How does alkene epoxidation with TBHP occur in MIL-47?

Matthias Vandichel,[a] *Karen Leus*,[b] *Ilke Muylaert*, [b] *Pascal Van Der Voort*,[b] *Michel Waroquier*,[a] *Veronique Van Speybroeck*,[a]

[a] *Center for Molecular Modeling, Ghent, Belgium*

[b] *Department of Inorganic and Physical Chemistry, Centre for Ordered Materials, Organometallics and Catalysis, Ghent, Belgium*

Matthias.Vandichel@Ugent.be

Introduction

Nowadays, the amount of catalytic applications for MOFs is expanding rapidly [1-3]. However, the catalytic reaction mechanisms in Metal Organic Frameworks and in particular at saturated coordinated centers are still poorly understood.

In a previous study by Leus et al. [4], we studied the catalytic potential of a coordinative saturated V-MOF; V-MIL-47 [5], for the liquid phase oxidation of cyclohexene with tert-butyl hydroperoxide (TBHP). The catalyst is believed to act partly heterogeneous, which can be seen from XRF and hot filtration experiments [4]. Apart from cyclohexene oxide (**1**), the product spectrum (Figure 1) also consist out of the consecutive formed cyclohexane-1,2-diol (**2**) and (radical) side products as tert-butyl-2-cyclohexenyl-1-peroxide (**3**) tert-butyl-2-cyclohexenyl-1-peroxide and cyclohexen-2-one (**4**).

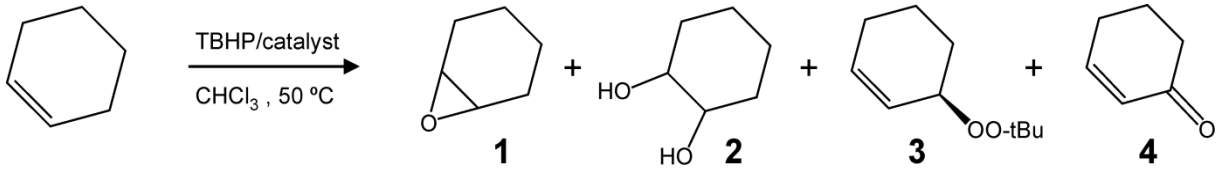

Figure 1: Products formed during the catalytic conversion of cyclohexene with the TBHP/MIL-47 system [4]

The conversion patterns of MIL-47 and the homogeneous catalyst $VO(acac)_2$ are very similar. Theoretical modeling on the latter more simple system brought us insight into the possible epoxidation mechanisms of MIL-47: successful epoxidation is accompanied by a ligand/linker exchange with TBHP [4]. Strikingly, this MIL-47

contains vanadium in a completely saturated form, while $VO(acac)_2$ only exhibits reactivity when an acetylacetone linker is exchanged with TBHP. This means, that for MIL-47, a similar mobility of two terephtalic ligands is required to explain a possible heterogeneous epoxidation route; which leads to an active V^{+IV} species (**Fig. 3-A**). For the activity of alkylperoxo-monovanadium-complexes, which can be considered as leached species from the MIL-47 catalyst, work is in progress [6]. A geometrical comparison between of the $VO(acac)_2$ and MIL-47 is shown in **Figure 2**.

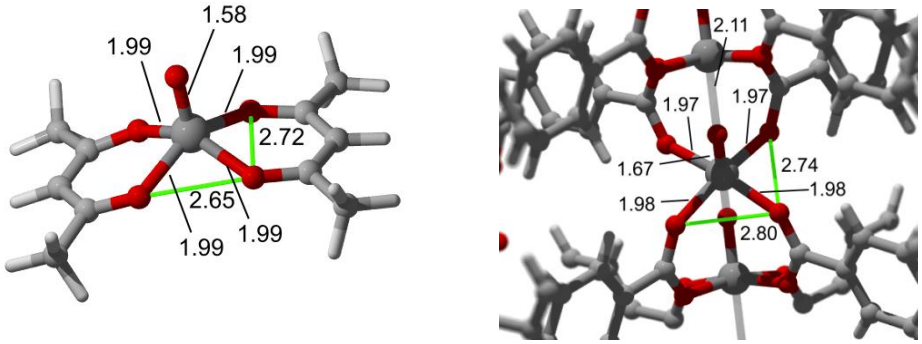

Figure 2: Comparison of distances (in Å) for $VO(acac)_2$ and MIL-47.

