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In Search of Catalytically Active Species in the Surfactant-Mediated Biphasic Alkene Epoxidation with Mimoun-Type Complexes

Dirk V. Deubel,* Jörg Sundermeyer, and Gernot Frenking*,†

*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse,
D-35032 Marburg, Germany, and Department of Chemistry, University of Calgary,
Calgary, Alberta, Canada T2N 1N4*

deubel@ucalgary.ca

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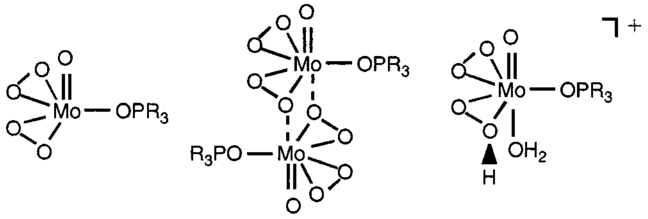
ABSTRACT



A biphasic protocol for the catalytic olefin epoxidation with Mimoun-type complexes [MoO(O$_2$)$_2$(OPR$_3$)] (1) was recently patented by BASF. Density-functional calculations have been carried out to identify potentially active species in addition to the parent complex 1. It has been found that the (μ_2,η^1:η^2-O$_2$)-bridged dimer [MoO(O$_2$)$_2$(OPR$_3$)]$_2$ is significantly less reactive than the monomer. The calculations show that the parent complex is strongly activated by protons coordinating with the peroxo functionalities.

A promising method for catalytic olefin epoxidation using molybdenum(VI) peroxo complexes for the activation of hydrogen peroxide in a biphasic protocol was recently developed by Sundermeyer and Wahl[1] and patented by BASF.[2] The perhydrolysis of molybdenum trioxide in the hydrogen peroxide/water phase gives the oxo-diperoxo compound.[3] The Mimoun-type complex[4] [MoO(O$_2$)$_2$(OPR$_3$)] (R = *n*-dodecyl) is formed at the interphase by coordination of the amphiphilic ligand OPR$_3$ and extracted into the chloroform/olefin phase where the epoxidation occurs.[1] The industrial importance and the academic challenge to end the long-standing controversy[5] about the reaction mechanism of olefin epoxidation with Mimoun-type diperoxo complexes [MoO(O$_2$)$_2$(OPR$_3$)] has stimulated the interest of theoreticians. Density-functional-theory (DFT) studies on the epoxidation of alkenes with transition-metal peroxo complexes have been recently reported by Wu and Sun,[6] Rösch and co-workers,[7] and us.[8−10] Very recently, it was shown[8] that

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† frenking@chemie.uni-marburg.de.

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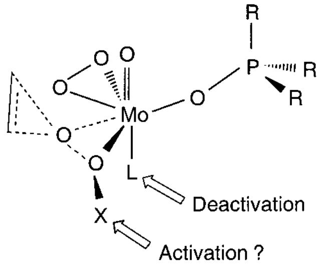
the ethylene epoxidation with $[MoO(O_2)_2(OPR_3)]$ ($R = Me$) follows a concerted mechanism. The transition state is shown in Scheme 1. This mechanism was suggested by Sharpless

Scheme 1. The Concept of the Deactivation and Activation of the Parent Complex **1** by an Additional Ligand L and Brönsted and Lewis Acids X. The Reactants Are Denoted **1**−**7**. The Transition States Have the Prefix TS. □ = Free Coordination Site



1 R = Me, L = □, X = □
2 R = Me, L = H_2O, X = □
3 R = H, L = □, X = □
4 R = H, dimer
5 R = Me, L = □, X = H^+
6 R = Me, L = H_2O, X = H^+
7 R = Me, L = OH^-, X = H^+

and co-workers.[11] The activation energy was theoretically predicted to be 18 kcal/mol.[8] In our DFT studies, the $OPMe_3$ ligand is an appropriate model for the actual $OP(n\text{-dodecyl})_3$ ligand, regarding the activation energy for olefin epoxidation.[9] Alkene epoxidation with molybdyl peroxides can be considered a metalla analogue to the epoxidation of olefins with dioxiranes, which were extensively studied by Bach and co-workers, Houk and co-workers, and others.[12] The topology of the transition state is coarctate.[13]

