Quantum Chemical Modeling of Propene and Butene Epoxidation with Hydrogen Peroxide

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The mechanism of hydrogen peroxide assisted epoxidation of propene, 1-butene, *trans*-2-butene, *cis*-2-butene, and isobutene was studied using density functional theory calculations. The results are rationalized in the context of the previously proposed direct pathway for epoxidation of ethene with hydrogen peroxide and compared to the indirect pathway involving Ti(IV) peroxide groups. The indirect Ti(IV) peroxide pathway displays a 57.8 kJ mol^{-1} activation enthalpy for the rate limiting step [*Phys. Chem. Chem. Phys.* **2007**, *9*, 5997]. In contrast, a lowering of the activation enthalpy is observed for the direct mechanism according to 72.3 (ethene), 53.9 (1-butene), 53.5 (propene), 46.9 (*trans*-2-butene), 46.6 (isobutene), and 42.6 (*cis*-2-butene) kJ mol^{-1} when the reaction takes place on a binuclear Ti(IV) dihydroxide site. These values clearly show that the direct pathway becomes the most favorable. The stability of the epoxides toward hydrolysis to the corresponding diols are also addressed. The present work clearly demonstrates the generality and efficiency of a binuclear dihydroxide site in catalyzing the epoxidation of olefins with hydrogen peroxide, thus avoiding the formation of a surface peroxide group.

1. Introduction

In two recent studies, a new mechanism for hydrogen peroxide assisted epoxidation was demonstrated, where the stabilization of the transition state was emphasized.[1,2] In the novel transition state, hydrogen peroxide is polarized to form a transient $H^{\delta+}-O-OH^{\delta-}$ structure. The subsequent recombination of $H^{\delta+}$ with $OH^{\delta-}$ to form H_2O is complementary to the epoxidation reaction. Microsolvation with water leads to stabilization of the polarized transition state and to a lowering of the activation enthalpy. A further decrease of the activation enthalpy was obtained by replacing molecular water by a binuclear (Ti(IV), Si(IV), Ge(IV)) dihydroxide unit. It is the improved ability of the hydroxide groups to stabilize the $OH^{\delta-}$ fragment, which is responsible for the further lowering of the barrier. The degree of uniqueness of Ti(IV)−OH in this respect was tested by replacing Ti(IV) by Si(IV) and Ge(IV). The similarity in obtained numbers emphasizes the importance of the binuclear dihydroxide site and demonstrates the nonuniqueness of Ti(IV) in this direct one-step reaction.[1] In Scheme 1 the energetics of ethene epoxidation is indicated for the direct one-step reaction and an indirect two-step reaction,[1] both appearing on a fully relaxed dihydroxide titanium site. The indirect two-step reaction involves formation of a Ti(IV)−OOH intermediate, which is avoided in the direct one-step reaction. In comparison, the corresponding data from a study of Limtrakul et. al[3] are also shown highlighting the mechanistic differences. In the latter work[3] the titanium ion is constrained within a zeolite structure making it reactive toward hydrogen peroxide. Formation of the surface peroxide group displays a negligible activation barrier. In contrast, the epoxidation reaction is associated with a substantial activation barrier, and the value resembles that obtained for ethene and hydrogen peroxide in vaccum.[2]

Vayssilov and van Santen[4] investigated a mechanism of ethene epoxidation in which Ti(IV) has a passive role in the actual epoxidation reaction. This mechanism was also incorporated in the study of Wells et. al[5] on propene epoxidation. A further development of this mechanism involved a defect site with hydroxide groups on the titanium site and on the adjacent silicon site.[5,6] The formation of a surface peroxide group as a first step in the epoxidation reaction with hydrogen peroxide was originally proposed by Bellussi[7−9] and also studied theoretically.[10−12] Sinclair and Catlow[12] perceived Ti(IV) to function as a Lewis acid. This mechanism emphasizes the activation of the O−O chemical bond beyond that in H_2O_2 by the formation of reactive Ti-(η^2 − OOH) hydroperoxy species.

The fate of the formed epoxide with respect to hydrolysis was also studied recently,[13] and it was shown that the reaction mechanism differs in neutral media compared to acid or alkaline conditions. Under neutral conditions, the ring-opening reaction involves only one water molecule, which is protolysed in the transition state. The activation barrier for this reaction is high, which is in agreement with the low reaction rate observed experimentally. Under acidic and alkaline conditions an S_N2 reaction is observed, with water and hydroxide ions acting as nucleophiles and oxonium ions and water acting as electrophiles, respectively. The activation enthalpies for these reactions are significantly lower than for the reaction under neutral conditions, which agrees well with experimental results.[14−20] The mechanism of hydrolysis of epoxides was recently reviewed, and it was emphasized that an understanding of the acid- and base-catalyzed mechanisms of epoxide hydrolysis in aqueous solutions is of special interest.[19]

The purpose of the present study is to demonstrate the characteristics of the direct one-step mechanism in case of propene, 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene epoxidation to clarify any degree of generality and demonstrate its relevance as a competing mechanism to the Ti(IV)-OOH mediated epoxidation channel.

