Quantum chemistry research structure and electronic properties of peroxides

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Abstract – *We have calculated the optimal structure, electronic properties and heat of formation ($\Delta_f H^\circ$) peroxide compounds with the help of semiempirical quantum chemical methods. Theoretically calculated values well coincide with the values found from thermochemical experiments.*

Key words: Geometric structure, electronic properties, heat of formation, reactivity.

I. Introduction

Quantum-chemical calculations can provide valuable information about physical and chemical properties of organic peroxides and they predict their reactivity. [1] We have done quantum-chemical calculations by the semiempirical method RM1 parameters for hydroperoxides, aralkyl peroxides and peroxyacids. We used the program MOPAK 2012 for our calculations [2] and the graphical interface Winmostar. [3]
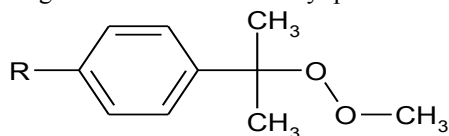
II. Experimental part

Quantum-chemical calculations were performed for the general formula of hydroperoxides:
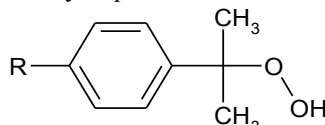
where R equals: $CH_2=C(CH_3)-$ (**I**); $BrCH_2-CH(CH_3)-$ (**II**); $CH_3-C(O)-$ (**III**); $HO-CH_2-$(**IV**); $H-$ (**V**); $(CH_3)_2CH-$ (**VI**).

and for the general formula for aralkyl peroxides:

where R equal CH_3-CH_2- (**VIII**), $BrCH_2-$ (**IX**), Br_2CH- (**X**), CH_3-O-CH_2- (**XI**), $CH_3-C(O)-OCH_2-$ (**XII**).
In addition, there are calculation results for peroxyacids with the general formula: $R- C(O)OOH$, where R equal CH_3- (**XIII**), CH_3-CH_2- (**XIV**), $CH_3-CH_2-CH_2-$ (**XV**), $CH_3-(CH_2)_4-$ (**XVI**), $CH_3-(CH_2)_7-$ (**XVII**), $CH_3-(CH_2)_8-$ (**XVIII**), C_6H_5- (**XIX**).

III. Results and discussions

Our work describes results of quantum chemical calculations of standart heat of formation ($\Delta_f H^{298}$), ionization potential (I_x) energy of higher occupied (E_{HOMO})

and the lower vacant (E_{LUMO}) molecular orbitals, dipole moments (D), volume (V) and area (S) molecules of aralkyl peroxides and hydroperoxides and peroxyacids. According to the energy E_{HOMO} and E_{LUMO} we calculated the electronic chemical potential (**μ**) and rigidity of molecules (**η**), using the next formulas: **μ**= ($E_{HOMO} + E_{LUMO}$)/2 and **η** = ($E_{LUMO} − E_{HOMO}$) [4, 5]. The obtained results for some hydroperoxides, aralkyl peroxides and peroxyacids are presented in tables 1 and 2.

TABLE 1

HEAT OF FORMATION, DIPOLE MOMENTS, ENERGY OF HIGHER OCCUPIED (E_{HOMO}) AND THE LOWER VACANT (E_{LUMO}) MOLECULAR ORBITALS, AND VOLUME OF EXAMINED MOLECULES OF HYDROPEROXIDES AND ARALKYL PEROXIDES

PEROXIDE	I	II	XI	XII
$\Delta_f H^\circ$ kJ/mole	-62.60	-152.30	-231.19	-442.00
D, debye	1.046	1.109	1.368	2.411
E_{HOMO},eB	-8.982	-9.301	-9.177	-9.353
E_{LUMO},eB	0.351	0.214	0.559	0.411
μ, eB	-4,667	-4,758	-4,868	-4,882
η, eB	9,333	9,515	9,736	9,764
S, Å^2	236.33	259.03	255.67	273.60
V, Å^3	252.59	289.19	269.06	297.15

