added in order to stop the reaction. The organic phase was then recovered and extracted with 20 mL of ethyl acetate (99% Carlo-Erba) and dried on $MgSO_4$. After evaporation of the solvent, the MO epoxide was obtained and analysed by GC. Methyl linoleate (ML: 99%, Sigma–Aldrich), trioleic sunflower oil (TSO: Stearinnerie Dubois) and rapeseed oil (RO: Novance; 58% oleic acid, 22% linoleic acid, 9% linolenic acid, 6% palmitic acid and 5% other) were also tested under the same experimental conditions; and the molar ratio H_2O_2/unsaturations of the reactant corresponds to an equimolar ratio. The ML, TSO or RO conversion is given starting from the amount of unsaturation remaining after the epoxidation reaction (obtained by iodine value after epoxidation reaction); the yield is calculated from the oxirane oxygen number. H_2O_2 efficiencies (%) were measured in few cases as the ratio between epoxide yield and H_2O_2 conversion taking into account the H_2O_2/MO molar ratio (H_2O_2 efficiency = 100 × ([H_2O_2] × epoxide yield)/(H_2O_2 conversion × [MO])).

2.3. GC analysis

All the compounds were analysed using a Varian 3350 GC equipped with an FID detector and an on column injector. A HT5 column (25 m × 0.32 mm × 0.1 μm) from SGE was used. The injector and detector temperatures were respectively of 323 and 573 K. For analyte separation, the GC oven temperature was fixed at 343 K for 1 min, then ramped at a rate of 10 K/min to 473 K, and ramped at 25 K/min to 573 K then kept constant for 1 min. An external standard (dodecan) was used.

2.4. Oxirane oxygen analysis

The percentage of oxirane oxygen was determined by the direct AOCS Official Method Cd 9-57. This analysis measures the amount of epoxide. (0.3–0.5) ± 0.0001 g of sample was introduced into a 50-mL Erlenmeyer flask. After the dissolution of the sample in 10 mL of glacial acetic acid (99.8% for analysis Prolabo); the coated stirring bar was added with five drops of crystal violet indicator. The sample was then stirred and titrated with a 0.1N HBr solution (Prolabo) to a blue-green end point persisting for 30 s.

$$\text{Oxirane oxygen}\,(\%) = \frac{\text{mL HBr to titrate sample} \times N \times 1.60}{\text{mass of sample}\,(\text{g})}$$

where N = normality of HBr solution.

2.5. Iodine value of fats and oils by the Wijs method analysis

The iodine value of oils was determined by the ISO 3961 method which measures the amount of unsaturation for 100 g of product. The sample was placed into a 500-mL iodine flask, 20 mL of cyclohexane (Fluka) + acetic acid (glacial Acros), 1:1, v/v and 25 mL of Wijs solution (Alfa Aaeser) were added. The flasks were blocked and agitated gently, then placed at the darkness during 1 h. After this time, 20 mL of a potassium iodide solution (Prolabo) and 150 mL of distilled water were added, and titrated with 0.1 M sodium thiosulfate solution (Prolabo), gradually under a constant and vigorous shaking. The titration was continued until the yellow color has almost disappeared. 1–2 mL of starch indicator solution (soluble extra pure Merck) was added and the titration was continued until the blue color just disappears.

$$\text{Iodine value} = \frac{12.6C(\upsilon_1 - \upsilon_2)}{m}$$

where C = concentration of sodium thiosulfate solution; υ_1 = volume of sodium thiosulfate solution, mL of blank; υ_2 = volume of sodium thiosulfate solution, mL of sample; m = mass of sample, g.

2.6. Epoxide NMR analysis

^{1}H and ^{13}C NMR spectra were carried out in an apparatus Bruker Avance 300 DPX with a 300 MHz frequency for protons and 75 MHz for carbon.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.90 (m, 2H), 2.31 (t), 1.63 (m), 1.49 (m), 1.00 (t). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 57.3, 51.5, 34.1, 31.8, 29.7, 29.6, 29.2, 29.0, 27.8, 26.5, 27.9, 22.7 and 14.1.

3. Results and discussion

Several parameters were examined during this study in order to improve the yield of the epoxides formed under green conditions.

