

Alkene epoxidation catalyzed by Ti-containing polyoxometalates: Unprecedented β -oxygen transfer mechanism

Pablo Jiménez-Lozano,[†] Igor Y. Skobelev,[‡] Oxana A. Kholdeeva,^{*,‡,§} Josep M. Poblet^{*,†} and Jorge J. Carbó^{*,†}

[†]Department de Química Física i Inorgànica, Universitat Rovira i Vigili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain

[‡]Boriskov Institute of Catalysis, Lavrentiev av. 5, Novosibirsk 630090, Russia

[§]Novosibirsk State University, Pirogova str. 2, Novosibirsk 630090, Russia

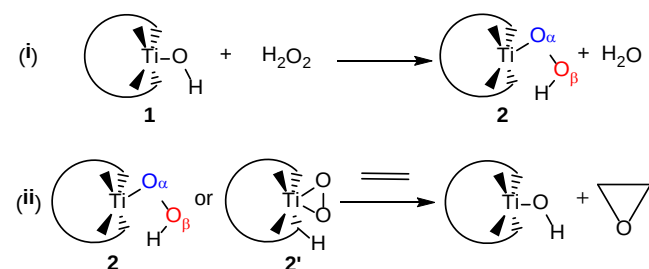
Supporting Information Placeholder

ABSTRACT: DFT study revealed that the mechanism of alkene epoxidation with hydrogen peroxide catalyzed by Ti-containing polyoxometalates (POMs) depends on the Ti coordination environment: for rigid and hindered Ti centers the unprecedented β -oxygen transfer from Ti-hydroperoxo species becomes favored over the α -oxygen one. Improving the model for catalyst description, the calculations were able to reproduce the Arrhenius activation energy values determined in kinetic studies. Unlike protonation, the possible ion-pairing between POMs and counteranions has a minor effect on the electrophilicity of the catalyst, and consequently, on the activity of epoxidation.

INTRODUCTION

Ti-containing heterogeneous catalysts have shown remarkable ability to accomplish selective oxidation of a wide variety of organic compounds using the green oxidant – aqueous H_2O_2 .¹ Understanding of the mechanisms governing catalysis by Ti at a molecular level is of particular importance for creation of new efficient catalytic systems and rational optimization of the existing ones. Ti-containing molecular metal-oxide clusters, also called polyoxometalates (Ti-POMs), have received significant attention as tractable molecular models for studying mechanisms of H_2O_2 activation over Ti centres.²

Scheme 1.



Previously, we characterized computationally the heterolytic mechanism for the oxidation of alkenes by H_2O_2 catalyzed by Ti(IV)-containing POMs.³ Scheme 1 depicts the proposed two-steps mechanism. First the Ti-hydroxo moiety activates the hydrogen peroxide to form the Ti-peroxo and -hydroperoxo intermediates. Then the more reactive hydroperoxo species transfers the electrophilic α -oxygen to the alkene yielding the epoxide. Theoretical studies have been also reported for H_2O_2 -based epoxidations by other type of POMs: lacunary polyoxotungstates,⁴ Se-containing dinuclear peroxotungstates,⁵ and divanadium-substituted polyoxotungstates.⁶ For the two latter systems the peroxo group is identified as the active species,^{5,6} whereas for lacunary polyoxotungstates both hydroperoxo-^{4a} and peroxo-type^{4c} mechanisms were proposed. We showed that the nature of substituted metal has a significant effect on the mechanism.³

Interestingly, with increasing the number of protons in Ti(IV)-substituted Keggin POMs $\text{Na}_{5-n}\text{H}_n\text{PTiW}_{10}\text{O}_{40}$, from $n = 1$ to $n = 2-5$, the reaction yields mainly heterolytic products in the cyclohexene oxidation with H_2O_2 .⁷ Posterior kinetic and DFT studies revealed that protonation results in a significant reduction of the activation energy (E_a) for cyclooctene oxidation catalyzed by $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OH})\text{W}_{10}\text{O}_{39}]$ (TBA-1K), from 17.0 to 11.6 kcal.mol⁻¹, due to the lowering of the energy barrier for the heterolytic oxygen transfer from the Ti hydroperoxo intermediate.⁸ Another interesting observation was that on going from TBA-1K with 6-coordinated Ti to the Ti-disubstituted sandwich-type $[\text{Ti}_2(\text{OH})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$ anion with 5-coordinated Ti environment, the activity and selectivity towards heterolytic oxidation products increases.⁹

