Inorganic Chemistry

ARTICLE

pubs.acs.org/IC

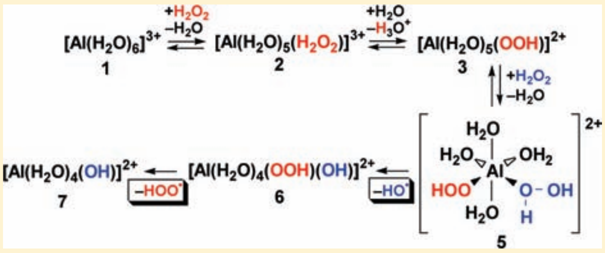
Mechanism of Al^{3+}-Catalyzed Oxidations of Hydrocarbons: Dramatic Activation of H_2O_2 toward O−O Homolysis in Complex $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$ Explains the Formation of $HO^\bullet$ Radicals

Maxim L. Kuznetsov,*,[†] Yuriy N. Kozlov,[‡] Dalmo Mandelli,[§] Armando J. L. Pombeiro,[†] and Georgiy B. Shul'pin*,[‡]

[†]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
[‡]Semenov Institute of Chemical Physics, Russian Academy of Science, Ulitsa Kosigina, dom 4, 119991 Moscow, Russia
[§]Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Rua Santa Adélia, 166, Santo André - SP, 09210-170, Brazil

Supporting Information

ABSTRACT: A radical mechanism of hydrocarbon oxidations with the environmentally friendly and cheap homogeneous nontransition metal system $[Al(H_2O)_6]^{3+}/H_2O_2/MeCN{-}H_2O$ was proposed for the first time on the basis of DFT calculations. A dramatic activation of H_2O_2 toward homolysis in the key intermediate $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$ due to the presence of the easily oxidizable OOH coligand provides, without a change of metal oxidation state, the generation of $HO^\bullet$ radicals, which then oxidize hydrocarbons. Nonradical mechanisms of the olefin epoxidation with the same catalytic system were also investigated.



INTRODUCTION

Selective oxidations of hydrocarbons with environmentally friendly hydrogen peroxide and molecular oxygen under mild conditions is an important field of catalytic chemistry.[1] These reactions are usually catalyzed by transition metal complexes (TMC), e.g., those of Fe,[2] V,[3] Mo,[4] Mn,[5] Ti,[6,7] Os,[8] Cu,[9,10] and others.[1] Many of them are highly dangerous for the environment and expensive as well, and this is the obvious disadvantage of the application of TMC in catalysis. An important exception is iron-based complexes which attract great attention for the oxidation of hydrocarbons[2,11] since the simple stoichiometric iron-containing oxidizing system $\{Fe^{2+} + H_2O_2\}$ was discovered by Fenton.[12]

In contrast, information about alkane oxidations catalyzed by non-TMC systems is much more scarce. If the *heterogeneous* reactions of this type are rather well-known,[13,14] the first exciting results on the *homogeneous* alkane oxidation with H_2O_2 catalyzed by a non-TMC (i.e., Al) have been reported only recently: alkanes were oxygenated with H_2O_2 in aqueous MeCN when $[Al(H_2O)_6]^{3+}$ (**1**) was used as a catalyst [in the form of $Al(NO_3)_3$].[15] The same system, **1**/H_2O_2, is also efficient for olefin epoxidations,[16] although other non-TMC compounds (e.g., derivatives of Bi, Se, As, Sn, Ge) were also applied for this reaction.[17] In contrast to many TMCs (except the iron complexes), the **1**/H_2O_2 system is promising from ecological and economical points of view because both the catalyst and oxidant are environmentally friendly, cheap, and accessible. At the same time, the area of homogeneous Al-salt catalyzed oxidations of hydrocarbons is now only at the initial stage of development, and the mechanisms of these processes are still a mystery.

In this work, we try to lift the veil from this mystery. The main goal is to study the plausible mechanisms of the hydrocarbon oxidations with the **1**/H_2O_2/MeCN−H_2O catalytic system using theoretical DFT methods. The article consists of two parts. In the first part, the mechanisms of alkane oxidation are discussed. To the best of our knowledge, this is the first attempt to explore the plausible mechanism of homogeneous alkane oxidation in the presence of H_2O_2 with a non-TMC catalyst using theoretical methods.[18,19] In the second part, the mechanisms of the olefin epoxidation with the same catalyst are discussed.

COMPUTATIONAL DETAILS

The full geometry optimization of all structures and transition states (TS) has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP)[20] with the help of the Gaussian 98[21] program package. The standard basis set 6-311+G(d,p) was applied for all atoms. No symmetry operations have been applied for any of the structures calculated. The O−O bond dissociation energy in H_2O_2 calculated at this level of theory (48.7 kcal/mol, the total energy gas-phase scale) is very close to the experimental value of 48.75 ± 0.005 kcal/mol.[22] The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) or saddle points (only one imaginary frequency) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C. The nature of all transition states was investigated by the analysis

Received: December 10, 2010
Published: April 01, 2011

Table 1. Energetic Characteristics (in kcal/mol) of the Formation of $HO^\bullet$ and $HOO^\bullet$ Radicals in the System **1**/H_2O_2 Calculated for CH_3CN Solution

entry	reaction	$\Delta H_s^\ddagger$	$\Delta G_s^\ddagger$	ΔH_s	ΔG_s
1	$[Al(H_2O)_6](H_2O_2)^{3+}$ (**1**) → $[Al(H_2O)_5](H_2O)(H_2O_2)^{3+}$ via **TS1**	18.4	17.9	+10.5	+10.1
2	$[Al(H_2O)_5](H_2O)(H_2O_2)^{3+}$ → $[Al(H_2O)_5(H_2O_2)](H_2O)^{3+}$ (**2**) via **TS2**	5.8	6.0	−4.0	−3.9
3	$[Al(H_2O)_5(OOH)](H_2O)^{2+}$ (**3**) + H_2O_2 → $[Al(H_2O)_4(OOH)](H_2O)(H_2O_2)^{2+}$ + H_2O via **TS3**	16.8	17.4	+7.9	+8.5
4	$[Al(H_2O)_4(OOH)](H_2O)(H_2O_2)^{2+}$ → $[Al(H_2O)_4(OOH)(H_2O_2)](H_2O)^{2+}$ (**5**) via **TS4**	5.6	5.6	+1.1	+1.2
5	$[Al(H_2O)_5(H_2O_2)](H_2O)^{3+}$ (**2**) → $[Al(H_2O)_5(^\bullet OH)](H_2O)^{3+}$ + $HO^\bullet$			+49.9	+42.2
6	H_2O_2 → $2HO^\bullet$			+45.1	+39.4
7	$[Al(H_2O)_4(OH)(H_2O_2)](H_2O)^{2+}$ (**4**) → *cis*-$[Al(H_2O)_4{}^\bullet(OH)_2](H_2O)^{2+}$ + $HO^\bullet$			+31.2	+25.0
8	$[Al(H_2O)_5(OOH)](H_2O)^{2+}$ (**3**) → $[Al(H_2O)_5(O^\bullet)](H_2O)^{2+}$ + $HO^\bullet$			+47.3	+39.9
9	$[Al(H_2O)_4(OOH)(H_2O_2)](H_2O)^{2+}$ (**5**) → $[Al(H_2O)_4(OOH)(OH)](H_2O)^{2+}$ (**6**) + $HO^\bullet$			+13.8	+6.1
10	$[Al(H_2O)_4(OOH)(OH)](H_2O)^{2+}$ (**6**) → $[Al(H_2O)_4(OH)](H_2O)^{2+}$ (**7**) + $HOO^\bullet$			+11.9	+3.0
11	$[Al(H_2O)_4(OH)](H_2O)^{2+}$ (**7**) + H_2O → $[Al(H_2O)_5(OH)](H_2O)^{2+}$ (**8**)			−22.5	−13.8

of vectors associated with the imaginary frequency and by the calculations of the intrinsic reaction coordinates (IRC) using the Gonzalez−Schlegel method.[23]

The starting geometry for the optimization of **TS1** was constructed using the equilibrium coordinates given in ref 24 for the TS of the water dissociation in $[Al(H_2O)_6](H_2O)_6{}^{3+}$. Taking into account the importance of the consideration of the second coordination sphere in the calculations of solvent effects for reactions involving highly charged species, one, two, or three solvent molecules (H_2O or H_2O_2) were included explicitly for the majority of the calculated structures (consult Tables 1 and 2 for each particular case).

