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MOLECULAR MODELLING OF ACRIDINE OXIDATION BY PEROXYACIDS

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Abstract. The optimal geometric structure and reactivity of some peroxyacids, acridine and products of their interaction were calculated by quantum-chemical methods. It was found that the heat of formation of peroxyacids (PA) and carboxylic acids (CA) grow with increasing length of a hydrocarbon radical. The dependencies of the area of PA and molecules of CA on the number of carbon atoms in the molecules are linear. The potentials of ionization of all studied PA are close and lie within the range of 11.22–11.39 eV depending on the calculation methods. The theoretically calculated dipole moments of acids, acridine, peroxyacids, and *N*-oxide of acridine are in good accordance with experimental values, which indicate the correctness of our calculations. Theoretical calculated values of the heats of formation (ΔH_f^0) of peroxyacids and acridine are in good accordance with the values obtained by thermo-chemical methods. Calculations indicate that the size of the hydrocarbon radical practically does not affect the value of ΔH^0_{exp}. The results of quantum chemical calculations for the oxidation reaction of acridine may be useful for prediction of other mechanisms of oxidative processes.

Keywords: peroxyacids, quantum-chemical calculations, oxidation, acridine, heat of formation.

1. Introduction

Organic peroxy-compounds are widely used as a source of free radicals, oxidizing agents, intermediates in organic synthesis, disinfectant agent, *etc*. [1-3]. Peroxyacids interact with sulfides, amines, ethylene hydrocarbons, demonstrate mild oxidative effect, and give valuable products.

The information about the structure and electronic properties of molecules is important for successful application of peroxide compounds. Quantum-chemical calculations are used for this. We can predict the reactivity, calculate the thermodynamic parameters and the optimal structure of peroxide compounds using them [4, 5].

The aim of our work was quantum-chemical calculations for the reaction of acridine oxidation by peroxyacids. Often, these reactions are used to produce *N*-oxides. Oxidation reactions of nitrogen-containing compounds by different oxidants allow receiving different conducting polymers [6, 7], biologically active compounds [8, 9] and apply these processes to neutralize substances harmful to the environment [10].

2. Experimental

The results of the theoretical calculations using quantum chemical methods are shown in this work. These are standard heats of formation (ΔH_f^0), ionization potential (I_X), energy of higher occupied molecular orbital (HOMO) and a lower unoccupied molecular orbital (LUMO), dipole moments (*D*), volume (*V*) and area (*S*) of molecules of certain peroxyacids (PA), carboxylic acids (CA), acridine and its *N*-oxides.

Chemical potential (μ) and rigidity of the molecule (η) were calculated by the energy of higher occupied molecular orbital (E_{HOMO}) and a lower unoccupied molecular orbital (E_{LUMO}):

$$\mu = (E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}})/2; \text{ and } \quad \eta = (E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}})$$

As is known, the frontier orbitals method, proposed by Fukui, identifies the relative reactive activity of the compounds by the energy of the molecular orbitals of E_{HOMO} and E_{LUMO} [11, 12]. The E_{HOMO} causes the interaction of the molecule with the electron acceptors, and the E_{LUMO} – electron donors. The positive energy of E_{LUMO} causes the nucleophile properties of the molecules, and the negative – the electrophilic ones.

All quantum-chemical calculations were carried out using semi-empirical methods implemented in the program MOPAC2016 [13] and using the graphical interface Winmostar [14]. The calculations were carried out using the methods AM1, PM3, PM6, PM7, MNDO, and RM1. All calculations were conducted for the gas phase. Based on the performed calculations, the heats of the reaction were obtained, and the possible mechanism of the reaction was predicted.

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3. Results and Discussion

Calculations for peroxyacids (PA) of the general formula:

R–C(O)–O–O–H

were carried out, were R is equal to: CH_3– (**I**); CH_3–CH_2– (**II**); CH_3–$(CH_2)_2$– (**III**); CH_3 –$(CH_2)_4$– (**IV**); CH_3–$(CH_2)_5$– (**V**); CH_3–$(CH_2)_6$– (**VI**); CH_3–$(CH_2)_7$– (**VII**); CH_3–$(CH_2)_8$– (**VIII**); C_6H_5– (**IX**).

