

THE THEORETICAL STUDY OF SOME REACTIONS WITH THE PARTICIPATION OF $\dot{O}H$ AND $H\dot{O}_2$ RADICALS

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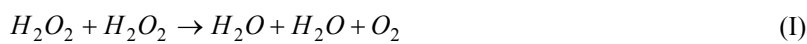
Abstract. The geometry of the H_2O_2 , $\dot{O}H$, $H\dot{O}_2$, O_2 particles and the energy profiles of the initial reactions between them, that are supposed to take place during the process of decomposition of hydrogen peroxide, were studied by *ab initio* calculations. It was shown that the differences between the energies of reactants and the products of all analysed reaction are positive values and correlate with the experimental data.

Keywords: the radicals reactions, decomposition of hydrogen peroxide, the thermodynamic stability

Introduction

The study of the elementary reactions that take place in the process of the H_2O_2 decomposition is of a great importance both from the theoretical point of view (in order to understand the mechanisms of the numerous processes in the chemical and biological systems, in the processes of photolysis, redox transformations of different organic substances, etc.) and from the practical point of view – the use of such compounds in many processes of oxidation. The knowledge of the mechanism of these reactions also presents interest for creating new catalytic systems for the oxidation of the organic substances.

In researches [1-3] it is supposed, that both at the direct decomposition of the hydrogen peroxide and at its decomposition in the presence of the complexes of transitional metals, at certain intermediate stages the following reactions take place:



In this paper it was proposed to study if the reactions **I-VI** really take place and if they are profitable from the thermodynamic point of view. For the realization of this goal the quantum-chemical calculations of the possible geometries of the H_2O_2 , $H\dot{O}_2$, $\dot{O}H$, H_2O and O_2 particles, the ways of interactions between them and the total energies of all systems were carried out.

Method of calculation

All calculations were performed with the help of the GAMESS programme [4], using MO LCAO Hartree-Fock-Roothaan SCF method in the restricted-open Hartree-Fock (ROHF) approximation with the STO-6G basis set for atomic functions.

Results and discussions

Calculation of the geometry of the investigated particles.

For every particle in reactions **I-VI**, (H_2O_2 , $H\dot{O}_2$, $\dot{O}H$, H_2O and O_2) the most propitious geometry was found and the total energies were calculated. In all cases it was considered that the spatial nuclear configuration of the investigated molecules corresponds to C_1 symmetry point group.

The values of equilibrium geometrical parameters and the total energies of the studied particles, obtained as a result of the geometry optimization, are presented in Table 1.

Table 1.

The values of geometrical parameters and the total energies.

	$R(O-H), (\text{Å})$	$\angle(HOO)$	$R(O-O), (\text{Å})$	$E, (a.e.u.)$
H_2O_2	1.00 (0.94 [6])	100.67 (99.5 [6])	1.40 (1.44[6])	-150.8595
$\dot{H}O_2$	1.00 (0.99 [5])	103.89 (104.96 [5])	1.35 (1.33 [5])	-149.6171
H_2O	0.99 (0.96 [5])	100 (104.45 [5])	-	-75.6812
$\dot{O}H$	1.01 (0.97 [5])	-	-	-75.0775
O_2	-	-	1.22 (1.20 [5])	-149.0504

Note that calculated values of the bond lengths (R) and the valence angles of investigated particles are in a rather good agreement with those obtained by other authors (Table 1).

Interaction of the studied particles.

Further, the optimization of the geometrical configuration of the pairs of molecules that take part in the I-VI reactions and were at the beginning in the immediate vicinity was done. In all the investigated reactions, the atoms of oxygen, at the beginning of optimization, are in a plane, a tendency that is kept to all along, this not being true for the atoms of hydrogen. A general analysis of these reactions, the way of approaching particles to each other, and the evolution of reactions are described and analysed below.

Reaction $H_2O_2 + H_2O_2$. Approaching these two molecules to each other and optimizing them together, one can see (Fig. 1) that at the beginning of reaction two hydrogen bonds appear between them (O1-H3 and O2-H4). Then there takes place the transfer of the (H3) and (H4) atoms towards the (O1) and (O2) atoms that provokes the breakage of the (O1-O2) bond ending up with the formation of two molecules of water and one molecule of oxygen. The dotted lines in Fig.1 show the hydrogen bonds and the weaker bonds between atoms of oxygen that are formed as a result of the interaction and are broken as a result of the reaction.