Total energies corrected for solvent effects (E_s) were estimated at the single-point calculations on the basis of gas-phase geometries using the polarizable continuum model in the CPCM version[25] with CH_3CN or, in some cases, H_2O as the solvent. The entropic term for the CH_3CN solvent (S_s) was calculated according to the procedure described by Wertz[26a] and Cooper and Ziegler[26b] using eqs C1−C4

$$\Delta S_1 = R \ln V^{s}{}_{m,\,liq}/V_{m,\,gas} \tag{C1}$$

$$\Delta S_2 = R \ln V^{\circ}{}_{m}/V^{s}{}_{m,\,liq} \tag{C2}$$

$$\alpha = \frac{S^{\circ,s}_{liq} - (S^{\circ,s}_{gas} + R \ln V^{s}_{m,\,liq}/V_{m,\,gas})}{(S^{\circ,s}_{gas} + R \ln V^{s}_{m,\,liq}/V_{m,\,gas})} \tag{C3}$$

$$\begin{aligned} S_s &= S_g + \Delta S_{sol} = S_g + [\Delta S_1 + \alpha(S_g + \Delta S_1) + \Delta S_2] \\ &= S_g + [(-12.21\ \mathrm{cal/mol\cdot K}) - 0.23(S_g - 12.21\ \mathrm{cal/mol\cdot K}) \\ &\quad + 5.87\ \mathrm{cal/mol\cdot K}] \end{aligned} \tag{C4}$$

where S_g is the gas-phase entropy of solute; ΔS_{sol} is the solvation entropy; $S^{\circ s}_{liq}$, $S^{\circ,s}_{gas}$, and $V^{s}_{m,liq}$ are standard entropies and molar volume of the solvent in liquid or gas phases (149.62 and 245.48 J/mol·K and 52.16 mL/mol, respectively, for CH_3CN), $V_{m,gas}$ is the molar volume of the ideal gas at 25 °C (24450 mL/mol), and $V^{\circ}{}_{m}$ is the molar volume of the solution corresponding to the standard conditions (1000 mL/mol). The S_s values for the H_2O solvent were calculated using the eq C5.[26b]

$$\begin{aligned} S_s &= S_g + [(-14.3\ \mathrm{cal/mol\cdot K}) \\ &\quad - 0.46(S_g - 14.3\mathrm{cal/mol\cdot K}) + 7.98\ \mathrm{cal/mol\cdot K}] \end{aligned} \tag{C5}$$

The enthalpies and Gibbs free energies in solution (H_s and G_s) were estimated using the expressions $H_s = E_s + H_g - E_g$ and $G_s = H_s - T\cdot S_s$, where E_g and H_g are the gas-phase total energy and enthalpy.

RESULTS AND DISCUSSION

1. Oxidation of Alkanes. In accord with the experimental data,[15] the oxidation of alkanes with H_2O_2 catalyzed by **1** occurs via a radical mechanism involving the formation of free $HO^\bullet$ and $HOO^\bullet$ radicals. The former more active radical oxidizes the alkane to corresponding alkyl radical $R^\bullet$ by hydrogen abstraction, and $R^\bullet$ then reacts with molecular oxygen, giving alkylperoxo radical $ROO^\bullet$, which is converted to the final product.[1i,27] However, the principal question—how the $HO^\bullet$ radicals are formed from H_2O_2 with **1**—remained absolutely unclear.

Initially, the mechanism of the $HO^\bullet$ generation from H_2O_2 catalyzed by TMCs was proposed by Haber and Weiss for the Fenton system.[28] It includes the electron transfer from Fe(II) to the hydrogen peroxide molecule, leading to the formation of $HO^\bullet$ [reaction 1]. The Fe(III) species then may be reduced by another H_2O_2 molecule with the generation of $HOO^\bullet$ radicals [reaction 2].[29] In a modified route proposed by Kozlov et al.,[30] the Fe(III) ion interacts simultaneously with two H_2O_2 molecules to give the Fe(II) ion and $HO^\bullet$, as well as O_2, which is the product of HOO^- oxidation by Fe(III) and the second H_2O_2 molecule (Scheme 1). Since that time, a number of mechanistic studies of the processes occurring in the Fenton or Fenton-like systems have been undertaken (some of them supporting the generation of radicals, others suggesting nonradical pathways).[2e,31,32]

$$[Fe^{II}(H_2O)_6]^{2+} + H_2O_2 \rightarrow [Fe^{III}(H_2O)_5(OH)]^{2+} + HO^\bullet + H_2O \tag{1}$$

$$[Fe^{III}(H_2O)_5(OH)]^{2+} + H_2O_2 \rightarrow [Fe^{II}(H_2O)_6]^{2+} + HOO^\bullet \tag{2}$$

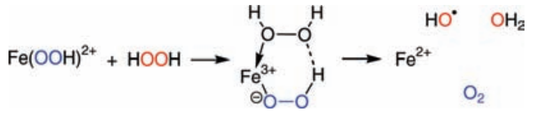
When the metal in the catalyst molecule is in the highest oxidation state, the first step of the reaction is the generation of the $HOO^\bullet$ radical accompanied by the reduction of the metal while $HO^\bullet$ is formed at a later stage. Such a mechanism (Scheme 2) was proposed[27] and theoretically studied[3a,33] for the V- and Re-based catalysts.

In all radical routes mentioned above, the oxidation state of the metal either increases or decreases. This is possible because transition metals usually have several stable oxidation states. However, the mechanism of radical formation catalyzed by the non-TMC **1** should be of a fundamentally different type because the unique stable nonzero oxidation state of Al is +III, and the

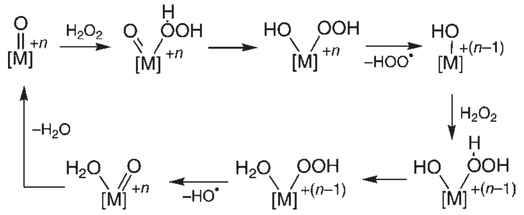
Table 2. Energetic Characteristics (in kcal/mol) of Ethylene Epoxidation with the System $1/H_2O_2$ Calculated for CH_3CN Solution

entry	reaction	$\Delta H_s^{\ddagger}$	$\Delta G_s^{\ddagger}$	ΔH_s	ΔG_s
	Sharpless mechanism				
1	$[Al(H_2O)_5(OOH)]^{2+}$ (**3**) → $[Al(H_2O)_4(OOH)](H_2O)^{2+}$ (**9**)			+6.6	+5.7
2	$[Al(H_2O)_5(OOH)]^{2+}$ (**3**) → $[Al(H_2O)_3(OOH)](H_2O)_2{}^{2+}$ (**10**)			+9.2	+5.9
3	$[Al(H_2O)_4(OOH)](H_2O)^{2+}$ (**9**) + C_2H_4 → $[Al(H_2O)_4(OH)(\underline{C}H_2CH_2\underline{O})](H_2O)^{2+}$ (**11**) via **TS5**	+9.0	+14.3	−63.2	−56.6
4	$[Al(H_2O)_3(OOH)](H_2O)_2{}^{2+}$ (**10**) + C_2H_4 → $[Al(H_2O)_3(OH)(\underline{C}H_2CH_2\underline{O})](H_2O)_2{}^{2+}$ (**12**) via **TS6**	+7.3	+14.0	−64.7	−56.9
5	$[Al(H_2O)_4(OH)(\underline{C}H_2CH_2\underline{O})](H_2O)^{2+}$ (**11**) → $[Al(H_2O)_4(OH)](H_2O)^{2+}$ (7) + $\underline{C}H_2CH_2\underline{O}$			+15.8	+8.3
6	$[Al(H_2O)_3(OH)(\underline{C}H_2CH_2\underline{O})](H_2O)_2{}^{2+}$ (**12**) → $[Al(H_2O)_3(OH)](H_2O)_2{}^{2+}$ (**13**) + $\underline{C}H_2CH_2\underline{O}$			+19.6	+12.4
7	$[Al(H_2O)_3(OH)](H_2O)_2{}^{2+}$ (**13**) → $[Al(H_2O)_4(OH)](H_2O)^{2+}$ (7)			−4.8	−4.0
	Mimoun mechanism				
8	$[Al(H_2O)_5(OOH)]^{2+}$ (**3**) + C_2H_4 → *trans*-$[Al(H_2O)_4(OOH)(C_2H_4)](H_2O)^{2+}$ (*trans*-**14**)			+15.3	+21.5
9	$[Al(H_2O)_5(OOH)]^{2+}$ (**3**) + C_2H_4 → *cis*-$[Al(H_2O)_4(OOH)(C_2H_4)](H_2O)^{2+}$ (*cis*-**14**)			+11.4	+17.8
10	$[Al(H_2O)_4(OOH)](H_2O)^{2+}$ (**9**) + C_2H_4 → $[Al(H_2O)_3(OOH)(C_2H_4)](H_2O)_2{}^{2+}$ (**15**)			+12.8	+20.1
11	$[Al(H_2O)_3(OOH)](H_2O)_2{}^{2+}$ (**10**) + C_2H_4 → $[Al(H_2O)_2(OOH)(C_2H_4)](H_2O)_3{}^{2+}$ (**16**)			+18.0	+23.2
12	*cis*-$[Al(H_2O)_4(OOH)(C_2H_4)](H_2O)^{2+}$ (*cis*-**14**) → $[Al(H_2O)_4(\underline{O}(H)OCH_2\underline{C}H_2)](H_2O)^{2+}$ (**17**)			−0.2	+1.4
13	*cis*-$[Al(H_2O)_4(OOH)(C_2H_4)](H_2O)^{2+}$ (*cis*-**14**) → $[Al(H_2O)_4(\underline{O}O(H)CH_2\underline{C}H_2)](H_2O)^{2+}$ (**18**)			+11.1	+10.8
14	$[Al(H_2O)_3(OOH)(C_2H_4)](H_2O)_2{}^{2+}$ (**15**) → $[Al(H_2O)_3(\underline{O}(H)OCH_2\underline{C}H_2)](H_2O)_2{}^{2+}$ (**19**) via **TS7**	21.7	23.0	−8.1	−6.9
15	$[Al(H_2O)_3(OOH)(C_2H_4)](H_2O)_2{}^{2+}$ (**15**) → $[Al(H_2O)_3(\underline{O}O(H)CH_2\underline{C}H_2)](H_2O)_2{}^{2+}$ (**20**)			+3.2	+3.4
16	$[Al(H_2O)_2(OOH)(C_2H_4)](H_2O)_3{}^{2+}$ (**16**) → $[Al(H_2O)_2(\underline{O}(H)OCH_2\underline{C}H_2)](H_2O)_3{}^{2+}$ (**21**)			+0.4	+2.5
17	$[Al(H_2O)_2(OOH)(C_2H_4)](H_2O)_3{}^{2+}$ (**16**) → $[Al(H_2O)_2(\underline{O}O(H)CH_2\underline{C}H_2)](H_2O)_3{}^{2+}$ (**22**)			+7.6	+9.5
	alternative stepwise mechanism				
18	$[Al(H_2O)_3(OOH)](H_2O)_2{}^{2+}$ (**10**) + C_2H_4 → $[Al(H_2O)_3(OOH)(C_2H_4)](H_2O)_2{}^{2+}$ (**15a**)			+10.8	+19.5
19	$[Al(H_2O)_3(OOH)(C_2H_4)](H_2O)_2{}^{2+}$ (**15a**) → $[Al(H_2O)_3(\underline{C}H_2CH_2\underline{O}OH)](H_2O)_2{}^{2+}$ (**23**) via **TS8**	4.6	5.3	−4.0	−3.1
20	**23** → **23a**			+3.7	+3.0
21	$[Al(H_2O)_3(\underline{C}H_2CH_2\underline{O}OH)](H_2O)_2{}^{2+}$ (**23a**) → $[Al(H_2O)_3(OH)(\underline{C}H_2CH_2\underline{O})](H_2O)_2{}^{2+}$ (**12a**) via **TS9**	4.2	4.5	−72.7	−73.1
22	$[Al(H_2O)_3(OH)(\underline{C}H_2CH_2\underline{O})](H_2O)_2{}^{2+}$ (**12a**) → $[Al(H_2O)_3(OH)](H_2O)_2{}^{2+}$ (**13**) + $\underline{C}H_2CH_2\underline{O}$			+17.2	+9.2

