Modelling citronellal cyclization in $Cu_3(BTC)_2$

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Recently, a new class of porous hybrid solids was discovered [1]. These highly tunable materials, known as metal-organic frameworks (MOFs), consist of both inorganic and organic moieties. They offer the high tunability of organic polymers, combined with porosity higher than aluminosilicate zeolites. Certain MOFs exhibit a very interesting adsorption and even catalytic behavior [2]. Within this study, we will focus on the easily synthesized and commercially available Lewis-acid $Cu_3(BTC)_2$ MOF: Cu connected with 1,3,5-benzenetricarboxylate linkers. The cyclization of citronellal [3], already tested experimentally on Cu_3BTC_2 [4] has been studied. The desired cyclization product is isopulegol (Figure 1), which can be hydrogenated to menthol, an organic compound often used in pharmaceuticals, cosmetics, food etc. Industrially, this cyclization reaction is performed with homogeneous $ZnBr_2$ catalyst. However, heterogeneous catalysts are more attractive since they offer easy separation and reuse of the catalyst.

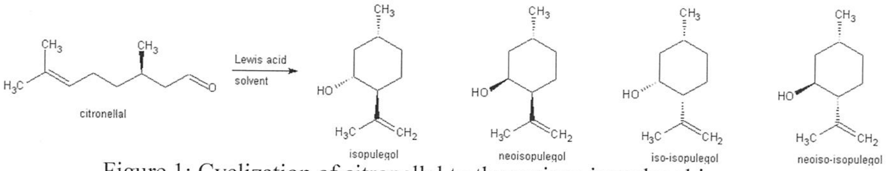

Figure 1: Cyclization of citronellal to the various isopulegol isomers.

This selectivity towards isopulegol can be increased by a Brønsted acid treatment of Cu_3BTC_2. The fact that this Brønsted acid has itself a lower selectivity towards isopulegol suggests a dual site catalytic mechanism operative at the modified active sites and offers a excellent opportunity to verify this by molecular modeling. Possible reaction routes leading to the various isopulegol isomers are studied from theoretical viewpoint on $Cu_3(BTC)_2$ and modified versions of this MOF. The theoretically obtained selectivities on small Cu-paddlewheels could already validate these promising experimental trends.

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