Quantum chemical studies of the olefin oxidation in the singlet and triplet states

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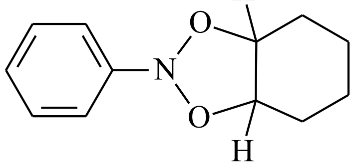
Photochemical oxidations of propylene by means of nitromethane and nitroethane were studied by UB3Lyp/6-31g in both the triplet and singlet states. It was studied the reaction paths giving propylene oxide. Gaussian03 was used to perform the calculations of the transition states of the reactions using QST2 and QST3 methods. Activation energies were calculated for every stage of the reactions. It was shown that the reaction proceeds mainly on the triplet potential surface energy.

Keywords: quantum chemical simulations, uB3Lyp, propylene oxide, olefins, the singlet state, triplet state, activation energy, Gaussian03w

INTRODUCTION

Studies of the olefins oxidations into oxygen containing compounds are among of the most important field of the modern industry oriented researches. The obtained results are useful to develop new low temperature oxidizing methods. Interesting reagents for the photochemical oxidation of olefins are aromatic nitrocompounds.

Buchi and Ierer [1] reported as early as in 1956 that the u.v. irradiation of the nitrobenzene – 2-methyl-2-butene mixture gave complicated mixture of the products but with low yields of them. It was concluded from the reaction products composition studies that the oxidation is directed onto the ethylenic bond. The authors assumed that 1,3,2-dioxazolidine (for example, see compounds 1 and 2) are to be intermediate particles.



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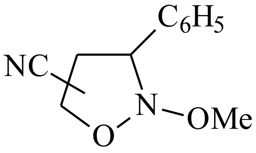

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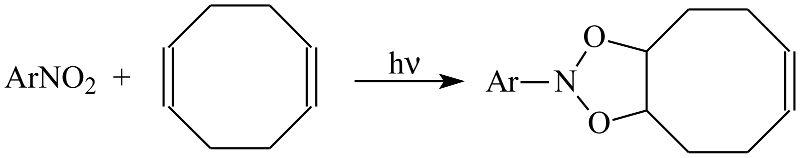
The hypothesis was proved in paper [2]. Its authors irradiated nitrobenzene – cyclohexene mixtures with u.v. light at room temperature. In that case they obtained very complicated reaction mixture, too. However, the irradiating of the reaction mixture up to complete removal of the nitrocompound at – 70 ^{0}C followed by evaporating of the solvent from reaction mixture gave solid crystalline compound. It was decomposed in few minutes at room temperature. There no absorption in the region characteristic for carbonyl group in its IR spectra. Besides, new absorptions appeared at 970 cm^{-1} and were related with the O – N bond [3, 4]. There were signals at 7.38 (benzoic) and 4.38 p.p.m. (protons situated near C – O group) in NMR spectra. After the reaction mixture being heated out, the intensities of these signals were decreased with synchronous appearance of aldehyde signal at 9.53 p.p.m. All facts mentioned are in accordence with the molecular structure 1. Due to the reaction scheme nirocompound reacts with olefin according to the 1,3-dipolar cycloaddition mechanism [5,6].



(1)

Room temperature decomposition of intermediate 1 and 2 gave the final products of the reaction.

Our paper is devoted to studying of photochemical oxidation of olefins (propylene) with nitrocompounds in the excited states of both singlet and triplet multiplicity.

There are several tasks to be solved to achieve the aims should be claimed.

In the first step it is desirable to be sure of the chosen strategy and methodology of investigation. In the second step geometries of the final (propylene oxide and nitrosocompound) and starting (nitrocompound and olefin) substances should be found. In the third step it is possible to determine geometry of the transition state for the reaction under study. And at last, to ensure ourselves that the structure of the transition state found is correct for the chosen reaction path we have to recover reaction coordinate. Let us discuss all these steps in more details.

COMPUTATIONAL PART

We have performed the quantum chemistry studying of the reaction paths of photochemical oxidation of olefins by nitrocompounds. As model reaction system we have used photochemical oxidation of propylene by nitromethane. UB3LYP/6-31(g) method was adopted. We have used results of paper [8] to do this choice. Our calculations were performed by means of Gaussian-03[7] program. The basis set was chose with Hartree-Fock method by enriching it from 3-21G till 6-311++G(d,p). Comparison of activation energies obtained permits to conclude that starting from 6-31G(d)-basis, activation energies lie within standard deviations for experiment (ca. 10 kJ mol^{-1}). All calculations were performed for this basis set. Activation energy is strongly dependent on the calculation method. The best agreement between calculation and experiment is observed in the case of hybrid functional B3LYP and B3PW91. Having all this in mind, we used DFT theory such as UB3LYP/6-31G.