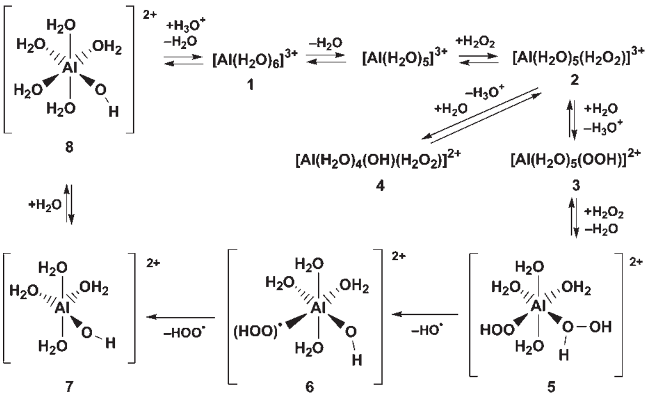
Scheme 1. Proposed Mechanism of the Iron-Catalyzed $HO^{\bullet}$ Generation Involving Two H_2O_2 Molecules



Scheme 2. Simplified Mechanism of $HOO^{\bullet}$ and $HO^{\bullet}$ Formation in the TMC/H_2O_2 Systems When the Metal Is in the Highest Oxidation State (The Oxidation State of the Metal Is Indicated)



Scheme 3. Mechanism of the $HO^{\bullet}$ and $HOO^{\bullet}$ Generation in the System $1/H_2O_2/MeCN-H_2O$ (Molecules of the Second Coordination Sphere Are Omitted)



formation of Al(II) or Al(IV) species is highly unfavorable. In this work, we propose such a mechanism (Scheme 3).

*i. Equilibria in the **1**/H_2O_2/H_2O System. Formation of the First H_2O_2 Complex.* Under experimental conditions when both H_2O and H_2O_2 are in comparable concentrations,[15] the substitution of a coordinated H_2O molecule in **1** for H_2O_2 is quite expected. The quantum-chemical calculations show that this reaction is slightly endoergonic (by 6.2 kcal/mol, Table 1, entries 1, 2), which is in agreement with a lower (but still high) donor ability of H_2O_2 compared to H_2O.

The previous studies of a similar water exchange process in **1** demonstrated that it proceeds via a dissociative mechanism.[24,34] In our work, we were also unable to find a seven-membered

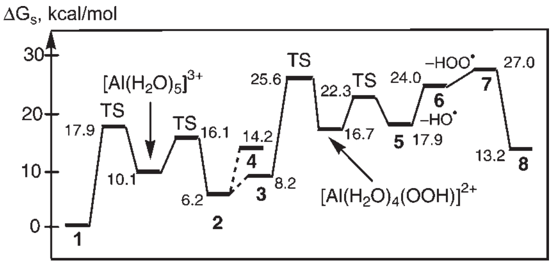


Figure 1. Energy profile of the $HO^\bullet$ and $HOO^\bullet$ generation in the system **1**/H_2O_2/MeCN−H_2O. Molecules of the second coordination sphere are omitted. Numbers indicate the relative energies. Only Al-bearing species are shown.

intermediate $[Al(H_2O)_6(H_2O_2)]^{3+}$ of the associative mechanism or any transition state of the concerted substitution (interchange mechanism). Thus, the rate limiting step of the H_2O-to-H_2O_2 substitution is the same as in the case of water exchange, i.e., cleavage of the Al−OH_2 bond.

The calculated activation barrier ($\Delta G_s^{\ddagger}$ value) of the water dissociation in **1** is 17.9 kcal/mol (Table 1, entry 1), which correlates very well with experimental results for the water exchange ($\Delta G^{\ddagger}$ of 17.0−17.3 kcal/mol[35]). The activation barrier of the second step, i.e., the coordination of H_2O_2, is 16.1 kcal/mol relative to **1**, being slightly lower than the $\Delta G_s^{\ddagger}$ of the first step (Table 1, entries 1, 2; Figure 1).

*ii. Equilibria in the **1**/H_2O_2/H_2O System. Proton Transfer and Formation of the Second H_2O_2 Complex.* It is well-known that the aluminum aqua-complexes undergo an effective proton transfer to a water molecule (protolysis) in aqueous solutions, providing the formation of an acidic medium. Analogously, the hydrogen peroxide complex **2** also should be involved in protolysis (Scheme 3). The protolysis of the ligated H_2O_2 is more favorable than that of the H_2O ligand. Indeed, product **3** is by 6.0 kcal/mol more stable than complex **4** (Table S3 in the Supporting Information). This is in agreement with the stronger acidic character of H_2O_2 compared to H_2O (pK_a is 11.7 for H_2O_2 vs 15.7 for H_2O).[36] For the same reason, the protolysis of H_2O_2 in **3** is also more effective than that of H_2O in **1**. As a result, the formation of complex **3** from **1** requires only 2 kcal/mol higher energy than the formation of **8**.

For the models used in this work, the CPCM method does not allow correct theoretical calculations of the solvent effects and, hence, of the ΔG_s and pK_a values of protolysis. However, using the experimental data,[37] the ΔG_s of the reaction $\mathbf{2}_{aq} + H_2O \rightarrow \mathbf{3}_{aq} + H_3O^+$ is estimated to be *ca.* 2 kcal/mol in MeCN−H_2O solution (see the Supporting Information for details).

The substitution of another H_2O ligand for a second H_2O_2 then occurs to give $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$ (**5**). The reaction is also endoergonic (by 9.7 kcal/mol) and occurs via the dissociative mechanism with an activation barrier similar to that of the ligand substitution in **1** (17.4 kcal/mol, Table 1, entries 3, 4).

iii. The Radical Formation. The most obvious way of generation of the free $HO^\bullet$ radical in the system **1**/H_2O_2 is homolytic O−O bond cleavage in the hydrogen peroxide molecule. First, we verified how the simple coordination of H_2O_2 to Al^{3+} affects the O−O bond. In accord with calculations, the energy of the homolytic cleavage of the O−O bond (in terms of Gibbs free energy in solution, ΔG_s) in complex **2** bearing one H_2O_2 molecule is 42.2 kcal/mol [reaction 3], which is even higher than the O−O bond energy in free H_2O_2 (39.4 kcal/mol, Table 1, entries 5, 6). The O−O bond energy in the protolytic product **4** is lower (25.0 kcal/mol, Table 1, entry 7) [reaction 4]. However, the general activation barrier of the $HO^\bullet$ formation relative to **1** in this case is still too high (39.2 kcal/mol, Figure 1).

$$[(H_2O)_5Al(H_2O_2)]^{3+}\ (\mathbf{2}) \rightarrow [(H_2O)_5Al(^\bullet OH)]^{3+} + HO^\bullet \tag{3}$$

$$[(H_2O)_4Al(OH)(H_2O_2)]^{2+}\ (\mathbf{4}) \rightarrow [(H_2O)_4Al(^\bullet OH)(^\bullet OH)]^{2+} + HO^\bullet \tag{4}$$

Second, the O−O bond cleavage of the OOH ligand in complex **3** was examined [reaction 5]. The generation of the $HO^\bullet$ radicals from the coordinated OOH ligand upon the O−O bond rupture was proposed and found to be effective for a number of TMCs [reaction 6].[1] In this case, the formed species $[ML_n(-O^\bullet)]^{m+}$ may be stabilized by an electron transfer to give $[ML_n(=O)]^{m+}$ accompanied by an increase of the metal oxidation state. A similar mechanism was found by Mayer and coworkers[38] for the Ti complexes $[Cp_2Ti(\eta^1\text{-OO}^t\text{Bu})L]$ (L = Cl^-, OTf^-, Br^-, OEt_2, Et_3P) in which the metal is in the highest oxidation state (+IV) and cannot be increased more. However, the product of the decomposition, $[Cp_2Ti(O)L]$, appeared to be also stabilized by electron delocalization: the spin density is distributed among the O and Ti atoms and Cp ligands, and the TiO bond has a significant double character due to π bonding. Thus, the real electronic structure of this complex is intermediate between the resonance structures $[Cp_2Ti(-O^\bullet)L]$ and $[(Cp^\bullet)(Cp)Ti(=O)L]$, and the Cp ligands play a key role in its stabilization.

$$[(H_2O)_5Al(-OOH)]^{2+}\ (\mathbf{3}) \rightarrow [(H_2O)_5Al(-O^\bullet)]^{2+} + HO^\bullet \tag{5}$$

$$[L_nM(-OOH)]^{m+} \rightarrow \{[L_nM(-O^\bullet)]^{m+} \leftrightarrow [L_nM(=O)]^{m+}\} + HO^\bullet \tag{6}$$

In contrast to all of these examples, the product of decomposition of the hydroperoxo complex **3**, $[(H_2O)_5Al(-O^\bullet)]^{2+}$ [reaction 5], has no ability to be stabilized since Al(III) cannot be oxidized, and there are no ligands which could provide the delocalization of the spin electron density in this complex. Indeed, the unpaired electron is almost completely localized on the oxo ligand (the spin density at this atom is 0.97). As a result, the O−O bond energy in **3** is very high (39.9 kcal/mol, Table 1, entry 8).

