REPORTS OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
ISSN 2224-5227
Volume 1, Number 311 (2017), 11 – 18

UDK 541.1+530.145

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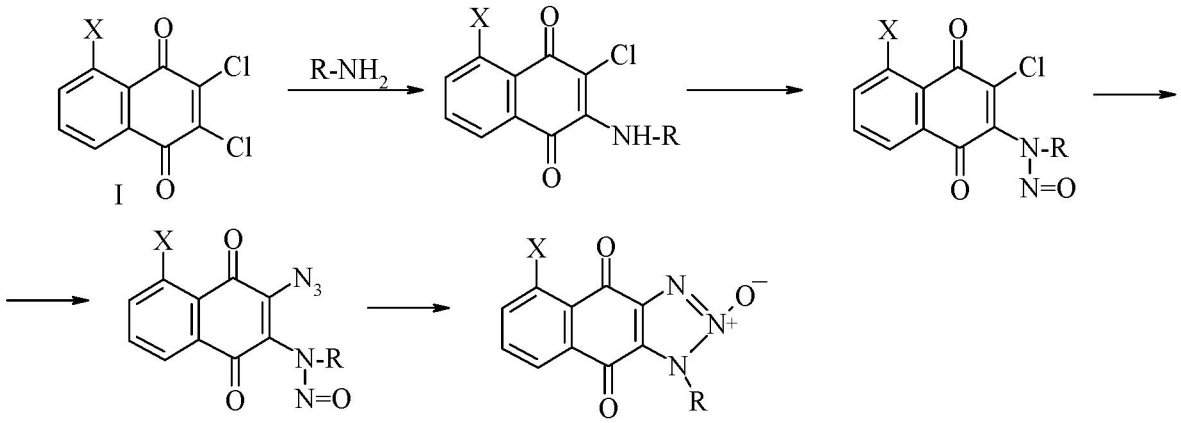
STUDY OF THE MECHANISM OF THE REACTION OF TRIAZOLIDE'S FORMATION OF USING THE DENSITY FUNCTIONAL THEORY

Abstract. We have analyzed the thermodynamic parameters of the reaction of the amination in the gas phase and in solution by calculation by density functional method using fully electronic basis set 6-31G(d). It was shown the dichlorojuglone aniline`s thermodynamic and kinetic possibility of a reaction of condensation. It was estimated the transition states, activation energies and rate constants for the reaction of condensation.

Keywords: the theory of functional density; B3LYP/6-31G (d); naphthoquinones; the mechanism of the reaction.

Introduction

Works [1-2] have described an experimental approach to triazole oxides. The interest in compounds of this structure is due to the fact that some of them [3] have antitumor activity. Given this and lack of in-depth information about the properties of the condensed triazole oxides we will consider experimental and quantum-chemical peculiarities of their formation, as was shown earlier [2]. It is known that the simplest way to naftatriazole oxides is the following scheme:



X = H, OH

The aim of this work was to study the density functional method of the mechanism of the first reaction stage of condensation dichlorojuglone with aniline and the explanation of the observed experimental data. For all calculations there were used fully electronic basis set 6-31G (d) with density functional B3LYP. This calculation method is widely used for analysis of thermodynamic parameters of organic compounds.

Experimental part

All calculations were carried out using standard software package GAUSSIAN'03 [4]. For the theoretical study, we used quantum-chemical density functional method (DFT, density function theory methods). The calculations were performed using the hybrid density functional method B3LYP with a functional exchange Beck (B3) [5] and the correlation functional of Lee, Yang and steam (not LYP) [6]. For all atoms basis set 6 fully electronic-31G (d) was used. The geometries of all calculated molecules were fully optimized, the lack of imaginary frequencies confirmed their stationary. Optimization of transition States was carried out using the STQN method [7], transition states with only one imaginary frequency. The calculations in ethanol solution are carried out by the same methods, using a polarized continuum (PCM) [8]. The energy is calculated compounds adjusted to the zero vibration energy (ZPVE) and reduced to standard conditions (298.15 K, 1 ATM.) using thermal corrections to enthalpy and free energy.

Results and discussion

The accuracy of any quantum-chemical calculations is determined by the agreement of experimental and calculated from molecular geometry. The calculated bond lengths and the bond angles of the studied molecules together with the available experimental data are represented in tables 1-2.

Table 1 - The geometrical parameters of the juglone

Bond	R (exper.), Å	R (calc.), Å	the valence angle	ω (exper.), degree	ω (calc.), degree
C-C	1.35 ± 0.02	1.34	O-C-C	120 ± 1	119.4
C-C	1.51 ± 0.03	1.49	C-C-C	123 ± 2	121.8
C-C	1.44 ± 0.02	1.48	C-C-C	120 ± 2	122
C-O	1.2 ± 0.02	1.23	C-C-O	121 ± 2	120.3
O-H	1.51 ± 0.02	1.49	C-C-C	119 ± 1	117.5
C-C	1.37 ± 0.02	1.42	C-C-C	118 ±1	120
C-C	1.51 ± 0.02	1.47	C-C-C	122 ± 1	120.7
C-O	1.33 ± 0.02	1.34	C-C-C	118 ± 1	118.2
C-C	1.44 ± 0.02	1.41	C-C-C	122 ± 1	120.1
C-C	1.38 ± 0.02	1.39	O-C-C	115 ± 2	118.2
C-C	1.42 ± 0.03	1.41	C-C-C	122 ± 1	119.4
C-C	1.36 ± 0.02	1.39	C-C-C	119 ± 2	120.2
C-C	1.4 ± 0.02	1.42	C-C-C	120 ± 2	121
			C-C-C	119 ± 2	119.5
			C-C-C	118 ± 1	120.6
			C-C-C	116 ± 1	119.3
			C-C-C	117 ± 1	119.4