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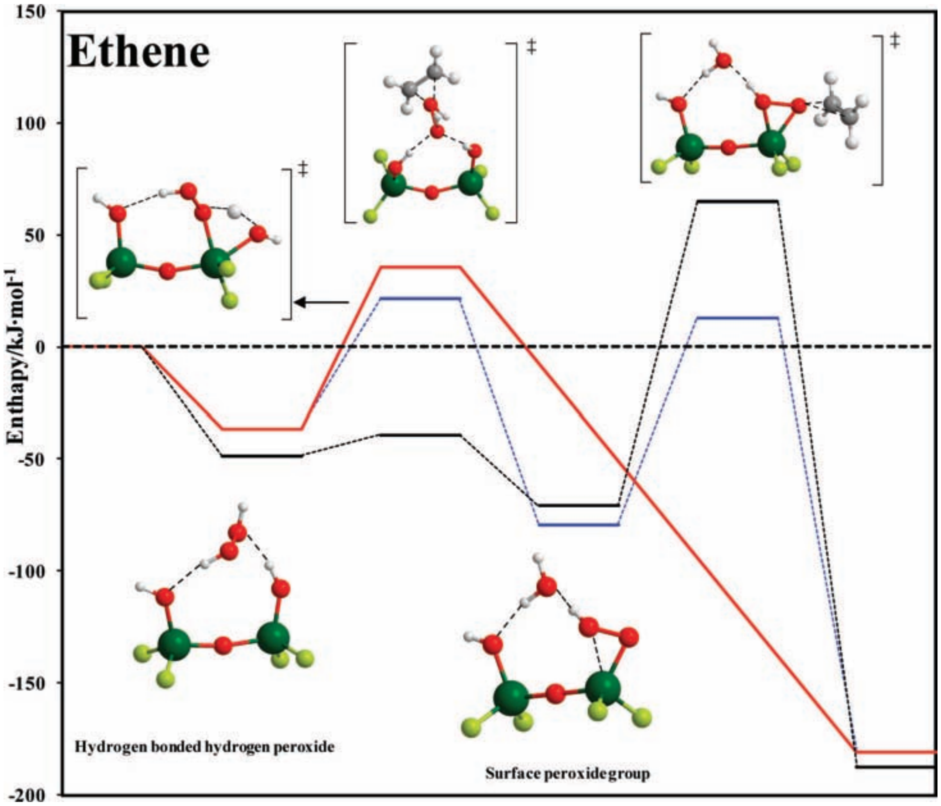
SCHEME 1: Ethene Epoxidation[a]



[a] Schematic reaction enthalpy diagrams corresponding to three different pathways for hydrogen peroxide assisted epoxidation of ethene on a Ti(IV) site showing direct epoxidation (red) and indirect epoxidation paths (blue, black[3]). The latter involve the formation of an intermediate Ti(IV)−OOH group). Results for a fully relaxed binuclear site (blue) and a constrained site in a zeolite (black[3]) are compared. The entities shown in brackets are related to the direct and indirect pathways (red and blue).

2. Computational Details

Level of theory and methodology were described and evaluated in detail in previous works.[1,2,13] Crucial for the applicability of density functional theory (DFT) to chemical reactions that involve bond breaking and bond formation is that (a) the ground-state potential energy surface displays a large HOMO−LUMO gap along the whole reaction path and that (b) the coupling between reactant and product states via the transition states must be strong. These requirements were demonstrated to be satisfied for the class of reactions considered in this work.

In particular, the B3LYP[21,22] hybrid density functional description was demonstrated to provide a reliable description. The triple-ξ basis, 6-311+G(d, p),[23] chosen for all atoms, was shown to give a balanced description of both hydrogen bonding and relevant bond breaking and bond formation.

The B3LYP/6-311+G(d,p) calculations were performed by employing the GAUSSIAN 03 program package.[24] Molecular structures were optimized, and analytical Hessians were subsequently evaluated for all the optimized geometries. All transition states are characterized by one imaginary eigenvalue of the Hessian matrix. Aside from the structural information and vibrational spectra, data from the Hessians was used for the thermochemical calculations.

3. Results

The present work repeats the ethene epoxidation[1,2] and hydrolysis[13] studies for propene. The results are presented in sections 3.1−3.3, where complementary data for 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene are also included. The stability of the epoxides with respect to hydrolysis is particularly addressed.

3.1. Propene Oxidation Upon Catalytic Microsolvation. The mechanism whereby hydrogen bonding facilitates access of a $H^{\delta+}-O-OH^{\delta-}$ transition state was described previously.[2] The corresponding results for the bare reaction between propene and hydrogen peroxide as well as those in the presence of 1, 2, and 4 water molecules are presented in Figure 1. Dramatic lowering of the activation enthalpy is observed, from 129.6 kJ mol^{-1} for the bare reaction down to 78.8 kJ mol^{-1} in case of microsolvation by four water molecules. This is in spite of the fact that in the reference state the oxidant H_2O_2 is microsolvated. The corresponding results in case of ethene epoxidation[2] are 136.6 and 92.4 kJ mol^{-1} for the bare and microsolvated systems, respectively. Interestingly, the 50.8 kJ mol^{-1} lowering of the activation enthalpy in case of propene is similar to the 44.2 kJ mol^{-1} found for ethene. However, the absolute activation enthalpy of propene epoxidation comes out 13.6 to kJ mol^{-1} lower than that of ethene. This difference can to some extent already be observed in the corresponding bare reactions, where a 7.0 kJ mol^{-1} difference is found.

3.2. Propene and Butene Oxidation on Binuclear Ti(IV) Dihydroxide Catalyst. The general features of the mechanism described for ethene.[2] were previously demonstrated for models of hydroxylated interfaces.[1] A binuclear dihydroxide site was postulated and results for Si(IV), Ge(IV), and Ti(IV) hydroxides were compared. For all three cases, some 20 kJ mol^{-1} further lowering of the activation enthalpy was observed for the epoxidation reaction as compared to microsolvation (four water

