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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.

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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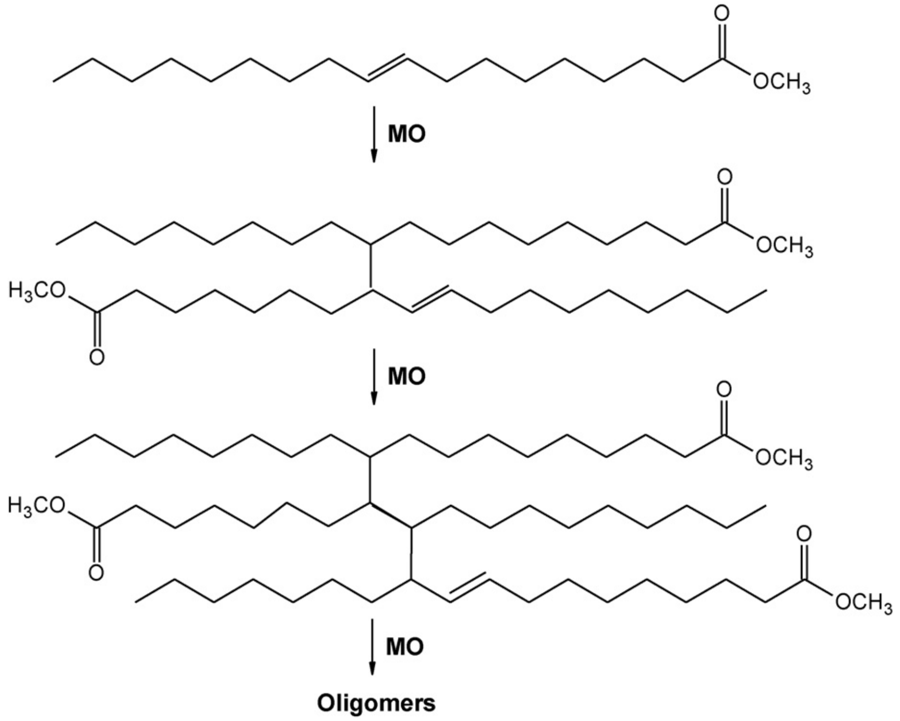

Scheme 1. Main by-products formed during the oligomerization of FAMEs.

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 O_2 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 O_2 in the epoxidation reaction atmosphere. Nevertheless, the use of an O_2 flow cannot replace the use of H_2O_2 as oxidant. Indeed, if the reaction was carried out without H_2O_2, 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 using the homogeneous POW catalyst under the above-mentioned reaction conditions.

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

2. Experimental

2.1. Preparation of the catalyst

The peroxophosphotungstate catalyst ($[(C_8H_{17})_3NCH_3]_3[PO_4[W(O)(O_2)_2]_4]$) 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 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%, v/v Prolabo) were added and this solution was diluted with 60 ml of distilled water. To the resultant solution, 4.18 g 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 $MgSO_4$ (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 ($RuCl_3$) 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