

DFT STUDY OF THE ENTIRE REACTION CYCLE OF H₂O₂ DECOMPOSITION AND O₂ GENERATION CATALYZED BY FENTON REAGENT

Ion Arsene^{a,b*}, Natalia Gorinchiy^b

^aTiraspol State University, 5, Gh. Yablocikin str., Chisinau MD 2069, Republic of Moldova

^bInstitute of Chemistry, 3, Academiei str., Chisinau MD 2028, Republic of Moldova

*e-mail: arsene_ion@mail.ru

Abstract. The reaction cycle of H₂O₂ decomposition and O₂ generation catalyzed by Fenton reagent was studied using density functional theory calculations. A four-stage mechanism for the oxygen production and the Fe²⁺ regeneration in the Fenton reaction is proposed based on the obtained results. The transition state for each step of the entire reaction cycle was localized and verified by intrinsic reaction coordinate analysis. It is shown that the O-O bond cleavage of coordinated H₂O₂ at the first step of reaction does not lead to a free HO• radical. Instead, a highly reactive intermediate [Fe^{IV}(H₂O)₄(OH)₂]²⁺ with two HO• radicals “trapped” in the complex is formed with the energy barrier of 15 kcal/mol. The result of the next two reaction steps is the formation of the two HO₂• radicals which can react on the triplet energy surface in order to produce O₂ in the triplet ground state and a H₂O₂ molecule.

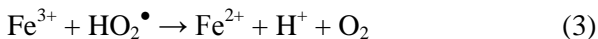
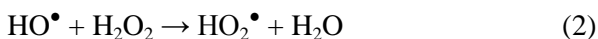
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Introduction

The Fenton reaction is known for a long time since Fenton, H.H. (1894) first observed the oxidation of tartaric acid by a mixture of iron sulphate and hydrogen peroxide. However, intensive discussions about the mechanism of this reaction and the nature of the active oxidizing intermediates continue to this day. In the 30s of the last century, almost simultaneously, two alternative models of this reaction were proposed in the literature, the so-called radical and non-radical mechanisms.

According to the first one, proposed by Haber, F. and Weiss, J. [1] and subsequently modified by Barb, W.G. *et al.* [2], the reaction of Fe(II) with hydrogen peroxide in an aqueous solution leads to the formation of free HO• and HO₂• radicals as active intermediates in reactions (Eqs.(1-5)):



It was assumed that the hydroxyl free radical HO• is the oxidative intermediate, whereas the HO₂• radical is the key intermediate in the O₂ production.

The second mechanism proposed by Bray, W.C. and Gorin, M.H. [3] involves the formation of the highly reactive ferryl-oxo complex Fe^{IV}O²⁺ (Eqs.(6,7)).



Since then, a great number of studies have been performed to elucidate the mechanism of these reactions and to determine whether the hydroxyl radical or another strongly oxidizing species are formed during the oxidation of Fe(II). The nature of these species is still a subject of controversy, since the direct experimental detection of intermediates is problematic because of their very short lifetime. So, experimental studies only indirectly confirm either one or the other reaction mechanism.

Some scientists consider that hydroxyl radicals in either “free” or “caged” form are the major oxidizing agent in the Fenton reaction [4-8]. The radical pathway seems to be preferable

also in the case of many catalytic systems based on other transition metals (the so-called non-ferrous Fenton catalysts) [9,10]. Another group of scientists supports an alternative mechanism in which the ferryl ion is regarded as the main oxidant in Fenton's reaction [11-18]. Some papers discuss that, depending on the experimental conditions, either a radical or non-radical reaction mechanism can be implemented [19-21]. A more complete discussion of the various points of view on the mechanisms of Fenton's reaction can also be found in a number of reviews [21-25].

Since, as already mentioned, the experimental identification of intermediates in the Fenton reaction is almost impossible because of their extremely short lifetime, a theoretical study of possible reaction paths can be helpful in understanding the mechanisms of this reaction. One such study based on the density functional theory (DFT) calculations was carried out by the group of Baerends, E.J. *et al.* [26-28]. In their thorough works [26,27] the authors have analyzed the possible mechanism for the oxygen evolution in the Fenton reaction assuming the formation of a ferryl-oxo complex as the key active intermediate. However, in our opinion, some aspects of the entire reaction cycle remain unclear (namely the localization of the transition states, the determination of the barriers heights and the reaction coordinates at every stage of reaction cycle). The authors start their study from the primary intermediate $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_5\text{H}_2\text{O}_2]$ which is formed by exchange of a water molecule in the hydration shell of the hexa-aqua- Fe^{2+} complex by H_2O_2 . At the same time, the first bond dissociation energy of ferrous hexa-aqua complex was found to be rather high, 24.5 kcal/mol [26]. The very process of exchange of the water molecule with the hydrogen peroxide, however, is not described.