More recently, some of us reported the E_a (14.5 $\pm$ 0.3 kcal.mol⁻¹) for cyclooctene epoxidation in the presence of $\text{TBA}_{5.5}\text{Na}_{1.55}\text{K}_{0.5}\text{H}_{0.5}[\text{Ti}_2(\text{OH})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$.^{2d} This E_a value lays between those of protonated and non-protonated Ti-monosubstituted Keggin-type anions. Initially, we identified the absence of dimer formation in the sandwich anion as a factor favoring the activity of the oxidation process.^{3a} However, the computed oxygen-transfer barrier (23.6 kcal.mol⁻¹)^{3a} for the bare anion $[\text{Ti}_2(\text{OH})_2\text{As}_2\text{W}_{19}\text{O}_{67}]^{8-}$ (1D) is significantly higher suggesting that important effects are missing in our molecular model. One possible reason for the low E_a determined could be the presence of additional protons or K^+

counter cations that might increase POM electrophilicity and lower activation barrier. It might also be a partial dissociation of the Ti-O-W bond(s) during catalysis, thereby leading to a more flexible and lower coordinated Ti environment that reduces the energy requirements of the strained oxygen-transfer transition state. Finally, the rigid and hindered Ti environment in **1D** might induce a change on the mechanism in which the β -oxygen atom transfers from the Ti-hydroperoxo group instead of the α -oxygen as shown in the sulfoxidation by Ti-POMs.¹⁰ Following our interest in the reactivity of Ti molecular oxides,^{3,8,10,11} here we extend the theoretical study on the alkene epoxidation with H_2O_2 catalyzed by **1D**. The new assessments include the modelling of effects such as protonation, countercations, structure lability, and mechanism dependence on the coordination environment. In addition, we present here further analysis of the previously reported kinetic studies.^{2d,3b}

RESULTS AND DISCUSSION

The rate law for the TBA-**1D**-catalyzed cyclooctene oxidation with H_2O_2 was described earlier,^{3b} and according to it, the Arrhenius activation energy can be expressed as

$$E_a \approx 0.3\Delta H_{\text{TiOOH}} + \Delta H^\ddagger$$

where ΔH_{TiOOH} is enthalpy of the formation of Ti hydroperoxo complex and $\Delta H^\ddagger$ is enthalpy barrier of oxygen transfer from active specie to substrate (see SI for details). From the determined equilibrium constant of hydroperoxo complex formation ($K = 3.5 \text{ M}^{-1}$),^{3b} we estimated ΔH_{TiOOH} in 0.6 kcal.mol⁻¹ (see SI for details). Thus, the contribution of ΔH_{TiOOH} on E_a (ca. 0.2 kcal.mol⁻¹) is lower than the experimental error in the E_a determination, and consequently, we can simply neglect the value of ΔH_{TiOOH} and assume that E_a is determined by the barrier of oxygen transfer to the alkene.

We carried out DFT calculations^{12,13} on different molecular models of Ti-monosubstituted Keggin-type anions [$\text{H}_n\text{PTi}(\text{OH})\text{W}_{11}\text{O}_{39}$]⁽⁴⁻ⁿ⁾⁻ ($n = 0$ and 1 , **1K** and **1KH**) and of Ti-disubstituted sandwich-type anions [$\text{K}_m\text{H}_n\text{Ti}_2(\text{OH})_2\text{As}_2\text{W}_{10}\text{O}_{67}$]^{(8-m-n)-} ($m = n = 0$ **1D**, $m = 0$ and $n = 1$ **1DH**, $m = 1$ and $n = 0$ **1DK** and $m = n = 1$ **1DHK**), using ethene as the simplest model substrate. We considered two mechanisms involving heterolytic oxygen transfer from hydroperoxo species, where the ethene can attack either the α - or β -oxygen (see Scheme 1). Table 1 compares the computed energy barriers for α - and β -oxygen transfer from Ti hydroperoxo species to alkene with the experimental Arrhenius activation barriers. Figures 1 and 2 show the computed energy profiles and the geometry of key transition states, respectively, for Ti-disubstituted anions.