The formation of radicals ($HOO^\bullet$) from complex **3** could also be possible upon homolytic cleavage of the Al−OOH bond [reactions 7 and 8]. However, this process corresponds to the reduction of Al to the oxidation state (+II) again without any possibility of the delocalization of the spin density. Respectively, the Al−OOH bond energy is very high [85.8 kcal/mol for reaction 7 and 86.5 kcal/mol for reaction 8].

$$[Al^{III}(H_2O)_5(OOH)]^{2+}\ (\mathbf{3}) \rightarrow [Al^{II}(H_2O)_5]^{2+} + HOO^\bullet \tag{7}$$

$$[Al^{III}(H_2O)_5(OOH)]^{2+}\ (\mathbf{3}) + H_2O \rightarrow [Al^{II}(H_2O)_6]^{2+} + HOO^\bullet \tag{8}$$

The same reason (a lack of the delocalization of spin density) accounts for the high O−O bond energies in **2** and **4** discussed

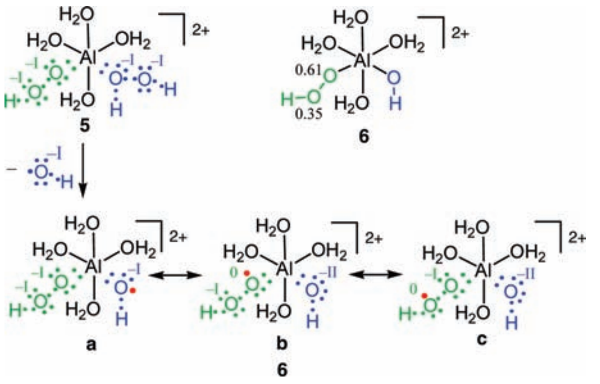


Figure 2. Atomic spin densities (Arabic numerals) in **6** and oxygen oxidation states (Roman numerals) in **5** and **6**.

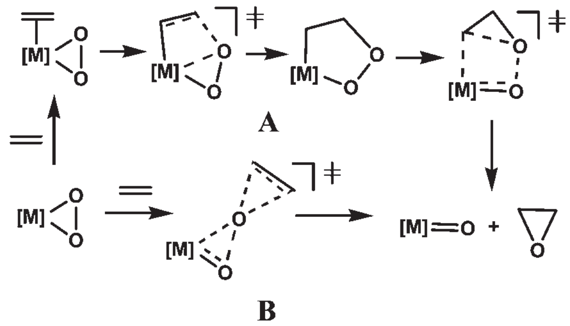
above [reactions 3 and 4]. In $[Al(H_2O)_5(^{\bullet}OH)]^{3+}$, the spin density is completely localized on the OH ligand. In $[Al(H_2O)_4{}^{\bullet}(OH)_2]^{2+}$, it is distributed among two OH ligands, providing some delocalization and the lower O−O bond energy in **4** than in **2** (25.0 vs. 42.2 kcal/mol). But, apparently, such delocalization is not sufficient for an effective homolysis of **4**.

Third, complex $[Al(H_2O)_4(H_2O_2)(OOH)]^{2+}$ (**5**) bearing both the OOH and H_2O_2 ligands was considered. The calculations predict that H_2O_2 coordinated to Al in **5** is *surprisingly highly activated* toward the homolytic O−O bond cleavage compared to free H_2O_2. The calculated O−O bond energy of H_2O_2 coordinated in **5** is only 6.1 kcal/mol vs 39.4 kcal/mol in free H_2O_2 (Table 1, entry 9). Thus, the activation of H_2O_2 toward the decomposition is 33.3 kcal/mol! Complex $[Al(H_2O)_4(OOH)(OH)]^{2+}$ (**6**) formed upon $HO^{\bullet}$ elimination from **5** can easily produce the $HOO^{\bullet}$ radical, the homolytic Al−OOH bond energy in **6** being only 3.0 kcal/mol (Table 1, entry 10).

It is interesting that the elimination of the $HOO^{\bullet}$ directly from **5** results in a spontaneous break of the O−O bond in the H_2O_2 ligand, and no minimum corresponding to complex $[Al(H_2O)_4(H_2O_2)]^{2+}$ was located. Thus, the formation of $HO^{\bullet}$ and $HOO^{\bullet}$ from **5** occurs via a stepwise process, and the higher reactive $HO^{\bullet}$ radical is formed before the less reactive $HOO^{\bullet}$ is generated. In the last step, the addition of a water molecule to the coordinatively unsaturated $[Al(H_2O)_4(OH)]^{2+}$ (**7**) leads to $[Al(H_2O)_5(OH)]^{2+}$ (**8**) which starts a new catalytic cycle. The $HO^{\bullet}$ radicals react with the alkane according to known reactions.[27]

Why are the HO−OH and Al−OOH bonds so highly activated in **5** and **6**? Obviously, the crucial factor in the great activation of H_2O_2 in **5** is the presence of the hydroperoxo OOH ligand since in similar species bearing the H_2O or OH ligand instead of OOH ($[Al(H_2O)_5(H_2O_2)]^{3+}$ (**2**) and $[Al(H_2O)_4(OH)(H_2O_2)]^{2+}$ (**4**)) the O−O bond energies are high (42.2 and 25.0 kcal/mol). The distinctive feature of the OOH ligand is its ability to be relatively easy oxidized by one electron. The calculations indicate that the spin density in **6** is delocalized among the two oxygen atoms of the OOH ligand (Figure 2, structures **6b** and **6c**) stabilizing this decomposition product. Therefore, the elimination of the $HO^{\bullet}$ radical from H_2O_2 in **5** results in a one electron oxidation of the hydroperoxide OOH ligand and a reduction of the Al-bound $HO^{\bullet}$ radical, without a change of the Al(III) oxidation state. Apparently, the oxidation of the OOH ligand should occur more easily than that of the H_2O or OH ligands. The oxidation of the OOH ligand also explains the weakness of the Al−OOH bond in **6**: the oxidation state of the donor O atom in the predominant resonance structure **b** is zero, and the bonding with Al should be weak. These results clearly indicate that two H_2O_2 molecules are involved in the radical generation: the first one is necessary for the formation of the OOH ligand in **5**, and the second one directly decomposes to give $HO^{\bullet}$. The results also demonstrate that the OOH ligand in **5** plays a role similar to that of the transition metal in TMC based catalysts; i.e., the one-electron oxidation of these species (^{-}OOH or the transition metal) stabilizes the product of the O−O bond cleavage.

Scheme 4. Mimoun (A) and Sharpless (B) Type Mechanisms of Olefin Epoxidation with Peroxo Complexes

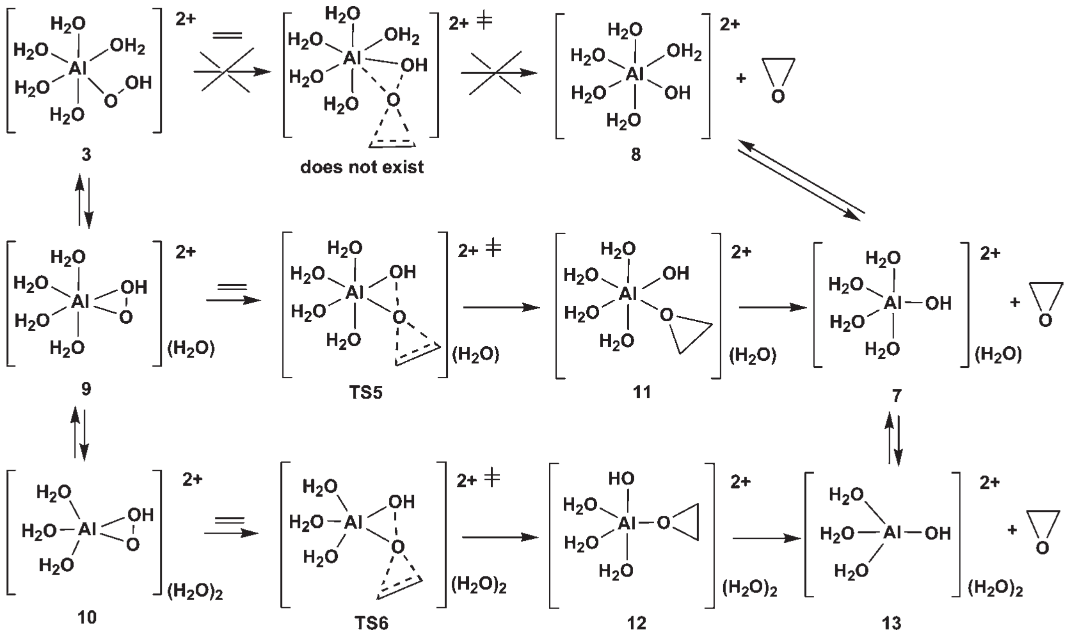


As can be seen in Figure 1, the rate limiting step of $HO^{\bullet}$ radical generation is the elimination of a water molecule in **3** upon the second H_2O-to-H_2O_2 substitution. The rate limiting step of the formation of the $HOO^{\bullet}$ radical is the monomolecular Al−OOH bond cleavage in **6**. The calculated apparent activation energies of formation of $HO^{\bullet}$ and $HOO^{\bullet}$ relative to **1** are 25.6 and 27.0 kcal/mol, respectively (in terms of G_s). These values are typical for reactions which occur at moderately elevated temperatures, and hence, they are consistent with experimental results.[15]