In the present paper, using DFT calculations, we propose a possible alternative mechanism of the entire reaction cycle for the catalytic decomposition of hydrogen peroxide and the concomitant evolution of O_2 , as well as the regeneration of the $\text{Fe}(\text{II})$ catalyst in the Fenton

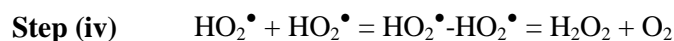
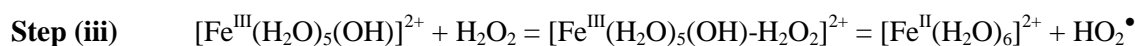
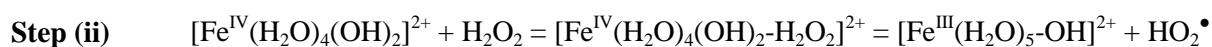
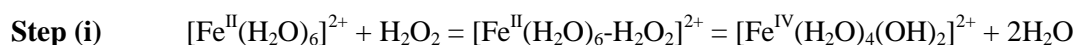
reaction. We consider here the processes occurring in the first solvation shell of the Fe^{2+} ion. There are a number of studies in which it is reported that the first solvation shell of Fe^{2+} consists of six water molecules [29], so we start with the hexa-aqua- Fe^{2+} complex.

We assume that the entire reaction cycle may proceed in the following four steps (i)-(iv).

The summary of the reaction cycle is: $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$, with regeneration of the complex $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$. In the calculations it is assumed an excess of hydrogen peroxide over Fe^{2+} ions, since oxygen evolution is actually observed experimentally under such conditions.

Computational details

The density functional theory (DFT) calculations of all the species involved in reaction steps (i)-(iv) were performed with the quantum-chemical program suite PRIRODA 06 [30-32], designed for the study of complex molecular systems by the density functional theory. The quantum-chemical code employed expansion of the electron density in an auxiliary basis set to accelerate evaluation of the Coulomb and exchange-correlation terms [30,31]. The generalized gradient approximation (GGA) with the functional proposed by Perdew, J.P., Burke, K. and Enzerhof, M. (PBE) [33] was used for treating both the exchange and correlation. The geometrical parameters for reactants, products, and transition states were fully optimized, using the all-electron correlation-consistent double- ζ polarized quality basis sets (implemented in the PRIRODA 06 package as the basis set L1, which is analogous to Dunning's basis sets cc-pVDZ [34]). For each species, the harmonic vibrational frequencies were calculated in order to validate the nature of stationary points: all positive frequencies for equilibrium structures and one imaginary frequency for transition states. After the transition state for each of the reaction steps (i)-(iv) was localized and verified to be a first-order saddle point, an intrinsic reaction coordinate (IRC) calculations were carried out to find out whether the founded transition state leads to the correct reactants and products.



Numerous calculations of the structure and properties of chemical compounds and the mechanisms of chemical reactions, performed using the PRIRODA 06 code, demonstrate the acceptability of the chosen calculation scheme for studying our systems (see, e.g. references in work [34]).

Results and discussion

Hexa-aqua Fe^{II} complex $[Fe^{II}(H_2O)_6]^{2+}$ study

To verify the accuracy of the method used, we performed calculations on the $Fe(II)$ -aqua complex in both the low-spin ($S=0$) and high-spin ($S=2$) states and compared the results with the data available in the literature. The minimum energy nuclear configuration of the ferrous complex in the $S=0$ state has T_h symmetry with the six water molecules at the vertices of the octahedron around the iron (Figure 1(a)). All the highest triply-degenerate t_g molecular orbitals (MO) are fully occupied giving rise the $^1A_{1g}$ ground state. The six Fe-O bond lengths are equal to 2.01 Å compared with 2.03 Å obtained in [26]. In the high-spin ($S=2$) electron configuration $(t_g)^4(e_g)^2$ the ground state of $Fe^{2+}(H_2O)_6$ is a triply degenerate 5T_g term. The doubly degenerate 5E_g state lays ~20 kcal/mol higher in energy [29]. In this 5T_g state, the T_h nuclear configuration is unstable with respect to both the doubly degenerate tetragonal (e_g type) and the triply degenerate trigonal (t_g type) displacements. This is the so-called $T_g \otimes (e_g + t_g)$ Jahn-Teller problem. Calculations show that in the present case the most active Jahn-Teller non-totally symmetric coordinate is the Q_θ one (e_g type), and the absolute minimum of energy is achieved at the nuclear configuration of D_{2h} symmetry (Figure 1(b)) with the elongated FeO_6 octahedron. Calculated Fe-O bond lengths are: $Fe-O_{ax}=2.18$ Å and $Fe-O_{eq}=2.11$ Å for the axial and equatorial