We think that other species might be more reactive than the parent complex $[MoO(O_2)_2(OPR_3)]$ in the biphasic protocol. The electrophilic nature of the oxidant attack to the olefin was recently supported by an analysis of donor−acceptor interactions[14] in the transition state (TS):[10] Charge donation from the olefin HOMO into the σ^* orbital of the O−O bond being cleaved is the predominant interaction.[10] A decrease of the energy of the latter orbital, for instance due to protonation at the peroxo functionality, is therefore expected to result in a higher reactivity. Bach and co-workers[15] showed that peroxy acids, which are commonly used as oxidants for olefins, can be activated by protons.[16] Moreover, in the biphasic protocol using Mimoun-type complexes,[1] the largest turnover frequencies are obtained at pH = 2.6 of the aqueous phase, indicating that protonated species might be transferred into the organic phase (e.g., $CHCl_3$). In addition to Brönsted acids, Lewis acids such as another coordinatively unsaturated d^0 metal center might activate the complex in a similar manner: a $(\mu_2,\eta^1:\eta^2\text{-}O_2)$-bridged dimer was recently suggested to play a key role in the catalytic process.[1] However, activation energies have been reported neither for the protonated species nor for the dimer.

Hence, the objective of this DFT study is to investigate a potential activation of the parent complex $[MoO(O_2)_2(OPR_3)]$ by protons and by dimerization. The calculations were based on the assumptions that (i) the reaction follows the concerted Sharpless mechanism, (ii) the peroxo oxygen *trans* to the phosphine oxide is transferred, which was recently proved for ethylene epoxidation with the parent complex,[8] and (iii) the same peroxo functionality is activated by the Brönsted or Lewis acid X coordinating with the oxygen *cis* to the phosphine oxide (Scheme 1).[17] We considered both the absence and the presence of an additional ligand L, such as water or hydrogen peroxide, at the metal (Scheme 1) since

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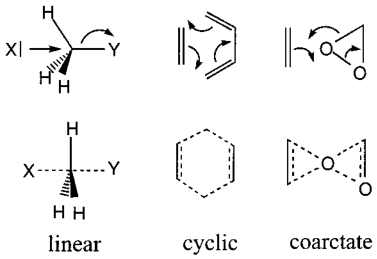
[13] Chemical reactions can be classified with respect to the topology of the transition state: (i) Reactions with a linear TS topology such as S_N2 reactions, (ii) pericyclic reactions, for instance, Diels−Alder reactions, and (iii) reactions with a coarctate TS topology such as olefin epoxidation with dioxiranes. Reactions of the latter class proceed by breaking and making two bonds at one or more atoms at a time. For details, see: (a) Herges, R. *Angew. Chem.* **1994**, *106*, 261. (b) Herges, R. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 91.



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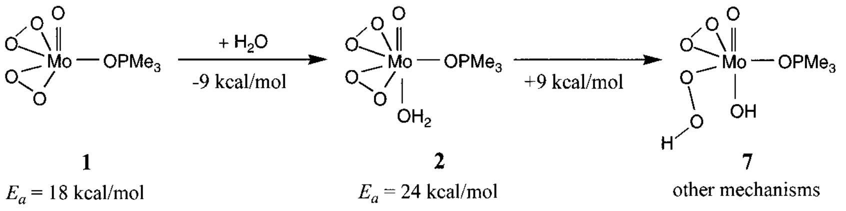
[16] However, the acid catalysis of olefin epoxidation with peroxy acids probably arises from coordination of the undissociated acid with the peroxy acid rather than from protonation. For details, see ref 15.

[17] In principle, several positions of the parent complex could be protonated: the oxo group, the phosphine oxide ligand, and the peroxo atoms *cis* and *trans* to the OPR_3 ligand. Moreover, the complex protonated anywhere can react at several positions, which tremendously increases the number of isomers to be taken into account in a systematic study. With finite computational resources, we have been able to investigate the influence of protonation at the *cis* position and olefin attack at the *trans* position of the protonated peroxo moiety (Scheme 1). We chose this approach since the protonation at the peroxo moiety will have the strongest effect on the energy of the σ^*(O−O) orbital.

