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Tridentate ONS vs ONO salicylideneamino(thio)phenolato [MoO₂L] complexes for catalytic solvent-free epoxidation with aqueous TBHP.

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Abstract

Comparison of molybdenum precatalysts with salicylideneaminothiophenolato (SATP; a tridentate ONS ligand) and salicylideneaminophenolato (SAP; a tridentate ONO ligand) in the solvent-free epoxidation of cyclooctene with aqueous TBHP yields better activity for the former. The DFT study of the catalytic cycle shows that the SATP catalyst follows the same pathway recently established for the SAP analogue and with a slightly smaller activation barrier in agreement with the experimental results.

1. Introduction

Within the quest of green chemistry, the implementation of solvent-free processes is one of the best options, especially with respect to the E-factor [1]. In addition, the elimination of solvents is a safety issue when these are potentially toxic (such as for instance the chlorinated solvents often used in academic research for epoxidation). Epoxides are interesting chemical intermediates, used extensively in fine chemistry through ring-opening and as precursors to different polymers [2, 3]. Epoxides are classically obtained using organic oxidants (m-CPBA, $\text{CH}_3\text{CO}_3\text{H}$, PhIO), needing the use of organic solvents (often chlorinated) or ionic liquids, but transition metal catalyzed epoxidation offers the possibility to use greener oxidants such as THBP, H_2O_2 , or even O_2 . Although being by-products of the reaction, tBuOH and water can be recycled, tBuOH being in addition useful for the synthesis of the gasoline additive MTBE [4].

Among the metals used for epoxidation catalysis, molybdenum is the most used both in academic research [5] and in industry [6]. In this area, we have shown catalytic efficiency of different types of molybdenum [7-9] and vanadium [10] complexes as well as polyoxometalates [11] for the epoxidation of cyclooctene and bio-sourced substrates [12], using aqueous TBHP as oxidant and no added organic solvent. Molybdenum(VI) complexes with the salicylideneaminophenolato (SAP) Schiff base ligand (a tridentate ONO ligand) were tested in organic solvents [13] and without solvent [9, 12]. The combination of the SAP ligand and molybdenum(VI) yielded reaction efficiency and catalyst stability. We were intrigued by the availability of an open coordination site in the 5-coordinate $[\text{MoO}_2(\text{SAP})]$, which is easily generated by dissociation of a weakly coordinating ligand (L) such as an alcohol from the 6-coordinate $[\text{MoO}_2(\text{SAP})(\text{L})]$ pre-catalyst, whereas most other active catalysts do not have the same possibility. Concerning the tridentate ONS donor set, only few contributions have dealt with their use in molybdenum catalyzed epoxidation [7, 14, 15] but only one of them, to the best of our knowledge, has used solvent-free conditions. The exception consists of a pyridoxal thiosemicarbazonato ligand having a different scaffold from SAP and a direct comparison of performance between the two systems is not possible [7]. The present article compares the SAP system with its sulfur analogue, the

salicylideneaminothiophenolato (SATP) ligand, revealing that the latter is much more active, and analyzes the possible reasons for this difference.

2. Experimental

Details on the starting materials and the characterization techniques can be found in the supporting information.