Fe-O bonds respectively. This result agrees with the data from the works [26,29], and with experimental data [35]. Thus, the ground state of the considered $[Fe^{II}(H_2O)_6]^{2+}$ complex is the high-spin electronic state ($S=2$) with the nuclear configuration of D_{2h} symmetry; the low-spin state ($S=0$) is 29.6 kcal/mol higher in energy than the high-spin one.

Reaction path from $[Fe^{II}(H_2O)_6]^{2+}$ to $[Fe^{IV}(H_2O)_4(OH)_2]^{2+}$ (step (i))

Consider the first step (i) of the entire reaction cycle in which the hydrogen peroxide molecule approaches the $Fe(II)$ -aqua complex in such a way that its oxygen atoms “look at” the two hydrogen atoms of adjacent water molecules. We found that in this case the stable complex $[Fe^{II}(H_2O)_6-H_2O_2]^{2+}$ with two hydrogen bonds is formed (complex **1** in Figure 2); the energy of stabilization is equal to 29.87 kcal/mol.

The transition state for this step with one imaginary frequency $918.94i$ cm^{-1} was localized (complex **TS-i** in Figure 2). The transition vector indicates that the molecular motion of this frequency is dominated by the transfer of a hydrogen atom H_1 from O_3 to O_1 and by the out-of-plane displacement of H_2 . Besides that, the torsion motion involving the four oxygen atoms also takes place. It is seen that geometry of **TS-i** complex differs significantly from that of the reactants. Firstly, the O_1-O_3 and O_2-O_4 distances between the oxygen atoms involved in hydrogen bonds decrease from 2.72 Å up to 2.44 Å and 2.48 Å, respectively. One of the hydrogen atoms of the Fe -aqua complex (H_1 in Figure 2) is displaced midway between the oxygen atoms O_1 and O_3 , becoming their shared atom. This leads to some charge transfer to the atom O_1 and the subsequent elongation of the O_1-O_2 bond length of coordinated H_2O_2 molecule up to 1.83 Å compared with 1.48 Å in free H_2O_2 molecule.

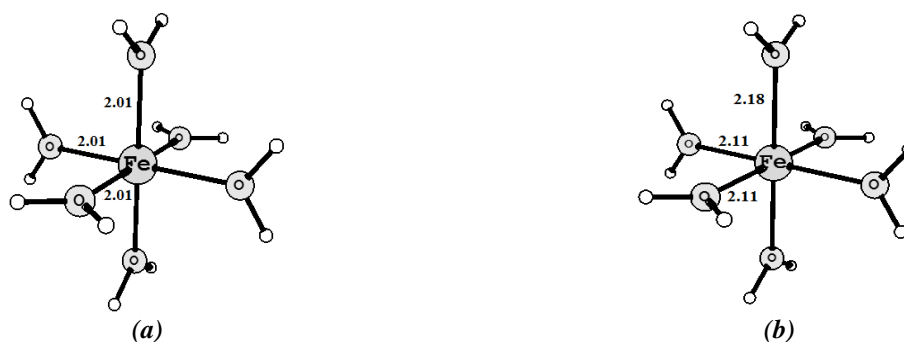


Figure 1. The structures of the $[Fe^{II}(H_2O)_6]^{2+}$ complex:
(a) T_h ($S=0$; $E_{total}=-1721.2268$ a.u.) and (b) D_{2h} ($S=2$; $E_{total}=-1721.2740$ a.u.).

Immediately after the transition state **TS-i** the vibrational motion of the complex corresponds to the displacement of the hydrogen atom H₂ (involved in the second hydrogen bond) towards the oxygen atom O₂. This, in turn, leads to further elongation and breaking of the O₁-O₂ bond.

