

N°215 / OC

TOPIC(s) : Clean reactions / Homogenous, heterogenous and biocatalysis

## Epoxidation of Limonene

## AUTHORS

Serge KALIAGUINE / UNIVERSITÉ LAVAL, PAVILLON A-POULIOT, QUÉBEC

## PURPOSE OF THE ABSTRACT

1,2-limonene oxide and limonene dioxide are key intermediates for the production of bio-based polymers such as epoxy resins, polycarbonates and isocyanate free polyurethanes (NIPU). First, the epoxidation of limonene was performed in the presence low-coordination titanium supported on 3D pore structure SBA-16 as the catalyst, using tert-bulyl hydroperoxide (TBHP) as the oxidizing agent in anhydrous conditions. Reaction operating parameters including temperature, TBHP/limonene molar ratio, solvent polarity and Ti/Si ratio were examined. The reaction should be carried out at 75°C in acetonitrile using a TBHP/limonene molar ratio of 11/6 for 24 h. Under these conditions, the conversion of limonene reached 80% with a selectivity of 80% 1,2-limonene oxide and 20% of 8,9-limonene oxide. No oxidation products such as carvone or carveol were observed in the reaction products. A comparison between the 3D cage structure of SBA-16 with 2D pore structure of SBA-15 was performed under the same conditions. SBA-16 favoured the mass transfer of the reactants and products yielding 65% of 1,2-limonene compared to only 27% when SBA-15 was used as the support under the same conditions. Ti/Si atomic ratio was varied and no difference in the catalytic activity was observed over the range 5 to 13.4 %. Repeated catalytic tests were performed and showed no change in activity after 3 cycles. This low coordination titanium supported on SBA-16 was however inefficient for the double epoxidation of limonene. When 1,2-limonene oxide was used as reactant, the yield of limonene dioxide was only 13% under the same conditions. A different relatively green approach was then considered to achieve the double epoxidation of limonene, DMDO using in-situ generated by the reaction of oxone (KSHO<sub>5</sub>) with acetone at room temperature in semi-batch conditions in the presence of NaHCO<sub>3</sub> as the buffer. The reaction conditions such as oxone/limonene molar ratio and the flowrate of the aqueous oxone solution were optimized. The double epoxidation of limonene using in-situ generated DMDO should be carried out with a flowrate of 1 mL min<sup>-1</sup> of 0.52 M aqueous oxone solution with a molar ratio of KHSO<sub>5</sub>/limonene of 2.6. The obtained yield reached 97% of limonene dioxide after 1.5 h of reaction time. However, the multiphasic character of using in-situ generated DMDO in semi-batch conditions requires strong agitation in order to favour the mass transfer of the oxidizing agent from the aqueous to organic phase. The epoxidation reaction was therefore studied under ultrasounds in order to enhance the mass transfer of DMDO and increase the reaction rate. The reaction conditions such as the flowrate and the ratio oxone/limonene were also optimized. The reaction should be carried out at a flowrate of 20 mL min<sup>-1</sup> of aqueous oxone solution with a stoichiometric excess 2.6. The obtained yield of limonene dioxide under ultrasounds was 100% in only 4.5 min at room temperature. In comparison, when conventional agitation using a magnetic stirrer was used, the required time to reach a 97% yield of limonene dioxide was 1.5 h. Based on the obtained results for the double epoxidation of limonene, other terpenes such as the two isomers of pinene, farnesol, carveol and carvone were also epoxidized in order to generalize the oxidation technique.  $\alpha$ - and  $\beta$ -pinene were completely converted yielding to 100% of pinene oxides after 4 min of reaction time. Farnesol, a triene, was also completely converted to farnesol trioxide after 8 min of reaction time. Carveol was completely converted yielding to 95% of carveol dioxide. Traces of the two monoepoxides and carvone were observed in the reaction medium. The epoxidation of carvone has resulted in 100% conversion, yielding only the 7,8-carvone epoxide.

## FIGURES

FIGURE 1

FIGURE 2

---

### KEYWORDS

Epoxidation processes | terpenes | limonene diepoxide

---

### BIBLIOGRAPHY