

Quantum chemical modeling of the olefin oxidation in the triplet state

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Abstract: The method uB3LYP/6-31g+(d) was used to simulate the reaction of photochemical oxidation of olefins such as ethylene with nitrobenzene and HNO₂ in the triplet state. It is found that photooxidation occurs in two stages. In a first step complex formation of the nitro compound with an olefin has place and in the second step its further degradation to nitroso compound and ethylene oxide occurs. The energies of activation for each stage of the transformation were determined.

Keywords: uB3LYP, reaction mechanism, the triplet state, transitional state, nitroso oxide imaginary frequency.

Introduction

Ethylene oxide is one of the target oxidation products of the olefin. It is widely used as a fumigant and are intermediates in the synthesis of solvents, lubricants, hydraulic liquids, emulsifiers. Usually [1] ethylene oxide is obtained through ethylene chlorohydrin and this method is currently the only industrial method of the oxide producing. Despite of the fact that the yield is high, the chlorine method has significant disadvantages [1]. Therefore, the researches in the field of the olefin oxidations to oxygenated compounds are relevant. Especially important is the development of new methods of the low-temperature oxidation. An interesting photochemical oxidants of olefins are aromatic nitro compounds. Buchi [2] reported that under irradiation a mixture of nitrobenzene and 2-methyl-2-butene by UV light a complex mixture of products with low yields forms. In the study of the qualitative composition of the reaction products it has become clear that the ethylene bond is susceptible to the nitrobenzene induced photochemical oxidation. These authors suggested that cyclic compounds are formed as intermediates. The proof of the hypothesis is given in [3].

The aim of our work is to study the photochemical oxidation of ethylene by nitrocompounds in the excited states of different multiplicity. To achieve the aim it is necessary

to solve several problems. At first, it needs to choose a method and a basis for the systems studying. At second, it is necessary to find the geometric structure of the initial reagents such as olefin, nitro compounds, and final products being ethylene oxide and nitroso compounds in the singlet ground and triplet excited states, as well as the geometric structure of the transition state for the oxidation reactions. Finally, in order to verify the correctness of the found structure of the transition state of the reaction route studied, it is necessary to recover the reaction coordinate.