The result of the first step (i) is the formation of the complex [Fe^{IV}(H₂O)₄(OH)₂]²⁺ with four water molecules and two OH radicals “trapped” in the complex, and two water molecules in the second coordination sphere (complex **2** in Figure 2). During the step (i) of reaction, the oxidation state of iron changes from Fe(II) to Fe(IV). The formation of such a highly reactive intermediate [Fe^{IV}(H₂O)₄(OH)₂]²⁺ has been postulated by Rush, J.D. and Koppenol, W.H. in their experimental study (stopped flow spectrophotometry) of the reaction between hydrogen peroxide and ferrous polyaminocarboxylate complexes [36]. In the work [37] the authors conclude that [LFe^{IV}(OH)₂]²⁺ (where, L= bispidine) is the key intermediate in the bispidine-iron-catalyzed olefin oxidation with H₂O₂. The same conclusion about existence of the intermediate [Fe^{IV}(H₂O)₄(OH)₂]²⁺ was also made by the authors of the work [26] on the basis of the DFT calculations, starting with the complex [Fe^{II}(H₂O)₅-H₂O₂]²⁺.

The calculated energy barrier of reaction step (i) is about 15 kcal/mol, which is more than four times smaller than the energy costs (~62 kcal/mol) to break the O-O bond in H₂O₂ in

the vacuum. This result demonstrates the significant catalytic effect of the Fe²⁺ ion in the O-O bond breaking of hydrogen peroxide.

The [Fe^{IV}(H₂O)₄(OH)₂]²⁺ and H₂O₂ interaction (step (ii))

The intermediate [Fe^{IV}(H₂O)₄(OH)₂]²⁺ formed during the step (i) of the entire reaction cycle can coordinate the second molecule of hydrogen peroxide to give the [Fe^{III}(H₂O)₅(OH)]²⁺ and the radical HO₂[•] (Figure 3). The step (ii) of reaction begins with the complexation of hydrogen peroxide with the compound [Fe^{IV}(H₂O)₄(OH)₂]²⁺ via the O₃-H₁ hydrogen bond with a bond length of 1.55 Å as shown in Figure 3. This interaction leads to the elongation of the bond O₁-H₁ in the complex **3** (1.04 Å versus 0.99 Å in the free H₂O₂ molecule) and to a decrease of the O₁-O₂ bond length in coordinated H₂O₂ molecule from 1.48 Å (free hydrogen peroxide) to 1.39 Å.

The transition state for this step (**TS-ii** in Figure 3) is characterized by one imaginary frequency with the value of 817.0i cm⁻¹, the vibrational vector corresponds to the movement of the hydrogen atom H₁ between the compound [Fe^{IV}(H₂O)₄(OH)₂]²⁺ and the hydrogen peroxide molecule. In this (**TS-ii**) state, the hydrogen atom H₁ is practically in the middle between the oxygen atoms O₁ and O₃, the distances O₁-H₁ and O₃-H₁ are 1.17 Å and 1.27 Å, respectively.

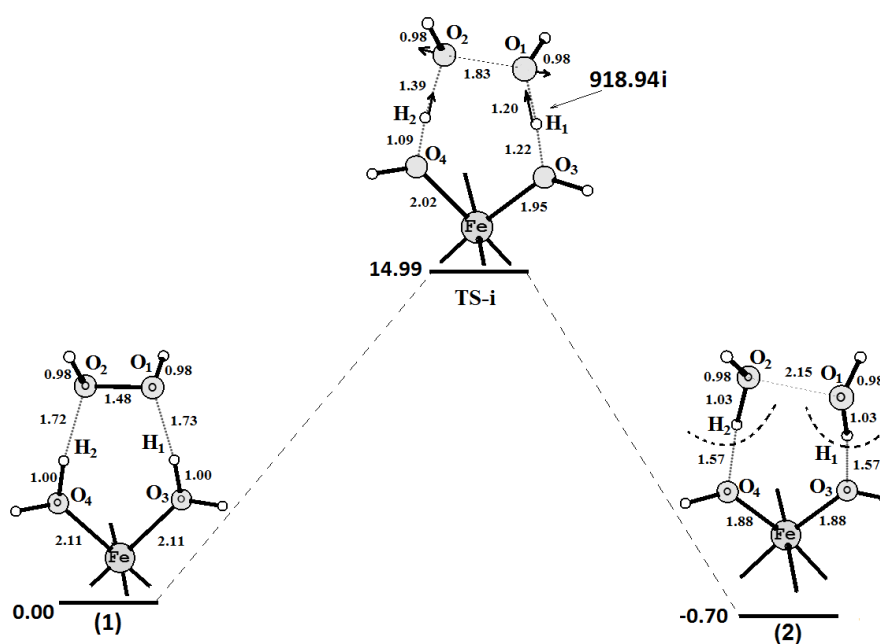


Figure 2. The calculated energy profile (kcal/mol) of step (i) of reaction along the IRC. The arrows schematically show the vibrational mode with the imaginary frequency for the transition state TS-i.

