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Selective epoxidation of unsaturated fatty esters over peroxophosphotungstic catalysts (POW) under solvent free conditions: Study of the POW catalyst's mechanism

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ABSTRACT

Methyl oleate epoxidation with a peroxophosphotungstate (POW) catalyst was performed under solvent free conditions. After underlying a synergistic effect of hydrogen peroxide and the dioxygen flow to obtain a total epoxide yield, new investigations were realized to understand this effect. The POW catalyst mechanism was studied using labeled oxygen flow and radical traps. We concluded that the reaction occurs in two parallel ways, a major one thanks to a concerted mechanism and a minor radicalar one leading to the formation of methyl stearate alcohol and diol intermediates. Oxygen flow is only necessary to perform the radicalar way.

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1. Introduction

Due to the increase of the greenhouse effect and the reduction of the petroleum oil resources, renewable oils and fats of vegetable origin is an important issue in chemistry since a shift from petrochemical feedstocks to renewable resources can contribute to a sustainable development. Vegetable oils such as rapeseed or sunflower oils are agroresources that can produce various compounds by hydrolysis, methanolysis, ... To extend the large scale potential of agroresources, new and green transformation of fatty acids must be developed. Numerous studies were focused on the carboxylic function transformation but it is also interesting to develop green process for the functionalization of the fatty alkyl chain and particularly the unsaturated function. Oleic acid is a mono unsaturated fatty acid which can be produced from a hybrid sunflower called "oleic sunflower" giving between 80 and 95% of oleic acid, is one of the most abundant one [1].

In this general context, we have focused our study on the synthesis of fatty epoxides from methyl oleate (MO) which are an important building block compound [2]. Indeed, MO epoxide is an intermediate of the polymers chemistry (such as the class of polyurethanes, polycyanates), in the lubricants and detergents synthesis, and in the formulation of biofuels [3] (as an additive for low temperature uses). On the other hand, the MO epoxide is more stable than the unsaturated fatty methyl starting ester.

Industrially the epoxidation of fatty esters uses a mixture of formic acid/hydrogen peroxide or peracids [4]. This process induces the formation of various by-products, and solvents elimination is needed. That is expensive and there are explosion risks.

The direct epoxidation of unsaturated fatty compounds by H_2O_2 as oxidant was investigated since H_2O_2 is a good candidate to develop a green process. It is cheap, readily available and transformed into water as the only by-product. Moreover, that is easy to eliminate by decantation because of the biphasic system. During the last decade, many different catalytic systems for the epoxidation using hydrogen peroxide have been studied [5–7]. Catalysts based on titanium [8], manganese [9], tungsten [10] and rhenium [11] have been described.

A peroxophosphotungstate (POW) based catalyst was successfully developed by Venturello and D'Aloisio [12] to perform epoxidation reaction in a biphasic media containing an organic solvent. Because many side reactions occur (hydrogen transfer, double bond shift, cis–trans isomerization, branching), a complex product mixture could be obtained. During the epoxidation of FAMEs, oligomerization by-products [13] can be formed; the main products are dimers, trimers, and isostearic acid (Scheme 1). Residual tungstic acid coming from the POW catalyst could also lead to another by-product formation, the 9,10-dihydroxystearic methyl ester as previously described by Santacesaria et al. [14].

During a first set of experiments [15], reaction parameters of the methyl oleate epoxidation reaction with a peroxophospho-



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Scheme 1. Main by-products formed during the oligomerization of FAMEs.

tungstate catalyst, hydrogen peroxide as oxidant and under solvent free condition were studied. After 0.5 h of reaction time, at 313 K and with a molar ratio MO/H_2O_2 (1/3), 97.4% of MO conversion and 73.3% of epoxide yield were obtained. To keep this yield while decreasing the amount of the oxidant (hydrogen peroxide) to an equimolar ratio MO/H_2O_2 , the reaction was performed with a gas flow.

The nature of the reaction atmosphere was then studied using different carrier gases (Table 1) with an equimolar ratio of the reactants. By replacing the air atmosphere (no flow), by an air flow bubbling in the reaction media, the epoxide yield was strongly increased from 71.4% to 95.0%. Moreover, we evidenced a synergistic effect when using both air and hydrogen peroxide, since after the replacement of air by nitrogen, a drastic decrease of the epoxide yield from 95% to 56% was obtained. If the reaction was carried out under an O₂ flow, 100% of epoxide selectivity was obtained with an equimolar amount of oxidant under greener conditions. These results confirmed the importance of the presence of O₂ in the epoxidation reaction atmosphere. Nevertheless, the use of an O₂ flow cannot replace the use of H₂O₂ as oxidant. Indeed, if the reaction was carried out without H₂O₂, no conversion was obtained.