TABLE 2

PEROXIDE	XIII	XIV	XVIII	XIX
$\Delta_f H^\circ$ kJ/mole	321,03	342,19	479,92	182,76
D, debye	2.552	2.531	2.432	3.111
E_{HOMO},eB	-11,270	-11,144	-10,897	-9,978
E_{LUMO},eB	0,864	0,910	0,941	-0,360
μ, eB	-6.067	-6.027	-5.919	-4.809
η, eB	12.134	12.054	11.838	9.618
S, Å^2	103,0	121,6	253,6	162,4
V, Å^3	85,4	106,7	257,7	155,4

Heat of formation, energy of higher occupied (E_{B3MO}) and the lower vacant (E_{HBMO}) molecular orbitals, area and volume of examined molecules of peroxyacids

Heat of formation $\Delta_f H^{298}$ of hydroperoxides and peroxyacids, which were calculated using the method RM1, matches well with the corresponding values determined thermochemical [6]. So $\Delta_f H^{298}$ for compound XYII was calculated using the quantum-chemical method and is equal to -479,92 whereas this value thermochemically found, is – 509,04±2,2 kJ/mole. Furthermore, we calculated the values **μ** and **η**, which are given in table. 1,2. It is known that the method of boundary orbitals was proposed by Fukui, determines the relative reactive activity of the compounds of the energy of molecular orbitals E_{HOMO} and E_{LUMO} [4, 5]. Energy of E_{HOMO} causes the interaction of the molecule with elektron acceptors, and E_{LUMO} − electron donor. Positive energy of E_{HOMO} causes the nucleophilic properties of molecules, and negative − electrophilic. Rigidity of molecules **η** and electronic chemical potential μ of hydroperoxides and aralkyl peroxides, which have similar structures are almost the same. For peroxyacids

(compounds XIII – XIX), these parameters differ from the values **η** and **μ** which were obtained for hydroperoxides and aralkyl peroxides. (table.2).

Electronic chemical potential and hardness of molecules of hydroperoxide tertbutyl (**VII**) and peroxybenzoic acid (**XIX**) significantly differ from the parameters of aralkyl hydroperoxide and aliphatic peroxyacids (table. 1, 2), which indicates that the reactivity of peroxides is different from all other examined compounds. Volume of molecule (V, Å^3) of hydroperoxide and peroxide are close. Volume of hydroperoxide tertbytul is significantly smaller. Area of molecules (S, Å^2) of aralkyl hydroperoxides and peroxides are not very different, which indicates the little effect of the radical R on this parameter. For peroxyacids (XIII – XIX) numeric values V and S grows with increasing values of the hydrocarbon radical bound to the peroxide group. (table. 2).

From the calculations derives the optimal structure of molecules of aralkyl hydroperoxides and peroxides (Fig. 1, 2). Structure of the molecule of hydroperoxide **III** are shown on Fig. 1.
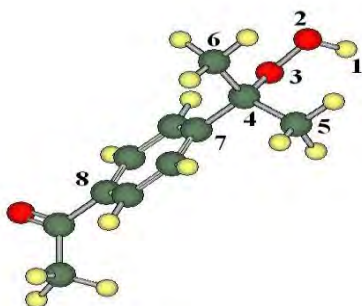

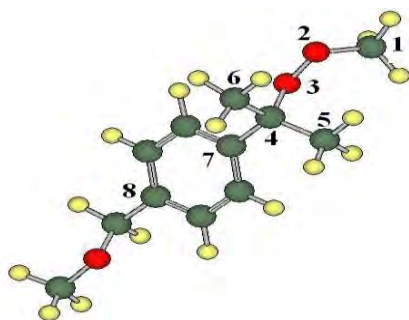Fig. 1. Optimal structure of molecule hydroperoxide **III**.

Fig. 2. Optimal geometric structure
of molecules of peroxide **XI**

The molecular structures of aralkyl hydroperoxides (I-IV) are similar. Phenyl nucleus is not deformed, and all connections between the carbon atoms there are close and are within 1,388 – 1,487 Å, and the angles between the carbon atoms are equal 120 degrees. Peroxide group is directed from the phenyl nucleus (Fig. 1). Molecular structures of aralkyl hydroperoxides (Fig. 2) **VIII – XII** are similar to molecular structures of hydroperoxides **I – VII**. As with aralkyl hydroperoxides phenyl core of the molecule of hydrogen peroxide is not deformed, and the distance between the carbon atoms is in the range 1,391 – 1,381 Å, and all of the angles change from 117 to 120

degrees. Replacement of a hydrogen atom of the peroxide group with the methyl radical leads to a change of the electronic density of oxygen atoms, that in turn changes the the reactivity of the molecules. The optimal geometric structure of the molecule of peroxide **XI** is shown on Fig. 2.