Table 1. Comparison of experimental activation energies (E_a) and computed energy barriers ($\Delta E^\ddagger$).

POM	E_a [ref.]	model	$\Delta E^\ddagger(\alpha)$	$\Delta E^\ddagger(\beta)$
TBA- 1K	17.0 [8]	2K	18.7	18.0
TBA- 1D	14.5 [2d]	2D	23.6	16.8
		2DH	21.0	14.7
		2DHK	20.2	13.3
TBA- 1K + H^+	11.6 [8]	2KH	12.7	13.2

(a) $\Delta E^\ddagger$ for heterolytic α - and β -oxygen transfer. Energies (kcal.mol⁻¹) in acetonitrile.

Within the series of studied Ti-containing POMs, the β -oxygen transfer becomes significantly favored for the 5-coordinated Ti-substituted sandwich-type anions (Table 1 and Figure 1). Note that the transition state **TS2DH β** might connect with an adduct in which the protonated epoxide interacts with the basic Ti-O moiety via H-bonding. However, attempts to obtain this adduct yielded the return of the proton to the POM basic oxygen atoms without apparent energy-barrier, resembling the mechanisms for alkene epoxidation by peracids,¹⁴ or sulfoxidation by Fe-hydroperoxo complexes.¹⁵ It is important to highlight that the mechanism involving heterolytic β -oxygen transfer to the alkene is unprecedented for Ti single-site catalysts. Initial computational studies on Ti complex models without structural constraints found a clear preference for the alkene attack to α -oxygen over the attack to β -oxygen.¹⁶ In Ti-hydroperoxo group, the $\sigma^*_{\text{O-O}}$ orbital is polarized towards the α -oxygen atom, which becomes better acceptor of the alkene nucleophilic attack in the absence of sterical hindrance. Then, posterior mechanistic studies using more sophisticated molecular models did only consider α -oxygen transfer.¹⁷ In a more general sense, the β -oxygen transfer mechanism has been unprecedented for d⁰-transition metal Ti-hydroperoxo complexes.¹⁸

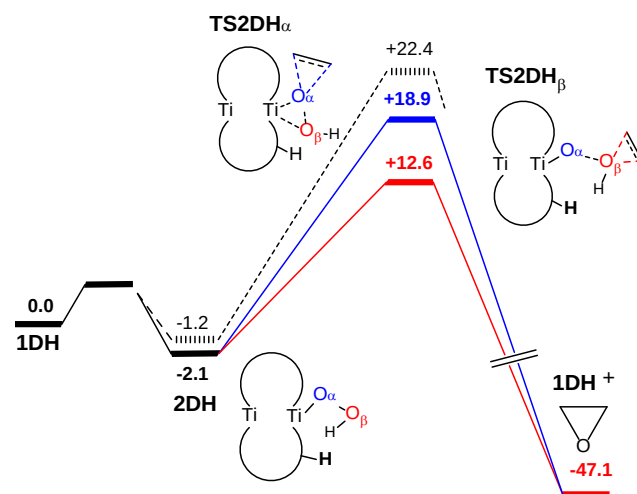


Figure 1. DFT potential energy profile in MeCN (kcal.mol⁻¹) for ethene epoxidation catalyzed by [$\text{HTi}_2(\text{OH})_2\text{As}_2\text{W}_{10}\text{O}_{67}$]⁷⁻ (**1DH**) anion (α - and β -oxygen transfer in blue and red). Dashed lines correspond to **1D** anion (ref. 3a).