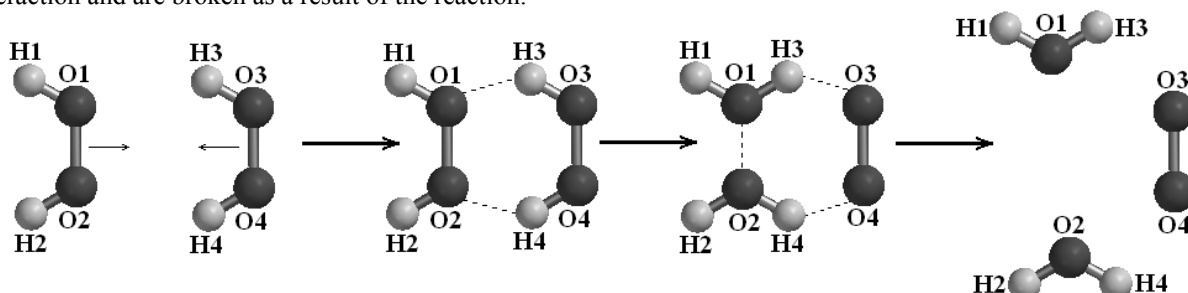
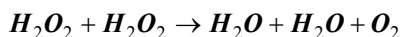


Fig. 1. The reaction of a pair of the hydrogen peroxide molecules with the formation of two molecules of water and a molecule of oxygen.

According to the quantum-chemical data (Table 2), the conclusion can be drawn that the investigated reaction takes place as it is supposed in the literature [7]. So, as a result of this process the reaction takes place the following way:



Reaction $H_2O_2 + \dot{O}H$. Further, the interaction of the hydrogen peroxide with the $\dot{O}H$ radical was analysed. At the beginning, the formation of the (O3-H1) hydrogen bond between the radical and the molecule of peroxide occurs that causes the transfer of the atom of hydrogen (H1) towards the radical of hydroxyl. During the reaction, the formation of a molecule of water and of a hydroperoxyl radical takes place (Fig. 2), the latter participates further in reaction III.

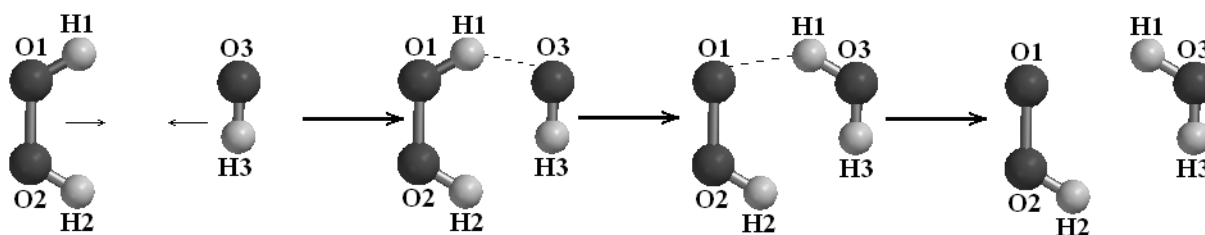
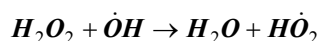


Fig. 2. The way of obtaining of the $\dot{H}O_2$ radical due to the interaction of the hydrogen peroxide with the $\dot{O}H$ radical.

Comparing the obtained results (Table 2) with the experimental ones [8-9], the conclusion was drawn that they are in a good concordance. The final reaction is:



Reaction $H_2O_2 + \dot{H}O_2$. Another reaction that has been investigated from the thermo-dynamic point of view is the interaction of the hydrogen peroxide with the hydroperoxyl radical $\dot{H}O_2$ [10]. When these two particles approach with each other the formation of the (O2-H3) hydrogen bond takes place followed by the transfer of the (H3) atom from the hydroperoxyl radical to the hydrogen peroxide that causes the (O1-O2) bond breaking, resulting in a new $\dot{O}H$ radical and two stable molecules: oxygen and water. Fig. 3 presents a general look of the development of the reaction and the obtained products:

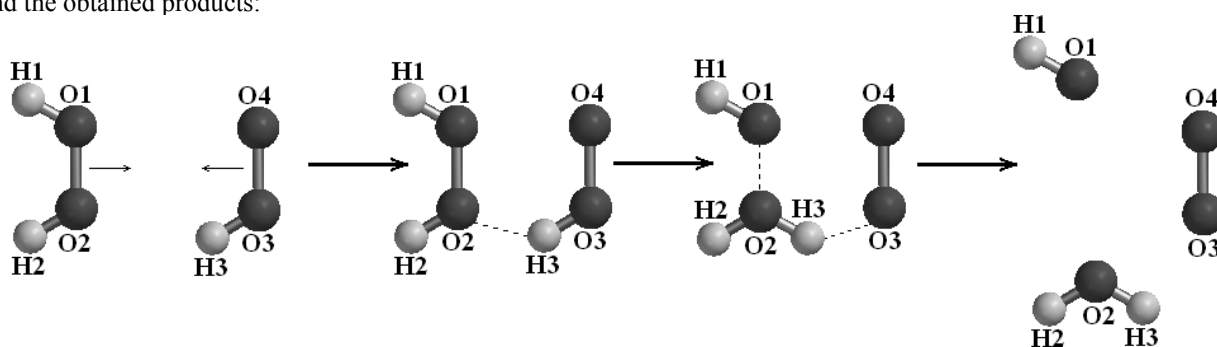
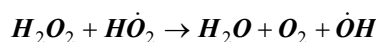


Fig. 3. The best way of approaching of the $\dot{H}O_2$ radical to the hydrogen peroxide to obtain the $\dot{O}H$ radical.



Both the obtained results (Table 2) and those from the literature confirm that this transformation takes place with the energy gain.

Reaction $\dot{H}O_2 + \dot{H}O_2$. The interaction between two $\dot{H}O_2$ molecules can be considered as a process of interruption of the $\dot{H}O_2 + \dot{H}O_2$ radical reactions. When combining two $\dot{H}O_2$ radicals, first of all the (O3-H2) hydrogen bond is formed, followed by the transfer of the (H2) atom. So, the formation of the molecules of the hydrogen peroxide and the oxygen (Fig. 4) takes place.

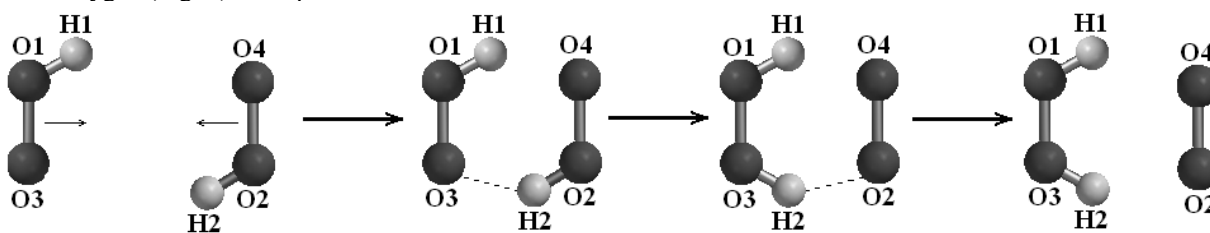
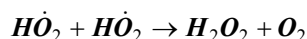
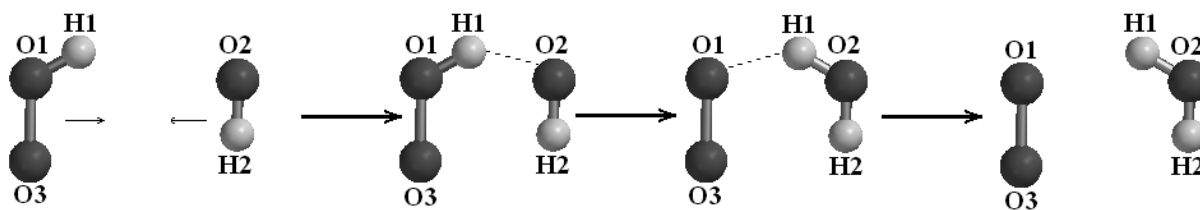


Fig. 4. The reaction of two $\dot{H}O_2$ radicals resulting in the formation of the molecules of the oxygen and peroxide.