3.1. Effect of temperature

Table 1 shows that, at 313 K under air atmosphere, a maximum of epoxide selectivity is obtained. Above this temperature, the epoxide yield dramatically decreases to 75% because the reaction of methyl oleate and/or its epoxide dimmer [20] formation becomes preponderant. The stability of the epoxide with the temperature was also studied. The epoxide alone is very stable even at high temperature (353 K). If the epoxide is in the presence of H_2O_2 (35%, w/v) and without catalyst it remains very stable even

Table 1

Effect of temperature on the reactant conversion, epoxide yield and H_2O_2 efficiency

Temperature (K)	Conversion (%)	Yield (%)	H_2O_2 efficiency (%)
293	65.8	62.1	–
303	91.0	79.7	–
313	96.9	94.0	33.0
333	98.1	77.2	–

Air (batch); H_2O_2/MO molar ratio 3/1, 30 min.

Table 2
Effect of time on the reactant conversion, epoxide yield and H_2O_2 efficiency

Time (h)	Conversion (%)	Yield (%)	H_2O_2 efficiency (%)
0.5	96.9	94.0	33.0
1	98.3	81.4	27.1
2	99.2	65.2	21.7

Air (batch), 313 K, H_2O_2/MO molar ratio 3/1.

Table 3
Effect of the concentration of the H_2O_2 on the methyl oleate epoxidation under air gas phase (batch) at 313 K, H_2O_2/MO (3/1), 30 min

H_2O_2 concentration, w/v (%)	Conversion (%)	Yield (%)	H_2O_2 efficiency (%)
20	58.9	50.2	–
35	96.9	94.0	33.0
50	99.4	81.0	–

at 333 K. In the same way, the epoxide is stable in the presence of the Tetrakis catalyst at 333 K without H_2O_2. On the contrary, if the epoxide is in contact with H_2O_2 (35%, w/v) and the catalyst, even at low temperature (313 K), a high reduction of the amount of epoxide is observed; it is thus degraded or oligomerizated. We can suppose that H_2O_2 dissociates more quickly with the increase of the temperature which leads to less H_2O_2 efficiency. We also observed 33% of H_2O_2 efficiency at 313 K which corresponds to the H_2O_2 needed to epoxidize all the unsaturations (H_2O_2/MO molar ratio 3/1).

3.2. Effect of reaction time

Table 2 shows that by increasing the reaction time, the epoxide yield decreases from 94% to 65.2% whereas the conversion of the reaction slightly increases until 99.2%. This reaction time effect was studied in air atmosphere (no flow) with a H_2O_2/MO molar ratio of 3. When increasing the reaction time from 0.5 to 2 h the decrease of the epoxidation yield is probably due to the epoxide degradation with the excess of H_2O_2 (epoxide oligomerization) [20].

3.3. Effect of the oxidant molar ratio

The effect of H_2O_2/MO molar ratio [(0.5/1) to (3/1)] was studied under air atmosphere (no flow) at 313 K. We observed (Fig. 1) that by increasing the H_2O_2/MO molar ratio, the conversion and the epoxide yield are also increased. A maximum is obtained using a molar ratio H_2O_2/MO of 3 giving a conversion and a yield of respectively, 96.9% and 94%.

3.4. Effect of the oxidant concentration

The effect of the H_2O_2 concentration was studied (Table 3). The best results were obtained using a H_2O_2 concentration of 35%, w/v. It is noticed that if the concentration of the hydrogen peroxide is higher than 35%, w/v, a reduction of the epoxide yield is observed. It seems that, with the increase of the oxidant concentration, there is a superoxygenation which induces the formation of by-products such as diols or cleavage products (methyl azelaidate and pelargonic acid detected by GC but not quantified) due to a stronger oxidation of the substrate. For a concentration lower than 35%, w/v, a decrease of the epoxide yield is also observed. Indeed, the reduction of the oxidizing agent concentration as well as the molar ratio lower than 3, leads to an increase in the MO dimerization.

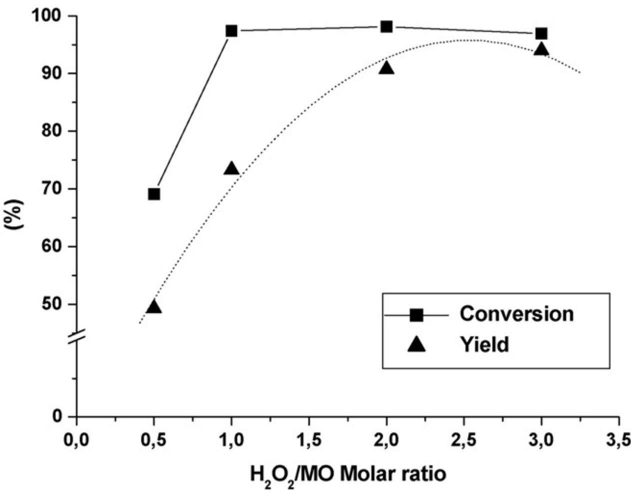

Fig. 1. Effect of H_2O_2/MO molar ratio on the reactant conversion and epoxide yield under air gas phase (batch) at 313 K, 30 min.

