The mechanism of the photochemical oxidation of substrates of different nature by nitro compounds

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Summary

Using quantum-chemical methods we studied the mechanism of the photochemical oxidation of epoxy olefins by nitro compounds. It was first found the structure of the corresponding transition states. DFT / 6-31g + (d) and DFT / 6-311 + g (d) methods were used to study the reaction of sulfur oxides (II, IV) with nitro compounds in the ground and excited states. It was first made an assumption that the transition states containing nitroso oxide fragment were formed in the course of the photochemical oxidation of various substrates by nitro compounds in the excited states. The nitroso compounds photochemical oxidation by nitro compounds in the excited states were studied by experimental and theoretical methods. By means of CASSCF method we determined the opportunity of the singlet - triplet transition involvement in the reactions with nitroso oxides participation. It was shown proximity of the S_0 and T_2 levels.

Introduction

Nitro compounds are the basis of explosives which recycling or disposal is an important task at the moment. Nitro compounds possess strong oxidizing properties and are capable to oxidize a great majority of organic compounds. They have a great potential as photochemical oxidants, but the mechanisms of oxidation with their participation have not been studied enough. Preparation of propylene oxide and ethylene oxide by photochemical oxidation of propylene and ethylene by nitro compounds may be useful in industry. Currently available methods for the preparation of epoxides lead to high yields of by-products, and the methods proposed in our work are free from the above-mentioned drawbacks. In addition, it is of interest to obtain nitroso oxides in the course of the photochemical isomerization of nitro compounds into nitroso oxides or in the course of the nitro compound interaction with nitroso compounds in the triplet and singlet states. They react with double bonds of olefin to form epoxides, with nitroso compounds readily oxidizing them into nitro compounds, with sulfoxides to transform them into sulfones, with divalent sulfur derivatives oxidizing them into sulfoxides and so on. For fundamental science it may be important to reveal mechanism oxidation by nitro compounds which includes the *in situ* formation of nitroso oxides.

Results and discussions

1. Isomerization of nitroso oxides in the nitro compound

As model used nitromethane and different nitroso compounds. Table 1 shows the activation energies of the nitromethane isomerization into the corresponding nitroso oxides in the singlet and triplet states. We studied both forward and backward reactions.

Table 1: Activation Energy (E_a) nitromethane isomerization to the corresponding N – nitroso oxides

Conformation of nitroso oxide	E_a, kcal mol^{-1}		imaginary frequency, см-^{1}
	Direct reaction	reverse reaction	
State S_0			
Trans	94.41	25.09	1129
Cis	56.60	42.54	817
state T_1			
Trans	30.60	3.17	93.69
Cis	29.83	2.63	173

It follows from table 1 that the reaction could easily proceed for participants being in the triplet state in the direction of obtaining nitro compounds from nitroso oxides. Consider the mechanism of the reaction in more detail for of *cis* - isomer of nitroso oxides, based the atomic spin density and geometry changes for the initial compounds, products and the transition state in the course of the reaction (Table 2).

Table 2: Calculated Data for CH_3NO_2 (T_1) ↔ CH_3NOO (T_1)

substance	M	r(O—O),нм	r(N—O), нм	Spin density
RNO_2	1	0.2173	0.1221	0
	3	0.2088	0.1308	O(1) 0.756 O(2) 0.756 N(3) 0.468
cis-RNOO	1	0.1392	0.1306	0
	3	0.1377	0.1514	O(1) 0.155 O(2) 0.975 N(3) 0.854
cis- RNOO – TS	1	0.1543	0.1353	0
	3	0.1350	0.1617	O(1) 0.153 O(2) 0.884 N(3) 0.923

Table 2 gives us an opportunity to conclude that distribution of spin density in cis-RNOO and in the transition state for the reaction are very similar and there is very long N-O bonds both in the nitroso oxides and the corresponding transition states. So we could say about early transition state for isomerization of nitroso oxide into nitro compounds. More clearly, this process is shown in Fig.1 where the reaction coordinate diagram for the reaction is shown.