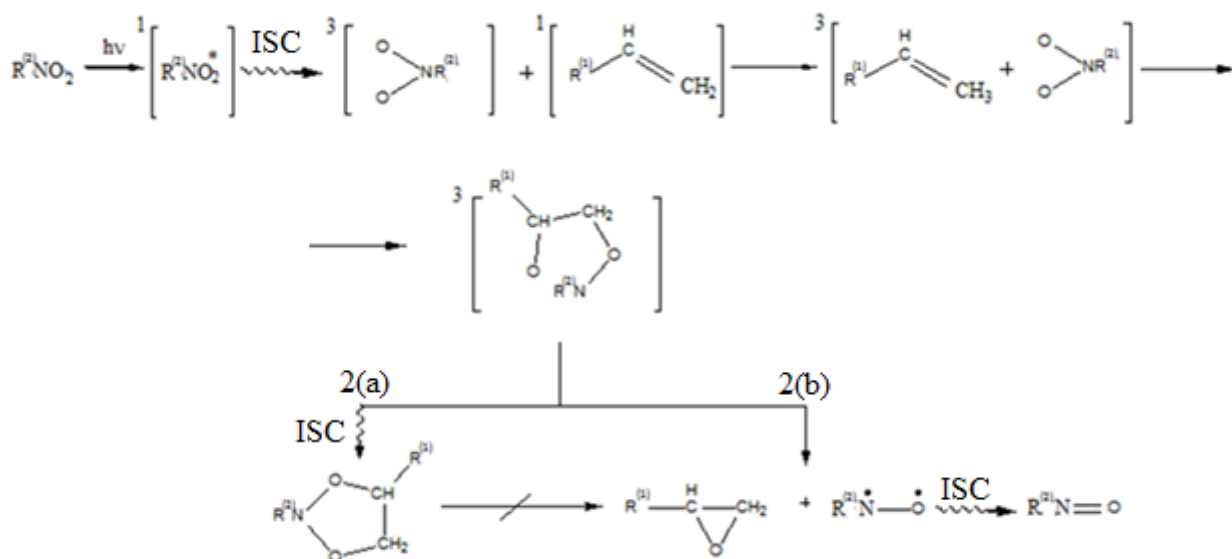
EXPERIMENTAL

The quantum - chemical modeling of reaction of photooxidation of olefins by nitro compounds was performed by uB3LYP/6-31g+(d) method. A software package Gaussian-03[4] was used for the calculations. The choice of method of calculation is based on the results of [5]. As model reactions to select the method of calculation cycloaddition reaction of diazomethane to butene-1, and methyl acrylate was chosen. By means of the Hartree-Fock method the authors [5] tested the election basis sets from 3-21g basis to 6-311++g(d, p). From the comparison of the activation energies it can be seen that starting from the 6-31g+(d) methods variations of the activation energies are not more than ca. 10 kJ mol^{-1} that is within the allowable error in the experiment. Therefore, all further calculations were carried out using this basic set. The value of the activation barrier is highly dependent on the method of calculation. The most good agreement between experimental and the DFT calculation data is observed for the hybrid functional B3LYP and B3PW91. Thus, to study the oxidation reactions of olefins nitro compounds selected method DFT uB3LYP with basis 6-31g+(d). The minimum of the molecular system was identified by the absence of "imaginary" vibration frequencies in the calculated IR spectrum. Searching of transition state geometries was performed by procedures TS, QST2 and QST3 of the software package Gaussian03 [6,7]. The criterion for the correctness of the transition state geometry finding was a presence of the only "imaginary" frequency. Refining of the transition state geometry was performed by the IRC method [8,9]. The activation energies of the reactions were calculated as the difference between the total energy of molecular systems based on zero-point energy.

RESULTS

The nitrocompound in the singlet ground state transfers into the first excited singlet state after light absorption. Undergoing intercombinational crossing (ISC) the nitrocompound molecule turns into the triplet state. Possibility of carrying out of the process was shown earlier [10]. The interaction of the triplet nitrocompound with ethylene molecule to form complex diradical triplet state. There are two possible reaction pathways. Origin - ISC to a cyclic compound which is then converted into we assumed ethylene oxide and a nitroso compound.

However, the implementation of this mechanism does not take place, as confirmed by our estimates of the fact that a stable compound is a cyclic compound. The second way of the diradical decomposition is to form propylene oxide and etilene - nitroso compounds.



Let us consider the reaction of 1.

Table 1 and Fig. 1 shows the spin density distribution in the starting materials, the transition state and the final product for all of the reactions.

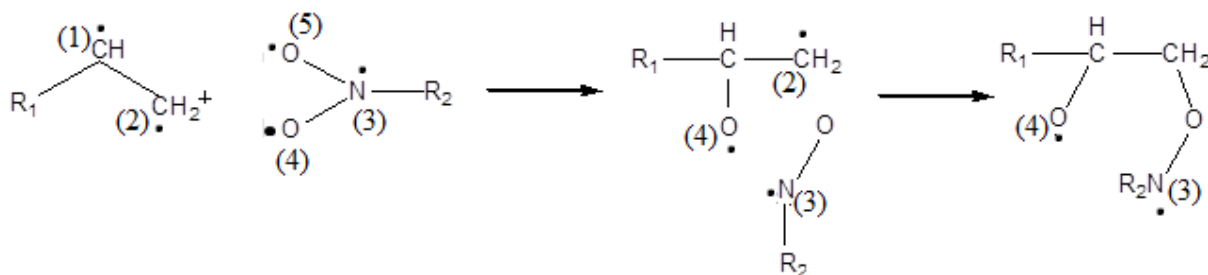


Fig. 1. The spin density distribution in the starting materials, the transition state and the reaction products 1. Points are the spin density maxima.

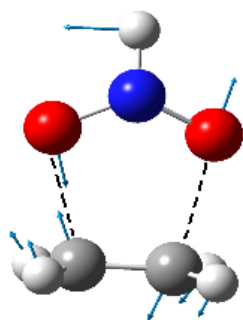
As the reaction proceeding nitrocompound being a diradical with spin density localized mainly on the oxygen atoms undergoes 1,2 attaching to a double bond with the formation of etilene fragment $C_8H_9O_2N$ when nitrobenzene and etilene $C_2H_5O_2N$ - etilene and HNO_2 are chosen as the starting materials. The reaction products 1 according to the data obtained as diradicals in the triplet state.

The activation energy of these reactions are presented in Table 2. The geometrical parameters of transition states are shown in Fig. 2. Table 1. The distribution of the spin density in the raw materials, the transition state and the reaction products

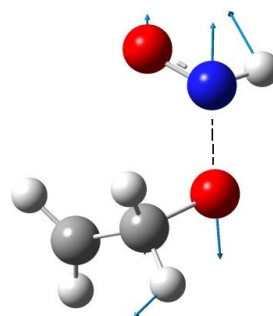
No. atom	basic components		transition state	reaction products
	$C_2H_4(S)$	HNO_2		$C_2H_5O_2N$
(2)C	-	-0.036	0.920	0.197
(3)N	-	0.546	0.647	0.519
(4)O	-	0.745	0.399	0.516
(5)O	-	0.745	0.053	0.447
	$C_2H_4(S)$	$PhNO_2(T)$		$C_8H_9O_2N(T)$
(2)C	-	-	0.743	0.009
(3)N	-	0.424	0.589	0.638
(4)O	-	0.723	0.525	0.922
(5)O	-	0.710	0.153	0.102