Physico-chemical parameters were calculated for the studied peroxyacids using semiempirical method AM1. They are presented in Table 1.

The heats of formation of peroxyacids coincide with the results of thermo-chemical data. Quantum-chemical calculations for peroxybenzoic acid (PBA) and benzoic acid (BA) were different from the corresponding values for aliphatic peroxyacids and their corresponding carboxylic acids.

The heat of formation of peroxyacids (PA) and carboxylic acids (CA) grow with increasing length of a hydrocarbon radical. The numerical values of the heat of formation and dipole moments of the PA and CA, with different number of carbon atoms in molecules (*N*) are given in Tables 2 and 3.

Table 1

Physico-chemical parameters of peroxyacids. Calculation method - AM1

Parameters	Peroxyacids								
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
$-\Delta H_f^0$, kJ/mol	298.69	324.48	352.91	410.16	436.30	462.32	496.69	516.70	152.26
D, Debye	2.443	2.515	2.573	2.607	2.658	2.396	2.675	2.567	3.241
E_{HOMO}, eV	-11.383	-11.258	-11.274	-11.247	-11.236	-11.089	-11.022	-10.999	-10.239
E_{LUMO}, eV	0.589	0.640	0.635	0.637	0.649	0.941	0.648	0.657	-0.671
μ, eV	-5.986	-5.307	-5.319	-5.303	-5.294	-5.074	-5.187	-5.171	-5.455
η, eV	11.997	11.898	11.872	11.873	11.885	12.030	11.670	11.674	9.568
S, Å^2	102.9	121.7	141.6	181.9	201.7	217.1	241.8	255.6	162.2
V, Å^3	85.51	106.7	128.7	173.0	195.2	215.2	238.9	259.5	155.8

Table 2

The dependence of the heats of formation of aliphatic peroxyacids (ΔH_f^0, kJ/mol) and dipole moments (*D*) on number of carbon atoms (*N*) in a molecule, calculated using various semi-empirical methods

N	2	3	4	5	6	7	8	9	10
$-\Delta H_f^0$, AM1	298,69	324.48	352.91	381.92	410.16	439.30	462.32	496.69	516.72
$-\Delta H_f^0$, PM3	325.72	344.51	369.16	389.78	414.45	435.17	454.76	480.60	498.71
$-\Delta H_f^0$, PM6	283,39	300.12	322.06	342.73	362.91	384.45	403.94	426.21	–
$-\Delta H_f^0$, PM7	307.06	325.51	347.05	368.08	389.06	410.85	430.58	453.58	471.66
$-\Delta H_f^0$, RM1	321.03	342.19	363.88	384.66	403.48	426.44	441.90	468.21	479.92
$-\Delta H_f^0$, MNDO	309.67	331.44	351.29	371.05	390.90	410.55	424.66	450.07	460.83
$-\Delta H_f^0$, exp.	–	–	–	–	428.3	448.9	469.5	490.1	510.7
D, RM1	2.55	2.53	2.59	2.58	2.53	2.60	2.43	2.61	2.42
D, exp.	–	–	–	–	–	–	–	2.37	2.27

Table 3

The dependence of the heats of formation of aliphatic acids (ΔH_f^0, kJ/mol) and dipole moments (*D*) on the number of carbon atoms (*N*) in a molecule, calculated using various semi-empirical methods