Several factors can explain this switch in the mechanism from α - to β -oxygen transfer. It was proposed that flexible and low-coordinated Ti environments favor the heterolytic α -oxygen transfer.^{3a} As well, reducing the negative charge of the POM promotes the transfer of electrophilic oxygens to alkene.⁸ In hydroperoxo species, **2D** or **2DH**, the Ti atom is strongly bounded to four neighbouring tungstates through oxygen bridges forming rigid square-planar $\text{Ti}(\text{OW})_4$ moiety, and it is embedded in POM framework. Thus, the corresponding transition states for α -oxygen transfer, **TS2D α** or **TS2DH α** , are far from the optimal non-sterically hindered and six-fold octahedral coordination observed for model mononuclear Ti complexes.^{16,19} On the other hand, the β -oxygen transfer proceeds without significant distortion of the Ti environment and farther from the active center (see Figure 2 for **TS2DH β** and Figure 3 for **TS2K β**) what enables to achieve lower energy barriers. If we compare Keggin- and

sandwich-type species, **2KH** and **2DH**, with the same charge density distribution (charge/metal ratio = 0.33), we observe that the energy barriers for β -oxygen anions are very similar (14.7 and 13.2 kcal.mol⁻¹ for **2DH** and **2KH**), whereas for α -oxygen transfer the energy barrier in **2DH** is significantly higher than in **1KH** (21.0 vs. 12.7 kcal.mol⁻¹). This indicates that the distortion of Ti environment for α -oxygen transfer is significantly larger in the 5-coordinated Ti of sandwich-type POM than in that of Keggin-type POM, and as a consequence, the preferred path for the sandwich-type species proceeds through β -oxygen transfer (Figure 2).

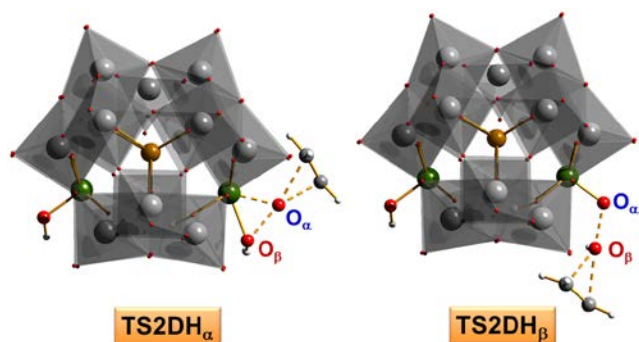


Figure 2. Representation (top view) of the transition states for α - and β -oxygen transfer to ethene from **2DH** anion.

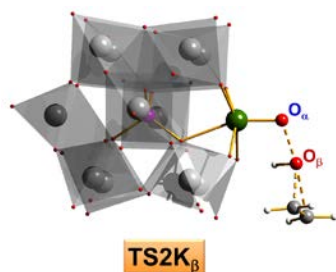


Figure 3. Representation (top view) of the transition state for β -oxygen transfer to ethene from **2K** anion.

Combining the mechanistic switch and protonation effects, the calculations nicely reproduce the activation energy values (see Table 1) and explain the activity and selectivity variation as a function of Ti environment. On-going from 6-coordinated Ti in **1K** to 5-coordinate in **1D**, the strain of the α -oxygen transfer transition states increases but the POM becomes more electrophilic (from charge/metal ratio = 0.42 to 0.38) reducing the energy barrier for the non-distorted β -oxygen transfer from 18.0 to 16.8 kcal.mol⁻¹. Adding a proton to the POM structure at the Ti-O-W bridging oxygen, **2DH**, the electrophilicity increases and the energy barrier lowers (14.7 kcal.mol⁻¹) reaching a value very close to the experimentally observed E_a energy (14.5 kcal.mol⁻¹). Thus, the protonated **2DH** structure represents better the catalytic species in agreement with experiments, in which the neutralization of the protons in TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}[Ti₂(OH)₂As₂W₁₀O₆₇] catalyst using TBAOH led to a drastic decrease of activity and selectivity toward heterolytic oxidation products.^{2d} For both types of POMs, our calculations tend to overestimate the energy barrier as compared to experimental values (see Table 1). In part, this is due to the use of model ethene instead of larger and more nucleophilic cyclooctene. In a combined experimental/computational approach, we showed that the

higher the nucleophilicity of the alkene, the higher the epoxidation activity by Ti-substituted sandwich-type anions.^{3b}