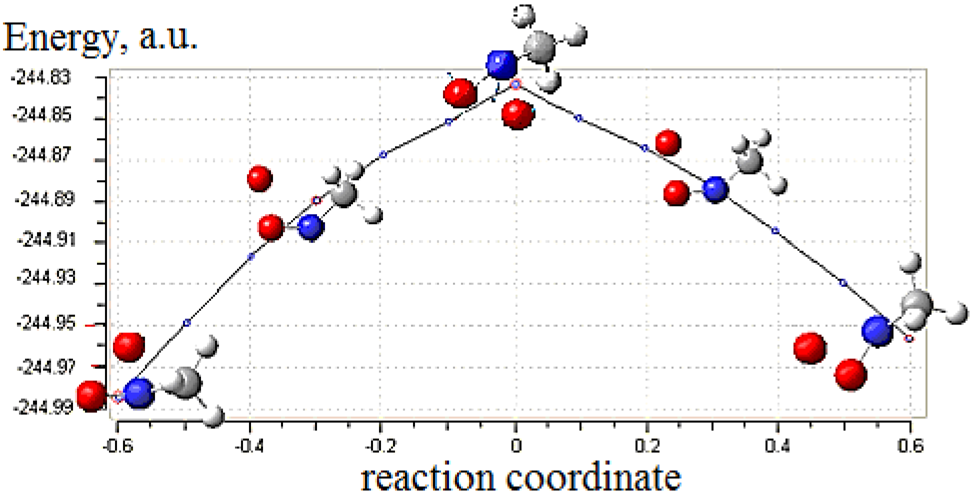
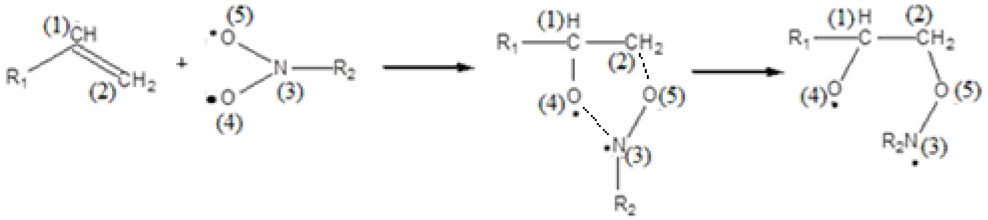


Fig. 1 Recovering of the reaction coordinate IRC method

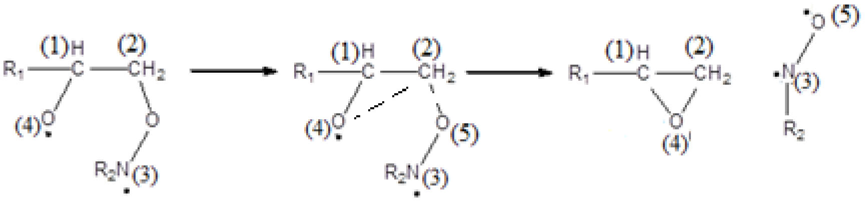
2. Oxidation of olefins

Consider the scheme of the oxidation of propylene by nitromethane. The initial reagents and reaction products are in the triplet state. The reaction proceeds in two stages.

The first step is an attachment the nitro compound CH_3NO_2 to propylene in the triplet state. The second step is further conversion of the first step product into an epoxy compound and nitroso derivative. Products and the initial compounds may be in the singlet and triplet state.



(1)



(2)

A reaction similar to reaction 1 in which the starting materials and products are in the singlet state can not occur to form *in situ* nitroso oxide. Apparently, it is caused the fact that the cyclic conformation is more advantageous in energy than propylene oxide. In the triplet state a cyclic compound is not formed. The activation energies for reaction 1 are shown in Table 3 and Fig. 2. Thus, the formation of ethylene oxide or propylene occurs only for participants that are in the triplet state.

Table 3: Activation energies of the propylene photooxidation by nitromethane.