Complete geometry optimizations were performed for the starting, intermediate and final substances in the ground and the lowest triplet state. The absence of “imaginary” frequencies in the calculated IR spectra was used as a criterion of the minimal point geometry achievement.

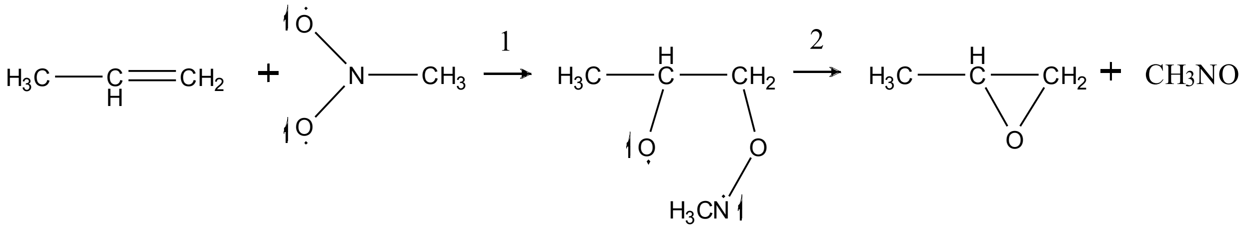
The transition state geometries were determined by means of QST2 and QST3 from Gaussian03 program package. The QST2 method permits to find the transition state structure starting from geometries of starting and final molecular systems. The QST3 method refines the transition state structure starting from the starting geometry, the assumed transition state geometry and the final product geometry [9,10]. The criteria that the geometry obtained belongs to the transition state serves the fact that there is only one “imaginary” frequency in the molecular system under consideration. The reaction route connecting the starting substances geometry, the transition state geometry and the final products along the reaction coordinate was found out by IRC method [11,12]. Activation energies were calculated as differences between the total energies of the transition state and the starting substances taking into account so called “Zero-point correction energies”.

So, the methodology we have adopted to perform our calculations seems to be adequate as a compromise between CPU time amount and quality of the results.

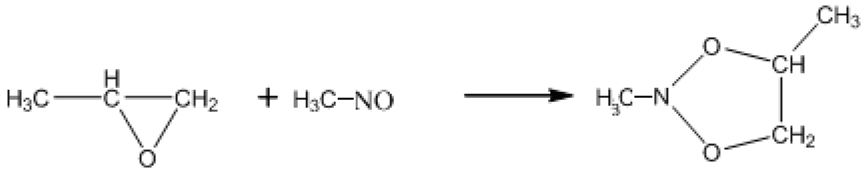
RESULTS AND DISCUSSION

Our aim is to study the epoxide compounds formation from olefins in the photochemical oxidation of them by nitrocompounds in both singlet and triplet states.

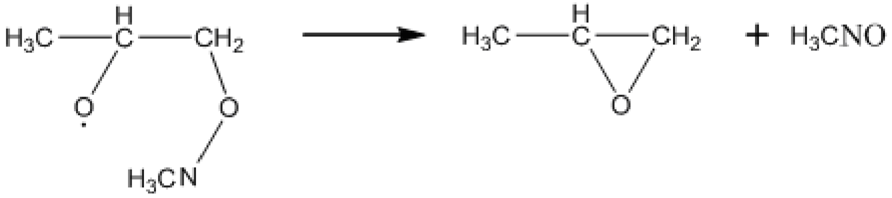
We assumed that the reaction scheme of the photochemical oxidation of propylene by nitromethane contains two main steps.



Reaction 1 is an addition of the nitromethane to a double bond. The addition reaction gives biradical adduct for the triplet state route (b). In the singlet state (a) reaction 1 proceeds in the reverse direction that is the starting materials (propylene and nitrocompound) are formed. Reaction 2 presents further transformation of the complex formed from reaction 1 into propylene oxide and nitrosocompound in the triplet state.



