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QUANTUM-CHEMICAL ANALYSIS
OF *a*–ALKYLACROLEINS STRUCTURE

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Abstract. The reactivity of different α-alkylacroleins has been described by semi-empirical quantum chemistry methods, their optimal geometric structure has been determined and heat of formation, as well as dipole moments of the molecules have been calculated. Theoretically calculated α-alkylacrolein parameters are in a good agreement with the experimental data presented in the literature for these compounds.

Keywords: α-alkylacroleins, quantum-chemical calculations, MOPAC2009, semiempirical methods, conformational analysis.

1. Introduction

Quantum-chemical calculations allow to receive information about molecule geometric and electronic structures, to predict the possible reaction mechanisms with their participation and to obtain data which can not be determined by the experiments. The reactivity of α-alkylacrolein (AA) molecules *via* the quantum chemistry methods were not calculated, so this research is actual and can allow to obtain more information for the clarification of the reaction mechanisms with their participation. The literature provides a number of experimental kinetic data of α-alkylacrolein dimerization [1-3]. Two AA molecules react with each other, whereby one molecule acts as heterodiene and another acts as dienophile. During this reaction 2,5-dialkyl-3,4-dihydro-2*H*-pyran-2-carbaldehyde – dimers of AA – are formed, where carbaldehyde group can be oriented equatorial or axial to the pyran cycle [4, 5]. The important peculiarity of α-alkylacrolein dimerization *via* Diels-Alder reaction is its regioselectivity, *cis-* principle of addition and *endo-*and *exo-*orientation of its substituents. Enantiomeric products are formed in the case of acyclic reagents use.

2. Experimental

The aim of our work was the study of geometric structure and electronic parameters of α-alkylacrolein molecular orbitals. The results of such studies allow to predict the molecules reactivity. We have carried out the quantum-chemical calculations for the molecules of acrolein (ACR), methacrolein (MA), α-ethylacrolein (EA), α-propilacrolein (PA), α-butylacrolein (BA) and α-amilacrolein (AMA). The structure optimization and electronic parameters of the studied α-alkylacrolein molecules were achieved by means of the quantum-chemical program MOPAC2009 [6] and GUI Winmostar [7]. To optimize the geometric structure and calculate the heat of molecular structures formation ($\Delta_f H^{298}$), energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, as well as charges on atoms by Mulliken different semiempirical methods were used.

3. Results and Discussion

Quantum-chemical calculations for EA in the gas phase were carried our using various semiempirical methods, namely AM1, PM3, RM1 and RM6; the results are shown in Table 1. These methods were used because they allow to optimize the geometry of molecules consisting of elements C, N, H, and O atoms, with the least error for bond lengths and angles between them, in comparison with other methods of diatomic differential overlap neglect [10].

Theoretically calculated heats of EA formation are within the range from -106.2 to -135.3 kJ/mol. The heat of EA formation, calculated on the basis of thermochemical data presented in [8], is -131.2 ± 2.6 kJ/mol. Numerical

$\Delta_f H^{298}$ value is theoretically obtained by RM1 method. It is in the best agreement with the experimental one (Table 1). EA dipole moments (μ), calculated *via* different semiempirical methods are within 2.48÷3.27 D. Experimental numerical value of μ for EA is 2.55 D [9] and coincides with the value theoretically calculated by RM1. The energy of higher occupied molecular orbital (HOMO) varies within (-10.06)–(-10.56) eV, while the numerical values of lower unoccupied molecular orbital (LUMO) are (-0.3)–(+0.3) eV. The absolute hardness (η) AA was determined by the formula: η = (LUMO-HOMO)/2. The calculated η values are shown in Table 1. As it might be expected, areas and volumes of EA molecule calculated by different methods are practically identical.

Further calculations for the studied α-alkylacroleins were performed by semiempirical RM1 method, since the heat of EA formation and its dipole moment calculated by this method are in the best agreement with the experimental ones (Table 1). Energy parameters for investigated α-alkylacroleins calculated by semiempirical RM1 method are shown in Table 2.