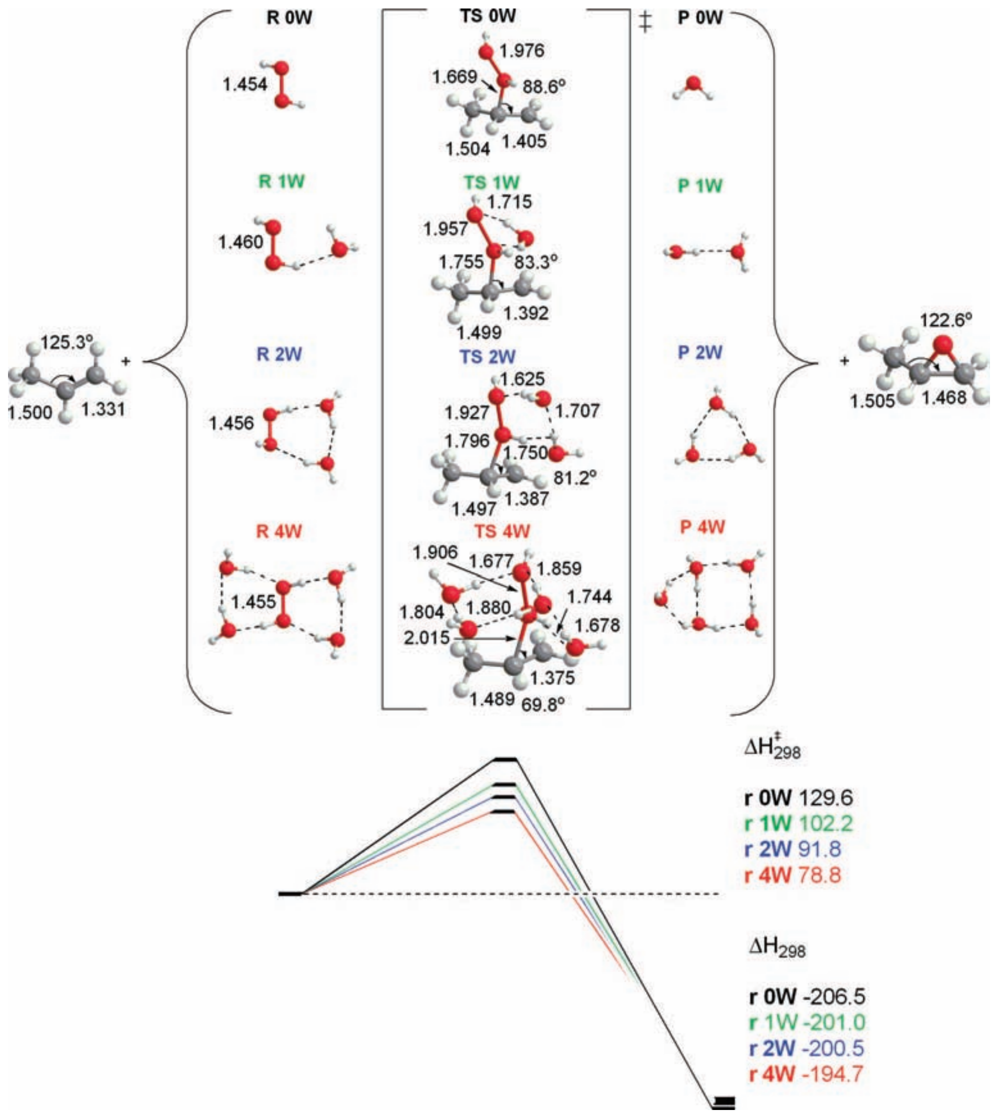


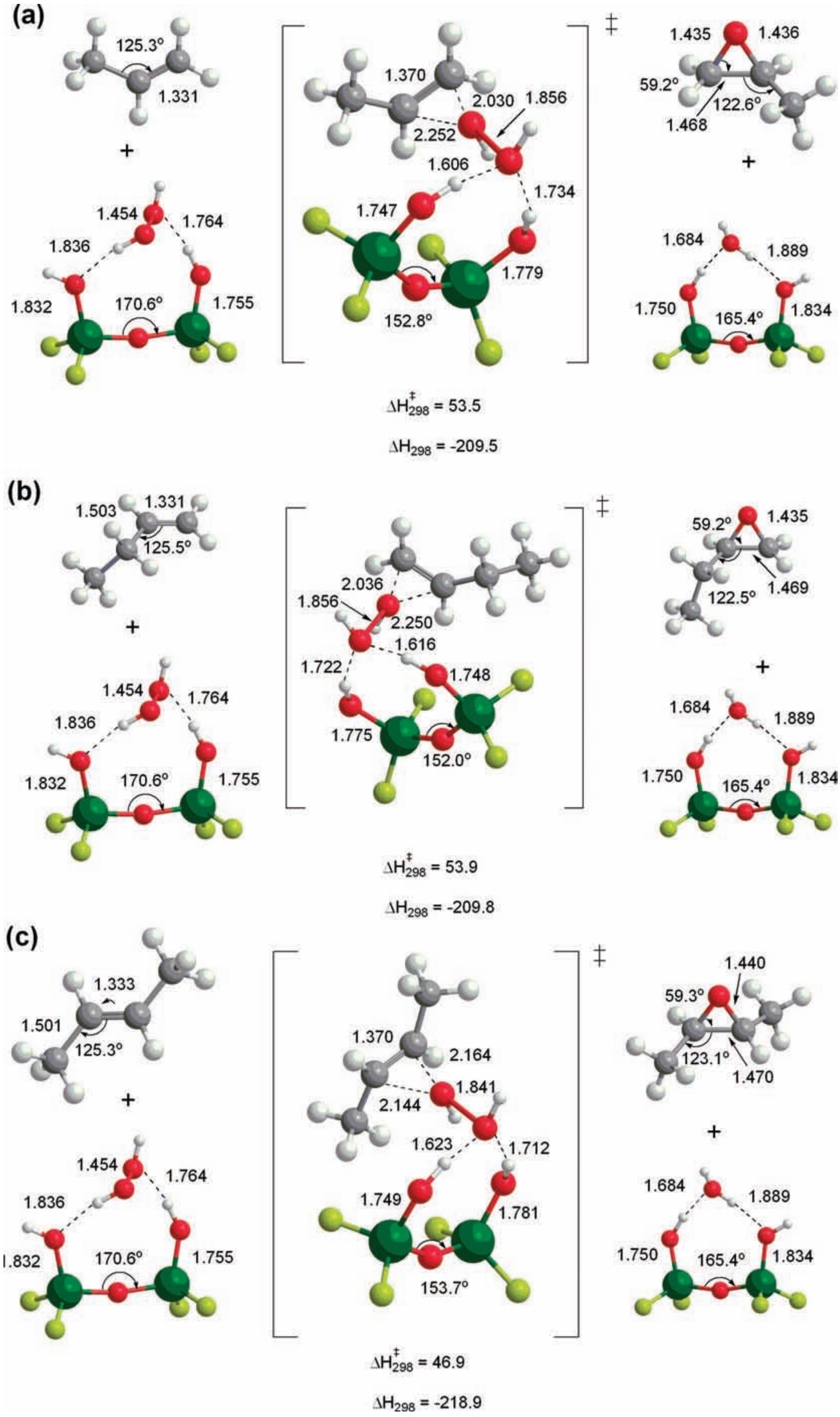
Figure 1. Hydrogen peroxide assisted propene epoxidation upon microsolvation. 0W−4W indicates the number of microsolvating water molecules. Bond distances are given in Ångströms and enthalpies in kJ mol^{-1}. The activation enthalpies $\Delta H^{\ddagger}_{298}$ and reaction enthalpies ΔH_{298} are given with respect to free propene and microsolvated hydrogen peroxide.

molecules). The corresponding results for propene are presented in Figure 2a for the case of a binuclear Ti(IV) dihydroxide catalytic site. The resulting 53.5 kJ mol^{-1} activation enthalpy comprises a further lowering by 25.3 kJ mol^{-1} relative to the microsolvation case (four water molecules).