(a)



(b)

This adduct decomposes to turn into propylene oxide and nitrosomethane (reaction 2). We calculated spin density distribution in the starting molecules, transitional state and the final molecules in the triplet state on Fig. 1

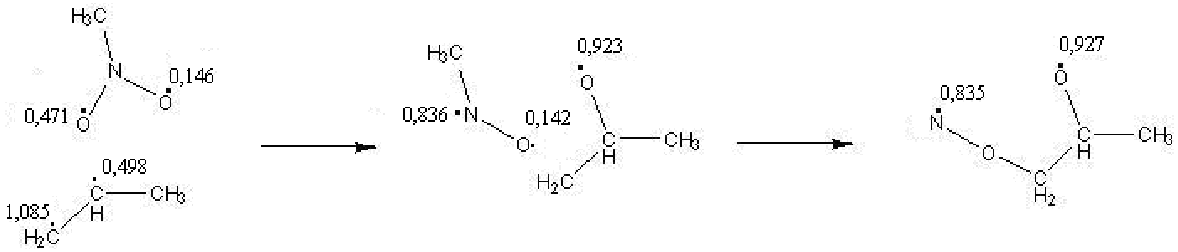


Fig. 1. The calculated spin density distribution in the starting molecules, transitional state and the final molecules on the triplet potential energy surface.

In the course of the reaction the triplet nitrocompound being a biradical with spin density localized mainly on oxygen atoms (0.471 and 0.146) is inclined to be involve into 1,2-addition to a double bond giving $C_4H_9O_2N$ moiety. The substance formed is also a biradical with spin densities 0.927 and 0.835 on oxygen and nitrogen atoms respectively. The activation energy of the reaction is estimated to be 21.99 kcal mole^{-1} (see Table 1). There has place only one imaginary frequency at 527.25*i* cm^{-1}.

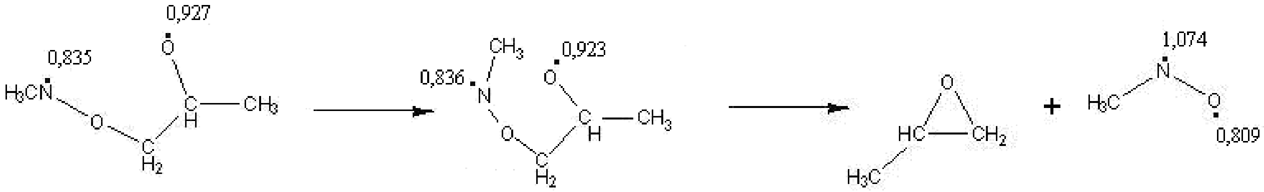
Table 1. Propylene photochemical oxidation with nitromethane

	$C_3H_6 + CH_3NO_2$	$C_3H_7O_2$	Transition state		*E_a, Kcal/mol*	
$E(T_0)$, a.u.	-362.618426	-362.635731	-362.583346		21.99	32.84
	$C_3H_6O + CH_3NO$	$C_3H_7O_2$	Transition state			
$E(S_0)$, a.u.	-362.652474	-362.677853	-362.569510		52.03	67.94
$E(T_0)$, a.u.	--362.638334	-362.635731	-362.619466		11.77	10.14

Here, *) - E is total electron energy of molecule (hartrees).

Reaction 1: Direct reaction is formation of $C_4H_9O_2N$ fragment starting from propylene and $C_2H_5NO_2$, reversal reaction is formation of C_3H_6 and CH_3NO_2. Reaction 2: Direct reaction is formation of $C_4H_9O_2N$ starting from propylene oxide and CH_3NO, reversal reaction gives propylene oxide.

Let us consider reaction 2 in more details.



(a) ***Starting and final substances in the singlet state.***

For singlet molecules reaction 2 proceeds mainly to the cycle compound formation ($C_4H_9O_2N$). The reason of it that the cyclic compound is more profitable (lower in energy) compared to propylene oxide and nitrosomethane (see Table 2). Activation energy of the reaction is 52.03 kcal mole^{-1}. Imaginary frequency in the transition state is 131.38*i* cm^{-1}. Geometry of the transition state is pictured on Fig. 2

(b) ***Starting and final substances in the triplet state.***

It is shown on Fig. 3 that there has place transformation of the complex formed in the course of the reaction 1 into direction of the propylene oxide formation. Activation energy of the process is 11.77 kcal mole^{-1}. Imaginary frequency in the transition state is 209.25*i* cm^{-1}.