N	2	3	4	5	6	7	8	9	10
$-\Delta H_f^0$, AM1	431.24	456.69	485.55	514.09	542.79	571.35	594.53	628.86	–
$-\Delta H_f^0$, PM3	426.51	445.32	467.94	490.48	513.27	535.96	555.43	581.35	–
$-\Delta H_f^0$, PM6	423.67	440.22	452.31	482.85	503.80	524.65	544.28	566.48	–
$-\Delta H_f^0$, PM7	427.79	445.53	468.51	489.35	510.95	532.28	550.68	575.01	596.36
$-\Delta H_f^0$, RM1	423.51	443.44	466.93	487.69	508.62	529.48	544.71	571.26	591.15
$-\Delta H_f^0$, MNDO	422.62	445.06	461.61	481.36	501.08	520.84	538.16	560.36	580.13
$-\Delta H_f^0$, exp.	433.0	455.8	475.9	491	512	536.5	554.5	575.6	624.2
D, RM1	1.766	1.766	1.755	1.72	1.75	1.73	1.86	1.73	1.954
D, exp.	1.77	1.75	1.58	1.74	–	–	–	–	–

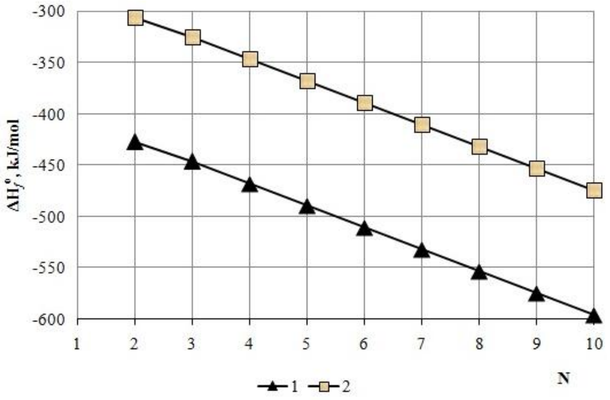


Fig. 1. The dependence of the heat of formation (ΔH_f^0) for carboxylic acids (1) and peroxyacids (2) on the number of carbon atoms (N) in molecules. Method of Calculation PM7

The dependencies of the heat of formation on the number of carbon atoms in molecule of peroxyacids or carboxylic acid calculated by different semiempirical methods are linear (Fig. 1). The numerical values of the heat of formation of peroxyacids or carboxylic acids with different values of N can be predicted with these dependencies.

The E_{HOMO} and E_{LUMO} are similar. Those characterize the oxidation-reducing properties of PA for compounds **I-VIII**. For peroxybenzoic acid, those differ slightly from the parameters for aliphatic peroxyacids. The parameters μ and η for peroxyacids **I-VIII** are almost the same (Table 1).

The numerical values of the areas and volumes of the compounds depend on their structure. The dependencies of the molecule area S of PA and CA on the number of carbon atoms in the molecules are linear. The difference between the areas of molecules of peroxyacid and carboxylic acid with the identical number of N calculated by various methods is within the range of 11.03–11.97 Å^2. This numerical value corresponds to the area of the oxygen atom in PA. Dependencies of volumes of molecules of PA and CA on the number of carbon atoms in molecules are linear too. The values of the volume of oxygen atom determined by the differences of PA and CA volumes are within the limits of 11.01–11.87 Å^3. The difference between the areas of PA containing N and N-1 atoms of carbon in the molecule will give the area of the CH_2 group in the investigated compounds. The numerical values of the CH_2 group area, depending on the calculation method, are within the range of 18.71–19.51 Å^2. The volumes of the CH_2 group are 21.25–22.04 Å^3. The potentials of ionization of all studied PA are close, and they are within the range of 11.220–11.389 eV depending on the calculation methods. Numerical values of I_X for carboxylic acids are similar to the values of PA and are changing within the limits of 11.054–11.492 eV.

The dipole moments of all studied PA and the structures of molecules of peroxyacids are similar. All PA in gas phase or in “inert” solvents form a compound with an intramolecular hydrogen bond (Fig. 2). Moreover, the hydrogen atom H(1) is bounding with oxygen of the carboxylic group O(5). The energy of hydrogen bond found based on the conformational analysis at the rotation of the OH group is 12.9 kJ/mol [15].