To consolidate this finding, the reaction mechanism was repeated for 1-butene, *cis*- and *trans*-2-butene, and isobutene, for which activation enthalpies of 53.9, 42.6, 46.9, and 46.6 kJ mol^{-1} were determined, respectively (parts b−e of Figure 2). The trend toward lower activation enthalpies for ethene (72.3 kJ mol^{-1}), propene (53.5 kJ mol^{-1}) and butene (42.6−53.9 kJ mol^{-1}) is discussed in section 4.

3.3. Propene Oxide and Butene Oxides Hydrolyses. The stability of ethene oxide toward hydrolysis to ethane diol in water was investigated.[13] Low activation barriers were determined under acidic and alkaline conditions (S_N2-type mechanism). Under neutral conditions an S_N1-type hydrolysis of the epoxide was characterized. This reaction path is repeated here for propene oxide and butene oxides. In case of propene oxide, two reaction channels were investigated comprising epoxide oxygen ending up on the central carbon, and epoxide oxygen ending up on the terminal carbon. The two pathways, depicted in Figure 3, are denoted Alpha and Beta, respectively. In the case of the Alpha hydrolysis pathway, water acts as nucleophile on the terminal carbon, while protonating the epoxide oxygen. In the case of the beta pathway, the nucleophilic attack occurs on the central carbon. The activation enthalpy for the Alpha pathway (206.8 kJ mol^{-1}) is found to be somewhat higher than the Beta pathway (189.8 kJ mol^{-1}). These results should be compared to that found for the hydrolysis of ethene oxide, where a 205.0 kJ mol^{-1} activation enthalpy was obtained.[13]

1-Butene oxide hydrolysis was investigated partly in order to place activation enthalpies of the Alpha and Beta pathways in a broader context. The values 207.2 kJ mol^{-1} (Alpha) and 194.9 kJ mol^{-1} (Beta) are similar to those obtained for propene, Figure 4a. The asymmetry of the Alpha and Beta hydrolysis pathways was investigated further by addressing the corresponding reaction for cis- and trans-2-butene oxide and isobutene oxide. 2-Butene oxide possesses only one unique hydrolysis pathway for each of the trans and cis configurations. 194.0 kJ mol^{-1} (trans) and 191.5 kJ mol^{-1} (cis) activation enthalpies were obtained, as shown in parts b and d of Figure 4. In the case of isobutene oxide, two pathways, Alpha and Gamma (See Figure 4c) can be distinguished with analogy to the Alpha and Beta pathways for propene oxide. Again, the pathway that performs the nucleophilic attack on the central carbon displays the lower


(a)
125.3°
1.331
+
1.454
1.764
1.836
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170.6°
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‡
1.370
2.030
1.856
2.252
1.606
1.734
1.747
1.779
152.8°
1.435
1.436
59.2°
122.6°
1.468
+
1.684
1.889
1.750
165.4°
1.834
$\Delta H^{\ddagger}_{298}$ = 53.5
ΔH_{298} = -209.5
(b)
1.503
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125.5°
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170.6°
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‡
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2.250
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152.0°
59.2°
1.435
122.5°
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+
1.684
1.889
1.750
165.4°
1.834
$\Delta H^{\ddagger}_{298}$ = 53.9
ΔH_{298} = -209.8
(c)
1.333
1.501
125.3°
+
1.454
1.764
1.836
1.832
170.6°
1.755
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1.370
2.164
1.841
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153.7°
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$\Delta H^{\ddagger}_{298}$ = 46.9
ΔH_{298} = -218.9