Table 1

**Physico-chemical parameters for EA,
calculated by semiempirical methods**

Parameters	Experimental	AM1	PM3	RM1	PM6
$\Delta_f H^{298}$, kJ/mol	-131.2±2.6	-126.24	-135.29	-128.45	-106.20
μ, D	2.55	2.67	2.48	2.55	3.27
HOMO, eV	-	-10.468	-10.559	-10.330	-10.055
LUMO, eV	-	0.015	-0.054	0.301	-0.298
η, eV	-	5.242	5.253	5.316	4.879
S, Å^2	-	132.77	132.38	132.01	132.51
V, Å^3	-	122.67	122.30	121.75	122.35

Table 2

**Physico-chemical parameters
for investigated α-alkylacroleins calculated by RM1**

Parameters	ACR	MA	EA	PA	BA	AMA
*$\Delta_f H^{298}$, kJ/mol	-71.28	-106.4 ± 2.0	-131.2 ± 2.6	-	-	-
$\Delta_f H^{298}$, kJ/mol	-68.84	-109.32	-128.45	-149.58	-170.47	-191.37
μ, D	2.40	2.56	2.55	2.58	2.57	2.59
HOMO, eV	-10.522	-10.274	-10.330	-10.312	-10.307	-10.307
LUMO, eV	0.203	0.250	0.301	0.290	0.291	0.290
η, eV	5.363	5.261	5.316	5.301	5.299	5.299
S, Å^2	96.03	114.36	132.01	151.85	171.64	191.69
V, Å^3	79.17	100.52	121.75	143.84	165.51	186.90

* the results were obtained by the thermochemical method [8]

The results show that the theoretically calculated heats of ACR, MA and EA formation are in agreement with the values experimentally obtained by the thermochemical method (Table 2). The numerical values of $\Delta_f H^{298}$ for PA, BA and AMA are absent in the literature, therefore with the high degree of reliability we can consider the calculated by RM1 heats of alkylacroleins formation close to the real ones. The difference between the numerical values for MA and ACR is 40.5 kJ/mol. The increase of alkyl radical by CH_2-group increases $\Delta_f H^{298}$ value by 19–21 kJ/mol for each of the next homologues. The numerical values of the AA homologous dipole moments are close to the values given in the literature [10]. The calculated values of the molecules area for acrolein homologues vary from 96.03 to 191.69 Å^2, *i.e.* the increase of hydrocarbon radical by CH_2-group increases the molecule area by 18–20 Å^2. Under the same conditions, the molecules volume increases by 21–22 Å^3 for the neighboring AA homologues.

Using the value of HOMO and LUMO energy we may determine the reactivity of the studied compounds. It is known that HOMO causes the interaction between the molecule and electronacceptors, and LUMO – between the molecule and electrondonors. LUMO positive energy is a reason for the molecules nucleophilic properties and negative energy – for electrophilic ones. In our case LUMO energy (Table 2) is positive so AA can be attributed to the weak nucleophiles. HOMO and LUMO numerical values are close for the studied AA. Absolute

hardness of the molecules is in the range of 5.26–5.36 eV and indicates that the investigated compounds belong to the soft reagents and may react with other soft ingredients. The geometrical structure of investigated AA molecules with numbering of atoms is shown in Fig. 1.
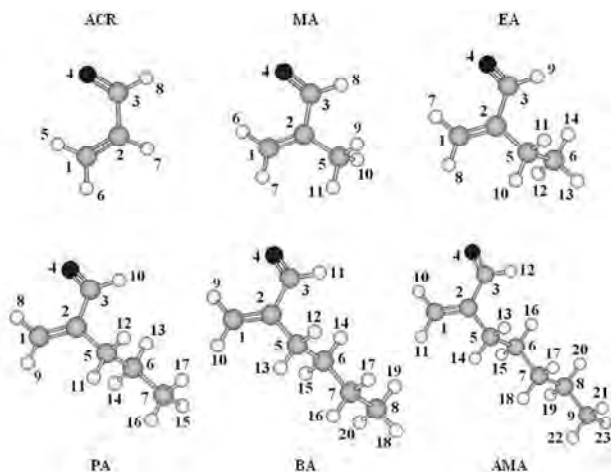