Table 2. The activation energies of the reactions $C_2H_4 + HNO_2$ and $C_2H_4 + PhNO_2$

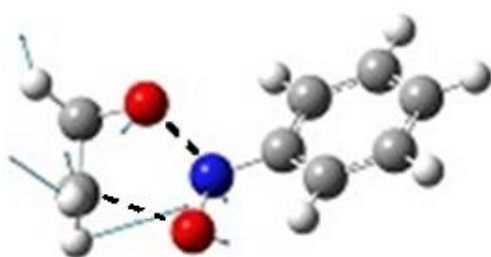
$C_2H_4 + HNO_2$	
reaction No.1	$E_a, \text{ kcal mol}^{-1}$
T_1	18.20
$C_2H_4 + PhNO_2$	
reaction No.1	$E_a, \text{ kcal mol}^{-1}$
T_1	0.06
$C_2H_4 + PhNO_2$	
reaction No.2	
T_1	2.02



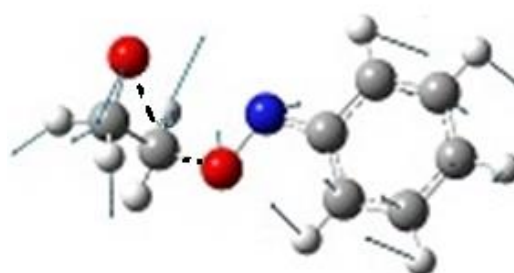
reaction No.1 $219i \text{ cm}^{-1}$



reaction No.2 b $270i \text{ cm}^{-1}$



reaction No.1 $588i \text{ cm}^{-1}$



reaction No.2 b $56i \text{ cm}^{-1}$

Fig. 2 The geometry of the transition state. The arrows indicate the displacement vector of the atoms.

Fig. 3 and Table 3 show the spin density distribution in the starting materials, the transition state and the final products for all reactions.

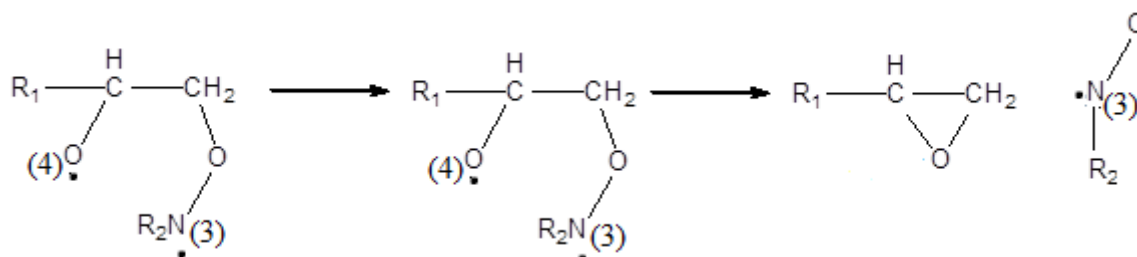


Fig. 3 The distribution of the spin density in the raw materials, the transition state of the reaction products, and 2. Consider the reaction 2.

Table 3. Distribution of the spin density in the raw materials, the transition state and the reaction products 1.

	C ₂ H ₅ O ₂ N	transition state	etilene oxide (S)	HNO(T)
(2)C	0.197	1.124	-	-
(3)N	0.519	0.400	-	1.074
(4)O	0.516	0.420	-	0.077
(5)O	0.447	0.222	-	0.849
	C ₈ H ₉ O ₂ N(T)	transition state	etilene oxide (S)	PhNO(T)
(3)N	0.638	0.621	-	0.944
(4)O	0.922	0.865	-	0.000
(5)O	0.102	0.109	-	0.768

Since the reaction 2 is a formation of cyclic compounds in the singlet state, the authors previously studied [16] and it is shown that for the molecules in the singlet state, reaction 2 occurs mainly in the direction of the formation of cyclic compounds. This is due to the fact that more advantageous (low energy) are cyclic compounds in comparison with the etilene oxide and nitroso containing substances.

For participants that are in the triplet state the reaction proceeds toward the formation of etilene oxide in the singlet state and diradicals nitroso containing substances that eventually undergo ISC and go into the singlet state. The activation energies are shown in Table 2, the

geometry of the transition states is given in Fig. 2. The distribution of spin density values are shown in Table 3 and Fig. 3

CONCLUSIONS

The method uB3LYP/6-31g+(d) was used to simulate the reactions of photochemical oxidation of ethylene by nitrobenzene and HNO₂. Transitional state of the oxidation reaction of the test substances were obtained. Oxidation takes place involving two stages: the first stage is the direct oxidation of ethylene to form cyclic compounds C₂H₅O₂N or C₈H₉O₂N. The second step is further transformation of the product in the first stage and ethylene oxide nitroso containing substance. Activation energy obtained for each stage of the transformation.

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