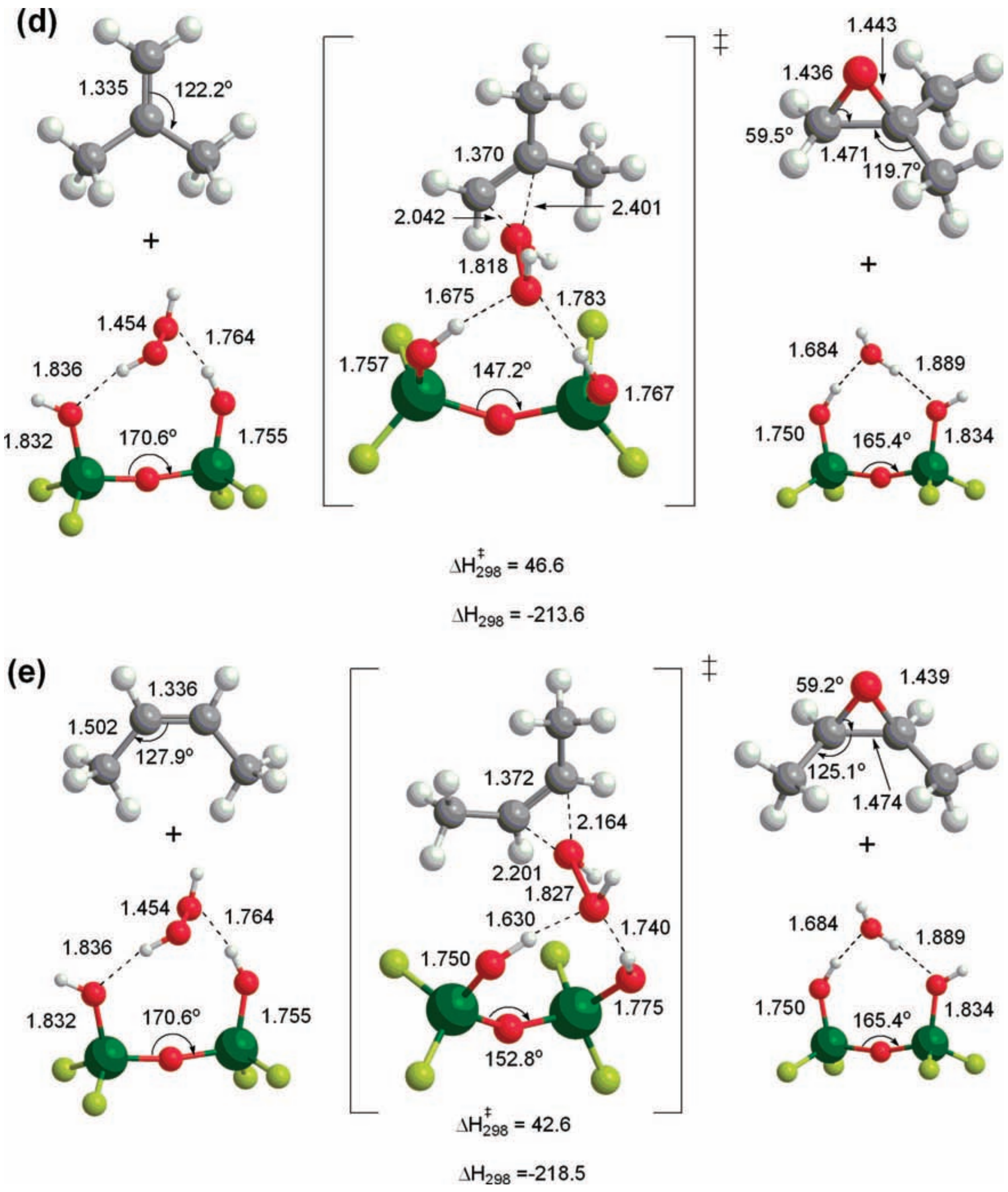


Figure 2. Direct one-step reaction pathway for (a) propene, (b) 1-butene, (c) *trans*-2-butene, (d) isobutene, and (e) *cis*-2-butene epoxidations by hydrogen peroxide at a binuclear Ti(IV) dihydroxide site. Bond distances are given in Ångströms and enthalpies in kJ mol^{-1}. The activation enthalpies $\Delta H^{\ddagger}_{298}$ and reaction enthalpies ΔH_{298} are given with respect to free propene and adsorbed hydrogen peroxide.

activation enthalpy, i.e., 210.1 vs 162.7 kJ mol^{-1} for the Alpha and Gamma pathways, respectively.

Two results are stressed. First, the activation enthalpies for hydrolysis of ethene oxide is similar to those found for the Alpha pathways of propene oxide, 1-butene oxide, and isobutene oxide, i.e., 205.0, 206.8, 207.2, and 210.1 kJ mol^{-1}, respectively. Second, a trend is observed toward lower activation enthalpies in the series ethene oxide, 2-butene oxide (trans and cis) and propene oxide, and isobutene oxide, i.e., 205.0, {194.0, 191.5, 189.8}, and 162.7 kJ mol^{-1}, respectively. Both these trends are discussed in section 4.

4. Discussion

A novel mechanism for olefin epoxidation, which exploits the ability of a microsolvating hydrogen bonding network to polarize the O−O σ bond in hydrogen peroxide has been demonstrated previously.[2] This reaction channel involves a transition state which has $H^{\delta+}O-OH^{\delta-}$ as key component. Decomposition of this species into "O" + H_2O provides an alternative route toward olefin epoxidation. Here, this mechanism was evaluated for propene epoxidation. Interestingly, when comparing ethene to propene, lower activation energies were found for the latter, both for the bare and microsolvated epoxidation reactions. Demonstration of the fundamental and general origins of this increased reactivity is a main objective of the present work. Thus, the hydrogen bonding network of the microsolvating water cluster was replaced by that of a binuclear Ti(IV) dihydroxide model site. A further downward shift of the propene activation enthalpy for epoxidation was observed, and the series 129.6 kJ mol^{-1} (bare), 78.8 kJ mol^{-1}

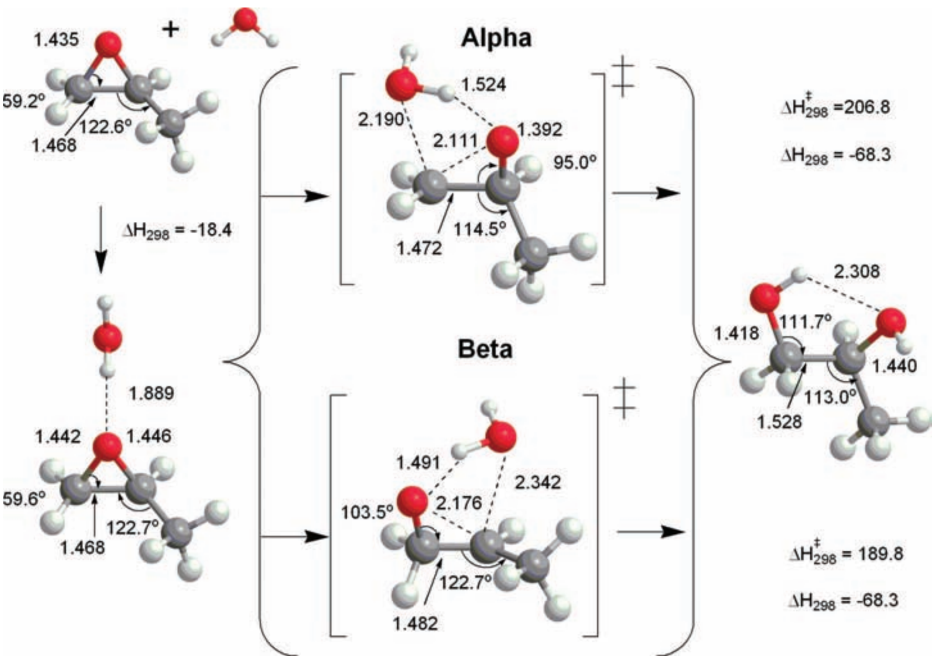


Figure 3. Propene oxide hydrolysis. Alpha and Beta refer to the order of the carbanion electrophile. Bond distances are given in Ångströms and enthalpies in kJ mol^{-1}. The activation enthalpies $\Delta H^{\ddagger}_{298}$ and reaction enthalpies ΔH_{298} are given with respect to free propene oxide and free water.