A shortening of the O₁-O₂ bond in the hydrogen peroxide molecule up to 1.37 Å is also observed (**TS-ii** in Figure 3). The calculated activation energy of this reaction is only 0.63 kcal/mol, and the energy gain is 1.7 kcal/mol, which means that the reaction is exothermic.

As a result of this reaction, the intermediate complex [Fe^{III}(H₂O)₅-OH]²⁺ (complex **4**, Figure 3) is formed, and a HO₂[•] free radical is released.

Regeneration of initial [Fe^{II}(H₂O)₆]²⁺ catalyst (step (iii))

In its turn, in excess of hydrogen peroxide, the complex [Fe^{III}(H₂O)₅-OH]²⁺ formed at the previous stage can interact with one more H₂O₂ molecule, resulting in the initial complex [Fe^{II}(H₂O)₆]²⁺ and a second radical HO₂[•] (Figure 4). Just as in the previous case, a stable hydrogen-bonded complex [Fe^{III}(H₂O)₅(OH)---H₂O₂]²⁺ (complex **5** in Figure 4) is formed by means of the hydrogen bond O₃-H₁ with a length of 1.52 Å. In the optimized configuration of the transition state (**TS-iii**), the imaginary frequency with the value of 550.63i cm⁻¹ corresponds to the motion of the hydrogen atom between the complex [Fe^{III}(H₂O)₅(OH)]²⁺ and the H₂O₂ molecule. In this configuration (**TS-iii**) the hydrogen atom H₁ is displaced towards the oxygen atom O₃, the distances being 1.24 Å for the O₁-H₁ bond and 1.19 Å for the H₁-O₃ bond.

The product of this reaction is the complex **6** (Figure 4) in which the radical HO₂[•] is bonded

to the complex [Fe^{II}(H₂O)₆]²⁺ by the hydrogen bond with a length of 1.48 Å. The O₁-O₂ bond length is 1.35 Å, which is characteristic for the hydroperoxyl radical HO₂[•]. The activation energy of this reaction is 4.27 kcal/mol. The reaction is endothermic with the calculated energy of 1.44 kcal/mol. This stage can also be considered as a reaction of regeneration of the initial complex [Fe^{II}(H₂O)₆]²⁺.

Bimolecular self-reaction HO₂[•] + HO₂[•] → HOOH + O₂ (step (iv))

Thus, as a result of the first three stages of the process under consideration, the initial complex [Fe^{II}(H₂O)₆]²⁺ is restored, and two hydroperoxyl radicals HO₂[•] are formed.

The gas-phase bimolecular self-reaction of HO₂[•] has been the subject of numerous experimental [38-40] and theoretical [41-45] studies because it plays an important role in the atmospheric chemistry [46,47]. It was shown that the most favourable channel of this interaction is the step (iv) HO₂[•] (²A'') + HO₂[•] (²A'') → H₂O₂(¹A) + O₂(³Σ_g⁻), which results in hydrogen peroxide H₂O₂ and the oxygen molecule in its ground electronic state O₂(³Σ_g⁻). It was postulated also that the step (iv) of reaction runs through the formation of stable intermediate H₂O₄. The nature of both the singlet and triplet H₂O₄ species was studied in a number of quantum-chemical calculations [43-45,48-50].