Noyori et al. [16] proposed a concerted mechanism, based on a labeled H_2O_2 study, to explain this catalyst working but Noyori did not study the influence of oxygen flow on the epoxidation reaction.

The present study is then dedicated to the understanding of the O_2 flow effect as well as the proposal of a reaction mechanism

Table 1

Effect of atmosphere gas phase on the reaction conversion and selectivity under the following conditions: $H_2O_2/MO(1/1)$, 313 K, 30 min.

Conditions	MO conversion (%)	MO epoxide selectivity (%)
N ₂ (200 ml/min)	83.0	81.8
Air (no flow)	97.4	75.3
Air (200 ml/min)	97.8	99.3
O ₂ (50 ml/min)	99.1	98.4

using the homogeneous POW catalyst under the above-mentioned reaction conditions.

2. Experimental

2.1. Preparation of the catalyst

peroxophosphotungstate catalyst $([(C_8H_{17})_3NCH_3]_3)$ The $[PO_4[W(O)(O_2)_2]_4])$ was prepared according to Venturello and D'Aloisio [12] and analyzed 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 H₂O₂ 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 H₃PO₄ 40% (w/v) (85%, v/v Prolabo) were added and this solution was diluted with 60 ml of distilled water. To the resultant solution, 4.18g of methyltrioctylammonium chloride (Fluka) in 80 ml of dichoromethane (Carlo-Erba) was added dropwise (2 min) under strong stirring. Then the mixture was stirred about 15 min. After decantation, the organic phase was dried over MgSO₄ (SDS) and gently evaporated on a rotary evaporator under reduced pressure at 308–313 K to obtain slightly yellow syrup.

The ruthenium catalyst was prepared following the incipient wetness impregnation. This method consists in blending the support with a volume of ruthenium chloride (RuCl₃) solution corresponding to volume pore of the support. The concentration of the solution is adjusted for obtaining the desired amount of ruthenium (5 wt%) in the final catalyst. After the impregnation, the catalyst is dried at 423 K under nitrogen.

2.2. Catalytic test

In a double-walled reactor (with internal diameter of 16 mm) the peroxophosphotungstate catalyst syrup was exactly weighted directly into the reactor (0.094 mmol), then the methyl oleate (MO) (99% Aldrich, 3.37 mmol) was added under strong stirring. When a temperature of 313 K was reached, H_2O_2 35% (w/v) (330 µl) were

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 MgSO₄. After evaporation of the solvent, the products were obtained and analyzed by GC.

Catalytic test in the presence of labeled ¹⁸O₂ molecule was carried out using a recycle closed system coupled to a mass spectrometer via a calibrated leak valve. This system was elsewhere detailed for oxygen mobility measurement on oxides [17]. The double-walled reactor described above was adapted to the system to perform the epoxidation reaction following the same protocol but replacing air by ¹⁸O₂/N₂ atmosphere. Total volume of the system was around 150 cm³ and recycle ¹⁸O₂/N₂ flow rate was 170 cm³ s⁻¹. All the volume was purged with nitrogen before introducing labeled oxygen in order to prevent the presence of ¹⁶O₂ in the gas phase. The variation of oxygen isotopomer partial pressures ¹⁸O₂ (*m*/*z* = 36), ¹⁸O¹⁶O (*m*/*z* = 34) and ¹⁶O₂ (*m*/*z* = 32) as well as N₂ (*m*/*z* = 28) were monitored every 40 s.

The experiments done in the presence of radical scavengers (0.2 mmol) were done under the same experimental conditions.

2.3. Analysis

2.3.1. GC analysis

All the compounds were analyzed using a Varian 3350 GC equipped with an FID detector and an on-column injector. An HT5 column ($25 \text{ m} \times 0.32 \text{ mm} \times 0.1 \mu \text{m}$) from SGE was used. The injector and detector temperatures were respectively of 323 and 573 K. The carrier gas was nitrogen. 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.

Before analysis, in a pillbox weight 0.1 g of the mixture product, 0.05 g of the external standard (dodecane) and 800 μ l of solvent (ethyl acetate) were added. After stirring, the sample was injected into GC (0.1 μ l).