Since the chemical formula of the Ti-disubstituted sandwich POM contains also alkali metal counter cations, in acetonitrile solvent the POM may form ion pairs with K⁺, producing an effect similar to protonation. We computed the oxygen transfer energy barriers from hydroperoxo anion [KTi(OOH)Ti(OH)As₂W₁₀O₆₇]⁷⁻ (**2DK**), where the potassium cation was placed at a W₄O₄ hole next to the Ti-OOH group. However, in this case, the calculated energy barriers for β -oxygen transfer is very close (17.2 kcal.mol⁻¹) to that of the bare anion **2D** (16.8 kcal.mol⁻¹). Similarly, adding K⁺ to **2DH** has also a marginal effect to the energy barrier of α - and β -oxygen transfer (see Table 1, **2DHK** anion). The direct interaction of the counter cation with the POM framework does not appreciably influence the electrophilicity of the POM in contrast to that observed for protonation. The K⁺...POM interaction has a strong ionic character, and consequently, the additional positive charge is retained in the potassium ion. Accordingly, the computed electrostatic-based atomic charge for the potassium in **2DK** is +0.93 e, whereas for the additional proton in **2DH** it is significantly lower +0.49 e. Thus, unlike protonation, the ion-pairing with K⁺ does not affect the rate of heterolytic oxygen transfer from the active Ti-hydroperoxo species.

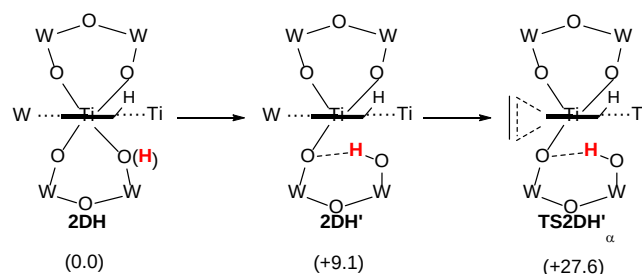


Figure 4. Schematic representation of a possible pathway for α -oxygen transfer to alkene involving a metal-oxygen bond breaking as a result of protonation. Relative energies in kcal.mol⁻¹.

Finally, we evaluated another possible mechanism consisting of the formation of a metastable structure from **2DH**. The protonation at the Ti-O-W bridging oxygen of **2D** may reversible dissociate one Ti-O(H) bond during the catalysis, thereby making the Ti centre lower coordinated. In this intermediate, **2DH'**, the new W-hydroxo group is stabilized via intramolecular hydrogen-bond with the adjacent Ti-O-W bridging oxygen (Figure 4). The energy required to form **2DH'** is moderate (+9.1 kcal.mol⁻¹) and the energy barrier for α -oxygen barrier from **2DH'** is lower than that from **2DH** species (18.5 vs. 23.6 kcal.mol⁻¹). However this path is unlikely because the energy cost of the overall process (27.6 kcal.mol⁻¹) is significantly higher than that for non-dissociative pathway.

CONCLUSIONS

We demonstrated an unprecedented mechanism for the alkene epoxidation with H₂O₂ catalyzed by Ti single-site. When Ti center is rigid and hindered, the transfer of the non-distorted β -oxygen to the alkene becomes significantly favored. This switch of the mechanism, along with the presence of protons in the POM structure that enhances electro-

philicity, explains the increase of activity and heterolytic selectivity of Ti-disubstituted sandwich-type $[\text{Ti}_2(\text{OH})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$ anion with respect to Keggin-type $[\text{PTi}(\text{OH})\text{W}_{11}\text{O}_{39}]^{4-}$ anion. Unlike protonation, the eventual formation of ion-pairing would not influence the electrophilicity of the POM catalyst during the oxidation process.

EXPERIMENTAL SECTION

Computational Details. Calculations were performed with Gaussian09 package²⁰ at the DFT level by means of the hybrid exchange-correlation B3LYP functional.²¹ For Ti, W and As atoms, the LANL2DZ pseudopotential was used.²² The 6-31G(d,p) basis set²³ was used for the C and H atoms, as well as for the O atoms of hydrogen peroxide and directly bound to Ti. For the rest of atoms, we employed a 6-31G basis set.²³ Geometry optimization in vacuum of all reactants, intermediates and of the transition states were performed without any symmetry constraints. The transition states were characterized by a single imaginary frequency and the normal mode which corresponds to the expected reaction path. Solvent effects were included by means of SMD model²⁴ single point calculations as implemented in Gaussian09,²⁰ using the most common experimental reported acetonitrile dielectric constant, $\epsilon = 36.64$. The use of continuum solvent models has revealed as absolutely fundamental for the modeling of these large anions (see ref. 13). C-HELP scheme²⁵ was used to compute atomic charges, in which charges are fitted to the electrostatic potential.

