Selective and solvent free epoxidation of unsaturated fatty esters over oxoperoxophosphotungstic catalysts

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Introduction

Fatty epoxides are an important class of chemicals used i) as intermediates and ii) in the near future, in the manufacture of bio-fuels additives. Such compounds were generally obtained from epoxidation of fatty esters with H_2O_2 in the presence of a sacrificial aldehyde. Among all the studies reported in the literature, a first set of experiments was done with H_2O_2 over molybdenum catalyst, starting from crude or purified vegetable oils [1]. A low yield of a mixture of epoxides was generally obtained [1]. From pure unsaturated esters or acids, this yield was improved when using similar catalysts but was lower than 60% [1]. In order to increase the selectivity and the yield to epoxides, the synthesis of new tungsten containing catalysts called "Tetrakis" was done [2]. Then we studied the catalytic properties of those compounds as homogeneous catalysts and after their grafting over a support. We present in this paper the first results of our study devoted to the methyl oleate (MO) epoxidation. The extrapolation of our results over pure or crude vegetable oils is also studied.

Figure 1. Reaction of methyl oleate epoxidation

H_2O_2-based catalytic epoxidation is of great advantage because i) it generates H_2O as by-product, and ii) is rather inexpensive and safer compared to organic peroxides and peracids generally used in the industry.

Materials and Methods

The "Tetrakis" catalyst (oxoperoxotungsto methyltrioctylammonium phosphate) is prepared from the addition of a phosphotungstate solution to a methyltrioctylammonium chloride solution [2]. The epoxidation reaction is carried out at 313 K in a batch reactor with hydrogen peroxide 35%w/v, without solvent and at atmospheric pressure.

Results and Discussion

Table 1 shows that under these experimental conditions MO is selectively transformed into the Cis epoxide with a yield above 90%, which is higher than the previous result [3]. In this case an excess of H_2O_2 is necessary to get a high epoxide yield. If, instead of being under atmospheric pressure, an air or O_2 flow passed through the MO (not shown), the epoxide yield is strongly increased (95% for air and 99% for O_2) with a molar ratio H_2O_2/MO (1/1). Moreover we are demonstrating a synergetic effect when using both air and hydrogen peroxide, since a drastic decrease of the epoxide yield (95% to 56%) was observed after replacing air with nitrogen.

Table 1. Effect of H_2O_2 concentration and molar ratio (versus MO) on the epoxidation of methyl oleate

H_2O_2 concentration (Molar ratio)	Atmosphere	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)
35% w/v (3/1)	air	40	0.5	97	91
35% w/v (1/1)	nitrogen	40	0.5	83	56
35% w/v (1/1)	air	40	0.5	97	71
60% w/v (1/0.74) [3]	air	60	0.83	95	84

This air or O_2 flow doesn't directly participate in the transformation of MO into its epoxide. We proved, thanks to experiments using a $^{18}O_2$ flow, that O_2 is not consumed during the reaction, while H_2O_2 is completely consumed to quantitatively epoxidize the MO. We suppose that the air or O_2 flow plays a role on the H_2O_2 decomposition equilibrium, so that this decomposition is slow down under these conditions.

This catalyst is also efficient for the transformation of methyl linoleate and vegetable oils (Table 2) under the same reaction conditions.

Table 2. Epoxidation of some fatty esters and crude vegetable oils

Substrate	Conversion (%)	Epoxide yield (%)
Methyl linoleate (ML)	91	68
Trioleic sunflower oil (TSO)	80	80
Rapeseed oil (RO)	75	56

Significance

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. It is performed with a stoechiometric 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 modification of the H_2O_2 decomposition equilibrium. Finally, this epoxidation method can be extended to other unsaturated fatty compounds and crude vegetable oils.

References

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