$C_3H_6 + CH_3NO_2$	
reaction 1	
state	E_a, kkal/mol
T_1	21.99
reaction 2	
S_0	52.03
T_1	2.26

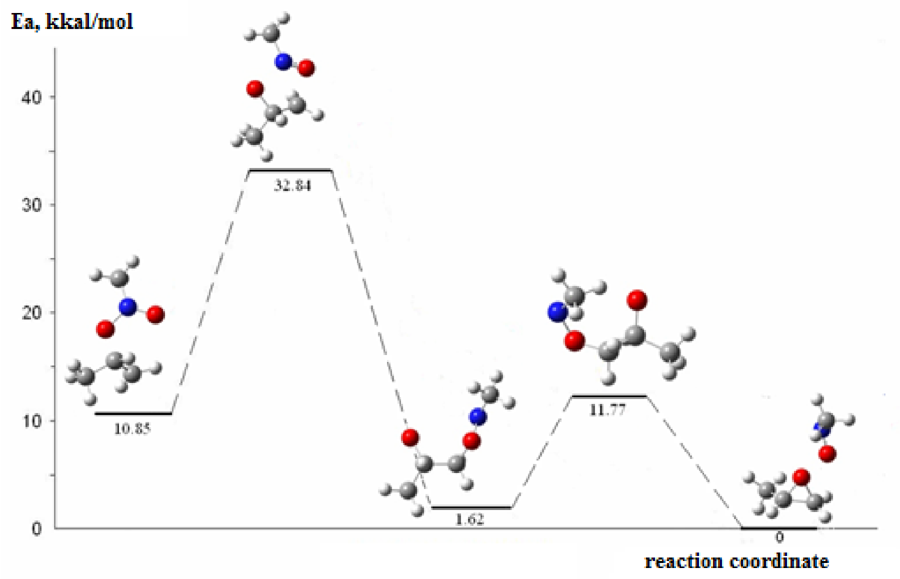


Fig. 2 Energy diagram of the oxidation of propylene by HNO_2 in the T_1 state

The corresponding transition states are shown on Fig. 3 and 4.

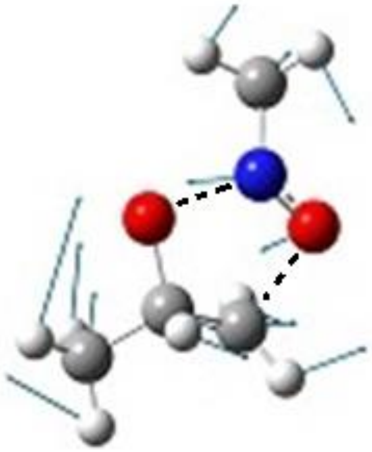


Fig. 3 The TS of reaction 1 with imaginary frequency at 527i cm^{-1} (T_1)

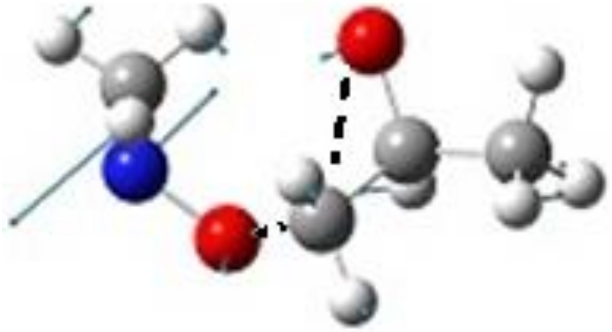


Fig. 4 The TS of reaction 2 with imaginary frequency at 209i cm^{-1} (T_1)

A detailed examination of the spin density distribution for the reaction 1 and 2 in the photooxidation of propylene by nitro compound can give us a possibility to conclude the following. Initially, there has place excitation of the nitro compound into the S_1 state. Then it undergoes intersystem crossing turning into the T_1 state. After that there is an interaction with propylene to form the triplet biradical. Values of the spin density are presented in Table. 4

Table 4. The values of the spin densities for the participants in reaction 1

No. & label of atom	Iinitial components		Transition state	Product
	C_3H_6(S)	CH_3NO_2(T)		$C_4H_9NO_2$(T)
(1)C	-		-0.0873	-0.0564
(2)C	-		0.6729	0.0010
(3)N	-	0.4680	0.6634	0.8423
(4)O	-	0.7560	0.5111	0.9333
(5)O	-	0.7560	0.1755	0.1395