2.1. Synthesis of $[MoO_2(SATP)]_2$

In a 100 mL Erlenmeyer flask, salicylaldehyde (0.50 g, 4.09 mmol) was dissolved in 50 mL of methanol and 2-aminothiophenol (0.50 g, 4.03 mmol) was added. After magnetic stirring for 0.5 h at room temperature, $[MoO_2(acac)_2]$ (1.34 g, 4.11 mmol) was added. The resulting mixture was further stirred for 4 h at room temperature. The resulting brown precipitate was separated by filtration, washed with CH_2Cl_2 and dried under reduced pressure for 24 h (Yield: 0.76 g, 53.3 %). TGA $\Delta m = \exp(\text{theo})$ 58.5 (59.5). IR (KBr, $\nu(\text{cm}^{-1})$) 781 (Mo-O-Mo), 920 (Mo=O), 1602 (C=N). 1H NMR (DMSO- d_6 , $\delta(\text{ppm})$): 6.89-7.81 (m, 7 H, Ar-H), 9.06 (s, 1 H, CH=N). ^{13}C NMR (300 MHz, DMSO- d_6): 163.0 (C_H-N), 161.3 (C_q-O), 148.1 (C_q-S), 138.6 (C_H-N), 137.0 (C_H-Ar), 136.8 (C_H-Ar), 129.8 (C_H-Ar), 129.1 (C_H-Ar), 125.8 (C_H-Ar), 123.1 (C_q), 120.9 (C_H-Ar), 119.6 (C_H-Ar), 119.1 (C_H-Ar).

2.2 Catalytic Procedures.

Routine experiments. CAUTION: a mixture of TBHP with organic compounds (especially without a solvent) is potentially explosive. In a typical experiment, cyclooctene (1 equiv) and the catalyst (x equiv, see tables) were mixed together and stirred in air in a round bottom flask. Acetophenone was added as internal standard. The reaction temperature (see tables) was regulated and then wet THBP (70% in water, y equiv, see tables) was added to the mixture, starting the reaction. Both $[MoO_2(SAP)]_2$ and $[MoO_2(SATP)]_2$ are slightly soluble at room temperature but appear to completely dissolve after addition of TBHP at the reaction temperature. The color indicates that both complexes are confined in the organic phase, whereas the water phase is colorless or only slightly colored. Samples of the organic phase were periodically withdrawn. The reaction was quenched by addition of MnO_2 , followed by

the addition of diethylether and removal of the manganese oxide and residual water by filtration through silica before GC analysis.

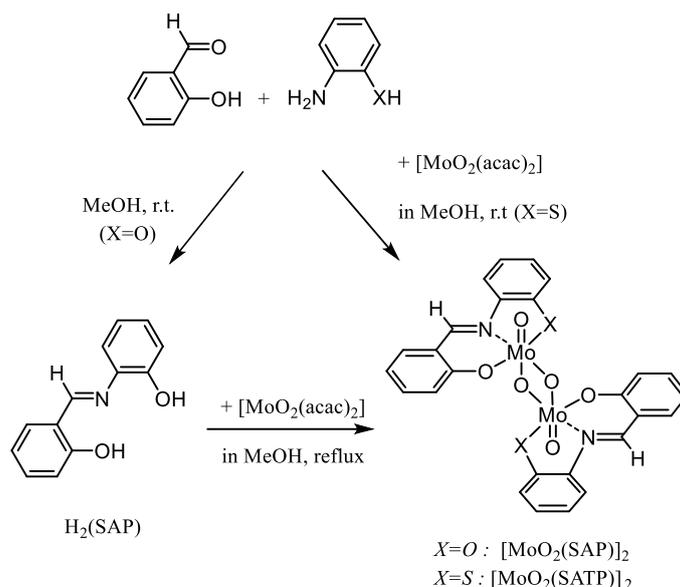
Water effect. The effect of water was tested using the same experimental conditions as the routine experiments, plus additional water was added to the reaction mixture, changing the water/TBHP ratio.

Computational Details.

The geometries of all species were optimized without any symmetry constraint with the Gaussian 09 program suite [16]. The input geometries were adapted from the X-ray structures of $[\text{MoO}_2(\text{SAP})(\text{EtOH})]$ [17], replacing one oxygen atom by a sulfur atom. The standard B3LYP three-parameter functional was used in conjunction with the 6-31G** basis set for C, H, N, O and S atoms and with the CEP-31G* basis set for molybdenum. The transition states were optimized using a preliminary scan of a relevant internal coordinate, followed by full optimization of the TS guided by knowledge of such coordinate. All optimized geometries were confirmed to be local minima (for stable molecules or reaction intermediates) or first order saddle points (for the TS's) by frequency analyses. For the TS's, analysis of the imaginary frequency confirmed the expected motion along the reaction coordinate. The calculated frequencies were also used to derive the thermochemical parameters at 298 K according to the standard ideal gas approximation.