Based on the performed calculations we can conclude, that the radical, which is near to the carbon atom C(8) in molecules such as hydroperoxides, aralkyl, practically doesn't change the reactivity of the O-O group.

Molecular structure of peroxyacids are similar. All peroxyacids create compounds with intramolecular hydrogen bonds. (Fig. 3). The energy bond is found, using the conformation analysis, at the rotation of the OH- group is 12,9 kJ/mole, and is close to the value calculated by the thermochemical data [7].
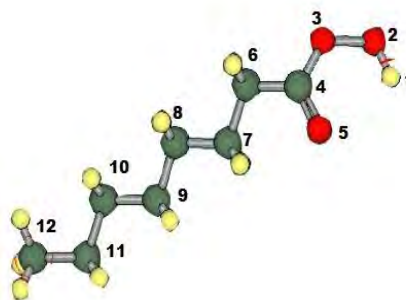

Fig. 3. Optimal structure of the molecule
of peroxyacid **XVII**.

Energy changing of the molecule of peroxyacid while rotating peroxy group, was remarked in works [8,9]. Results of the conformating analysis of aralkyl hydroperoxide and peroxides are shown on the Fig. 4,5. Potential energy change was calculated by the rotation of the OH – group of the hydroperoxide, or CH$_3$-O – peroxy group. We can spectate three maximums for both occasions on the curve of the change of the potential energy (Fig. 4, 5).
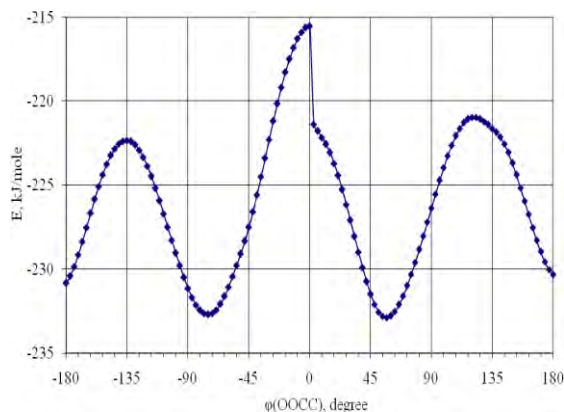

Fig. 4. Energy change of the molecule of hydroperoxide VI
while rotating the O-H group around the C-O bond

Given fact testifies that in examined molecules of peroxides of hydrogen peroxide groups, or CH$_3$0- groups need to take position relatively to the phenyl core and other methyl radicals, so they can provide minimal

energy. In accordance with the obtained results in the case of the hydroperoxide such positions of OH – group are three. In the case of aralkyl peroxide XI on the curve of the potential energy change, we also can see three minimums.
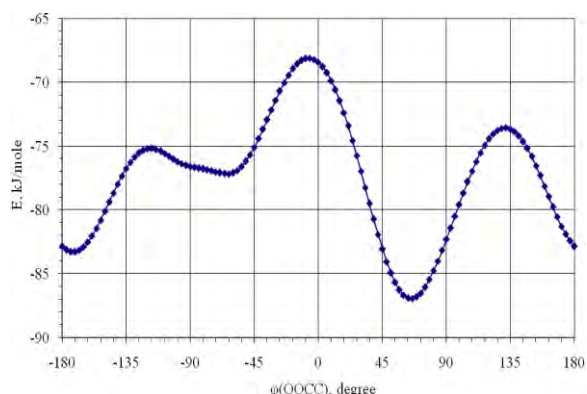

Fig. 5. Energy change of the molecule of peroxide XI while rotating O-CH3 group around the C-O bond.

Studying of partial charges on the atoms in the examined molecules (table 3) confirm the conclusion about minimum influence of the radical, which is positioned by the carbon atom C(8), phenyl core of the hydroperoxide or the aralkyl peroxide.