Scheme 2. Energy Profile for the Addition of an Aqua Ligand to the Parent Complex **1** and Subsequent Intramolecular Proton Transfer. Activation Energies E_a for Ethylene Epoxidation



the protonated complexes might also be stabilized by this ligand.

We report the calculated structures and energies of the molecules **1**−**7** and the corresponding transition states listed in Scheme 1.[18] The calculated geometries of selected molecules and TS are shown in Figures 1 and 2.[28] The theoretically predicted activation energies E_a are summarized in Schemes 2−4. For the complexes with an additional ligand L, stabilization energies were also calculated; activation energies are then given with respect to the stabilized complexes. In previous studies,[8,9] the activation energy for ethylene epoxidation with the parent complex **1** was predicted to be 18 kcal/mol. The coordination of water with the metal stabilizes the complex by 9 kcal/mol but results in a significantly higher activation barrier (E_a = 24 kcal/mol).[28] The reason for the deactivation by an additional ligand L coordinating with the parent complex is the greater electron density at the reaction center, which results in a smaller reactivity.

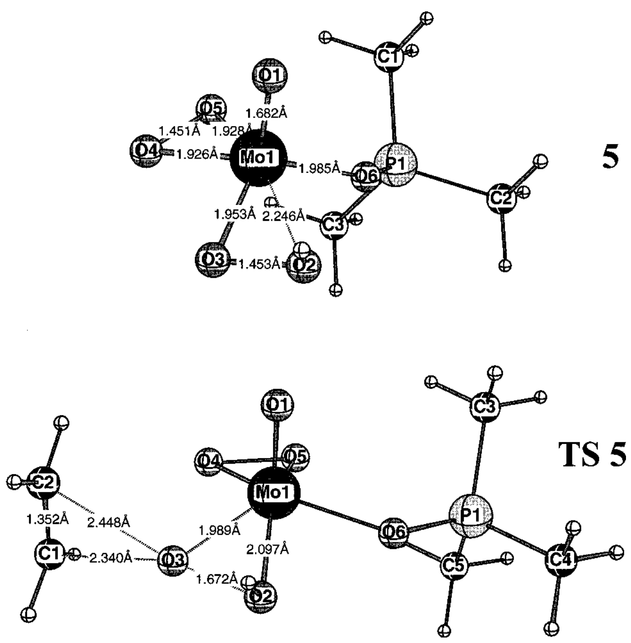


Figure 1. Calculated structure of the protonated species **5** and transition state **TS 5**.

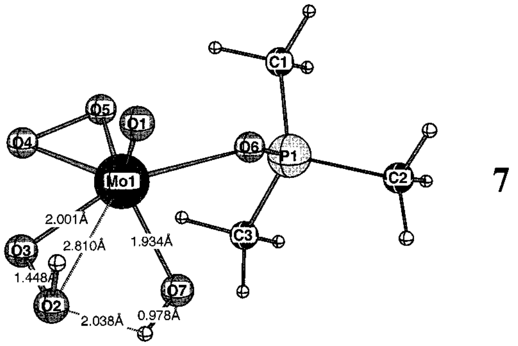


Figure 2. Calculated structure of complex **7** formed via intramolecular proton transfer from the aqua ligand of **2** to the peroxo moiety.

We now discuss the role of the dimer $[MoO(O_2)_2(OPR_3)]_2$ **4** in the catalytic system. Model complexes with R = H were

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[18] For geometry optimizations, Becke's three-parameter hybrid functional (B3, ref 20) together with the correlation functional of Lee, Yang, and Parr (LYP, ref 21) were employed as implemented in Gaussian 98 (ref 22). Our standard basis set II (ref 23) was used, which consists of relativistic small-core ECPs (ref 24) and a (441/2111/31) valence basis set for Mo, while the 6-31G(d) (ref 25) all-electron basis set was employed for the other atoms. All stationary points were characterized by the calculation of vibrational frequencies. Energies reported have been corrected with respect to unscaled zero-point energies (ZPE). Improved total energies were calculated at the B3LYP level using the same ECP and valence basis set at Mo, but totally uncontracted and augmented with one set of f-type polarization functions (ref 26), together with the 6-31+G(d) basis set at the other atoms (ref 27). This basis-set combination is denoted III+ (ref 19).