3. Results and Discussion

The molybdenum complex of the ONO tridentate ligand SAP, $[\text{MoO}_2(\text{SAP})]_2$, has been reported previously [9, 12, 18]. The corresponding ONS ligand [19] has also been previously used to synthesize various complexes of Ti, Mn, Tc, Re, Co, Ni, Cu, Zn, [19, 20] and also a molybdenum complex $[\text{MoO}_2(\text{SATP})(\text{L})]$ (L = substituted imidazole) [21]. A ligand-free $[\text{MoO}_2(\text{SATP})]_2$ derivative, however, has apparently not yet been described. Because of the air sensitivity of the H_2SATP ligand [20], the complex was obtained in a one-pot process from salicylaldehyde, 2-aminothiophenol and the freshly prepared molybdenum precursor $[\text{MoO}_2(\text{acac})_2]$ in methanol at room temperature (Scheme 1).



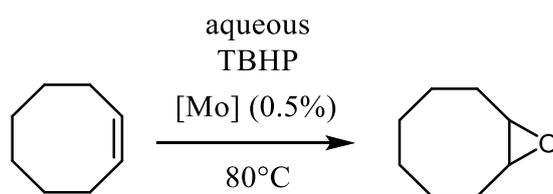
Scheme 1- Synthetic routes for ligands and complexes

The spectroscopic and other characterization shows identical properties for complex $[\text{MoO}_2(\text{SATP})]_2$ and the previously reported $[\text{MoO}_2(\text{SAP})]_2$ analogue. Formation and coordination of the SATP ligand is indicated by the C=N stretching vibration at 1602 cm^{-1} (vs. 1608 cm^{-1} for the SAP analogue). The vibrational pattern of the $\{\text{MoO}_2^{2+}\}$ fragment is also characteristic: whereas mononuclear $[\text{MoO}_2(\text{SAP})(\text{L})]$ complexes show two Mo=O stretching vibrations between 850 and 940 cm^{-1} , dinuclear $[\text{MoO}_2(\text{SAP})]_2$ exhibits only one Mo=O vibration at 937 cm^{-1} and a lower frequency band at 790 cm^{-1} corresponding to a vibrational mode of the bridging Mo-O-Mo unit [17]. For the $[\text{MoO}_2(\text{SATP})]_2$ complex, these vibrations are observed at lower frequencies, 920 and 781 cm^{-1} respectively, suggesting greater electron donating ability for SATP. These data also exclude a monomeric 5-coordinate geometry for the compound, at least in the solid state. The ^1H NMR spectrum of $[\text{MoO}_2(\text{SATP})]_2$ in d^6 -DMSO (which probably generates the monomeric $[\text{MoO}_2(\text{SATP})(d^6\text{-DMSO})]$ *in situ*) shows the CH=N resonance at δ 9.06 (vs. 9.23 for the SAP analogue). The absence of an aldehydic resonance at $\delta > 10$ and broad OH resonances confirms the generation of the desired complex from the one-pot procedure.

The thermogravimetric analysis (TGA) is the simplest method to determine whether the compound contains a donor solvent molecule. For instance, complex $[\text{MoO}_2(\text{SAP})(\text{EtOH})]$ shows release of the weakly coordinated EtOH molecule at ca. 100°C [17]. The TGA of the isolated SATP complex shows the absence of a mass loss at low temperatures and the

presence of a single mass loss at T ca. 249-543 °C (*cf.* 245-543°C for the corresponding SAP system), related to the loss of the SATP ligand with formation of MoO₃ as residue. Interestingly, while labile alcohol adducts are generally obtained under these conditions with SAP and other similar ONO Schiff base ligands [17, 18, 22], a methanol-free product is obtained with SATP. This suggests that the O/S substitution makes the formation of a monomeric MeOH adduct thermodynamically less favorable.