Atom Hydrogen of the hydroperoxides characterized by the deficit of the electronic density. For peroxyacid (table 4)the positive charges on the atom hydrogen H(1) is a slightly larger. It means, that the acids properties of peroxyacids are bigger than appropriate values for the hydroperoxides. This conclusion is confirmed by literature data. [10]

TABLE 3

PARTIAL CHARGES ON THE ATOMS (BY MALLIKEN) OF THE EXAMINED PEROXIDES. NUMBERS OF ATOMS MATCH THE NUMBERS OF THE FIG. 1,2

PERO-XIDES	ATOMS AND NUMBER OF ATOMS				
	H(1), *C(1)	O(2)	O(3)	C(4)	C(5)
I	0,198	-0,197	-0,172	0,172	-0,212
II	0,195	-0,192	-0,170	0,170	-0,214
III	0,200	-0,191	-0,173	0,164	-0,212
IV	0,199	-0,196	-0,173	0,171	-0,212
V	0,198	-0,197	-0,173	0,174	-0,212
VI	0,198	-0,196	-0,173	0,171	-0,212
VII	0,196	-0,195	-0,174	0,143	-0,193
VIII*	-0,043	-0,149	-0,171	0,174	-0,215
IX*	-0,045	-0,147	-0,171	0,169	-0,216
X*	-0,045	-0,147	-0,170	0,166	-0,217
XI*	-0,041	-0,151	-0,174	0,174	-0,214
XII*	-0,044	-0,148	-0,170	0,169	-0,126

It should be noted, that the excess charges of the atoms oxygen O(2) and O(3) of the hydroperoxides molecules are differ, than for peroxyacids, atomic charges are practically equal. It is known, than in reaction of electrophilic oxidation, attack on the reactive centre carries atom oxygen O(2). This statement is true for reaction that involve hydroperoxides. In the case of peroxidyacid attack on the aliquot bond, or on the atom nitrogen can perform atom O(2) or O(3). Creating a transitional complex for reaction of oxidation of the pyridine peroxide acetic acid confirm this conclusion. (Fig. 6)

TABLE 4

ATOMIC CHARGES OF THE PEROXYACIDS BY MALLIKEN. NUMBERS OF ATOMS MATCH THE NUMBERS ON THE FIG. 3

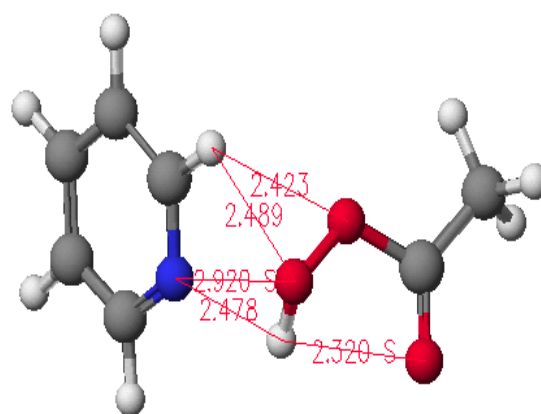| PEROXY ACIDS	H(1)	O(2)	O(3)	C(4)	C(5)
XIII	0,203	-0,156	-0,166	0,335	-0.317
XIV	0,202	-0,156	-0,170	0,322	-0.316
XV	0,202	-0,157	-0,165	0,321	-0.317
XVI	0,203	-0,156	-0,161	0,365	-0.325
XVII	0,201	-0,156	-0,168	0,325	-0.318
XVIII	0,202	-0,156	-0,170	0,323	-0.318
XIX	0,202	-0,157	-0,165	0,321	-0.317

Fig. 6. Transitional complex for reaction of oxidation of the pyridine peroxide acetic acid

According to obtained data distance to the reaction center of nitrogen atom for O (2) and O (3) is practically the same and is 2.42 – 2.48 Å. It should be noted that in the intermediate state of pyridine molecule and peroxyacids molecule (XIII) should be aligned relative each to other.

Conclusion

Thus, quantum-chemical calculations allow to find the optimal geometric structure of the studing peroxides and to predict its reactivity and the possibillity of predicting of the reaction mechanisms with peroxides.

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