Molecular modeling of the isoquinoline and hinaldyne reaction of oxidation by peroxyacids

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Abstract – Optimal-geometric structures of molecules was calculated with semi-empirical quantum-chemical methods. The heat of formation (ΔH_f), the heat of reaction (ΔH_{ex}) was found. Numerical values of ΔH_f was calculated theoretically is satisfactorily coincide with the data obtained experimentally.

Key words – heat of formation, oxidation, isoquinoline, hinaldyne, N-oxides, peroxydecanoid acid, structure of molecules.

I. Introduction

Modern computer technology empirical and semiempirical quantum chemistry allow predict geometric structure, energy and other properties of the molecules. Not spending experimental studies using methods of quantum chemistry we can predict the properties of materials, but between studies of the molecules in this way and experimentally there is a fundamental difference: the calculations can be conducted for nonexistent or unstable connections, and the existing components, with which conducting experimental studies in the laboratory [1].

Complexes of quantum chemistry program: empirical (GAUSSIAN and GAMESS) and semi-empirical (MORAS and Hyper Chem) are widely used in practice [2, 3]. All quantum-chemical calculations we carried out using MOPAC 2012 [4] with graphic interface Winmostar 3.75 [5].

Choose of the methods of quantum-chemical calculations it is important, as this can provide valuable information for the elucidation of the mechanism of reaction on which we can predict the reactivity of molecules.

II. Results and discussion

In our work, the results of quantum-chemical calculations of molecules isoquinoline, hinaldyne and their N-oxides are presented. In literature there are no data from studies of quantum-chemical oxidation of organic compounds, so we carried out molecular modeling these processes by peroxydecanoic acid oxidation.

Quantum chemical calculations give valuable information about the optimal geometric structure of molecules, heat of formation, potential of ionization, dipole moments, and other important characteristics. A special interest is the choice of method of calculation as packet of program MOPAC 2012 contains several semi-empirical methods of calculation. To calculate the heats of formation adopted the following methods: AM1, PM3, PM5, PM6, RM1.

An important characteristic of oxidative process is the heat of reaction ΔH_{ex}. To find ΔH_{ex} performed quantum-chemical calculations of optimum geometrical structure and the heats of formation ΔH_f starting materials and products of reaction and comparing the received results with thermochemical data. Optimal geometric structures of isoquinoline, hinaldyn and products of their oxidation are shown in Figure 1.
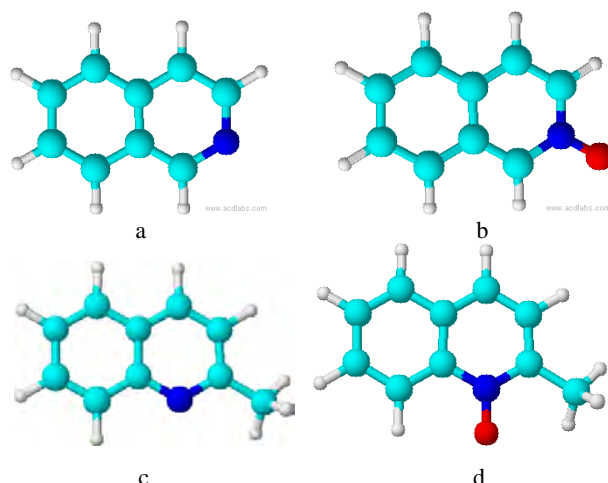

Fig. 1. Optimal geometric structures of isoquinoline (a), hinaldyne (c) and products of their oxidation (b, d)

Molecules of isoquinoline, hinaldyne and their –oxides – flat, and the data of quantum-chemical calculations show that the oxidation of organic compounds does not lead to deformation of the phenyl nucleus. Angles in atoms of the compounds are close to 120°.

Table 1 shows the results of quantum chemical calculations of isoquinoline molecules various semi-empirical methods.

We receiving heat of formation (ΔH_f), dipole moment (D), energy the highest occupied (HOMO) and lower vacant molecular orbitals (LUMO), the area (S) and volume (V), potential ionization of molecule (I_x). During the calculation ΔH^0_f For energy HOMO and LUMO we calculated electronic chemical potential (μ) and stiffness molecules (η).

It is noteworthy that, isoquinoline ΔH^0_f was calculated theoretically is in the range 188.05-209.33 kJ/mol and well coincides with the data obtained by thermochemical methods, numerical value which is $\Delta_f H°_{gas} = 204.61$ kJ/mol. The dipole moment isoquinoline found experimentally equal 2,53 ± 2,73 Debye [6], while in the calculations numerical value D = 2.15 - 2.72, that is well-designed setting matches the experimentally found.