The methyl oleate conversion is expressed as follows at *t* time:

Conversion (%) =
$$\frac{(S_{\text{oleate}}^{i}/S_{\text{dod}}^{i}) - (S_{\text{oleate}}^{t}/S_{\text{dod}}^{t})}{(S_{\text{oleate}}^{i}/S_{\text{dod}}^{i})} \times 100$$

where S_{oleate}^{i} : surface of the methyl oleate chromatographic peak at time zero; S_{dod}^{i} : surface of the dodecane chromatographic peak at time zero; S_{oleate}^{i} : surface of the methyl oleate chromatographic peak at time t; S_{dod}^{t} : surface of the dodecane chromatographic peak at time t.

The epoxide yield is expressed as follows at t time:

Yield (%) =
$$\frac{(S_{epox}^{t}/S_{dod}^{t}) \times K_{oleate}}{(S_{oleate}^{i}/S_{dod}^{i}) \times K_{epox}} \times 100$$

where S_{epox}^t : surface of the epoxide chromatographic peak at time t; S_{dod}^t : surface of the dodecane chromatographic peak at time t; S_{oleate}^i : surface of the methyl oleate chromatographic peak at time zero; S_{dod}^i : surface of the dodecane chromatographic peak at time zero; K_{oleate} : relative response factor of the MO compared with dodecane; K_{epox} : relative response of the epoxide compared with dodecane.

The epoxide selectivity is expressed as follows:

Selectivity (%) =
$$\frac{\text{yield (\%)}}{\text{conversion (\%)}} \times 100$$

The carbon balance is calculated from the initial mole of reactants from GC analysis. All the yields were determined thanks to calibrated GC peaks area.



Fig. 1. The MO conversion and its epoxide yield at short reaction time (O_2 , 313 K, H_2O_2/MO (1/1)).

2.3.2. LC analysis

All the fatty compounds were analyzed using a Waters HPLC 600 Controller equipped with a Waters UV 486 Tunable Absorbance Detector and a Waters 600 Pump. The column was a Nucleosil C₁₈ (250 mm × 4.6 mm × 5 μ m) from Supelco and an autosampler Waters 717 plus was used. The analyses were done at room temperature and the solvent was methanol (Aldrich HPLC grade) with a flow of 1 ml/min. The wavelength used to detect the fatty compounds was 205 nm.

3. Results and discussion

In a first time a mechanistic study was performed by analysis of the reaction media at short reaction time under O_2 flow to determine what are the primary and secondary products. After, to evaluate the effect of oxygen on the reaction and particularly its influence on radical mechanism, some radical scavengers were added at the beginning of the reaction. Finally, labeled ¹⁸O₂ was used to determine how the oxygen flow is involved in the epoxidation reaction.

3.1. Study of the MO conversion and selectivity at short reaction time

The epoxidation reaction was performed under O_2 flow at lower reaction time to prove that the maximum of MO epoxide selectivity is obtained at 0.5 h of reaction time and to determine the catalyst activity at the early stage of the reaction.

First of all, we can observe in Fig. 1 that the peroxophosphotungstate catalyst is very effective in the very first minutes of the reaction. Indeed, it can be underlined that after only 5 min of reaction; the conversion of the MO determined by GC analysis is already of 32% and the epoxide yield of 13%. Furthermore, between 5 and 10 min of reaction time, the MO conversion is multiplied by 3 from 32% to 87%. At 10 min of reaction time the MO conversion is very high (87%) but the MO epoxide yield is only 53%; so the carbon balance is uncompleted. Nevertheless, after 30 min of reaction time, the conversion of the MO reaches 99% and the MO epoxide yield reaches 99%. Only the peaks of MO and MO epoxide are identified by GC analysis and it is impossible, using this technique, to determine the by-products of the MO conversion that would complete the carbon balance.

In order to determine the presence of GC undetected intermediate products, all the mixture samples were analyzed by HPLC with a C_{18} Nucleosil column (Fig. 2).

After 5 min of reaction, the LC analysis shows the main presence of MO and the presence of MO epoxide. Two other products



Fig. 2. The MO epoxidation between 5 and 25 min of reaction time. HPLC analysis of the mixtures.

at 4.18 and 4.50 min (retention time) were identified by LCMS (not shown) as the mono and diol of the MO, respectively methyl-10hydroxyoctadecanoate and methyl-9,10-dihydroxyoctadecanoate. The two others peaks at 1.61 and 1.91 min of retention time were attributed by LC to the organic cation of the homogeneous POW catalyst; as confirmed by the HPLC analysis of the catalyst alone.



Fig. 3. Variation of the MO, MO epoxide and MO diols amounts (HPLC analysis).