A diagram on Fig.2 shows energy characteristics of the propylene oxidation on the triplet potential energy surface.

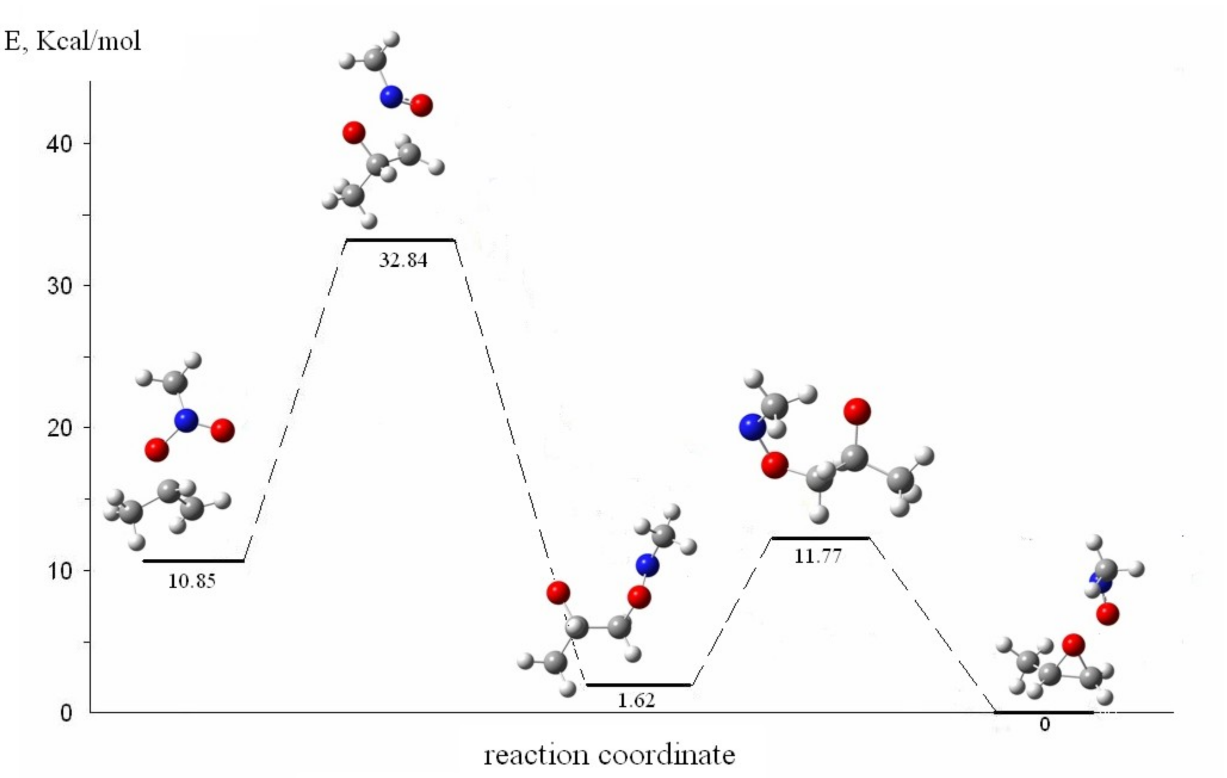
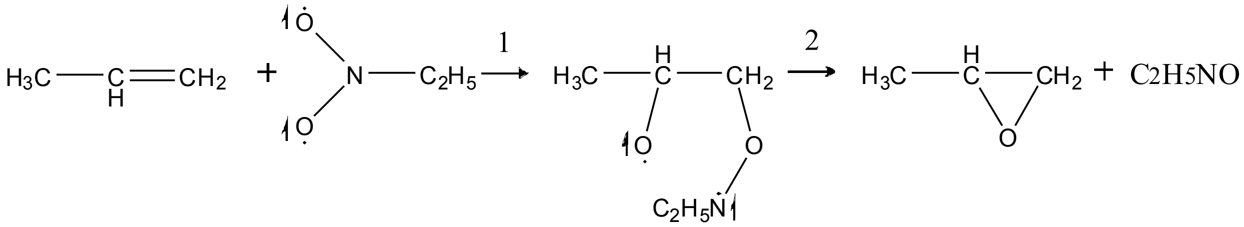


Fig. 2. Energy diagram of the propylene oxidation reaction proceeding on the triplet potential energy surface.