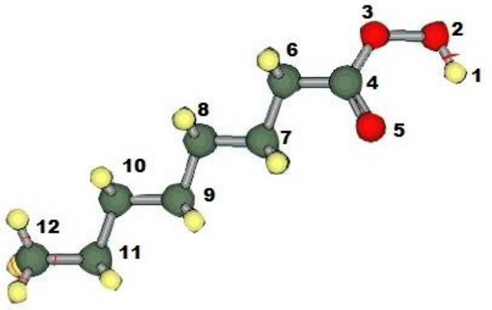


Fig. 2. The optimal molecular structure of peroxyacid **VI**

The length of O–O bond, according to the quantum-chemical calculations, is 1.399 Å. The length of this bond determined from X-ray diffraction data of peroxynonanic acid is equal to 1.442 Å [16]. The length of bond of the carbonyl group is 1.231 Å and the results of the theoretical calculations provide the value of 1.229 Å. The C–O–O angle obtained as a result of X-ray diffraction is 112.0^{o}, whereas according to the quantum-chemical calculations it is 129.5^{o}. Thus, experimental values and results of theoretical studies are in agreement. Small differences can be explained by the fact that X-ray diffraction was conducted for crystalline specimens in a solid state, while quantum-chemical calculations were performed for a molecule in the gas phase.

Valuable information can be obtained by investigating the partial charges on the atoms of PA. Partial charges on atoms calculated by semiempirical quantum-chemical methods AM1 are presented in the Table 4.

The atom H(1) has a deficiency of electron density, which indicates its “acid” character. The acidity of PA is less than for the corresponding carboxylic acids. The values of pKa for peroxyacids are within the limits of 7.01–8.7 [17]. The partial charges are almost identical at atoms of oxygen in peroxide group. It should be noted that the partial charges on the oxygen atoms of O(2) and O(3) in molecules of hydroperoxide are different, unlike molecules of PA [18].

The attack on the reaction center in the reactions of electrophilic oxidation is performed by an oxygen atom O(2). This statement is true for reactions involving hydroperoxides [2]. The attack on a multiple bond or a nitrogen atom in the case of peroxyacids can be carried out by O(2) and O(3) atom. The carbonyl group in molecules of PA is strongly polarized (Table 6). A partial charge on all other atoms for the investigated PA does not change with the radical change near the peroxide group of the PA. The partial charges for the molecule of peroxybenzoic acid are different from the parameters calculated for all aliphatic PA.

The infrared spectra of the PA calculation allowed detecting the bands characteristic of these compounds. The characteristic band in the IR spectrum of the PA is the absorption at 3280 cm^{-1}, which corresponds to the absorption frequency of the OH group, bound by the intramolecular hydrogen bond. In addition, the absorption band at 2000 cm^{-1} is observed in the spectrum. This corresponds to the oscillation of the group C=O of PA. The absorption band of the O–O bond in the theoretically calculated spectrum is observed at 1500 cm^{-1}. In the spectrum of the PDA solution in carbon tetrachloride, the absorption band of the peroxide bond is observed at the wavelength of 865 cm^{-1}. The absorption band at 3280 cm^{-1} corresponds to the absorption frequency of the OH-group associated with the intramolecular hydrogen bond, which coincides with the value theoretically calculated. The absorption band at 1760 cm^{-1} corresponds to the absorption of the carbonyl group C=O, whereas, for the calculated spectrum, the quantum-chemical absorption method is observed at 2000 cm^{-1}.

In our opinion, some discrepancy between theoretically calculated and experimentally calculated wavelengths in IR spectra can be explained by the fact that those theoretical calculations of IR spectra are carried out for an individual molecule in a vacuum, while experimental measurements were carried out in a solution of carbon tetrachloride. It should be noted that according to the obtained data; the intra-molecular hydrogen bond is characterized by considerable strength. Spectroscopic studies in the wavelength range from 4000 to 2500 cm^{-1} for solutions of PDA with different concentrations practically do not change the position and nature of absorption bands. The change in the PDA concentration from 0.0125 to 0.2 mol/l in a solution of carbon tetrachloride gives a proportional increase in the optical density of the 3280 cm^{-1} band. This suggests that at the moderate concentrations of the peroxyacid molecules exist in a monomer state with intramolecular hydrogen bonds [19, 20].