Fig. 3 shows the variation of the amount (based on peaks area) of the MO, MO epoxide and MO diols during the epoxidation reaction from the HPLC analysis presented previously in Fig. 2.

At 10 and 15 min of reaction time, the two relative amounts of the mono and diol of the MO decreases while the MO epoxide relative amount increases. At 20 min of reaction time, there is still rise of the MO epoxide relative amount and a decrease of the MO amount. The mono and diol of MO have disappeared. Finally at 25 min of reaction, MO is nearly fully converted into MO epoxide.

Finally, when the reaction time increases, it seems that first, mono and diol of MO are formed, but these products decrease leading to an increase of the MO epoxide (Figs. 1 and 3). These data seem indicate that MO mono and diols are reaction intermediates under our reaction conditions. The diol is then transformed into epoxide by dehydration because of the reaction media acidity (pH 1); it was indeed confirmed from the pure diol which was fully transformed into epoxide under our reaction conditions. The intermediate alcohol is also dehydrated to go back to the MO (Scheme 2). However this observation is not in agreement with the catalytic mechanism demonstrated by Noyori et al. [16], but this work concerned the epoxide formation of less lipophilic molecules by a concerted mechanism, in that case no alcohols were detected.

The formation of these intermediates could come from a radicalar decomposition of H_2O_2 or from the reaction of MO with tungstic acid as described by Santacesaria et al. [14] but under other reaction conditions (70 °C, H_2O_2 excess, 6 h of reaction time). We verified this last possibility, but under our reaction conditions, no



Scheme 2. Reaction scheme proposal for the epoxidation of FAMEs by H₂O₂ with POW catalyst.

diol formation was observed using tungstic acid as catalyst.

3.2. Reaction in the presence of radical scavengers

To know if the epoxidation reaction with a peroxophosphotungstate catalyst and hydrogen peroxide is occurring through a radical mechanism, the reaction was performed in the presence of radical scavengers (0.2 mmol). If the catalyst mechanism involves a radical mechanism in the presence of O_2 , the use of a radical trap during the catalytic test, could prevent the MO epoxide formation. The different traps used were histidine, BHT (2,6-di-ter-butyl-4methylphenol), and ascorbic acid. The histidine is a radical trap for 1O_2 radicals; the BHT is a hydrogen donor and a radical trap for 1O_2 and 3O_2 radicals and a trap of all sorts of radicals. Fig. 4 shows the results of MO epoxidation in the presence of each kind of radical traps.

The addition of the histidine during the MO epoxidation does not prevent the MO epoxide formation. This catalytic test proves that the epoxidation reaction thanks to a peroxophosphotungstate catalyst does not involve ¹O₂ radicals. The same reaction in the presence of BHT and ascorbic acid does not prevent the formation of MO epoxide. Therefore, the epoxidation reaction does not involve hydrogen donor and all sorts of radicals.

We can think that the epoxidation reaction with peroxophosphotungstate and hydrogen peroxide as oxidant does not involve a radical mechanism, as Noyori et al. [16] already explained.

However, we can mention that the use of these traps slows down the reaction as the MO is not completely converted after 30 min of reaction time.

When the MO epoxidation was performed with ascorbic acid as radical trap (Fig. 4), no mono and diols of the MO were obtained at short reaction time (10 min). In fact, it seems that there is a radical initiation for the alcohols formation and that two parallels mechanisms during the epoxidation reaction occurs (Scheme 2); one minor one that involve a radicalar formation of mono and diols, and a major one that follow a concerted mechanism as described by Noyori et al. [16].

The radicalar formation of mono and diols only occurs under O_2 or air flow while no alcohols were detected under a N_2 flow (not shown) meaning that the radicalar mechanism pathway does not occur under N_2 . This is the reason why the reaction is slow down under a nitrogen flow. So O_2 only increase the reaction rate.



Fig. 4. MO epoxidation reactions in the presence of various radical scavengers (a, BHT; b, ascorbic acid; c, histidine: 0.5 h of reaction time; d, ascorbic acid: 10 min of reaction time).



Fig. 5. Evolution of the gas phase during the MO epoxidation reaction in the presence of H_2O_2 , POW and 50 mbar of $^{18}O_2$ in N_2 .