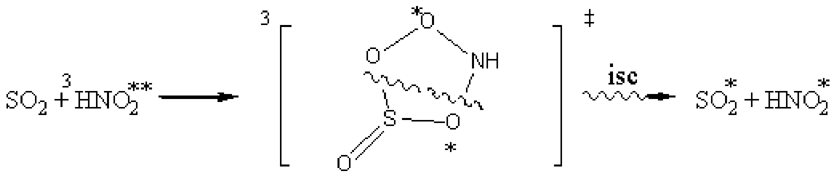
There are two possible reaction pathways. The first way is a deactivation of the triplet biradical to form a singlet product followed by the formation of propylene oxide and nitroso compounds. However, as it was shown by the calculations of the activation energy this process is impossible. The second way is the destruction of the resulting biradical into propylene oxide and nitroso compounds. There has place a spin density redistribution to form in the transition state a nitroso compound-like fragment (in the triplet state) with the maxima of the spin density on nitrogen atom and one of the oxygen atom. Further redistribution could form nitroso compound in the triplet state and the propylene oxide precursor. As a result, as shown in Table 5 there had place formation of triplet nitroso compound and propylene oxide.

Table 5. Spin densities for the participants in the reaction 2

No. & label of atom	Initial components	Transition state	reaction products	
	$C_4H_9O_2$(T)		propylene oxide	CH_3NO(T)
(1)C	-0.0564	-0.0494	-	
(2)C	0.0010	0.0043	-	
(3)N	0.8423	0.8359	-	1.0739
(4)O	0.9333	0.9230	-	
(5)O	0.1395	0.1425	-	0.8088

3. The study of the photochemical oxidation of sulfur compounds by nitro compounds

The third part is devoted to the study of the oxidation of sulfur (IV) by nitro compounds. Reaction schemes (3) and (4) can serve as a way to explain the obtained.



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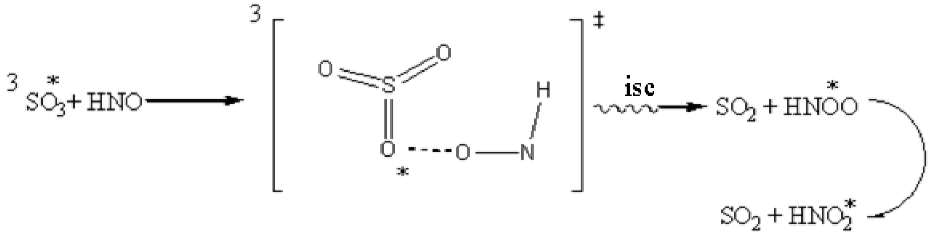
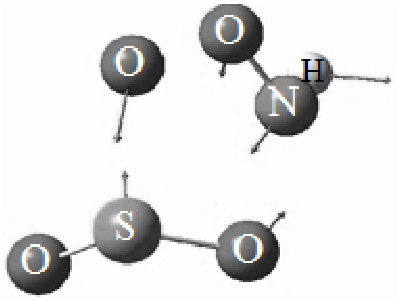
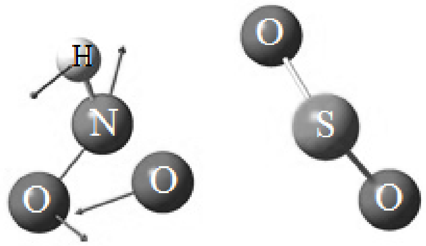
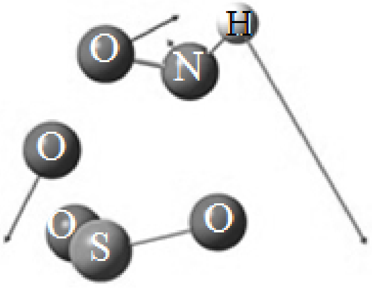
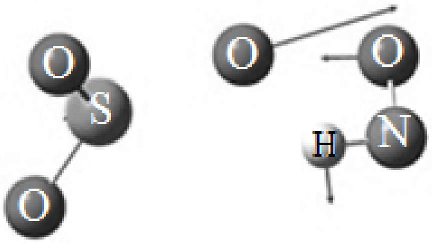


4

Here *isc* denotes intersystem crossing.