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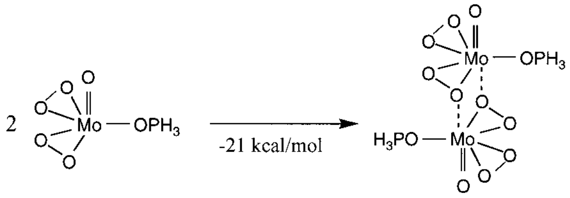
calculated. The formation of the dinuclear complex $[MoO(O_2)_2(OPR_3)]_2$ is predicted to be exothermic by 22 kcal/mol, or 11 kcal/mol per molybdenum unit (Scheme 3). Dimerization might both activate the peroxo moieties due to the coordination of another metal center, i.e., a Lewis acid, and at the same time deactivate the complex because of the coordination of the other peroxo ligand with the first metal center. The calculated energy for the corresponding transition state **TS 4** is surprising: The activation barrier is higher by 6 kcal/mol than that for the monomer (Scheme 3), indicating that the dimer plays a minor role in the catalytic process.

Scheme 3. Energy Profile for the Formation of Dinuclear Complex **4**, Using OPH_3 Model Ligands, and Activation Energies E_a for Ethylene Epoxidation

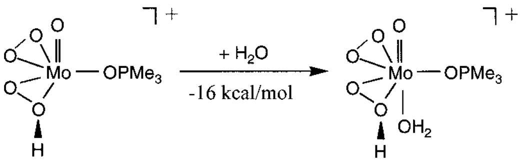


3
E_a = 15 kcal/mol

4
E_a = 22 kcal/mol

The calculated geometries of the protonated peroxo complex **5** and the corresponding transition state **TS 5** are shown in Figure 1. We predict a tremendous increase of reactivity due to protonation (Scheme 4): The activation energy is computed to be only 1 kcal/mol.[29] The cationic molecule **5** is more stabilized by an additional ligand L than the parent complex **1** (stabilization energies −16 and −9 kcal/mol, respectively, for H_2O coordination). Note that the additional ligand scarcely influences the reactivity of the protonated species; compound **6** is almost as reactive as the nonhydrated complex **5** (E_a = 3 kcal/mol). Therefore, compounds of type **6** probably belong to the key species in the catalytic process. Protonated dimers, which have not been studied, might certainly also play a role in the BASF system.

Scheme 4. Energy Profile for the Coordination of an Aqua Ligand with Protonated Complex **5** and Activation Energies E_a for Ethylene Epoxidation



5
E_a = 1 kcal/mol

6
E_a = 3 kcal/mol

Finally, we would like to point out that the peroxo functionality might not only be activated by an *intermolecular* proton transfer but also by an *intramolecular* proton transfer (Scheme 2). After the coordination of an aqua ligand L with the parent complex, a proton can move from L to the peroxo group. This gives the complex $[MoO(\eta^2\text{-}O_2)(\eta^1\text{-}OOH)(OH)(OPR_3)]$ (**7**) shown in Figure 2. During intramolecular proton transfer, which is exothermic by 9 kcal/mol, one η^2 peroxo moiety is opened, yielding a complex with a η^1-OOH ligand. For these compounds, different mechanisms must be considered, as have been suggested by Sheldon,[31] Chong and Sharpless,[31] and Thiel and co-workers[32] for the Mo-calatyzed epoxidation with alkylhydroperoxides.

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(29) The most significant influence of the solvent can be expected for the protonated complexes. Since **TS 5** is larger than reactant **5** and the positive total charge is therefore better stabilized in **TS 5** than in **5**, the activation energy will probably be underestimated. Furthermore, the presence of the counterion might increase the activation barrier.

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