All of these results are also interesting from a practical point of view and may be used for the optimization of the experimental reaction conditions. The substitutions of H_2O for H_2O_2 in the coordination sphere of Al(III) are energetically demanding processes which give the main contribution to the total activation barrier (Figure 1). However, if a catalyst molecule $[Al(H_2O)_nL_m]^{3+}$ will already initially bear an easily oxidizable ligand L, the substitution of only one H_2O molecule is necessary. The O−O bond energy in thus formed species $[Al(H_2O)_{(n-1)}(H_2O_2)L_m]^{3+}$ is expected to be low since the ligand L should play the same role that the OOH ligand does in **5**. The skip of one energetically demanding step (the ligand substitution) in the reaction mechanism may provide a lower overall activation barrier than was found for the catalyst **1**. The verification of this hypothesis is the subject of future experimental and theoretical studies.

2. Epoxidation of Alkenes. There are a number of theoretical works devoted to mechanistic studies of olefin epoxidation catalyzed by complexes of Ti, V, Cr, Mo, W, Mn, Re, Fe, Ru, Pt, and Cu.[39,40] Two main types of mechanisms are usually considered for the metal-catalyzed epoxidations with H_2O_2, i.e., the Mimoun[41] and the Sharpless[42] mechanisms. The classical version of the first route includes the formation of a π complex between the catalyst and the olefin followed by the generation of a five-membered metallacyclic intermediate which, upon decomposition, affords the epoxide (Scheme 4A). The second route represents a concerted one-step process when the olefin molecule directly attacks the peroxo ligand of the catalyst (Scheme 4B).

Scheme 5. Sharpless Mechanisms of Ethylene Epoxidation with Complexes 9 and 10



For the system $1/H_2O_2$—which was also successfully used for the epoxidation of olefins[16]—both Sharpless and Mimoun mechanisms as well as other alternative stepwise routes were studied in the present work for the epoxidation of C_2H_4.

i. Sharpless-Type Mechanism. The hydroperoxo complex $[Al(H_2O)_5(OOH)]^{2+}$ (**3**) formed from **1** upon ligand substitution and protolysis (see above, Scheme 3) might be an active catalytic species for olefin epoxidation. However, we were unable to locate any transition state of the Sharpless mechanism for this complex. All attempts resulted in the extrusion of one water molecule from the inner coordination sphere. Thus, we examined complexes $[Al(H_2O)_4(OOH)](H_2O)^{2+}$ (**9**) and $[Al(H_2O)_3(OOH)](H_2O)_2^{2+}$ (**10**) with Al coordination numbers of 5 and 4, respectively, assuming that the ligated OOH occupies one coordination position (Scheme 5). The formation of these complexes from $[Al(H_2O)_5(OOH)]^{2+}$ (**3**) requires +5.7 and +5.9 kcal/mol, respectively (Table 2, entries 1, 2). For both of these species, transition states **TS5** and **TS6** were found. The IRC calculations demonstrate that these TSs are indeed of the Sharpless-type.

The $\Delta G_s^{\ddagger}$ values of epoxidations via **TS5** and **TS6** are 14.3 and 14.0 kcal/mol, respectively (Table 2, entries 3, 4). The apparent activation barriers of these two channels relative to **1** are also practically the same (28.2 and 28.1 kcal/mol, in terms of ΔG_s, Figure 3, and 24.1 and 25.0 kcal/mol, in terms of ΔH_s neglecting the entropic term of the protolysis of **2**). The epoxidations are strongly exothermic and exoergonic and lead to the formation of complexes **11** and **12** with the epoxide coordinated to Al via the oxygen atom. The decomposition of these species liberates the epoxide and regenerates the catalyst in the form $[Al(H_2O)_{(5-x)}(OH)]^{2+}$ ($x = 0-2$; Table 2, entries 5, 6). The hydroxo complex with the saturated coordination sphere of Al, **8**, appears to be more stable than complexes 7 and **13** (Table 1, entry 11; Table 2, entry 7).

ii. Mimoun-Type Mechanism. For this mechanism, three routes based on the complexes **3**, **9**, and **10** were considered (Scheme 6). The first step of the classic Mimoun mechanism is the formation of a π complex of olefin with the catalyst. The structures of the π complexes *trans-/cis*-**14**, **15**, and **16** formed as a result of the substitution of one H_2O ligand for C_2H_4 were located for all three routes. The most stable structure is *cis*-**14**, followed by *trans*-**14**, **15**, and **16**. The addition of the ethylene molecule is a strongly endoergonic process with ΔG_s values of 17.8−23.2 kcal/mol (Table 2, entries 8−11). In fact, the energy of *cis*-**14** is only by 2.1 kcal/mol lower than the energy of **TS6**. The structures *cis*-**14**, **15**, and **16** with neighboring positions of the C_2H_4 and OOH ligands are precursors for the formation of five-membered metallacyclic intermediates.

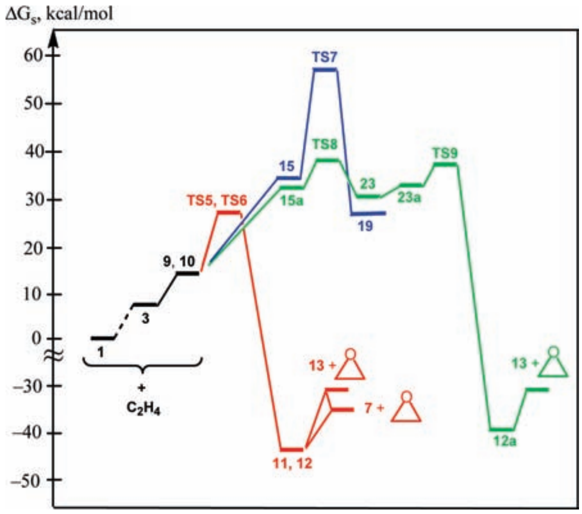


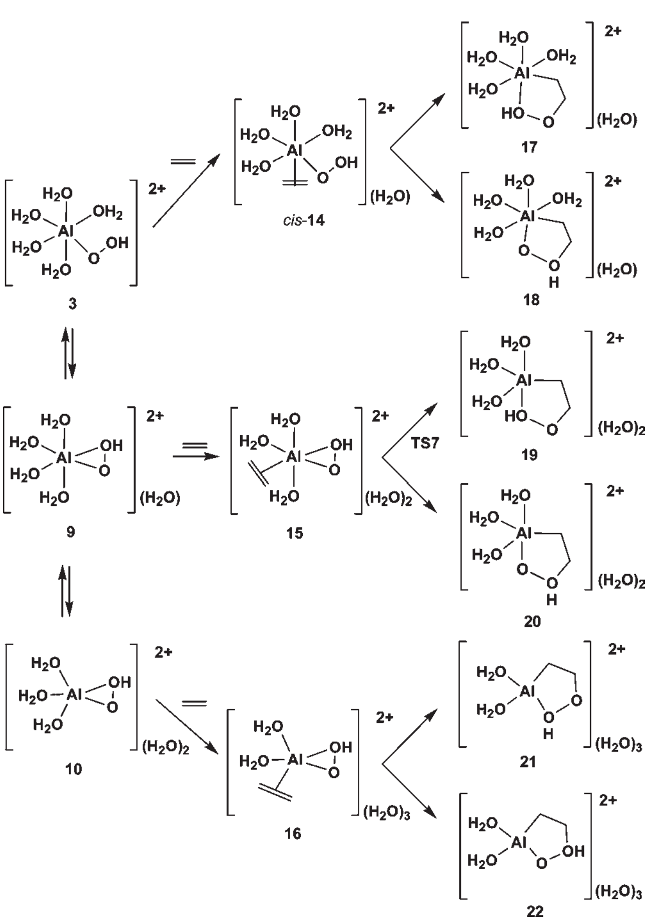
Figure 3. Energy profiles corresponding to Sharpless (red), Mimoun (blue), and alternative stepwise (green) mechanisms of Al-catalyzed ethylene epoxidation.

Two types of the five-membered metallacyclo intermediates with different protonated oxygen atoms [the −CCOO(H)Al− type

(**17**, **19**, **21**) and the −CCO(H)OAl− type (**18**, **20**, **22**)] were found for each of the three Mimoun routes. The intermediates of the −CCOO(H)Al− type are more stable than the corresponding structures of the −CCO(H)OAl− type. In the first triad, **17** and **19** have similar stabilities while **21** is by 12.5−12.7 kcal/mol less stable. The formation of the intermediates is strongly endoergonic relative to the $[Al(H_2O)_5(OOH)]^{2+}$ (**3**) + C_2H_4 system (by 18.9−38.6 kcal/mol, Table 2, entries 12−17).