Reaction of 3 is a photo-oxidation of sulfur oxide (IV) by the nitro compound molecule in the triplet state. During the reaction the separation of the oxygen atom and the formation of nitroso oxide which is then converted into the nitro compound. The reaction takes place, apparently, through the five-member transition state. The yield of reaction products depends upon the relative magnitudes of the energy for the transition state. Reaction 4 is the separation of the oxygen atom of the triplet sulfur trioxide and its transfer to a molecule of the nitroso compound. In the course of it there may also be formed nitroso oxide in the triplet state followed by rearrangement of it into nitro compound. In other words, the reaction of SO_2 with HNO_2 does not lead to the formation of SO_3 and HNO, and the mechanism is similar to the mechanism discussed in reaction 3. Table 6 shows characteristics of the transition states and energies of the corresponding reactions in the singlet and triplet states.

Table 6: Transition states in these reactions

Singlet transition state, the imaginary frequency $226.83i$ cm^{-1}(S_0) 	Multiplicity	E_a, kcal/mol	Triplet transition state, the imaginary frequency $878.92i$ cm^{-1}(T_1) 
	S_0	115.22	
	T_1	66.25	
Singlet transition state for the imaginary frequency $537.25i$ см$^{-1}$(S_0) 	Multiplicity	E_a, kcal/mol	Triplet transition state for the imaginary frequency $461.92i$ см$^{-1}$(T_1) 
	S_0	27.47	
	T_1	1.45	

4. Possibility of formation of nitroso oxides during oxidation reactions of nitro compounds

In this part of our work the mechanism of formation of nitroso oxides on the example of the reaction of nitro compounds with nitroso compound $HNO_2^* + HNO^* \leftrightarrow HNO + HNO_2^{**}$ was suggested.

When modeling the aforementioned reaction, as well as similar to it, we can note that the transition state is formed as a compound having the geometry similar to nitroso oxide. Optimal geometry of nitroso oxides corresponding to the minimum energy is shown in Fig. 5 and

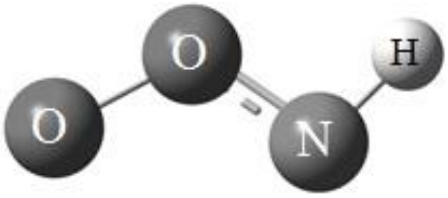


Fig 5. Nitroso oxide (S_0)

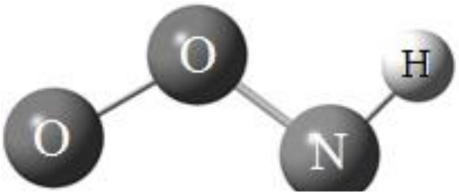


Fig 6. Nitroso oxide (T_1)

6. During further study of the geometry, as well as the calculated IR spectra of the transition states we identified similarities in the structure and vibrations of the atoms of the corresponding compounds. Geometry of nitroso oxides transients compared with the geometry of nitroso oxides. The calculation was performed by uB3LYP / 6-311 + g (d) *. The results are shown in Table 7.

Table 7. The geometric parameters of nitroso oxides (S_0 and T_1)

Method of calculation	O-O, nm	N-O, nm	ν(N-O), cm^{-1}	ν(O-O), cm^{-1}	Δ(N-O)-(O-O), cm^{-1}
uB3LYP/6-311g+(d) (S)	0.1293	0.1275	1279.42	1115.71	163.71
uB3LYP/6-311g+(d) (T)	0.1328	0.1427	829.42	1061.11	152.26

Let us consider the interaction of nitro compound with nitroso compound in the triplet state.

$$HNO_2^{*} + HNO^{*} \leftrightarrow HNO + HNO_2^{**}$$

Ability to flow this reaction is described. In the course of calculations we obtained the transition state which is we can see easily the nitroso oxide fragment particiupation. Comparison of its geometrical parameters calculated for a nitroso oxide molecule is given in Table 8.

