

Limonene Epoxidation Studies in Order to Obtain Natural Monomers

Bonon, Anderson J.^{1*}; Mandelli, Dalmo²; Shul'pin, Georgiy B.³; Maciel, Rubens¹.

¹School of Chemical Engineering, State University of Campinas, Brazil; ²Human and Natural Sciences Center, Federal University of ABC, Brazil; ³Semenov Institute of Chemical Physics, Russian Academy of Sciences, Russia.

Statement of Purpose: Epoxides are key raw materials for a wide variety of chemicals and polymers. The simplest oxirane, ethylene oxide, is obtained by the vapor-phase oxidation of ethylene with air, using a supported silver catalyst. Unfortunately, this method isn't applicable to olefins with allylic C-H bonds, due to the oxidation of this position, giving several different oxidation products. The epoxidation of olefins with peracids is still the most widely used method for the epoxide obtention, leading a production of large amounts of carboxylic acids as by-products¹. Terpenes are found in several Brazilian plants and their epoxides are used as starting materials for the synthesis of flavors, fragrances and bio-polymers such as polylimonene epoxide carbonate². This work propose the studies of (*R*)-Limonene epoxidation with H₂O₂ in friendly conditions, 25 °C and atmospheric pressure, with methyltrioxorhenium (MTO, CH₃ReO₃)^{3,4}, in order to evaluate kinetic parameters and the initial concentration influence of substrate, catalyst and oxidant in the yield, conversion, selectivity and dependence of initial oxygenate accumulation rate (W₀).

Methods: The epoxidation reactions were carried out in air in thermostatic vessels under vigorous stirring. Typically, the reaction started by the addition of an aliquot of catalyst solution in to the mixture containing (*R*)-Limonene, H₂O₂ 70 %_(aq), Pyridine, CH₂Cl₂ (2 mL) and butoxi-butane (1.2 mmol, internal standard). The mixture was kept at 25°C under magnetic stirring for 1 h. Aliquots were taken, and the reaction was quenched by adding MnO₂ to decompose the remaining H₂O₂. The suspension was then filtered in 0.45 μm

HPLC filter and samples were analyzed by GC/MS and the quantified by GC-FID with calibration curves.

An experimental design 2⁴⁺¹ was realized.

Results: The main products found in the reactions (fig.1) were *cis* & *trans* internal epoxides (2), *cis* & *trans* external epoxides (3), and the diepoxides (4), in some reactions it was found traces of carvone and *cis*-carveol.

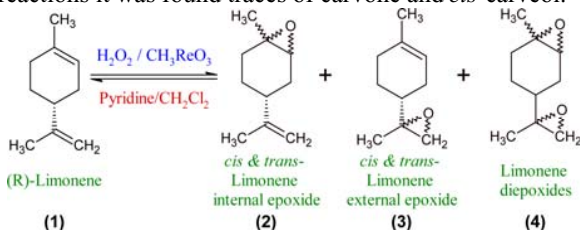


Figure 1. Limonene epoxidation and its main products.

The figure 2 shows the result where the yield reaches 96.9 % in 30 min, with 81.0 % of selectivity in respect to internal epoxides, and 1701 turnover number.

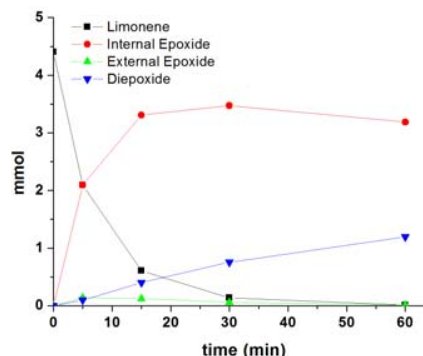


Figure 2: Epoxidation of limonene (4.4 mmol) with H₂O₂ (8.0 mmol), pyridine (0.64 mmol) and CH₃ReO₃ (0.0025 mmol).

Decreasing the amount of pyridine and increasing the reaction time it's possible to control the system in order to obtain large amount of limonene's diepoxides (fig.3).

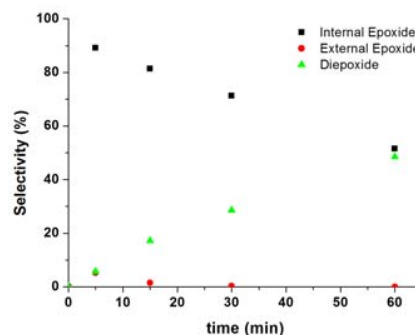


Figure 3: Epoxidation of limonene (4.3 mmol) with H₂O₂ (7.8 mmol), pyridine (0.3 mmol) and CH₃ReO₃ (0.025 mmol).

Conclusions: CH₃ReO₃/H₂O₂ is an active catalytic system for the epoxidation of terpenes. The activity and selectivity of this system can be increased by the addition of pyridine, an efficient co-catalyst.

References: ¹(A. J. Bonon, D. Mandelli, O. A. Kholdeeva, M. V. Barmatova, Y. N. Kozlov, G. B. Shul'pin, *Appl. Catal. A: General*. **2009**; 365:96–104.); ²(C.M. Byrne, S. D. Allen, E. B. Lobkovsky, G. W. Coates. *J. Am. Chem. Soc.* **2004**; 126(37):11404–11405). ³(Yan N. Xiao C. Kou Y. *Coord. Chem. Rev.*, **2010**; 254:1179–1218.); ⁴(A. Stamatidis, D. Giasafaki, K. C. Christoforidis, Y. Deligiannakis, M. Louloudi., *J. Mol. Catal. A: Chem.* **2010**; 319:58-65.); ⁴(R. Saladino, R. Bernini, V. Neri, C. Crestini. *Appl. Catal. A: General*. **2009**; 360:171–176.).