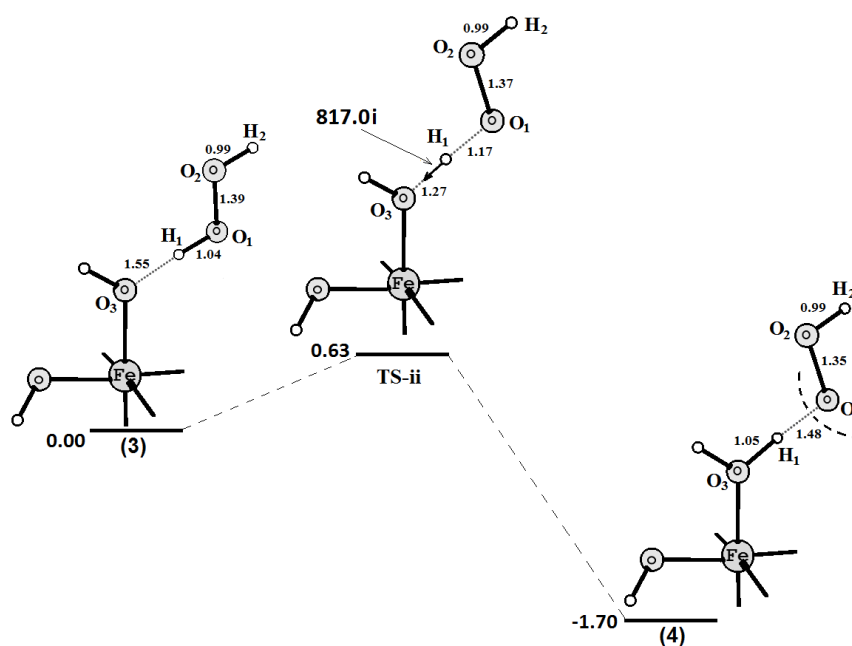


Figure 3. The calculated relative energies (kcal/mol) of the reagents, transition state (TS-ii) and the products for step (ii) of reaction. The arrows schematically show the vibrational mode with the imaginary frequency for the transition state TS-ii.

Two HO_2^\bullet radicals in their ground electronic state ($^2A''$) can form a common H_2O_4 system either in the singlet or in the triplet spin state. Since we are interested in the products of the step (iv) of reaction, in their electronic ground state, namely $\text{H}_2\text{O}_2(^1A)$ and $\text{O}_2(^3\Sigma_g^-)$, all calculations for the reactants, intermediates, products and the transition state of this reaction were performed for the triplet spin states. Calculations show that the most stable structure of the intermediate H_2O_4 in its triplet spin state is a doubly hydrogen-bonded planar six-member ring of C_{2h} symmetry (complex 7 in Figure 5).

This complex is formed from two HO_2^\bullet radicals without any energy barrier; relative to the reagents, its stabilization energy is 15.7 kcal/mol. The lengths of two equal hydrogen bonds are 1.58 Å, the HOO bond angles are equal to 103.9°. These results agree rather well with the data from other studies [42-45].

The transition state for dissociation of the intermediate complex H_2O_4 to the products was localized (TS-iv in Figure 5), which is only 1.07 kcal/mol higher than the stable triplet intermediate H_2O_4 structure (7).

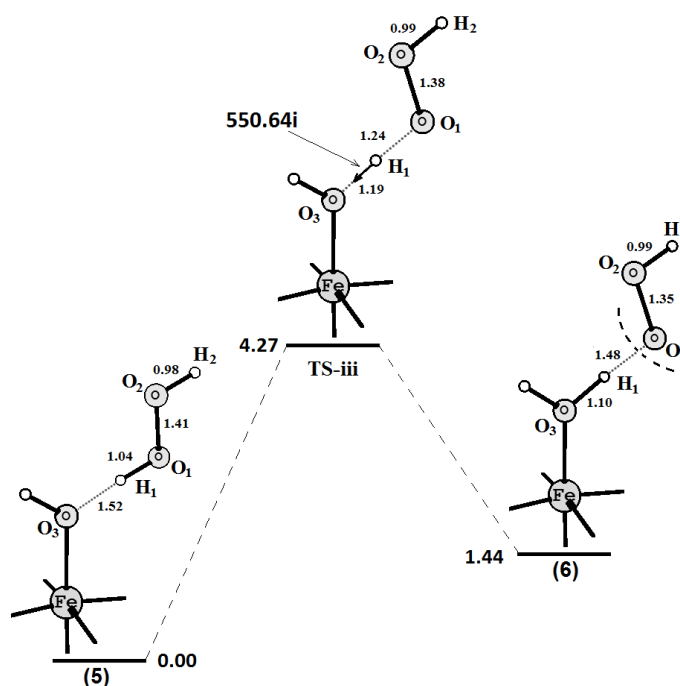


Figure 4. The calculated relative energies (kcal/mol) of the reagents, transition state (TS-iii) and the products for step (iii) of reaction. The arrows schematically show the vibrational mode with the imaginary frequency for the transition state TS-iii.