For the route involving the most stable intermediate, **19**, a transition state of its formation (**TS7**) was calculated. The activation barrier of the formation of **19** is very high, i.e., 57.0 kcal/mol relative to **1** vs 28.1 kcal/mol for the Sharpless mechanism (Figure 3). Thus, the Mimoun mechanism of the Al-catalyzed olefin epoxidation is not favorable.

Scheme 6. Formation of Intermediates of the Mimoun Mechanisms



iii. Alternative Stepwise Mechanism. Besides the Mimoun-type mechanism, another stepwise route was examined. It starts with the formation of the adduct **15a** of ethylene with the catalyst **10** (Scheme 7, Table 2, entry 18). Complex **15a** transforms via transition state **TS8** to the four-membered metallacyclic species **23**, which undergoes isomerization to **23a**. The epoxide coordinated to Al through the oxygen atom (complex **12a**) is then afforded from **23a** in one step via **TS9**. The energies of **TS8** and **TS9** are similar, the latter being slightly more stable, by 0.9 kcal/mol (Table 2, entries 19, 21). The activation barrier of the discussed mechanism is 38.9 kcal/mol relative to **1**, which is by 10.8 kcal/mol higher than the barrier of the Sharpless mechanism (Figure 3). Another even less plausible stepwise mechanism of the olefin epoxidation with the **1**/H_2O_2 catalyst is discussed in the Supporting Information.

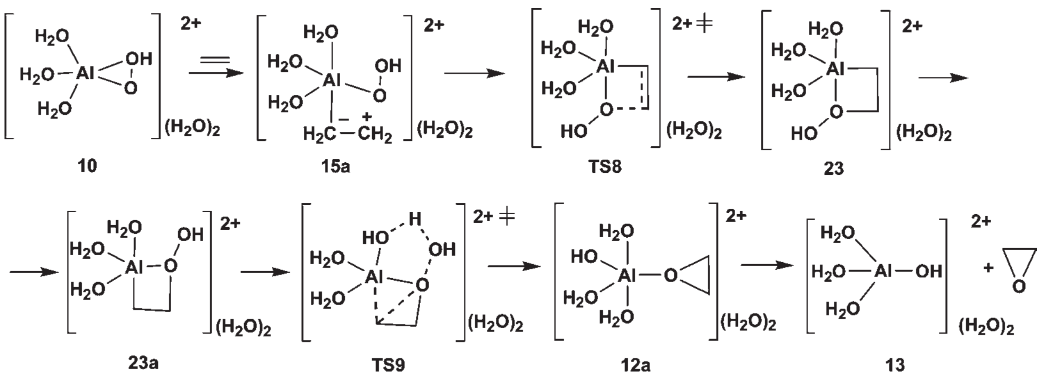
It is interesting that, as discussed above, the activation barriers of the $HO^•$ and $HOO^•$ radical formation in the **1**/H_2O_2 system are *lower* than the barrier of the Sharpless epoxidation (25.6 and 27.0 kcal/mol vs 28.1 kcal/mol). Thus, the oxidation of olefins by the highly reactive $HO^•$ radicals is quite competitive with the Sharpless epoxidation. This is consistent with the experimental data about the formation of a mixture of products containing not only epoxides and diols but also alcohols, ketones, and products of C−C bond cleavage.[16]

■ FINAL REMARKS

In summary, in the present work, the first attempted theoretical mechanistic studies of alkane and olefin oxidations with the promising "green" and cheap catalytic system $[Al(H_2O)_6]^{3+}$/H_2O_2/MeCN−H_2O have been undertaken. The mechanism of the generation of $HO^•$ and $HOO^•$ radicals—the former is able to directly oxidize even very inert saturated hydrocarbons—includes (*i*) the substitution of a H_2O molecule for H_2O_2 in the starting complex $[Al(H_2O)_6]^{3+}$, (*ii*) the H-transfer from the coordinated H_2O_2 to water (protolysis), and (*iii*) the second substitution of the ligated H_2O for H_2O_2 to give the hydroperoxo complex $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$ (**5**) (Scheme 3). This complex plays a crucial role in the mechanism due to unusual weakness of the HO−OH and Al−OOH bonds (the homolytic O−O bond energy of H_2O_2 ligated in **5** is 6.1 kcal/mol vs 39.4 kcal/mol in free H_2O_2).

The presence of the OOH ligand was found to be a fundamental factor of the H_2O_2 activation in complex **5**. The ability of the OOH ligand to be relatively easy oxidized by one electron

Scheme 7. Alternative Stepwise Mechanism of Ethylene Epoxidation with Complex 10



provides the delocalization of the spin density in the decomposition product $[Al(H_2O)_4(OOH)(OH)]^{2+}$, dramatically decreasing the HO−OH bond energy in **5**. In addition, it is expected that the introduction of another easily oxidizable ligand to the catalyst molecule instead of OOH will play a similar role in the activation of H_2O_2 at a metal which cannot change its oxidation state. This practically useful prediction opens possibilities to favorable catalyst modifications. Among the mechanisms of olefin epoxidation, the Sharpless route is the most favorable one. However, the oxidation of olefins by free radicals is quite competitive with the nonradical epoxidation, explaining the low selectivity of this reaction.

It is important also that the mechanism of the $HO^{\bullet}$ and $HOO^{\bullet}$ generation proposed in this work may have a general character and be feasible not only for the specific catalyst **1** but also for other catalytic systems with the metal having a unique stable nonzero oxidation state. To confirm this hypothesis, additional studies are necessary, and they are underway in our groups.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of the calculation of the ΔG of protolysis, discussion of an outer-sphere nonradical mechanisms of the olefin epoxidation, tables with energies and atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: max@mail.ist.utl.pt (M.L.K.), shulpin@chph.ras.ru (G.B.S.).

ACKNOWLEDGMENT

This work was supported by the FCT (Ciência 2007 and PPCDT programmes) (Portugal), FAPESP (grant 2006/03996-6), CNPq (grants 478165/2006-4, 305014/2007-2) (Brazil) and the Russian Foundation for Basic Research (grant 06-03-32344-a). MLK is grateful to the FCT and IST for a research contract within the Ciência 2007 scientific programme. GBS expresses his gratitude to the FCT and IST for making it possible for him to stay at IST as invited Professor and to perform a part of the present work.

REFERENCES

(1) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932. (b) Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, *103*, 2457–2473. (c) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. *Green Chem.* **2003**, *5*, 1–7. (d) Brégeault, J.-M. *Dalton Trans.* **2003**, 3289–3302. (e) Labinger, J. A. *J. Mol. Catal. A* **2004**, *220*, 27–35. (f) Conley, B. L.; Tenn, W. J., III; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.; Mironov, O.; Oxgaard, J.; Gonzales, J.; Goddard, W. A., III; Periana, R. A. *J. Mol. Catal. A: Chem.* **2006**, *251*, 8–23. (g) Muzart, J. *J. Mol. Catal. A* **2007**, *276*, 62–72. (h) Díaz-Requejo, M. M.; Pérez, P. J. *Chem. Rev.* **2008**, *108*, 3379–3394. (i) Shul'pin, G. B. *Mini-Rev. Org. Chem.* **2009**, *6*, 95–104. (j) Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 575 and references in these reviews.

(2) (a) England, J.; Britovsek, G. J. P.; Rabadla, N.; White, A. J. P. *Inorg. Chem.* **2007**, *46*, 3752–3767. (b) Sorokin, A. B.; Kudrik, E. V.; Alvarez, L. X.; Afanasiev, P.; Millet, J. M. M.; Bouchu, D. *Catal. Today* **2010**, *157*, 149–154. (c) Romakh, V. B.; Therrien, B.; Süss-Fink, G.; Shul'pin, G. B. *Inorg. Chem.* **2007**, *46*, 3166–3175. (d) Tanase, S.; Marques-Gallego, P.; Browne, W. R.; Hage, R.; Bouwman, E.; Feringa, B. L.; Reedijk, J. *Dalton Trans.* **2008**, 2026–2033. (e) Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2010**, *75*, 3705–3714. (f) Gomez, L.; Garcia-Bosch, I.; Company, A.; Benet-Buchholz, J.; Polo, A.; Sala, X.; Ribas, X.; Costas, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5720–5723. (g) Gosiewska, S.; Lutz, M.; Spek, A. L.; Gebbink, R. J. M. K. *Inorg. Chim. Acta* **2007**, *360*, 405–417. (h) Taktak, S.; Ye, W.; Herrera, A. M.; Rybak-Akimova, E. V. *Inorg. Chem.* **2007**, *46*, 2929–2942. (i) Monfared, H. H.; Amouei, Z. *J. Mol. Catal. A* **2004**, *217*, 161–164.