Most of the previously published catalytic epoxidation of Mo^{VI} complexes of ONO and ONS ligands were conducted in organic solvents [13-15, 22-31]. Complex [MoO₂(SATP)]₂ was tested for the epoxydation of cyclooctene by aqueous TBHP under solvent-free conditions at 80°C (Scheme 2) and the results compared with those of the previously investigated SAP analogue, as well as with [MoO₂(acac)₂], under the same operating conditions. The results are summarized in Figure 1. The most active catalyst is [MoO₂(acac)₂] (96% conversion after 4 h, initial TOF = 270 h⁻¹). Compound [MoO₂(SATP)]₂, however, shows only slightly lower activity (90% conversion after 4 h, TOF_{init.} = 253 h⁻¹), but much greater than [MoO₂(SAP)]₂ (76% conversion, TOF_{init.} = 70). The epoxide selectivity is high and similar for all three complexes (91, 93 and 94% for [MoO₂(acac)₂], [MoO₂(SAP)] and [MoO₂(SATP)], respectively). In spite of its higher activity, however, complex [MoO₂(acac)₂] is of lesser interest because of its decomposition under the catalytic conditions as pointed out before [9].



Scheme 2 - Solvent-free epoxidation of cyclooctene

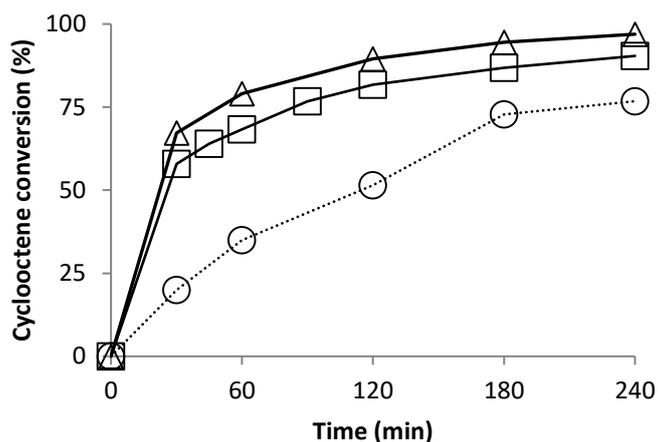


Figure 1 - Cyclooctene conversion vs. time catalyzed by $[\text{MoO}_2(\text{acac})]_2$ (Δ), $[\text{MoO}_2(\text{SAP})]_2$ (\square) and $[\text{MoO}_2(\text{SATP})]_2$ (\circ). Experimental conditions: Mo/TBHP/cyclooctene = 0.5/100/200; T = 80°C.

A decrease of catalyst loading down to 0.025% (250 ppm) while maintaining the same substrate amount and TBHP/substrate ratio still allowed to attain high conversions after 4 h for the $[\text{MoO}_2(\text{SATP})]_2$ catalyst, higher than with a greater loading of the $[\text{MoO}_2(\text{SAP})]_2$ catalyst, see Figure 2. The selectivity remains high for the $[\text{MoO}_2(\text{SATP})]_2$ catalyst while it is slightly eroded at the lowest loadings of $[\text{MoO}_2(\text{SAP})]_2$, see Table S1. The increase of initial TOF as the catalyst loading is decreased (up to 2697 h⁻¹ with 0.025% of the SATP complex) suggests that at high concentrations the catalyst is not entirely in its active form, although optical evidence is in favor of complete dissolution and confinement in the organic phase at the high temperature of the catalytic runs. A possible interpretation is equilibrium dissociation of the stable dimer into catalytically active monomer. No catalyst activation phase is apparent in any of these runs. Since a decrease of catalyst loading entails an increase of the water/catalyst ratio, the effect of water was independently investigated while keeping the catalyst loading and TBHP/substrate ratio constant. Increasing amounts of water have only a slightly negative effect on the conversion (see Table S2 in SI), which could simply be related to a decreasing TBHP concentration in the olefin phase. The selectivity does not appear to be significantly affected by the water amount.