Fig. 1. The optimal geometrical structure of the α-alkylacrolein molecules

Stereometric analysis of AA molecules structure indicates that they may exist as two conformers. *Cis*-conformer has the minimum energy, which is confirmed by calculation of potential energy changes of MA molecule during its rotation around C(2)-C(3) axis (Fig. 2). The numerical value of MA *cis*-conformer energy is -109.32 kJ/mol, whereas for *trans*-conformer it is -107.54 kJ/mol. Thus we can conclude that the *cis*-conformation is more stable.

Calculation of the optimal molecular structure indicates that atoms C(1), C(2), C(3) and O(4) for ACR and MA lie in one plane. The growth of alkyl substituent size in AA (EA, PA, BA, AMA) molecule slightly changes the dihedral angle of acrylic fragment, resulting in the deviation of O(4) atom from the plane by ± 18°. The numerical values of AA molecules bond lengths are shown in Table 3.

Table 3

Bond lengths (d, Å) between atoms of investigated AA

d, Å	ACR	MA	EA	PA	BA	AMA
C(1)-C(2)	1.329	1.331	1.331	1.331	1.331	1.331
C(2)-C(3)	1.476	1.480	1.479	1.479	1.479	1.479
C(3)-O(4)	1.218	1.217	1.217	1.217	1.217	1.217
C(2)-C(5)	1.094*	1.485	1.492	1.492	1.492	1.492
C(5)-C(6)	-	-	1.521	1.528	1.529	1.529
C(6)-C(7)	-	-	-	1.520	1.527	1.527
C(7)-C(8)	-	-	-	-	1.520	1.527
C(8)-C(9)	-	-	-	-	-	1.520

*bond length of the C(2)-H(7)

Reactivity of AA molecules does not depend on the length of alkyl substituent. The bond length between the acrylic fragment atoms indicates this fact. It should be noted also that the length of C(2)-C(5) bond in the investigated AA molecules is 1.485–1.492 Å and it is slightly lower than that for single C–C bonds in the alkyl substituent. Obviously, such decrease of C(2)-C(5) bond takes place due to the conjugation effect [1, 11] affecting the reaction mechanisms in the presence of alkylacroleins. The rotation of methyl group hydrogen atoms in the MA molecule relative to C(2)-C(5) axis leads to the energy changes. Moreover, the dependence of the energy on the rotation angle has three maximums and three minimums (Fig. 3). The system energy is minimal when C(1), C(2), C(5) and H atoms are in the same plane. The molecule has the maximum energy while rejecting the H atom from C(1)-C(2)-C(5) plane by ± 60°. The conformational analysis allows to calculate the hydrogen atom conjugation energy, which is 2.35 kJ/mol. In the case of higher AA (EA, PA, BA and AMA) the C(5) atom is connected with two H atoms, therefore the dependence of the potential energy on the rotation angle is more complex during C(2)-C(5) bond rotation.
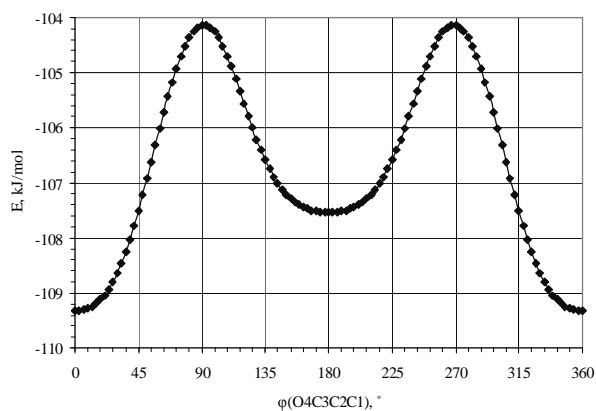