(3) (a) Kirillova, M. V.; Kuznetsov, M. L.; Romakh, V. B.; Shul'pina, L. S.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Shul'pin, G. B. *J. Catal.* **2009**, *267*, 140–157. (b) Kozlov, Yu. N.; Romakh, V. B.; Kitaygorodskiy, A.; Buglyo, P.; Süss-Fink, G.; Shul'pin, G. B. *J. Phys. Chem. A* **2007**, *111*, 7736–7752. (c) Kirillova, M. V.; Kuznetsov, M. L.; Reis, P. M.; da Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Am. Chem. Soc.* **2007**, *129*, 10531–10545. (d) Adão, P.; Pessoa, J. C.; Henriques, R. T.; Kuznetsov, M. L.; Avecilla, F.; Maurya, M. R.; Kumar, U.; Correia, I. *Inorg. Chem.* **2009**, *48*, 3542–3561. (e) Si, T. K.; Chakraborty, S.; Mukherjee, A. K.; Drew, M. G. B.; Bhattacharyya, R. *Polyhedron* **2008**, *27*, 2233–2242. (f) Maity, D.; Marek, J.; Sheldrick, W. S.; Mayer-Figge, H.; Ali, M. *J. Mol. Catal. A* **2007**, *270*, 153–159. (g) Gekhman, A. E.; Stolyarov, I. P.; Moiseeva, N. I.; Moiseev, I. I. *C. R. Chim.* **2004**, *7*, 833–844. (h) Wei, X.; Ye, L.; Yuan, Y. *J. Nat. Gas Chem.* **2009**, *18*, 295–299. (i) Teramura, K.; Tanaka, T.; Hosokawa, T.; Ohuchi, T.; Kani, M.; Funabiki, T. *Catal. Today* **2004**, *96*, 205–209. (j) Conte, V.; Fabbianesi, F.; Floris, B.; Galloni, P.; Sordi, D.; Arends, I. W. C. E.; Bonchio, M.; Rehder, D.; Bogdal, D. *Pure Appl. Chem.* **2009**, *81*, 1265–1277.

(4) (a) Herbert, M.; Alvarez, E.; Cole-Hamilton, D. J.; Montilla, F.; Galindo, A. *Chem. Commun.* **2010**, *46*, 5933–5935. (b) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Royo, B. *Catal. Lett.* **2010**, *136*, 222–227. (c) Dinoi, C.; Ciclosi, M.; Manoury, E.; Maron, L.; Perrin, L.; Poli, R. *Chem.—Eur. J.* **2010**, *16*, 9572–9584.

(5) (a) Mardani, H. R.; Golchoubian, H. *J. Mol. Catal. A* **2006**, *259*, 197–200. (b) Nakayama, N.; Tsuchiya, S.; Ogawa, S. *J. Mol. Catal. A* **2007**, *277*, 61–71. (c) Shul'pin, G. B.; Kozlov, Y. N.; Kholuiskaya, S. N.; Plieva, M. I. *J. Mol. Catal. A* **2009**, *299*, 77–87. (d) Serafimidou, A.; Stamatis, A.; Louloudi, M. *Catal. Commun.* **2008**, *9*, 35–39.

(6) (a) Khouw, C. B.; Dartt, C. B.; Labinger, J. A.; Davis, M. E. *J. Catal.* **1994**, *149*, 195–205. (b) Clerici, M. G. *Appl. Catal.* **1991**, *68*, 249–261.

(7) (a) Xiong, D.; Wu, M.; Wang, S.; Li, F.; Xia, C.; Sun, W. *Tetrahedron Assym.* **2010**, *21*, 374–378. (b) Matsumoto, K.; Oguma, T.; Katsuki, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 7432–7435. (c) Berkessel, A.; Brandenburg, M.; Leitterstorf, E.; Frey, J.; Lex, J.; Schaefer, M. *Adv. Synth. Catal.* **2007**, *349*, 2385–2391.

(8) (a) Yuan, Q.; Deng, W.; Zhang, Q.; Wang, Y. *Adv. Synth. Catal.* **2007**, *349*, 1199–1209. (b) Shul'pin, G. B.; Kirillova, M. V.; Kozlov, Y. N.; Shul'pina, L. S.; Kudinov, A. R.; Pombeiro, A. J. L. *J. Catal.* **2011**, *277*, 164–172. (c) Ell, A. H.; Jonsson, S. Y.; Borje, A.; Adolfsson, H.; Backvall, J. E. *Tetrahedron Lett.* **2001**, *42*, 2569–2571.

(9) (a) Roy, P.; Manassero, M. *Dalton Trans.* **2010**, *39*, 1539–1545. (b) Balandina, T. A.; Larina, T. Yu.; Kuznetsova, N. I.; Bal'zhinimaev, B. S. *Kinet. Catal.* **2008**, *49*, 499–505. (c) Ohta, T.; Tachiyama, T.; Yoshizawa, K.; Yamabe, T.; Uchida, T.; Kitagawa, T. *Inorg. Chem.* **2000**, *39*, 4358–4369. (d) Barton, D. H. R.; Delanghe, N. C.; Patin, B. *Tetrahedron* **1997**, *53*, 16017–16028. (e) Okuno, T.; Ohba, S.; Nishida, Y. *Polyhedron* **1997**, *16*, 3765–3774. (f) Silva, A. C.; Fernández, T. L.; Carvalho, N. M. F.; Herbst, M. H.; Bordinhão, J.; Horn, A., Jr.; Wardell, J. L.; Oestreicher, E. G.; Antunes, O. A. C. *Appl. Catal., A* **2007**, *317*, 154–160.

(10) (a) Kirillova, M. V.; Kirillov, A. M.; Kuznetsov, M. L.; da Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Chem. Commun.* **2009**, 2353–2355. (b) Silva, T. E. S.; Alegria, E. C. B. A.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Adv. Synth. Cat.* **2008**, *350*, 706–716.

(11) (a) Stephenson, N. A.; Bell, A. T. *J. Mol. Catal. A* **2007**, *275*, 54–62. (b) Correa, A.; Mancheño, O. G.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108–1117. (c) Pignatello, J. J.; Oliveros, E.; McKay, A. *Crit. Rev. Environ. Sci. Tech.* **2006**, *36*, 1–84 and reference therein.

(12) Fenton, H. J. H. *J. Chem. Soc.* **1894**, *65*, 899–910.

(13) (a) Mandelli, D.; do Amaral, A. C. N.; Kozlov, Y. N.; Shul'pina, L. S.; Bonon, A. J.; Carvalho, W. A.; Shul'pin, G. B. *Catal. Lett.* **2009**, *132*, 235–243. (b) Dissanayake, D.; Kharas, K. C. C.; Lunsford, J. H.; Rosynek, M. P. *J. Catal.* **1993**, *139*, 652–663. (c) Mota, C. J. A.; Bhering, D. L.; Ramírez-Solís, A. *Int. J. Quantum Chem.* **2005**, *105*, 174–185. (d) Colorio, G.; Vedrine, J. C.; Auroux, A.; Bonnetot, B. *Appl. Catal., A* **1996**, *137*, 55–68. (e) Qian, G.; Ji, D.; Lu, G.; Zhao, R.; Qi, Y.; Suo, J. *J. Catal.* **2005**, *232*, 378–385.

(14) (a) Stoica, G.; Santiago, M.; Jacobs, P. A.; Perez-Ramirez, J.; Pescarmona, P. P. *Appl. Catal., A* **2009**, *371*, 43–53. (b) Pescarmona, P. P.; Jacobs, P. A. *Catal. Today* **2008**, *137*, 52–60. (c) Rinaldi, R.; Fujiwara, F. Y.; Schuchardt, U. *J. Catal.* **2007**, *245*, 456–465. (d) Uguina, M. A.; Delgado, J. A.; Rodriguez, A.; Carretero, J.; Gomez-Diaz, D. *J. Mol. Catal. A* **2006**, *256*, 208–215. (e) Choudhary, V. R.; Patil, N. S.; Chaudhari, N. K.; Bhargava, S. K. *J. Mol. Catal. A* **2005**, *227*, 217–222. (f) Pillai, U. R.; Sahle-Demessie, E. *Appl. Catal., A* **2004**, *261*, 69–76. (g) Fraile, J. M.; Garcia, J. I.; Marco, D.; Mayoral, J. A. *Appl. Catal., A* **2001**, *207*, 239–246.

(15) Mandelli, D.; Chiacchio, K. C.; Kozlov, Y. N.; Shul'pin, G. B. *Tetrahedron Lett.* **2008**, *49*, 6693–6697.

(16) Rinaldi, R.; de Oliveira, H. F. N.; Schumann, H.; Schuchardt, U. *J. Molec. Catal. A* **2009**, *307*, 1–8.

(17) (a) Salvador, J. A. R.; Silvestre, S. M. *Tetrahedron Lett.* **2005**, *46*, 2581–2584. (b) Bonvin, Y.; Callens, E.; Larrosa, I.; Henderson, D. A.; Oldham, J.; Burton, A. J.; Barrett, A. G. M. *Org. Lett.* **2005**, *7*, 4549–4552. (c) Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 8409–8411. (d) Goodman, M. A.; Detty, M. R. *Synlett* **2006**, 1100–1104. (e) Betzemeier, B.; Lhermitte, F.; Knochel, P. *Synlett* **1999**, 489–491. (f) ten Brink, G.-J.; Fernandez, B. C. M.; van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 224–228. (g) Chaudhari, K.; Das, T. K.; Rajmohanan, P. R.; Lazar, K.; Sivasanker, S.; Chandwadkar, A. J. *J. Catal.* **1999**, *183*, 281–291. (h) Sever, R. R.; Root, T. W. *J. Phys. Chem. B* **2003**, *107*, 10521–10530. (i) Ionescu, R.; Pavel, O. D.; Brjega, R.; Zăvoianu, R.; Angelescu, E. *Catal. Lett.* **2010**, *134*, 309–317. (j) van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Tetrahedron Lett.* **1999**, *40*, 5239–5242. (k) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689–1697. (l) García-Marín, H.; van der Toorn, J. C.; Mayoral, J. A.; García, J. I.; Arends, I. W. C. E. *Green Chem.* **2009**, *11*, 1605–1609.