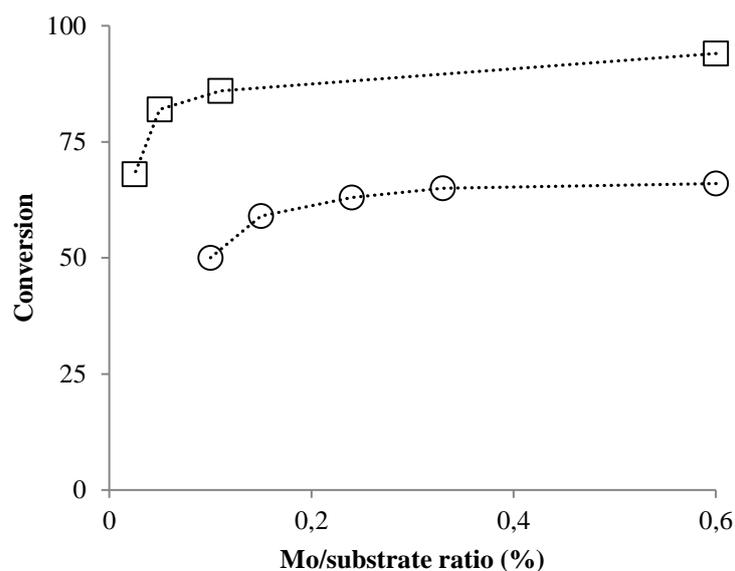
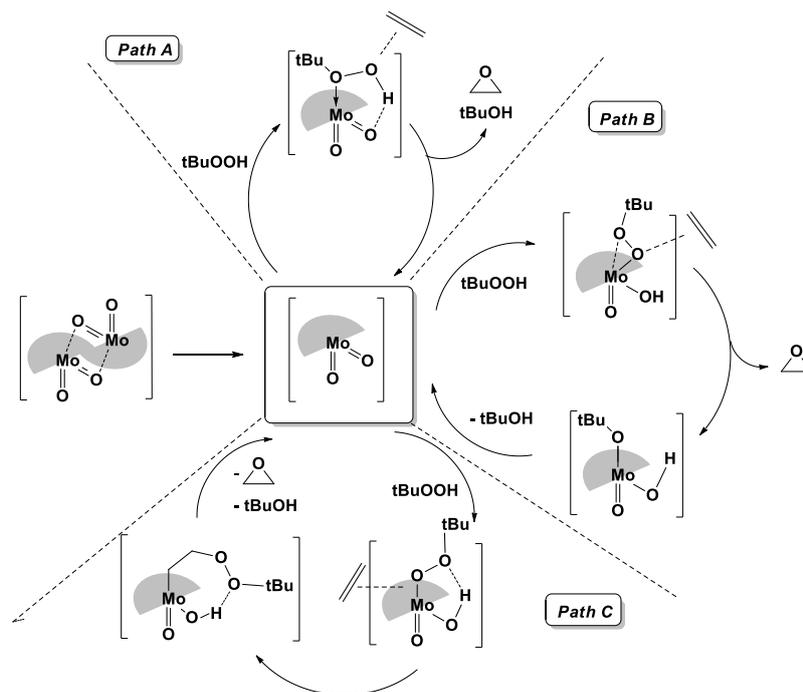


Figure 2 - Cyclooctene conversion after 4 h as a function of the catalyst loading for $[\text{MoO}_2(\text{SAP})]_2$ (○) and $[\text{MoO}_2(\text{SATP})]_2$ (□). Conditions: $T = 80^\circ\text{C}$, $[\text{Mo}]/\text{cyclooctene}/\text{TBHP} = x/100/200$.