Fig. 2. The potential energy change of MA molecule depending on the size of dihedral angle
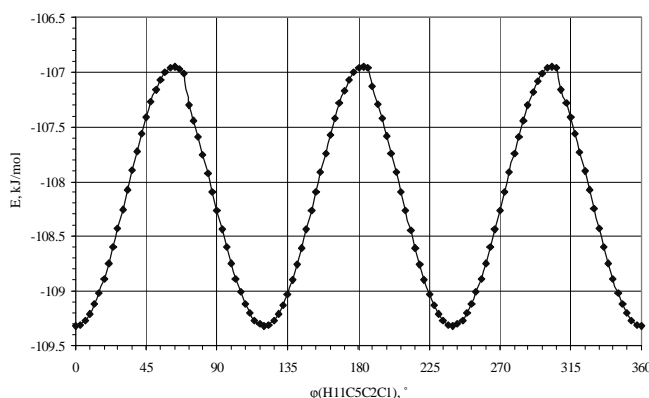

Fig. 3. Dependence of MA molecule energy upon the change of methyl group rotation angle around C(5)-C(2) axis

Reactivity of AA molecules can be characterized by a charge on atoms by Mulliken. The calculation results are represented in Table 4.

**Charges on atoms by Mulliken
for the investigated alkylacroleins**

Atom (No.)	ACR	MA	EA	PA	BA	AMA
C(1)	-0.066	-0.091	-0.092	-0.090	-0.090	-0.090
C(2)	-0.270	-0.198	-0.205	-0.207	-0.207	-0.207
C(3)	0.267	0.268	0.270	0.269	0.269	0.269
O(4)	-0.308	-0.307	-0.307	-0.307	-0.307	-0.307
C(5)		-0.139	-0.071	-0.082	-0.082	-0.082
C(6)			-0.180	-0.113	-0.124	-0.125
C(7)				-0.179	-0.113	-0.123
C(8)					-0.178	-0.113
C(9)						-0.178

Charges on acrylic fragment atoms for all investigated AA (except ACR) are practically identical, which confirms the small effect of alkyl substituent on the molecule reactivity. For all AA the charge on O(4) atom is equal to -0.307, and on C(3) it is 0.269, indicating the same electronic parameters of the carbonyl group. According to the obtained calculations, the lowest negative charge is observed on C(2) atom for ACR, while for other AA the numerical value of the charge is higher and ranges from -0.198 to -0.207. The charges on C(1) atom for MA, EA, PA, BA, and AMA are practically identical and equal to -0.091 (Table 4). Numerical value of this parameter for ACR is higher (-0.066). The difference between ACR and other AA reactivity appears in different rates of the dimerization reaction [12].

4. Conclusions

Using the semiempirical quantum chemistry methods we described the reactivity of different alkylacroleins, found their optimal geometric structure and calculated the heat of molecules formation and their dipole moments. Theoretically calculated parameters for AA are in a good agreement with the experimental data presented in the literature for these compounds.

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**КВАНТОВО-ХІМІЧНИЙ АНАЛІЗ БУДОВИ
α-АЛКІЛАКРОЛЕЇНІВ**

Анотація. *За допомогою напівемпіричних методів квантової хімії охарактеризовано реакційну здатність різних α-алкілакролеїнів, знайдено їх оптимальну геометричну будову та розраховані теплоти утворення та дипольні моменти молекул. Теоретично обчислені параметри для α-алкілакролеїнів добре співпадають з експериментальними даними, які наведені в літературі для цих сполук.*

Ключові слова. *α-алкілакролеїни, квантово-хімічні розрахунки, МОРАС2009, напівемпіричні методи, конформаційний аналіз.*