Let us consider a scheme the photochemical propylene oxidation by nitroethane.

The scheme consists of two steps, too. Reaction 1 is direct propylene oxidation by triplet nitroethane, and reaction 2 shows transformation of the complex formed into propylene oxide. The general reaction scheme of the reaction is very analogous to the scheme in the nitromethane – propylene reaction system.



Here, the final products and the starting reagents are in both singlet (a) and triplet (b) state.

Spin density distributions in the starting substances, the transition state and the final products from reaction 1 are shown on Fig. 3.

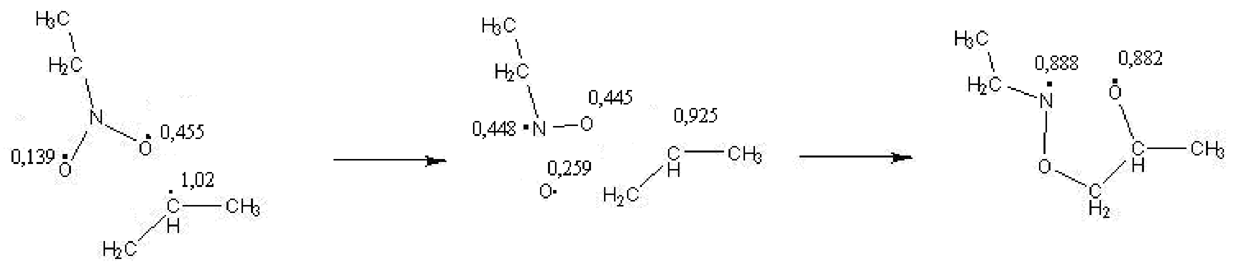


Fig.3. Spin density distribution in the starting substances, the transition state and the final products in reaction 1.

In the course of the reaction the triplet nitrocompound being a biradical with spin density localized mainly on oxygen atoms (0.455 and 0.139) undergoes 1,2-addition to a double bond of propylene to give the $C_5H_{11}O_2N$ fragment. Substance $C_5H_{11}O_2N$ formed is also a triplet biradical having spin density on oxygen and nitrogen atoms of 0.882 and 0.888, respectively. Activation energy for the reaction is 8.09 kcal mole^{-1} (see Table 2). Imaginary frequency is 128.32*i* cm^{-1}.

Let us discuss reaction 2 in more details.

(a) The starting and final substances in the singlet state.

For singlet molecules reaction 2 proceeds mainly in the direction of the cyclic substance formation. This way has place because the cyclic compound is the most lower in energy (see Table 2). Activation energy of the reaction is 39.76 kcal mole^{-1}. Imaginary frequency in the transition state is 659.80*i* cm^{-1}. Geometry of the transition state is shown on Fig. 4.

(b) The starting and final substances in the triplet state.

Fig. 3 says that there has place conversion of the complex formed as a result of reaction 1 to give propylene oxide. Activation energy of the reaction is 3.60 kcal mole^{-1}. Imaginary frequency in the transition state is 148.38*i* cm^{-1}. Geometry of the transition state are shown on Fig. 4