(four water molecules), and 53.5 kJ mol^{-1} (binuclear dihydroxide) was found (vide supra, sections 3.1. and 3.2). This series of activation enthalpies should be compared to that for ethene epoxidation, i.e., 136.6 kJ mol^{-1} (bare), 92.4 kJ mol^{-1} (four water molecules), and 72.3 kJ mol^{-1} (binuclear dihydroxide).[1,2] The hypothesis that the differences between the ethene and propene series originates from the different abilities of the olefins to stabilize a carbocation−carbanion pair, resulting from the polarization of the π bond, was tested by considering 1-butene, *cis*- and *trans*-2-butene, and isobutene epoxidation at the binuclear dihydroxide site. Indeed, an even lower activation enthalpy than that found for propene was determined for isobutene, while 1-butene is similar to propene and 2-butene comes out similar to isobutene, supporting the hypothesis. Thus, at the binuclear dihydroxide site, the trend 72.3 kJ mol^{-1} (ethene), 53.9 kJ mol^{-1} (1-butene), 53.5 kJ mol^{-1} (propene), 46.9 kJ mol^{-1} (*trans*-2-butene), 46.6 kJ mol^{-1} (isobutene), and 42.6 kJ mol^{-1} (*cis*-2-butene) emerges for the activation enthalpies.

The reactivity of epoxides toward hydrolysis, to form the corresponding diols, have been demonstrated to be sensitively dependent on pH, both experimentally[14−20] and by means of theory.[13] The epoxides are only stable in a regime close to pH 7. The hydrolysis pathway under neutral conditions, corresponding to that considered for ethene oxide,[13] i.e., nucleophilic attack on carbon while protonating the epoxide oxygen, was investigated for both propene oxide and butene oxides (vide supra section 3.3). By consideration of the trend in activation enthalpies for hydrolyses, i.e., 194.9 (1-butene; Beta channel), 189.8 (propene oxide; Beta channel), and 162.7 kJ mol^{-1} (isobutene oxide; Gamma channel), a possible explanation is that it reflects the *different* abilities of the olefins to stabilize a carbocation site. Support for this hypothesis is produced by considering the *similarity* in hydrolysis barriers resulting from nuclear attacks on the α carbon, i.e., 205.0 (ethene oxide), 206.8 (propene oxide), 207.2 (1-butene oxide), and 210.1 kJ mol^{-1} (isobutene oxide). Apparent exceptions to this rule are *trans*-2-butene and *cis*-2-butene, which produce intermediate activation enthalpies of hydrolysis, between the Alpha and Beta/Gamma pathways, i.e., 194.0 and 191.5 kJ mol^{-1}, respectively. This is because these possess only one hydrolysis pathway, which is observed to average over the easy (Beta/Gamma) and difficult (Alpha) pathways.

The competing *indirect pathway* for catalytic olefin epoxidation employs Ti(IV)OH as catalyst and has the formation of the Ti(IV)−OOH peroxide as the rate limiting step. A 57.8 kJ mol^{-1} activation enthalpy for this step was determined,[1] in agreement with previous studies.[5,10−12] While this value is arguably significantly lower than that obtained for the *direct pathway* in case of ethene (72.3 kJ mol^{-1}), in the case of both the propene (53.5 kJ mol^{-1}), 1-butene (53.9 kJ mol^{-1}), *trans*-2-butene (46.9 kJ mol^{-1}), isobutene (46.6 kJ mol^{-1}), and *cis*-2-butene (42.6 kJ mol^{-1}) epoxidation reactions, the *direct pathway* prevails. The energy diagrams for epoxidation of propene and butene are summarized in Schemes 2 and 3.

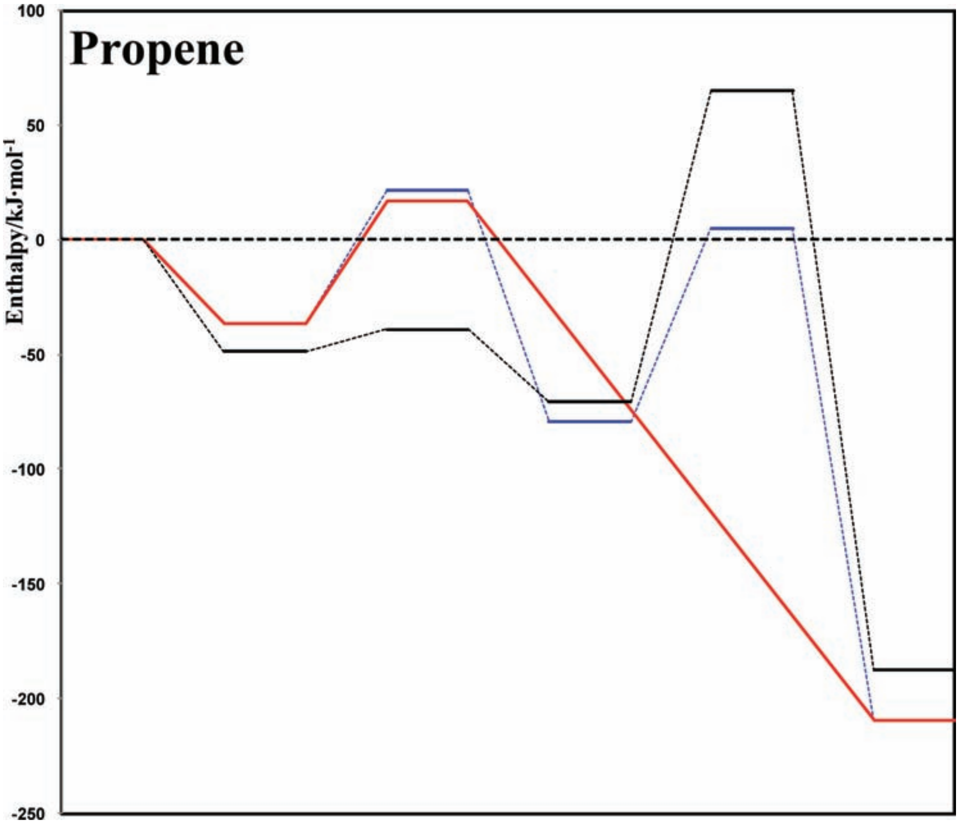
5. Conclusions

A direct one-step reaction channel for epoxidation of olefins by means of hydrogen peroxide, which passes over a $H^{\delta+}{-}O{-}OH^{\delta-}$ transition state was previously described for ethene.[1,2] Crucial for the strategy to form epoxides in aqueous media is the stability of the products. Hydrolysis to the corresponding diols occurs readily under alkaline and acidic conditions, while the products are found to be stable in neutral media. Here, these findings were generalized to apply to the oxidation of propene and butene.