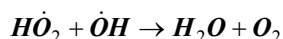
This reaction takes place as it is described in the literature [11], the final reaction being:



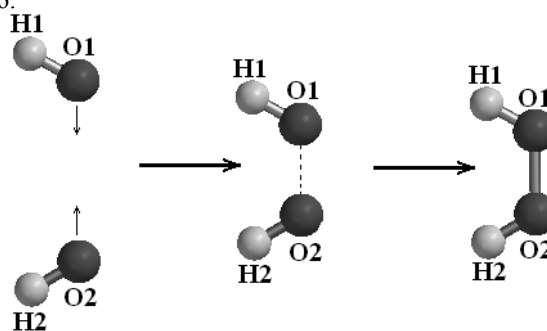
Reaction $\dot{H}O_2 + \dot{O}H$. Another studied reaction is the interaction between $\dot{O}H$ hydroxyl radical and $\dot{H}O_2$ radical [12]. If we make a general analysis of this reaction, it will be noticed that, first, there occurs the formation of the (O2-H1) hydrogen bond, and then the transfer of the (H1) hydrogen atom with the formation of a molecule of water and oxygen. (Fig. 5)


 Fig. 5. The interaction of the $\dot{O}H$ and HO_2 radicals

The interaction of these radicals can also be considered as a stage of interruption of the studied reactions followed by the obtaining of the molecules of water and oxygen that are stable.



Reaction $\dot{O}H + \dot{O}H$. From the experimental data [3] it is known that $\dot{O}H$ radical is more suitable to be combined with another $\dot{O}H$ radical, followed by the formation of a molecule of the hydrogen peroxide. The theoretical analysis of this reaction demonstrates that the bond of two $\dot{O}H$ radicals can occur. The scheme of the development of this reaction is presented in Fig. 6.


 Fig. 6. The recombination of the $\dot{O}H$ radicals to the hydrogen peroxide

Analyzing the processes I-VI we can conclude that the reactants and the products of reactions are separated by rather significant energetical barrier ΔE_1 , followed by an energetical gain ΔE_2 (Table 2). Using the calculated values of the total energy for the investigated systems and calculating the energy of the reaction according to the formula:

$$\Delta E_2 = \sum_i E_i^{(prod.)} - \sum_j E_j^{(react.)}$$

it is possible to draw the energetical profile of the reactions (Fig. 7). According to the scheme (Fig. 7) the products of the reactions are energetically more profitable than the initial substances. The values of the total energy gains are presented in Table 2.

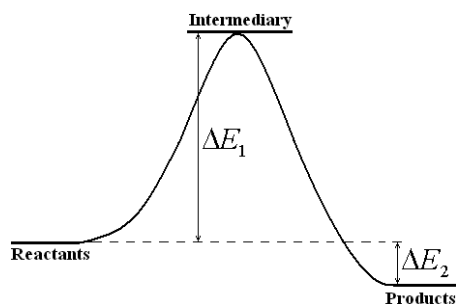


Fig. 7. Schematic drawing of the energetical profile of considered reactions

Table 2

Energetical barrier ΔE_1 and energetical gain ΔE_2		
Reaction	ΔE_1 (kcal/mol)	ΔE_2 (kcal/mol)
I	493.95	32.28
II	77.71	20.29 (32.2 [7])
III	144.82	2.08 (30 [13])
IV	240.75	2.99 (41 [7])
V	115.07	23.29 (70 [7])
VI	149.66	20.98 (51 [7])

From the Table 2 it is seen that the obtained values of the barriers are too large. The reason is that the energies of transition states were calculated without re-optimization of their geometry. So these values can be considered only as semi-quantitative estimations.

Proceeding from the obtained data for the energies of the reactions ΔE_2 , one can note a rather good correlation between the theoretical and experimental results for reactions **II**, **V** and **VI** (Table 2).

These processes were also studied from the point of view of the charge transfer between the studied particles during the reactions. The calculated charges of the reaction products in all the cases are equal to zero. This agrees with the experimental data which stands that only neutral particles are forming.

Conclusions

1. It was proved that the differences between the energies of the reactants and the products of all analysed reactions are positive values that correlates with the experimental data.
2. Obtained theoretical results show that the products of all reactions **I-VI** have total charge equal to zero.

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