3.5. Effect of the reaction atmosphere

The nature of the reaction atmosphere was also studied using different carrier gases (Table 4). By replacing the air atmosphere (no flow), by an air flow bubbling in the reaction media, the epoxide yield is strongly increased from 73.3% to 97.1% with an equimolar ratio of the reactants instead of a molar ratio of 3; and a H_2O_2 efficiency equal to 100%. Moreover, we evidenced a synergetic effect when using both air and hydrogen peroxide, since after the replacement of air by nitrogen, a drastic decrease of the epoxide yield from 97.1% to 67.9% is obtained. If the reaction is carried out under O_2 flow, the results are similar to those obtained with an air flow. These results confirm the importance of the presence of O_2 in the epoxidation reaction atmosphere. In the presence of an oxygen flow, the catalyst is always saturated in oxygen; therefore the epoxidation reaction is faster than the MO dimerization reaction.

Thanks to an O_2 flow, 100% of epoxide yield is obtained while having decreased the amount of oxidant; we are thus under greener conditions. Nevertheless the use of an O_2 flow cannot replace the use of H_2O_2 as oxidant. Indeed, if the reaction is carried out without H_2O_2, no conversion is obtained.

We suggest that the presence of O_2 in the flow leads to a slower decomposition of H_2O_2 because the H_2O_2 decomposition equilibrium is modified. So, all the hydrogen peroxide is used for the epoxidation and the side dimerization reaction cannot occur.

3.6. Extrapolation to more complex substrates

After the optimisation of the reaction parameters, we extended our procedure to others fats compounds such as the methyl linoleate (C18:2), the trioleic sunflower oil, and the rapeseed oil (Table 5). Using the ML we found a very high conversion and yield

Table 4
Effect of gas phase on the reactant conversion, epoxide yield and H_2O_2 efficiency under the following conditions: H_2O_2/MO (1/1), 313 K, 30 min

Conditions	Conversion (%)	Yield (%)	H_2O_2 efficiency (%)
N_2 200 mL/min	83.0	67.9	70.1
Air (no flow)	97.4	73.3	77.2
Air 200 mL/min	97.8	97.1	100
O_2 50 mL/min	99.1	97.5 (100[a])	100

[a] Results obtained by ^1H NMR and ^{13}C NMR.

Table 5
Epoxidation of some fatty esters and crude vegetable oils, 313 K, 30 min, O_2 50 mL/min

Substrate	Conversion (%)	Epoxide selectivity (%)
Methyl linoleate (ML)	91	75
Trioleic sunflower oil (TSO)	80	100
Rapeseed oil (RO)	75	75

in ML epoxide. Moreover, the oxirane oxygen analysis shows that the two unsaturations of the ML are epoxidized. The more the starting product has a complex composition, the more it is difficult to epoxidize its unsaturations. Nevertheless when crude vegetable oil is used (rapeseed oil: RO) the yield into epoxide is very high whereas the operating conditions are the same ones as those used for the MO. 56% of yield is obtained while the reaction lasts only 30 min at 313 K using an equimolar ratio of oxidant compared to the number of unsaturations. The decrease of the epoxide yield of the rapeseed raw oil is also due to the presence of impurities.

4. Conclusion

The use of the ‘‘Tetrakis’’ phosphotungstate catalyst leads to a rather complete and selective transformation of *cis* MO into *cis* epoxide under greener conditions than what was obtained in previous studies because it is performed with a stoichiometric amount of hydrogen peroxide, without solvent and at a lower temperature leading to a maximal H_2O_2 efficiency. Such a high yield is the result of a synergetic effect of hydrogen peroxide and air (or oxygen) used as oxidizing agents at a rather low temperature (313 K). This really high yield is also probably due to the low MO dimerization under these conditions because of the catalyst saturation by oxygen and also because of the modification of the H_2O_2 decomposition equilibrium. Finally this epoxidation method can be extended to other unsaturated fatty compounds and crude vegetable oils.

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