Dramatic lowering of activation enthalpies toward epoxidation from 129.6 kJ mol^{-1} (bare), 78.8 kJ mol^{-1} (four water molecules), and 53.5 kJ mol^{-1} (binuclear dihydroxide site) were found for propene. In the case of ethene epoxidation, a parallel trend was observed,[1,2] i.e., 136.6 (bare), 92.4 (four water molecules), and 72.3 kJ mol^{-1} (binuclear dihydroxide).

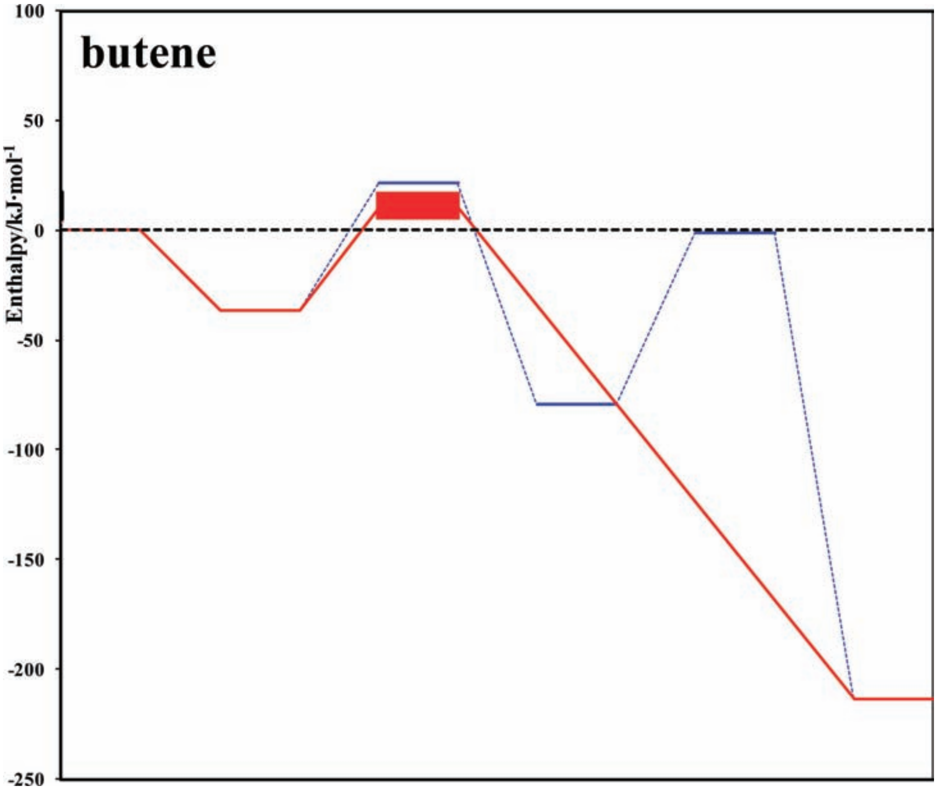
Activation enthalpies obtained at the binuclear dihydroxide site are 72.3 (ethene), 53.9 (1-butene), 53.5 (propene), 46.9 (*trans*-2-butene), 46.6 (isobutene), and 42.6 (*cis*-2-butene) kJ

SCHEME 2: Propene Epoxidation[a]