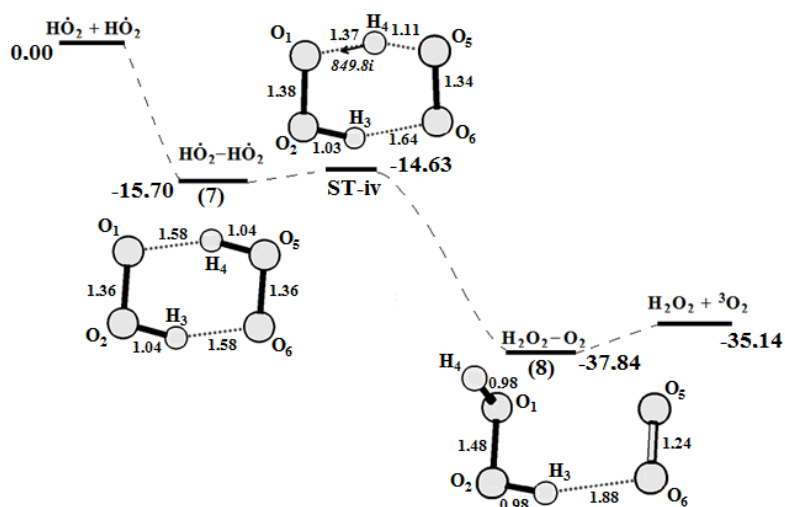


Figure 5. Schematic energy profile (kcal/mol) for reaction $\text{HO}_2^\bullet(^2A'') + \text{HO}_2^\bullet(^2A'') \rightarrow \text{H}_2\text{O}_4(^3A_g) \rightarrow \text{H}_2\text{O}_2(^1A) + \text{O}_2(^3\Sigma_g^-)$.

Harmonic vibrational frequency calculations show that the obtained transition state is indeed the first-order saddle point, since it is characterized by one imaginary frequency equal to 849.8i. The transition vector indicates that the molecular motion of this frequency is dominated by transfer of the hydrogen atom H₄ from O₅ to O₁ and by the out-of-plane displacement of the hydrogen H₃. The O₅-H₄ bond length becomes equal to 1.11 Å, while the value of R(O₁-H₄) is decreased by 0.21 Å up to 1.37 Å. The dihedral angle H₄-O₁-O₂-H₃ in the **TS-iv** is equal to 16.20°. Besides that, the torsion motion involving the four oxygen atoms also takes place.

As a result of the reaction step (iv), we obtain the hydrogen-bonded complex H₂O₂-O₂ which is 23.21 kcal/mol lower than the **TS-iv** structure. The total energy gain of the reaction is 35.14 kcal/mol compared to the experimental value of 38.28 kcal/mol [51].

The summary reaction cycle for the hydrogen peroxide decomposition, the Fe²⁺ regeneration and the molecular oxygen production

Thus, as a result the above four steps we have the summary reaction cycle for the hydrogen peroxide decomposition and the molecular oxygen production:

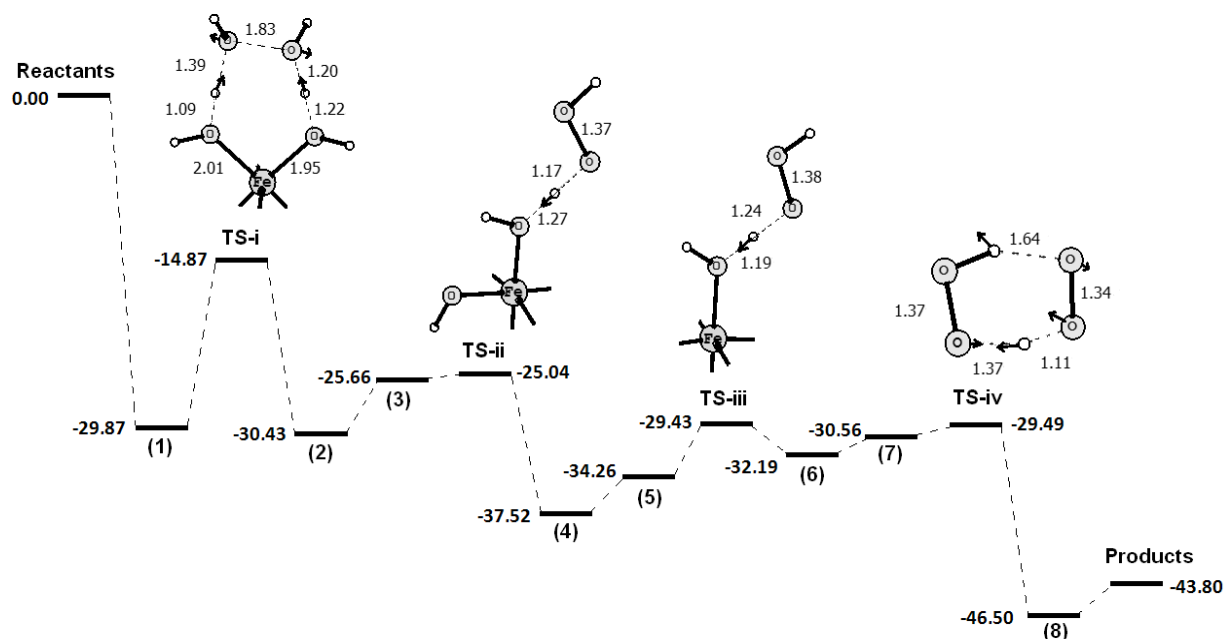
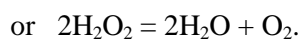
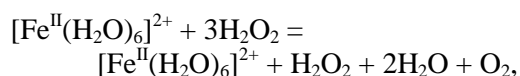