The reason for the greater activity of the SATP system was explored by DFT calculations by extending the recently published investigation of the catalytic cycle for the SAP system, where ethylene was used as the model olefin [9]. On the basis of experimental mechanistic information gathered on the SAP system, it was concluded that the active form of the catalyst is the mononuclear 5-coordinate $[\text{MoO}_2(\text{SAP})]$ species. Of the three possible pathways, which are recalled in Scheme 3, path A was found to have the lowest activation barrier with a rate determining transition state located at 22.5 kcal/mol from the rate-determining intermediate, the $[\text{MoO}_2(\text{SAP})]\cdots\text{TBHP}$ adduct. This pathway, previously proposed without supporting experimental evidence [13, 26, 27], involves an O atom transfer from the $[\text{MoO}_2(\text{SAP})]\cdots\text{TBHP}$ intermediate, which is stabilized by an intramolecular H-bond, to the external olefin and is closely related to that proposed by Bartlett [32] for the epoxidation by peracids [9]. Pathways B and C, on the other hand, are more commonly accepted mechanisms based on initial hypotheses of Sharpless [33] and Mimoun, [34] both involving TBHP activation by proton transfer to an oxido ligand and formation of a $\text{Mo}(\text{OH})(\text{OO}t\text{Bu})$ moiety.



Scheme 3 – Possible mechanisms for the epoxidation catalytic cycle with $[\text{MoO}_2(\text{SAP})]$ and $[\text{MoO}_2(\text{SATP})]$.

The results of the calculations on the SATP system, summarized in Figure 3, completely parallel those of the analogous SAP system, pathway A being again characterized by the lowest energy rate-determining transition state. The association of the pentacoordinated monomer with either TBHP, leading to the path A intermediate \mathbf{I}_A , or with itself, yielding the di(μ -oxido)bridged dimer, has lower exothermicity for the SATP system (stabilizations by 5.0 and 1.9 kcal/mol, respectively) than for the SAP analogue (8.4 and 4.9 kcal/mol). This is consistent with the experimental trends discussed above, indicating reduced electron deficiency for the 5-coordinate SATP complex. Like for the SAP system, the \mathbf{I}_B and \mathbf{I}_C intermediates of the other two pathways, produced by proton transfer activation of TBHP, are located at higher energy relative to the 5-coordinate dioxido complex. The transition states of the three pathways (energies in kcal/mol from the $[\text{MoO}_2(\text{SATP})]$ monomer), \mathbf{TS}_A (17.3), \mathbf{TS}_B (33.6) and \mathbf{TS}_C (30.0), have structures (details in Table S3 in the SI) and relative energies comparable to those of the SAP catalyst. A detailed comparison of the \mathbf{TS}_A geometries for the SAP and SATP systems (details in SI, Figure S6) shows very similar features, with a slightly more pronounced Mo-O*t*Bu bond formation and a less pronounced O-ethylene bond formation for the TS with the ONS ligand. Like for the SAP system, an organometallic intermediate as originally proposed by Mimoun could not be located and the reaction

coordinate involved instead a direct O atom transfer to the external olefin to produce the epoxide product, which remains coordinated in a 6-coordinate adduct, plus *t*BuOH in a single step.

The energy span [35] for the lowest energy pathway, $[E(\text{TS}_A) - E(\text{I}_A)]$, 22.3 kcal/mol, is quite close to that of the SAP analogue, 22.5 kcal/mol [9]. It is difficult to make firm conclusions out of a calculated energy difference of only 0.2 kcal/mol, but we nevertheless observe that this difference is in the right direction (smaller barrier for the SAPT complex). Assuming that the TS contribution to the activation Gibbs energy is identical for the two catalysts, application of the Eyring expression on this $\Delta(\Delta E)$ yields a reactivity ratio ($k_{\text{SAPT}}/k_{\text{SAP}}$) of 17 at 80°C, which is close to the ratio of ca. 10 from the TOF of the two catalysts determined under the conditions where the dinuclear precatalyst is most extensively dissociated, *i.e.* at the lowest catalyst loading (Table S1).