ASSOCIATED CONTENT

Supporting Information

Additional experimental details, additional structure representations, relative energies of different isomers, and xyz coordinates for the most relevant structures.

AUTHOR INFORMATION

Corresponding Author

* E-mail: j.carbo@urv.cat

* E-mail: josepmaria.poblet@urv.cat

* E-mail: khold@catalysis.ru

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Research at Universitat Rovira i Virgili was supported by Spanish Ministry of Science and Innovation (CTQ2014-52774-P) and the Generalitat de Catalunya (2014SGR199 and XRTQC).

REFERENCES

- (1) For recent reviews, see (a) Clerici, M. G.; Domine, M. E. in *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications* (Eds. Clerici, M. G. and Kholdeeva, O. A.) Wiley, New Jersey, 2013, Ch. 2; (b) Kholdeeva, O. A. *ibid.*, Ch. 4; (c) Kholdeeva, O. A. *Catal. Sci. Technol.* **2014**, *4*, 1869; (d) Moliner, M.; Corma, A. *Microporous Mesoporous Mater* **2014**, *189*, 31.
- (2) (a) Kholdeeva, O. A. *Topics Catal.* **2006**, *40*, 229; (b) Kholdeeva, O. A.; Maksimovskaya, R. I. *J. Mol. Catal. A: Chemical* **2007**, *262*, 7; (c) Nomiya, K.; Sakai, Y.; Matsunaga, S. *Eur. J. Inorg. Chem.* **2011**, 179; (d) Kholdeeva, O. A. *Eur. J. Inorg. Chem.* **2013**, 1595.