The calculation parameters using quantum chemical methods for isoquinoline-N-oxide molecules are shown in Table 2.

The heat of formation of isoquinoline-N-oxide was calculated theoretically is in the range 194.39 - 252.56 kJ/mol and well coincides with the data obtained by thermochemical methods, numerical value which is $\Delta_f H°_{gas} = 204.61$ kJ/mol isoquinoline found.

TABLE 1

PHYSICO-CHEMICAL PARAMETERS OF ISOQUINOLINE
CALCULATED BY SEMI-EMPIRICAL METHODS

Parameters	Method				
	AM1	PM3	PM6	PM7	RM1
Heat of formation, kJ/mol	204.1	194.3	209.3	203.3	188.1
Dipole moment, Debye	2.2	2.2	2.7	2.7	2.4
E_{HOMO}, eV	-9.2	-9.3	-9.3	-9.3	-9.0
E_{LUMO}, eV	-0.3	-0.5	-0.7	-0.8	-0.3
μ, eV	-4.7	-4.9	-5.0	-5.1	-4.6
η, eV	8.9	8.7	8.5	8.4	8.7
Area, Å^2	162.4	162.2	163.2	162.5	161.8
Volume, Å^3	160.5	160.3	161.8	160.9	159.9
Potential ionization, Ev	9.2	9.2	9.2	9.3	8.9

The dipole moment of of isoquinoline-N-oxide found experimentally equal 3.73 Debye [6], while in the calculations numerical value D = 3.73 - 4.26 Debye, that is well-designed setting matches the experimentally found.

TABLE 2

PHYSICO-CHEMICAL PARAMETERS OF ISOQUINOLINE-N-OXIDE
CALCULATED BY SEMI-EMPIRICAL METHODS

Parameters	Method				
	AM1	PM3	PM6	PM7	RM1
Heat of formation, kJ/mol	252.5	211.2	194.9	204.5	194.3
Dipole moment, Debye	3.7	3.9	4.2	3.8	3.7
E_{HOMO}, eV	-9.0	-9.0	-9.0	-8.8	-8.8
E_{LUMO}, eV	-0.4	-0.7	-0.9	-1.1	-0.3
Area, Å^2	171.9	171.5	172.2	171.5	171.0
Volume, Å^3	171.3	170.7	171.7	170.9	170.2
Potential ionization, Ev	8.8	8.9	8.9	8.7	8.6

The heat of reaction of isoquinoline oxidation to isoquinoline-N-oxide by peroxydecanoic acid designed by law Hess shown in Table 3. The numeric value for this reaction ΔH_{ex} was calculated by thermochemical data in literature missing, because it has not given opportunities to compare it with data ΔH_{ex} obtained on the basis of quantum-chemical methods.

TABLE 3

THE HEAT OF REACTION OF ISOQUINOLINE OXIDATION
BY PEROXYDECANOIC ACID CALCULATED BY VARIOUS
SEMI-EMPIRICAL METHODS

Method of calculation	ΔH_{ex}, kJ	Method of calculation	ΔH_{ex}, kJ
AM1	-83.5	PM7	-138.9
PM3	-80.8	RM1	-96.8
PM6	-151.7	Thermochemical data	-

It should be noted that ΔH^0_f hinaldyne was calculated theoretically is in the range 151.41 - 187.13 kJ/mol and well coincides with the data obtained by thermochemical methods, numerical value which is $\Delta_f H°_{gas} = 159.1 \pm 3.1$ kJ/mol. The dipole moment of hinaldyne experimentally found equal 1,86 ± 1,95 Debye [6], while in the calculations numerical value D = 1.67 - 1.98, is well calculated parameter found to match experimentally. Potential of ionization of the molecule hinaldyne-N-oxide was calculated theoretically is in the range 8.33-8.61 eV and well coincides with the literature, which constitute 8.00 ± 0.05 eV. The dipole moment is 4.0 Debye experimentally found [6], while in the calculations received during D = 2,94-3,43 Debye.

Conclusion

Thus quantum chemical calculations make it possible to obtain results and predict the reactivity of substances. Based on the results for the oxidizing isoquinoline and hinaldyne by peroxydecanoic acid we can conclude that the mechanisms of these substances are similar.

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