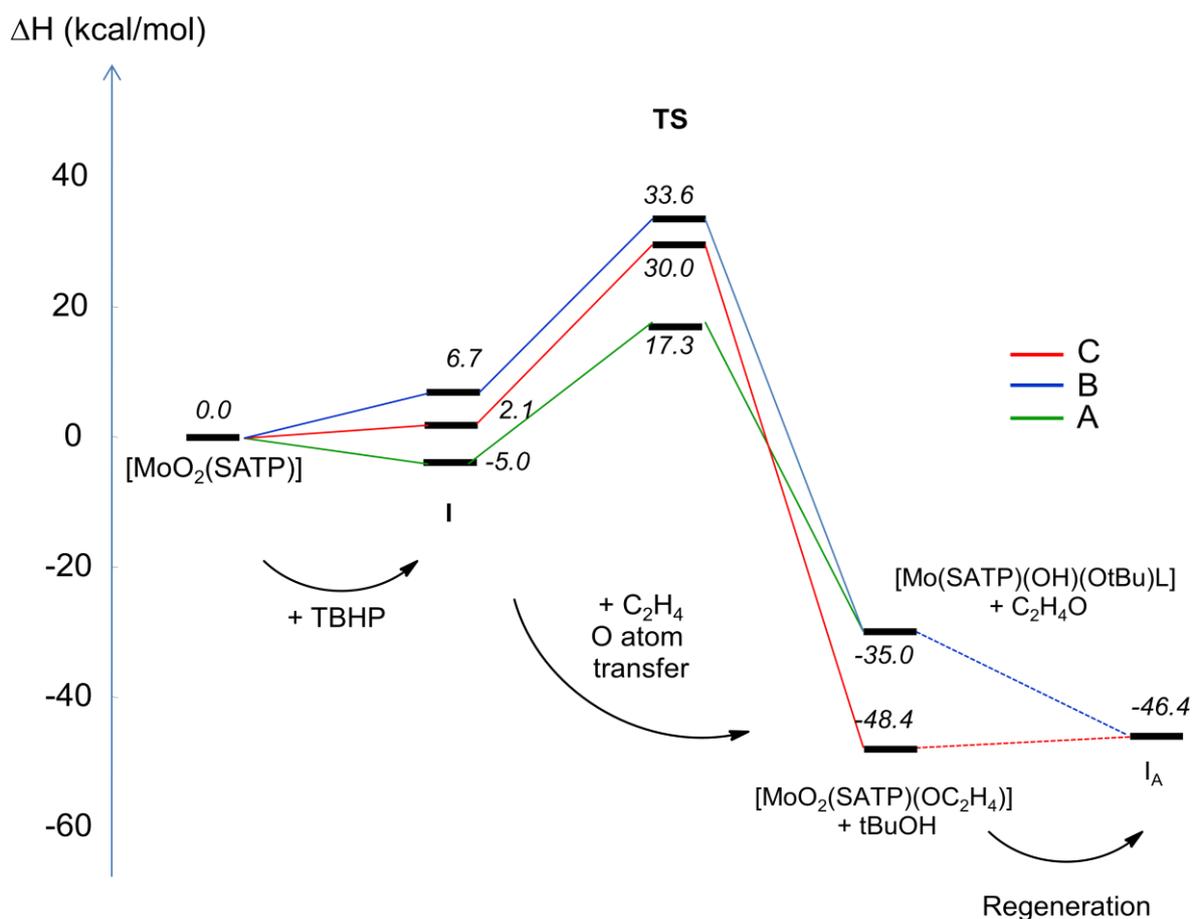


Figure 3 – Energy profile of the reaction along the three catalytic cycles of Scheme 3.

4. Conclusions

In conclusion, we have reported the first direct comparison of two ligands that are related by an O/S atom substitution in Mo^{VI}-catalyzed olefin epoxidation and have shown that the S ligand yields a much more efficient catalytic system than the O ligand. This difference is related to a subtle electronic effect of the O/S substitution that slightly lowers the energy span of the catalytic cycle.

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