- (3) (a) Antonova, N. S.; Carbó, J. J.; Kortz, U.; Kholdeeva, O. A.; Poblet, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 7488; (b) Donoeva, B. G.; Trubitsina, T. A.; Antonova, N. S.; Carbó, J. J.; Poblet, J. M.; Al-Kadamany, G.; Kortz, U.; Kholdeeva, O. A. *Eur. J. Inorg. Chem.* **2010**, 5312.
- (4) (a) Prabhakar, R.; Morokuma, K.; Hill, C. L.; Musaev, D. G. *Inorg. Chem.* **2006**, *45*, 5703; (b) Sartorel, A.; Carraro, M.; Bagno, A.; Scorrano, G.; Bonchio, M., *Angew. Chem. Int. Ed.*, **2007**, *46*, 3255; (c) Sartorel, A.; Carraro, M.; Bagno, A.; Scorrano, G.; Bonchio, M., *J. Phys. Org. Chem.*, **2008**, *21*, 596.
- (5) (a) Kamata, K.; Hirano, T.; Kuzuya, S.; Mizuno, N., *J. Am. Chem. Soc.*, **2009**, *131*, 6997; (b) Kamata, K.; Ishimoto, R.; Hirano, T.; Kuzuya, S.; Uehara, K.; Mizuno, N., *Inorg. Chem.*, **2010**, *49*, 2471; (c) Zhu, B.; Lang, Z. L.; Yan, L. K.; Ramzan, M.; Janjua, S. A.; Su, Z. M.; *Int. J. Quant. Chem.*, **2014**, *114*, 458.
- (6) (a) Nakagawa, Y.; Mizuno, N. *Inorg. Chem.* **2007**, *46*, 1727; (b) Kuznetsov, A. E.; Geletii, Y. V.; Hill, C. L.; Morokuma, K.; Musaev, D. G. *Inorg. Chem.* **2009**, *48*, 1871; (c) Kamata, K.; Sugahara, K.; Yonehara, K.; Ishimoto, R.; Mizuno, N., *Chem. Eur. J.*, **2011**, *17*, 7549.
- (7) Kholdeeva, O. A.; Trubitsina, T. A.; Timofeeva, M. N.; Maksimov, G. M.; Maksimovskaya, R. I.; Rogov, V. A. *J. Mol. Cat. A: Chem.* **2005**, *232*, 17.
- (8) Jiménez-Lozano, P.; Ivanchikova, I. D.; Kholdeeva, O. A.; Poblet, J. M.; Carbó, J. J. *Chem. Commun.*, **2012**, 48, 9266.
- (9) (a) Hussain, F.; Bassil, B. S.; Kortz, U.; Kholdeeva, O. A.; Timofeeva, M. N.; de Oliveira, P.; Keita, B.; Nadjo, L. *Chem. Eur. J.* **2007**, *13*, 4733; (b) Kholdeeva, O. A.; Donoeva, B. G.; Trubitsina, T. A.; Al-Kadamany, G.; Kortz, U. *Eur. J. Inorg. Chem.* **2009**, 5134.
- (10) Skobelev, I. Y.; Zalomaeva, O. V.; Kholdeeva, O. A.; Poblet, J. M.; Carbó, J. J. *Chem. Eur. J.* **2015**, *21*, 14496.
- (11) Aguado-Ullate, S.; Carbó, J. J.; González-del Moral, O.; Martín, A.; Mena, M.; Poblet, J. M.; Santamaría, C. *Inorg. Chem.* **2011**, *13*, 6269.
- (12) Parr, R. G.; Yang, W. in *Density Functional Theory of Atoms and Molecule*, Oxford University Press, Oxford, UK, 1989.
- (13) For reviews on the use of computational methods in polyoxometalate chemistry, see: a) López, X.; Miró, P.; Carbó, J. J.; Rodríguez-Fortea, A.; C. Bo, C.; Poblet, J. M. *Theor. Chem. Acc.*, **2011**, *128*, 393; b) López, X.; Carbó, J. J.; Bo, C.; Poblet, J. M. *Chem. Soc. Rev.*, **2012**, *41*, 7537.
- (14) Houk, K. N.; Liu, J.; DeMello, N. C.; Condroski, K. R., *J. Am. Chem. Soc.*, **1997**, *119*, 10147.
- (15) Kim, Y. M.; Cho, K. B.; Cho, J.; Wang, B.; Chunsen, L.; Shaik, S.; Nam, W., *J. Am. Chem. Soc.*, **2013**, *135*, 8838.
- (16) (a) Neurock, M.; Manzer, L. E., *Chem. Commun.*, **1996**, 1133; (b) Tantanak, D.; Vincent, M. A.; Hillier, I. H., *Chem. Commun.*, **1998**, 1031.
- (17) See for example: (a) Kudo, T.; Gordon, M. S., *J. Phys. Chem. A*, **2003**, *107*, 8756; (b) Sever, R. R.; Root, T. W., *J. Phys. Chem. B*, **2003**, *107*, 4080; (c) Wells, D. H. Jr.; Delgass, W. N.; Thomson, K. T. *J. Am. Chem. Soc.* **2004**, *126*, 2956; (d) Lundin, A.; Panas, I.; Ahlberg, E. J. *Phys. Chem. A* **2009**, *113*, 282; (e) Wu, X.; Yang, G.; Zhou, L.; Han, X. *Comp. Theor. Chem.* **2013**, *1017*, 109.
- (18) Rösch, N.; Di Valentin, C.; Yudanov, I. V. *Mechanism of Olefin Epoxidation by Transition Metal Peroxo Compounds in Computational Modeling of Homogenous Catalysis* (Eds. F. Maseras, A. Lledós), Kluwer Academic Publishers, Dordrecht, **2002**.
- (19) Sever, R. R.; Root, T. W. *J. Phys. Chem. B* **2003**, *107*, 10521, and references therein.
- (20) Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gom-

perts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(21) (a) Lee, C.; Yang, C.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785; (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648; (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623.

(22) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 270.

(23) (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, 77, 3654; (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, 56, 2257; (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, 28, 213.

(24) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, 113, 6378.

(25) Breneman, C. M.; Wiberg, K. B., *J. Comp. Chem.*, **1990**, 11, 361.

DFT study revealed that the mechanism of alkene epoxidation with hydrogen peroxide catalyzed by Ti-containing polyoxometalates (POMs) depends on the Ti coordination environment: for rigid and hindered Ti centers the unprecedented β -oxygen transfer from Ti-hydroperoxo species becomes favored over the α -oxygen one.