3.3. Effect of O_2 by using ${}^{18}O_2$

Taking into account the results presented previously with the effect of an O₂ flow, the epoxidation reaction was performed with labeled oxygen to understand the role of O₂ flow on the reaction mechanism. By using ${}^{18}O_2/N_2$ flow in the catalytic test and analyzing the products by GC-MS, it could be possible to discriminate the origin of the oxygen of the epoxide formed. A consumption of ${}^{18}O_2$ from the gas phase could have two reasons: (i) a consumption due to the epoxidation reaction. In that case, the presence of ¹⁸O must be found in the oxirane cycle of the epoxide molecule which could be determined by GC/MS. (ii) A consumption due to the exchange between oxygen from the gas phase and oxygenated molecules of the reactants or the catalyst (POW, H₂O₂, MO for instance). In that last case the disappearance of ¹⁸O₂ should match with appearance of ¹⁸O¹⁶O and/or ¹⁶O₂ partial pressures in the gas phase. To check this hypothesis, evolution of all the oxygen isotopomers were collected on-line.

Fig. 5 shows the gas composition during the MO epoxidation in the presence of H_2O_2 , POW as catalyst and under ${}^{18}O_2/N_2$ recycling flow. After 30 min of reaction MO was totally converted whereas ${}^{18}O_2$ partial pressure was kept constant and thus no other isotopomer of oxygen appeared in the gas phase. To confirm the reliability of this technique, a ruthenium-based catalyst was tested. This catalyst is known to be active for the epoxidation reaction by using only O_2 as oxidizing agent [18].

Using a ruthenium on silica-based catalyst (5 wt% Ru) prepared from a classical incipient wetness impregnation method, a consumption of ¹⁸O₂ was observed (Fig. 6). No other isotopomer of oxygen were observed during the reaction showing the absence of exchange phenomenon. The total pressure in the mass spectrometer being maintained constant, the disappearance of ¹⁸O₂ only involved an increase of the N₂ pressure. Then, the resulting products of these two reactions were analyzed by GC–MS.

Fig. 7 shows the GC–MS analysis of the epoxidation reaction performed with the POW catalyst. As it was shown in Fig. 1, during this epoxidation reaction, no ¹⁸O₂ consumption is observed. The GC–MS analysis of the product shows that the MO epoxide is obtained with two characteristic radical ions at m/z = 155 and at m/z = 199 corresponding to a ¹⁶O epoxide (Fig. 7).

The epoxidation reaction performed with Ruthenium catalyst was also analyzed by GC–MS (Fig. 8). During this reaction, a consumption of labeled oxygen isotope 18 was observed as previously shown (Fig. 6). Fig. 8 shows that the GC–MS analysis corresponds to the MO epoxide is obtained but all the characteristic radical ions have the value of the standard MO epoxide + 2. In fact the molecu-



Fig. 6. Evolution of the gas phase during the MO epoxidation reaction in the presence of a ruthenium based catalyst and 500 mbar of $^{18}O_2$ in N₂.



Fig. 7. GC–MS analysis of the MO epoxide obtained with the POW catalyst under a $^{18}\mathrm{O}_2$ flow.

lar ion is at m/z = 157 instead of 155 corresponding to the presence of labeled oxygen isotope. The same observation is done for the second characteristic radical ion at m/z = 201 (199+2).

In the case of the POW catalyst, no labeled oxygen is consumed during the epoxidation reaction, but as it was previously shown, the epoxidation reacted total yield thanks to an O_2 flow. So, if under an O_2 flow no epoxide were formed, but the MO epoxidation was still performed, what is the role of oxygen?



Fig. 8. GC–MS analysis of the MO epoxide obtained with the ruthenium based catalyst under a $^{18}O_2$ flow.

The most probable answer is that O_2 initiate the radicalar decomposition of H_2O_2 leading to the formation of MO mono and diols; this additional parallel reaction pathway leading to an acceleration of the all epoxidation process.

The reuse of the catalyst is still a problem while its separation from the reaction media is not possible without degradation. To solve this problem, we studied the heterogeneisation of the active species; which will be the object of future publications.

4. Conclusion

We studied the influence of an oxygen flow on the reactivity of a peroxophosphotungstate catalyst for the epoxidation of methyl oleate (MO) with hydrogen peroxide. Thanks to labeled oxygen experiments, we proved that the oxygen atoms coming from the gas phase were not directly involved in the epoxide formation. We also detected some new intermediates during this reaction; the mono and the diol of MO are formed at the early stage of the reaction by a radicalar mechanism. This mechanism is the minor way of a parallel epoxidation mechanism which also involve a major concerted mechanism way. The reaction is faster under O₂ or air flow because the radicalar mechanism does not occur under a nitrogen flow, and the influence of O₂ on the reaction kinetic is due to its participation in the radicalar transformation of methyl oleate into its epoxide by way of the formation of the MO mono and diol intermediates.

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