(18) The Ca^{2+} and Mg^{2+} catalyzed carbonylation of alkanes in the presence of $K_2S_2O_8$ as an oxidant was reported earlier: (a) Asadullah, M.; Kitamura, T.; Fujiwara, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 2475–2478. (b) Asadullah, M.; Kitamura, T.; Fujiwara, Y. *Appl. Organomet. Chem.* **1999**, *13*, 539–547.

(19) The mechanism of heterogeneous activation of the alkane C–H bond on unsaturated Al ions or on Al_n or $(Al_2O_3)_x^+$ clusters and the oxidation of methane by the HOO$^\bullet$ radical complexed to the lithium cation in the absence of H_2O_2 were previously theoretically studied: (a) Fărcaşiu, D.; Lukinskas, P. *J. Phys. Chem. A* **2002**, *106*, 1619–1626. (b) Alexandrou, E. I.; Gross, A.; Bacalis, N. C. *J. Chem. Phys.* **2010**, *132*, 154701–154714. (c) Feyel, S.; Döbler, J.; Höckendorf, R.; Beyer, M. K.; Sauer, J.; Schwarz, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1946–1950. (d) Clark, T.; Hofmann, H. *J. Phys. Chem.* **1994**, *98*, 13797–13803.

(20) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785–789.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Peterson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) Luo, X.; Fleming, P. R.; Rizzo, T. R. *J. Chem. Phys.* **1992**, *96*, 5659–5667.

(23) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853–5860.

(24) Qian, Z.; Feng, H.; Yang, W.; Miao, Q.; He, L.; Bi, S. *Chem. Commun.* **2008**, 3930–3932.

(25) Barone, V.; Cossi, M. *J. Phys. Chem.* **1998**, *102*, 1995–2001.

(26) (a) Wertz, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 5316–5322. (b) Cooper, J.; Ziegler, T. *Inorg. Chem.* **2002**, *41*, 6614–6622.

(27) Shul'pin, G. B.; Kozlov, Y. N.; Nizova, G. V.; Süss-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1351–1371.

(28) Haber, F.; Weiss, J. *Naturwiss.* **1932**, *20*, 948–950.

(29) Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. *Trans. Faraday Soc.* **1951**, *47*, 591–616.

(30) Kozlov, Y. N.; Nadezhdin, A. D.; Purmal', A. P. *Kinet. Katal.* **1973**, *14*, 141–148.

(31) (a) Sawyer, D. T.; Sobkowiak, A.; Matsushita, T. *Acc. Chem. Res.* **1996**, *29*, 409–416. (b) Walling, C. *Acc. Chem. Res.* **1998**, *31*, 155–157. (c) Goldstein, S.; Meyerstein, D. *Acc. Chem. Res.* **1999**, *32*, 547–550. (d) MacFaul., P. A.; Wayner, D. D. M.; Ingold, K. U. *Acc. Chem. Res.* **1998**, *31*, 159–162. (e) Dunford, H. B. *Coord. Chem. Rev.* **2002**, *233*, 311–318. (f) Groves, J. T. *J. Inorg. Biochem.* **2006**, *100*, 434–447.

(32) For example: (a) Paczesniak, T.; Sobkowiak, A. *J. Mol. Catal. A* **2003**, *194*, 1–11. (b) Ensing, B.; Buda, F.; Gribnau, M. C. M.; Baerends, E. *J. Am. Chem. Soc.* **2004**, *126*, 4355–4365. (c) Bautz, J.; Bukowski, M. R.; Kerscher, M.; Stubna, A.; Comba, P.; Lienke, A.; Münck, E.; Que, L., Jr. *Angew. Chem., Int. Ed.* **2006**, *45*, 5681–5684. (d) Rush, J. D.; Koppenol, W. H. *J. Inorg. Biochem.* **1987**, *29*, 199–215. (e) Kremer, M. L. *J. Inorg. Biochem.* **2000**, *78*, 255–257. (f) Kremer, M. L. J. *J. Phys. Chem. A* **2003**, *107*, 1734–1741. (g) Perez-Benito, J. F. *J. Phys. Chem. A* **2004**, *108*, 4853–4858. (h) Bassan, A.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Que, L. *J. Am. Chem. Soc.* **2002**, *124*, 11056–11063. (i) Comba, P.; Rajaraman, G.; Rohwer, H. *Inorg. Chem.* **2007**, *46*, 3826–3838. (j) Chandrasena, R. E. P.; Vatsis, K. P.; Coon, M. J.; Hollenberg, P. F.; Newcomb, M. *J. Am. Chem. Soc.* **2004**, *126*, 115–126. (k) Michel, C.; Baerends, E. J. *Inorg. Chem.* **2009**, *48*, 3628–3638. (l) Das, S.; Bhattacharyya, J.; Mukhopadhyay, S. *Dalton Trans.* **2008**, 6634–6640. (m) Nam, W.; Han, H. J.; Oh, S. Y.; Lee, Y. J.; Choi, M. H.; Han, S. Y.; Kim, C.; Woo, S. K.; Shin, W. *J. Am. Chem. Soc.* **2000**, *122*, 8677–8684. (n) Derat, E.; Kumar, D.; Hirao, H.; Shaik, S. *J. Am. Chem. Soc.* **2006**, *128*, 473–484. (o) Kamachi, T.; Yoshizawa, K. *J. Am. Chem. Soc.* **2003**, *125*, 4652–4661. (p) Ogliaro, F.; Harris, N.; Cohen, S.; Filatov, M.; de Visser, S. P.; Shaik, S. *J. Am. Chem. Soc.* **2000**, *122*, 8977–8989.

(33) (a) Khaliullin, R. Z.; Bell, A. T.; Head-Gordon, M. *J. Phys. Chem. B* **2005**, *109*, 17984–17992. (b) Kuznetsov, M. L.; Pombeiro, A. J. L. *Inorg. Chem.* **2009**, *48*, 307–318.

(34) (a) Hanauer, H.; Puchta, R.; Clark, T.; van Eldik, R. *Inorg. Chem.* **2007**, *46*, 1112–1122. (b) Kowall, T.; Caravan, P.; Bourgeois, H.; Helm, L.; Rotzinger, F. P.; Merbach, A. E. *J. Am. Chem. Soc.* **1998**, *120*, 6569–6577. (c) Evans, R. J.; Rustad, J. R.; Casey, W. H. *J. Phys. Chem. A* **2008**, *112*, 4125–4140.

(35) (a) Phillips, B. L.; Casey, W. H.; Crawford, S. N. *Geochim. Cosmochim. Acta* **1997**, *61*, 3041–3049. (b) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545–554.

(36) *Catalytic oxidations with hydrogen peroxide as oxidant*; Strukul, G., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; p 60.

(37) Sposito, G. *The Environmental Chemistry of Aluminium*, 2nd ed.; CRC: Boca Raton, FL, 1995.

(38) (a) DiPasquale, A. G.; Hrovat, D. A.; Mayer, J. M. *Organometallics* **2006**, *25*, 915–924. (b) DiPasquale, A. G.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 14534–14535.

(39) Kuznetsov, M. L.; Pessoa, J. C. *Dalton Trans.* **2009**, 5460–5468 and references therein.

(40) (a) Kamata, K.; Ishimoto, R.; Hirano, T.; Kuzuya, S.; Uehara, K.; Mizuno, N. *Inorg. Chem.* **2010**, *49*, 2471–2478. (b) Costa, P. J.;

Calhorda, M. J.; Kühn, F. E. *Organometallics* **2010**, *29*, 303–311. (c) Yamaguchi, K.; Yamanaka, S.; Shimada, J.; Isobe, H.; Saito, T.; Shoji, M.; Kitagawa, Y.; Okumura, M. *Int. J. Quantum Chem.* **2009**, *109*, 3745–3766. (d) Li, H.-B.; Tian, S. X.; Yang, J. *Chem.—Eur. J.* **2009**, *15*, 10747–10751. (e) Benet-Buchholz, J.; Comba, P.; Llobet, A.; Roeser, S.; Vadivelu, P.; Wadepohl, H.; Wiesner, S. *Dalton Trans.* **2009**, 5910–5923. (f) Stare, J.; Henson, N. J.; Eckert, J. *J. Chem. Inf. Model.* **2009**, *49*, 833–846. (g) Kuznetsov, A. E.; Geletii, Y. V.; Hill, C. L.; Morokuma, K.; Musaev, D. G. *Inorg. Chem.* **2009**, *48*, 1871–1878. (h) Lundin, A.; Panas, I.; Ahlberg, E. *J. Phys. Chem. A* **2009**, *113*, 282–290. (i) Kamachi, T.; Lee, Y.-M.; Nishimi, T.; Cho, J.; Yoshizawa, K.; Nam, W. *J. Phys. Chem. A* **2008**, *112*, 13102–13108. (j) Haras, A.; Ziegler, T. *Can. J. Chem.* **2009**, *87*, 33–38. (k) Comas-Vives, A.; Lledos, A.; Poli, R. *Chem.—Eur. J.* **2010**, *16*, 2147–2158. (l) Tse, M. K.; Bhor, S.; Klawonn, M.; Anilkumar, G.; Jiao, H. J.; Spannenberg, A.; Dobler, C.; Magerlein, W.; Hugl, H.; Beller, M. *Chem.—Eur. J.* **2006**, *12*, 1875–1888.

(41) Mimoun, H.; Seree de Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37–50.

(42) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295–296.