Quantum-chemical calculations for acridine (AN) and acridine *N*-oxide (OAN) were carried out by semi-empirical methods. Optimal geometric structures of acridine and acridine *N*-oxide are given in Fig. 3.

According to quantum-chemical calculations, the acridine and acridine-10-oxide molecules are flat. All flat angles in both molecules are 120°. The heat of formation of acridine and acridine-10-oxide and other parameters calculated by semiempirical methods AM1, PM3, PM7, RM1, and MNDO are given in Tables 5 and 6.

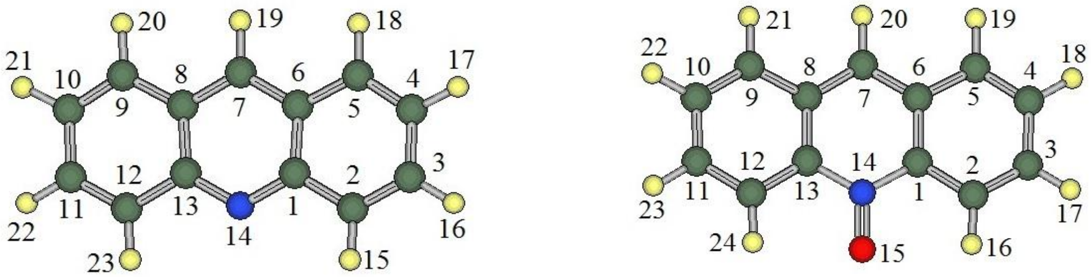
The calculated heats of formation of acridine are within the range from -213.17 to -299.61 kJ/mol. The value of ΔH_f^0 which was found *via* thermo-chemical method, is equal to -273.9±2.0 kJ/mol, and corresponds well to the values calculated theoretically. The theoretically calculated dipole moments of acids, acridine, peroxyacids, and *N*-oxide of acridine are in good agreement with experimental values [21], which may indicate the correctness of our calculations. The values of partial charges on atoms can give important information about the reactivity of the molecules. The results of such calculations are presented in Table 7.

Table 4

Partial charges on the peroxyacids atoms (by Mulliken)

Peroxyacid	Atom label						
	H(1)	O(2)	O(3)	C(4)	O(5)	C(6)	C(7)
I	0.203	-0.156	-0.166	0.335	-0.317	-0.223	–
II	0.202	-0.156	-0.170	0.322	-0.316	-0.158	-0.214
III	0.202	-0.157	-0.165	0.321	-0.317	-0.158	-0.159
IV	0.203	-0.156	-0.161	0.365	-0.325	-0.158	-0.158
V	0.201	-0.156	-0.168	0.325	-0.318	-0.159	-0.158
VI	0.202	-0.156	-0.170	0.323	-0.318	-0.157	-0.152
VII	0.202	-0.157	-0.165	0.321	-0.317	-0.158	-0.158
VIII	0.211	-0.137	-0.168	0.269	-0.325	-0.157	-0.156
IX	0.213	-0.166	-0.132	0.316	-0.330	-0.123	-0.067

Notes: Atom labels correspond to the numbers in Fig. 2. Calculation method AM1.



a) b)

Fig. 3. Optimal geometric structure of acridine (a) and its oxidation product – acridine-*N*-oxide (b)

Table 5

Physico-chemical parameters for acridine calculated using various semi-empirical methods