Figure 6. Energy profile of the entire reaction cycle of H₂O₂ decomposition and the O₂(³Σ_g⁻) generation in the presence of the [Fe^{II}(H₂O)₆]²⁺, calculated at the DFT-BPE cc-pVDZ level of theory.

Figure 6 illustrates the general process of hydrogen peroxide decomposition and the molecular oxygen generation in the Fenton reaction. This process consists of four steps, each of which passes through a transition state (**TS-i**, **TS-ii**, **TS-iii**, and **TS-iv** in Figure 6).

The initial step, (1)→(**TS-i**)→(2), involves formation of the stable complex [Fe^{II}(H₂O)₆-H₂O₂]²⁺ (1) with two hydrogen bonds, the hydrogen peroxide O-O bond cleavage, and formation of the intermediate compound [Fe^{IV}(H₂O)₄(OH)₂]²⁺ with two HO[•] radicals “trapped” in the complex. At the second stage, (3)→(**TS-ii**)→(4), interaction of the above complex [Fe^{IV}(H₂O)₄(OH)₂]²⁺ with the H₂O₂ molecule leads to formation of the intermediate hydrogen bonded complex [Fe^{III}(H₂O)₅(OH)---HO₂]²⁺ (4). The subsequent interaction of the [Fe^{III}(H₂O)₅(OH)]²⁺ with another molecule of H₂O₂ at the third stage, (5)→(**TS-iii**)→(6), restores the initial iron aqua-complex [Fe^{II}(H₂O)₆]²⁺ and generates the second radical HO₂[•]. During the last, step (iv) of the reaction, (7)→(**TS-iv**)→(8), the interaction of the two HO₂[•] radicals gives an oxygen molecule in its ground triplet state and a hydrogen peroxide molecule.

It can be seen that the entire reaction cycle is an energetically favourable process with an energy gain of 43.8 kcal/mol, so that the above four-stage reaction mechanism seems reasonable.

In the present paper, we considered the processes occurring in the first solvation shell of the Fe²⁺ ion. The role of the solvent effect will be the subject of further research.

Conclusions

A consistent picture of the entire reaction cycle of hydrogen peroxide decomposition and the molecular oxygen generation in the Fenton reaction is provided by means of DFT calculations. The proposed four-stage mechanism assumes implicitly an excess of hydrogen peroxide over Fe^{2+} ions, since oxygen evolution is actually observed experimentally under such conditions. The transition states for all steps of the reaction cycle were localized and verified by intrinsic reaction coordinate analysis.

Starting from the Fe^{II} -aqua-complex, we have shown that the O-O bond breaking of coordinated H_2O_2 at the first step of reaction does not lead to formation of free HO^\bullet radicals as intermediates. Instead, a highly reactive intermediate $[\text{Fe}^{\text{IV}}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$ with two OH radicals “trapped” in the complex is formed with a calculated energy barrier of 15 kcal/mol, which is more than four times lower than the energy costs to break the O-O bond in H_2O_2 in the gas phase. In the second step, interaction of this intermediate with another molecule of hydrogen peroxide leads to the formation of the HO_2^\bullet radical and the complex $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$. Reaction of the latter with another H_2O_2 molecule results in the formation of a second HO_2^\bullet radical and regeneration of the initial iron aqua-complex. Then, the HO_2^\bullet self-reaction occurring through the formation of a stable six-member double-hydrogen bonded $(\text{HO}_2^\bullet)_2$ intermediate, gives hydrogen peroxide molecule and the oxygen molecule in its ground triplet state, $\text{O}_2(^3\Sigma_g^-)$. It is shown that the entire reaction cycle is an energetically favourable process with an energy gain of 43.8 kcal/mol.

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