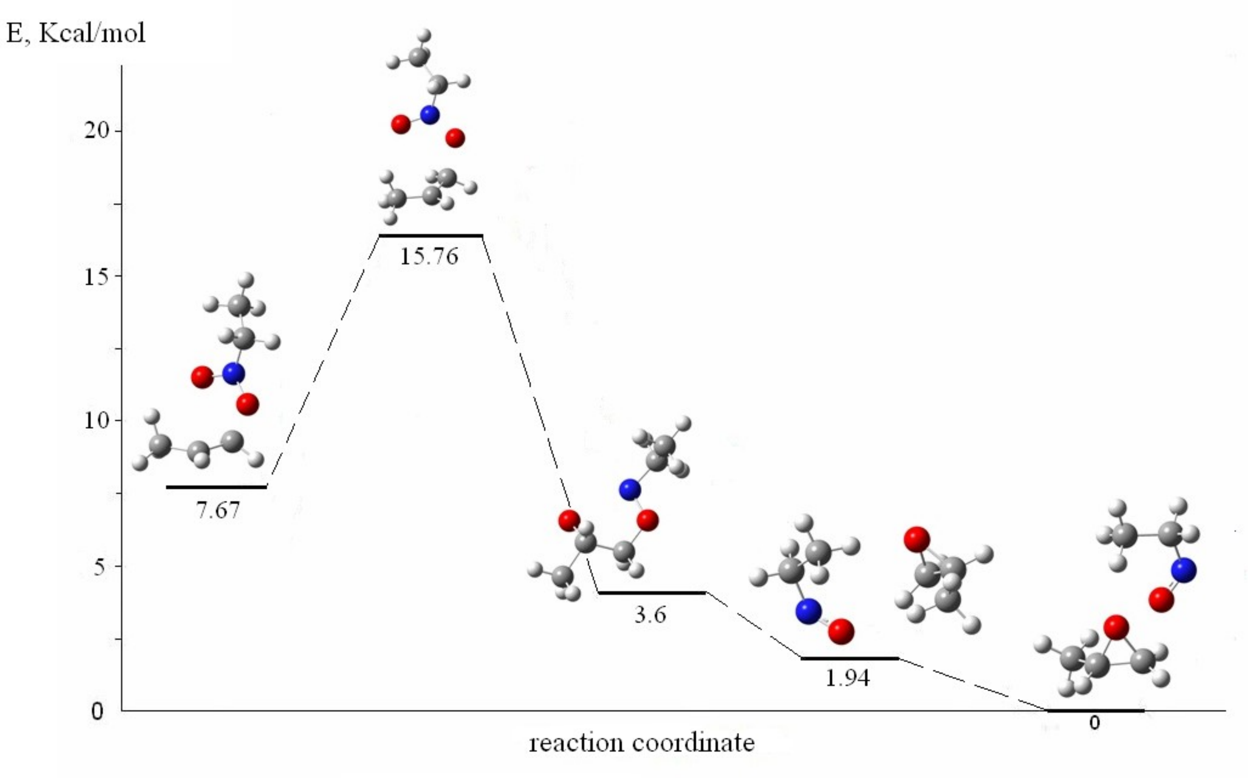


Fig. 4. Energy characteristics of oxidation of propylene by the triplet nitroethane.

One can observed that the most high barrier of 8.09 kcal mole^{-1} is observed in the first step of the reaction namely in reaction of the triplet nitrocompound with propylene followed by $C_5H_{11}O_2N$ formation. $C_5H_{11}O_2N$ turns into propylene oxide with zero activation energy in the next step. There is no realization of the second part of the reaction, that is the formation of propylene oxide and nitroethane, on the triplet potential energy surface formation of the cyclic compound. At the same time the last stage proceeds with zero activation energy. For the reaction in the singlet state the second part does not realize.

Table 2. Photochemical propylene oxidation in the presence of nitrocompound.

	$C_3H_6 + C_2H_5NO_2$	$C_3H_{11}O_2$	Transition state		*E_a, Kcal/mol*	
$E(T_0)$, a.u.	**-401.899497**	**-401.886605**	**-401.911732**		**8.09**	**15.76**
	$C_3H_6O + C_2H_5NO$	$C_5H_{11}O_2N$	Transition state			
$E(S_0)$,a.u.	**-401.932371**	**-401.955604**	**-401.868948**		**39.76**	**54.33**
$E(T_0)$, a.u.	**-401.917474**	**-401.914376**	**-401.911732**		**3.6**	No

Here, *) - E is total electron energy of molecule (hartrees). Reaction 1: Direct reaction is formation of $C_5H_{11}O_2N$ fragment starting from propylene and $C_2H_5NO_2$, reversal reaction is formation of C_3H_6 and $C_2H_5NO_2$. Reaction 2: Direct reaction is formation of $C_5H_{11}O_2N$ starting from propylene oxide and C_2H_5NO, reversal reaction gives propylene oxide.

We performed a quantum chemical study of the photochemical oxidation of propylene in the presence of nitromethane or nitroethane by means of UB3LYP/6-31g method. It was determined the structure of the transition state for the reaction was determined.

It was shown that the photochemical oxidation proceeds as the two stage process. In the first stage there has place direct oxidation of propylene to form 1,2,3-dioxazole. In the second stage the further transformation of the intermediate into propylene oxide occurs on the triplet potential energy surface. We determined activation energies of all reactions involved in the oxidation. The results were checked by means existance of the only imaginary frequency and successful recovering of the reaction coordinate by the IRC method. The reaction in the direction of propylene oxide and nitrosocompound does not take place in the singlet state.

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