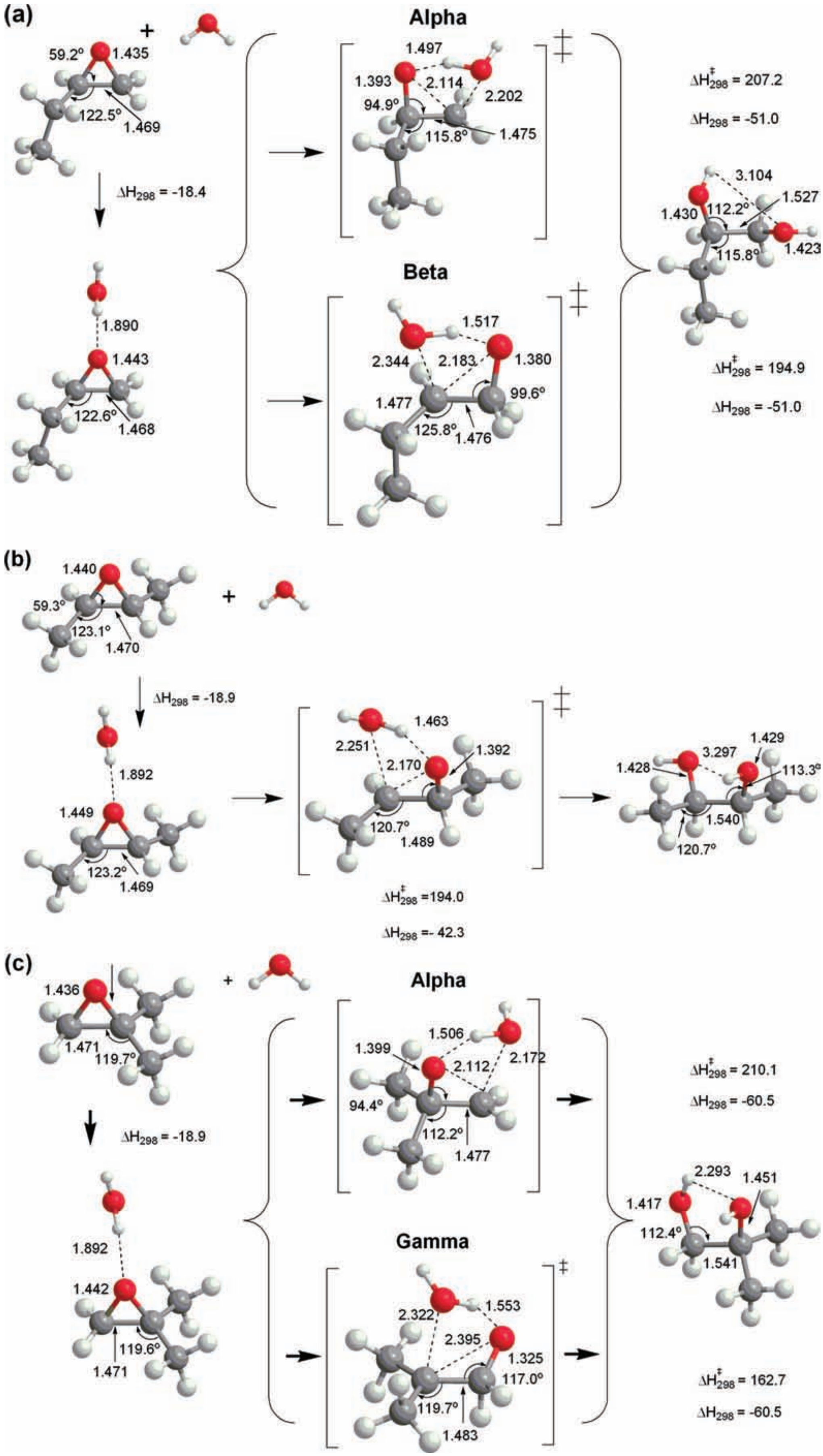


[a] Schematic reaction enthalpy diagrams corresponding to three different pathways for hydrogen peroxide assisted epoxidation of propene on a Ti(IV) site showing direct epoxidation (red) and indirect epoxidation paths (blue, black[3]). The latter involve the formation of an intermediate Ti(IV)−OOH group). Results for a fully relaxed binuclear site (blue) and a constrained site in a zeolite (black[3]) are compared.

SCHEME 3: Butene Epoxidation[a]



[a] Schematic reaction enthalpy diagrams corresponding to two different pathways for hydrogen peroxide assisted epoxidation of the butenes investigated on a Ti(IV) site showing the direct epoxidation path (red) and indirect epoxidation path (blue).


(a)
+
59.2°
1.435
122.5°
1.469
ΔH298 = -18.4
1.890
1.443
122.6°
1.468
Alpha
1.497
1.393
2.114
2.202
94.9°
115.8°
1.475
‡
Beta
1.517
2.344
2.183
1.380
1.477
99.6°
125.8°
1.476
‡
ΔH‡298 = 207.2
ΔH298 = -51.0
3.104
1.527
1.430
112.2°
115.8°
1.423
ΔH‡298 = 194.9
ΔH298 = -51.0
(b)
1.440
59.3°
123.1°
1.470
+
ΔH298 = -18.9
1.892
1.449
123.2°
1.469
1.463
2.251
2.170
1.392
120.7°
1.489
‡
ΔH‡298 =194.0
ΔH298 =- 42.3
1.429
1.428
3.297
113.3°
1.540
120.7°
(c)
1.436
+
1.471
119.7°
ΔH298 = -18.9
1.892
1.442
119.6°
1.471
Alpha
1.506
1.399
2.112
2.172
94.4°
112.2°
1.477
ΔH‡298 = 210.1
ΔH298 = -60.5
2.293
1.451
1.417
112.4°
1.541
Gamma
‡
2.322
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2.395
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117.0°
119.7°
1.483
ΔH‡298 = 162.7
ΔH298 = -60.5

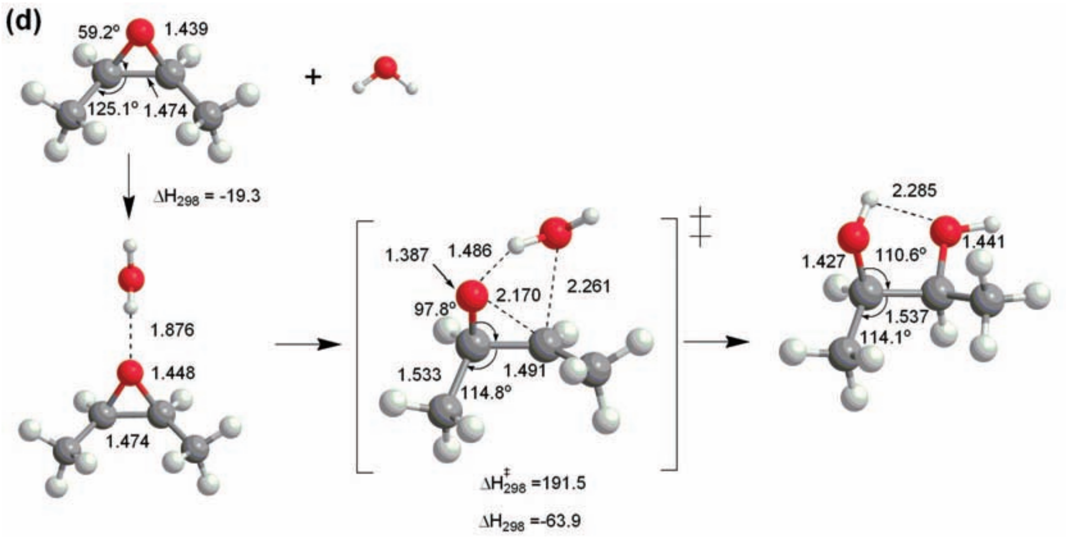

Figure 4. Hydrolysis of butene oxides (a) 1-butene, (b) *trans*-2-butene, (c) isobutene, and (d) *cis*-2-butene. Alpha, Beta, and Gamma refer to the order of the carbanion electrophile. Bond distances are given in Ångströms and enthalpies in kJ mol^{-1}. The activation enthalpies $\Delta H^{\ddagger}_{298}$ and reaction enthalpies ΔH_{298} are given with respect to free isobutene oxide and free water.

mol^{-1}. This trend was understood mainly to be due to the different abilities of the olefins to stabilize a carbocation–carbanion pair.

The direct one-step reaction was contrasted by the indirect two-step reaction. The latter involves formation of a Ti(IV)–OOH intermediate, for which a barrier of 57.8 kJ mol^{-1} was determined,[1] while the second barrier, i.e., toward epoxide formation, was found to be 49.5 kJ/mol. Thus, the direct one-step reaction becomes the route to prefer for propene, 1- and 2-butene, as well as for isobutene.

The barriers for epoxide hydrolysis under neutral conditions were found to be high, i.e., 205.0 kJ mol^{-1} (ethene oxide), 194.9 kJ mol^{-1} (1-butene; Beta channel), 189.8 kJ mol^{-1} (propene oxide; Beta channel), and 162.3 kJ mol^{-1} (isobutene oxide; Gamma channel). These values clearly show the stability of the different epoxides under neutral conditions.[13]

This work has demonstrated the generality and efficiency of a binuclear dihydroxide site in catalyzing the epoxidation of olefins with hydrogen peroxide via a direct one-step reaction, which avoids the formation of a Ti(IV)–OOH intermediate.

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