Parameter	Method of calculation				
	AM1	PM3	PM7	RM1	MNDO
$-\Delta H_f^0$, kJ/mol	297.59	268.91	299.61	260.96	213.72
D, Debye	1.681	1.681	1.456	1.871	1.595
E_{HOMO}, eV	-8.949	-8.974	-8.854	-8.719	-9.102
E_{LUMO}, eV	-0.604	-0.807	-1.232	-0.175	-0.394
μ, eV	-4.777	-4.891	-5.044	-4.447	-4.748
η, eV	8.345	8.167	7.622	8.532	8.708
S, Å^2	209.32	208.90	209.38	208.67	212.04
V, Å^3	215.07	214.44	215.51	214.10	218.76
I_X, eV	8.949	8.974	8.854	8.719	9.102

Table 6

Physico-chemical parameters for acridine-*N*-oxide calculated using various semi-empirical methods

Parameter	Method of calculation				
	AM1	PM3	PM7	RM1	MNDO
$-\Delta H_f^0$, kJ/mol	288.64	242.73	251.31	217.48	240.36
D, Debye	3.149	3.376	2.82	3.092	2.955
E_{HOMO}, eV	-8.751	-8.882	-8.516	-8.489	-8.898
E_{LUMO}, eV	-0.115	-0.365	-0.796	-0.049	-0.022
μ, eV	-4.433	-4.259	-4.656	-4.369	-4.460
η, eV	8.636	8.517	7.49	8.440	8.876
S, Å^2	215.96	215.43	215.40	215.12	219.15
V, Å^3	225.82	225.49	225.39	225.04	230.08
I_X, eV	8.75	8.593	8.516	8.489	8.898

Table 7

Partial charges on the atoms (by Mulliken) of the studied molecules of acridine and acridine *N*-oxide

Atom label	Acridine	Acridine-*N*-oxide	Atom label	Acridine	Acridine-*N*-oxide
1C	0.003	-0.026	8C	-0.066	-0.026
2C	-0.099	-0.105	9C	-0.116	-0.116
3C	-0.127	-0.123	10C	-0.123	-0.123
4C	-0.123	-0.123	11C	-0.127	-0.123
5C	-0.116	-0.116	12C	-0.099	-0.105
6C	-0.066	-0.026	13C	0.003	-0.026
7C	-0.095	-0.126	14N	-0.105	0.200
			15O	–	-0.350

Notes: The numbers of the atoms correspond to the numbers in Fig. 3. Method of calculation AM1.

Partial charges in the molecules of acridine and *N*-oxide of acridine for carbon atoms, which are in the identical positions, are almost identical. At the atom of nitrogen in the molecule of acridine, the partial charge is -0.105, and in the *N*-oxide of acridine, the corresponding value becomes positive and equal to 0.200. The oxygen atom in the *N*-oxide of acridine has a partial charge of -0.350, which indicates the polarization of the N–C bond.

The thermal effects of the reaction based on the quantum-chemical calculations were obtained. The scheme of oxidation reaction of acridine:

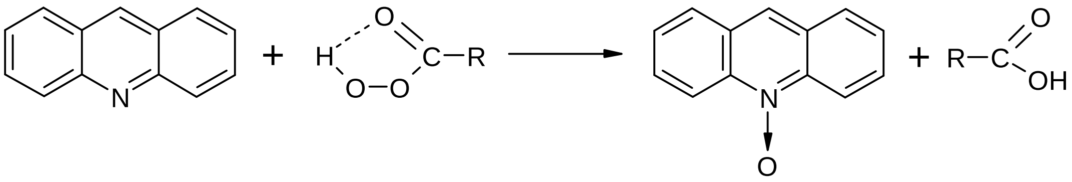


Table 8

The heat of formation of molecules and thermal effect of acridine oxidation by peroxydecanoic acid, calculated using different semiempirical methods

Method of calculation	The heat of formation of molecules ΔH_f^0, kJ/mol				Thermal effect of acridine oxidation ΔH_{exp}, kJ/mol
	Acridine	Peroxydecanoic acid	Decanoic acid	Acridine-*N*-oxide	
AM1	297.5	-516.7	-657.4	288.6	-149.6
PM3	268.9	-498.7	-604.2	242.7	-131.7
PM7	299.6	-471.6	-587.4	251.3	-164.1
RM1	260.9	-479.9	-587.4	217.4	-150.7
MNDO	213.7	-460.8	-592.2	240.3	-102.8
Thermo-chemical data	273.9±2	-509.4±2.2	-680.5	–	–