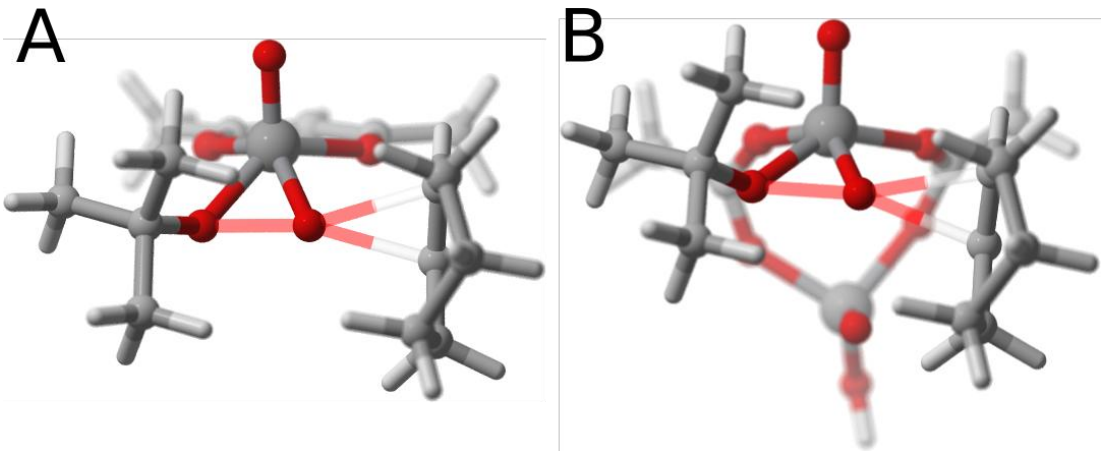

Figure 3: Investigated models for epoxidation, transition states of (A) VOacac-(OOtBu) and (B) MIL-47small-(OOtBu).

Methodology

Geometry optimizations were first performed with the Gaussian03 [7] package using the B3LYP hybrid functional [8-9]. The double-zeta Pople basis set 6–31+G(d) was used for all the atoms except vanadium, for which the LANL2DZ effective core potential was applied [10]. Even though this methodology was used for the calculation of the frequencies, the energies were refined by single point energy

calculations at the b3lyp/6-311+g(3df,2p) level of theory. This type of procedure is common when dealing with transition metal catalysis [11-13].

Results and conclusions

The epoxidation of cyclohexene has been investigated for various model systems, able to represent MIL-47. **Fig. 3** shows two transition states of them: the VO(acac)(OOtBu) system, for which we proposed an initial cycle [4] (**Fig. 4**) and a cluster model resembling MIL-47, denoted as MIL-47small-(OOtBu). The complexes are first activated with TBHP (A in **Fig. 4**), to form the active alkylperoxo species [14-15] after which epoxidation can occur, followed by cyclohexene oxide production (**Fig. 3**).

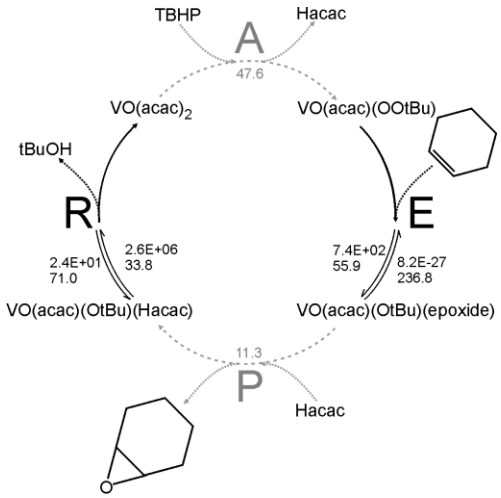

Figure 4: An $VO(acac)_2$ epoxidation cycle. The complex is first activated (A) after which epoxidation (E) can occur, followed by cyclohexene oxide production (P). The complex can be regenerated (R). A and P represent equilibrium steps (gray, reaction energies (below) are shown in kJ/mol). E and R are modeled as unimolecular reactions (black, reaction barriers are shown in kJ/mol while reaction rates at 323 K (above) are shown in 1/s). The used level of theory is described in the methodology section.

Table 1 gives us an overview of the bimolecular kinetic parameters for model systems A and B (**Fig. 3**). All parameters are very similar, however, model system B has slightly more favorable kinetic parameters. Other extended models will be discussed more in detail in our future work.

Table 1: Bimolecular kinetic data for the epoxidation reaction at 323 K.

Model system	$k_{EPOXIDATION}$ (m^3 mol^{-1} s^{-1})	A (m^3 mol^{-1} s^{-1})	E_a (kJ/mol)
A	$6.81\ 10^{-7}$	$4.49\ 10^{3}$	60.67
B	$1.24\ 10^{-5}$	$1.33\ 10^{4}$	55.78

In conclusion, theoretical calculations on two model systems reveal that successful epoxidation is accompanied by a linker exchange with TBHP. A similar mobility of the terephthalic linkers is required to explain the catalytic activity of MIL-47(V^{+IV}).

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