Comparison of the calculated geometric parameters with experimental data shows that the calculated lengths of bonds mostly underestimated, and bond have been completed. However the analysis leads to good quality there was a problem with the correlation between the calculated and experimental bond lengths of and valence angles [9-12] for some of the studied molecules:

$$R^{exp.} = -0.04 + 1.03\ R^{calc.} \qquad (r = 0.996;\ s = 0.02;\ n = 22) \qquad (1)$$

$$\omega^{exp.} = -17.9 + 1{,}14\ \omega^{calc.} \qquad (r = 0.982;\ s = 1.5;\ n = 32) \qquad (2)$$

In these and the following correlation equations, r is the correlation coefficient, s is standard deviation and n is the number of compounds included in the correlation.

Table 2 - The geometrical parameters of the naphthazarine

Bond	R (exper.), Å	R (calc.), Å	the valence angle	ω (exper.), degree	ω (calc.), degree
C-C	1.431 ± 0.006	1.47612	C-C-H	120 ± 2	122.4
C-C	1.342 ± 0.007	1.34598	C-C-O	118.5 ± 0.4	119.8
C-C	1.413 ± 0.007	1.42717	C-C-H	120 ± 2	115.8
C-C	1.427 ± 0.005	1.4062	C-C-O	122.2 ± 0.4	122.4
C-C	1.436 ± 0.006	1.41946	C-O-H	104 ± 2	106.5
C-C	1.342 ± 0.007	1.37442	O-H-O	152 ± 4	147.3
C-O	1.301 ± 0.004	1.24774	H-O-C	99 ± 2	101.1
C-O	1.288 ± 0.004	1.33758	O-C-C	121.4 ± 0.4	122.4
C-H	0.96 ± 0.005	1.08626	C-C-C	119.7 ± 0.4	119.7
C-H	0.98 ± 0.005	1.08533	C-C-H	117 ± 3	117.9
O-H	1.06 ± 0.05	0.99638	C-C-H	122 ± 3	121.3
H-O	1.59 ± 0.05	1.7001	C-C-C	120.6 ± 0.4	121.8
			C-C-C	119.2 ± 0.3	117,8
			C-C-C	120 ± 0.4	120.3
			C-C-C	119.5 ± 0.4	119.9
			C-C-C	121.9 ± 0.4	120.8
			C-C-C	119 ± 0.4	119.3

The table 3 shows the calculated and experimental [13-15] values of wavelength UV spectra (λ), IR spectra (ω) spectra and the ^{1}H and ^{13}C NMR (δ) of some quinone molecules.

The correlation equations (3-5) show that our calculations allow to estimate the spectral parameters with a sufficient degree of accuracy.

$$\lambda^{exp.} = -16 + 1.06\ \lambda^{calc.} \qquad (r = 0.998;\ s = 7;\ n = 22) \qquad (3)$$

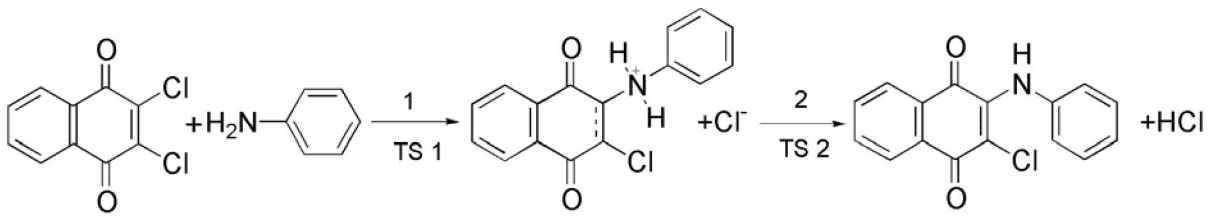
$$\delta^{exp.}\ {}^{1}H = 1.23 + 0.83\ \delta^{calc.}\ {}^{1}H \qquad (r = 0.995;\ s = 0.2;\ n = 19) \qquad (4)$$

$$\delta^{exp.}\ {}^{13}C = 4.7 + 0.92\ \delta^{calc.}\ {}^{13}C \qquad (r = 0.996;\ s = 2.2;\ n = 8) \qquad (5)$$

$$\omega^{'rcg/} = 32 + 0.99\ \omega^{calc.} \qquad (r = 0.995;\ s = 30;\ n = 18) \qquad (6)$$

We obtained a correlation ratio suggest that expected thermodynamic parameters are quite close to experimental values. In addition, in [16] it is shown that among the methods of the density functional (BLYP, B3LYP, PB86, B3P86, BPW91, B3PW91 and SVWN) B3LYP method most accurately predicts thermodynamic parameters with an absolute error of 13 kJ/mol.

On the basis of the experiment we can assume the mechanism for the first reaction stage of the formation of intermediate and transition states:



3-хлор-1,4-диоксо-1,4-дигидро
-2-нафталенил(фенил)аммониум хлорид

The table 4 shows the results of quantum-chemical calculations of the enthalpies (ΔH) and free Gibbs energies of the amination's reactions for some naphthoquinones with aromatic amines. From table 4 it is shown that all the reactions are thermodynamically favorable in the gas phase and in solvent. However, the solvent Gibbs energy is approximately two times larger value due to the salvation of the reagents in ethanol.