Table 9

Thermal effect of acridine oxidation by various peroxyacids, calculated using different semiempirical methods

Method of calculation	Thermal effect of acridine oxidation by various peroxyacids, $-\Delta H^0_{exp}$, kJ/mol								
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
AM1	141.14	141.15	141.58	140.95	140.99	141.15	141.11	–	141.44
PM3	126.06	126.99	124.97	125.01	126.97	126.86	126.93	–	125.60
PM7	169.03	169.32	168.30	170.19	169.72	168.40	169.79	164.10	169.00
RM1	145.95	144.74	146.53	148.61	146.51	146.28	146.52	–	146.28

The heat of reaction of acridine by peroxydecanoic acid (PDA) using various methods calculated by the Hess equation is given in Table 8.

The numerical values of the heat of formation of PDA, decanoic acid and acridine well coincide with the corresponding values of ΔH_f^0 found thermo-chemically [22, 23]. The thermo-chemical data for *N*-oxide of acridine are absent in literature. According to quantum-chemical calculations, the numerical values of ΔH_f^0 are within the range of 217.4–288.6 kJ/mol. The reaction of oxidation of acridine is exothermic.

The thermal effect was calculated by different semiempirical methods. For this reaction, it is from -102.8 to -164.1 kJ/mol. The data on the thermal effects of the acridine oxidation by various peroxyacids, calculated using different semiempirical methods are presented in Table 9. Calculations indicate that the size of the hydrocarbon radical practically does not affect the value of ΔH^0_{exp}. Using the AM1 method, the numerical values of ΔH^0_{exp} are equal to 140.95–141.44 kJ/mol. In the case of use of peroxybenzoic acid as an oxidant, the thermal effect of the process is also -141.44 kJ/mol.

4. Conclusions

Quantum-chemical calculations allow to find the optimal geometric structure of molecules and predict the reactivity of peroxyacids. In our work, optimal geometric structures, the heats of formation of the starting compounds and the products of the reaction of acridine oxidation by peroxyacids were calculated. The obtained results can be considered reliable due to the good correspondence between the theoretical and calculated values. The results of quantum chemical calculations for the oxidation reaction of acridine may be useful for prediction of other mechanisms of oxidative processes.

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МОЛЕКУЛЯРНЕ МОДЕЛЮВАННЯ ОКИСНЮВАЛЬНОЇ РЕАКЦІЇ АКРИДИНУ ПЕРОКСИКИСЛОТАМИ

Анотація. *Квантово-хімічними методами розраховано оптимальну геометричну будову та реакційну здатність деяких пероксикислот, акридину та продуктів їхньої взаємодії. Встановлено, що теплота утворення пероксикислот (ПК) і карбонових кислот (КК) збільшується із підвищенням довжини вуглеводневого радикалу. Залежності площ молекул ПК та молекул КК від кількості атомів карбону в молекулах є лінійними. Потенціали йонізації всіх досліджених ПК близькі і знаходяться в діапазоні 11.22–11.39 еВ, залежно від методів розрахунку. Теоретично обчислені дипольні моменти кислот, акридинів, пероксикислот та N-оксидів акридину непогано узгоджуються з експериментальними значеннями, що вказує на правильність розрахунків. Теоретично обчислені значення теплоти утворення* (ΔH_f^0) *пероксикислот та акридину непогано узгоджуються зі значеннями, отриманими термохімічними методами. Розрахунки показують, що розмір вуглеводневого радикалу практично не впливає на величину* ΔH^0_{exp}. *Результати квантово-хімічних розрахунків для реакції окиснення акридину можуть бути корисними для прогнозування інших механізмів окиснювальних процесів.*

Ключові слова: *пероксикислоти, квантово-хімічні розрахунки, реакційна здатність окиснення, акридин, теплоти утворення.*