Table 8. Comparison of geometric parameters and IR spectra in the transition state of the reaction and nitrosooxide molecule in the triplet states.

	HNOO(в TS)	HNOO (theory)	HNOO(experiment*)
O-O, nm	0.1436	0.1368	-
N-O, nm	0.1421	0.1369	-
ν(N-O), cm^{-1}	893	829	1088
ν(O-O), cm^{-1}	788	1061	1029

* The experimental data were taken from [1]

From Table 8 it can be noted that the geometry of nitroso oxide in a vacuum is almost identical to the geometry of the nitroso oxide-like fragment in the transition states. Such a coincidence is observed for the vibration frequencies of groups of atoms NO 829.42 and 893.16 cm^{-1}, respectively. For groups of atoms OO coincidence of oscillation is observed. This is caused by, apparently, the fact that nitroso oxide-like fragment affects a group of atoms in a transient state. Calculated IR spectra are shown on Fig. 7 and 8.

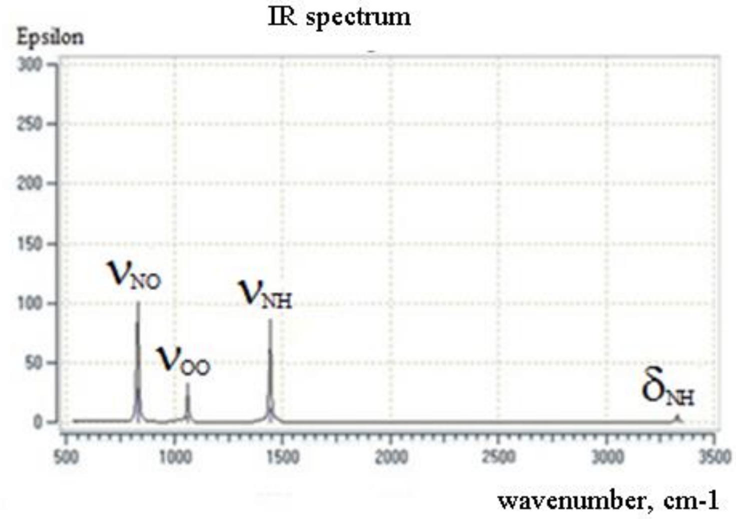


Рис. 7 IR spectrum of a nitroso oxide molecule HNOO(T_1).

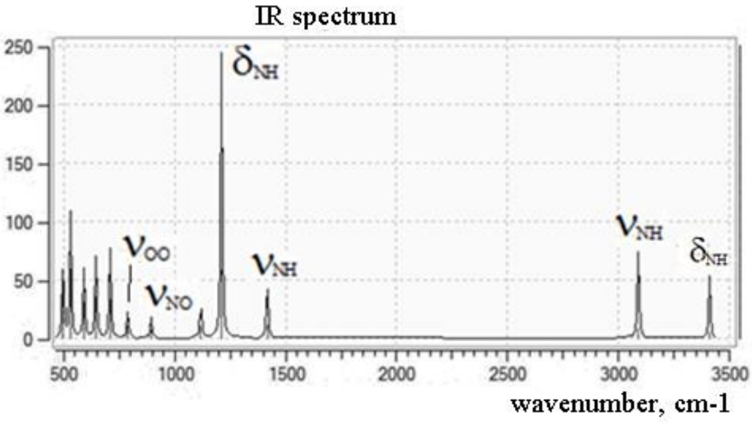


Рис. 8 The IR spectrum of the transition state in the T_1 state.

Thus, when modeling reactions $R1NO_2 + R_2NO \leftrightarrow R_1NO^* + R_2NO_2$, where $R_1 = H, CH_3$, t-Bu, $R_2 = H, CH_3$, Ph, and $SO_2 + HNO_2^{**} \leftrightarrow SO_2^* + HNO_2^*$ we observed that in the transition state there is formed a fragment of a compound having the geometry similar to nitroso oxide.

5. The energy levels of nitroso oxides

It is known that nitro compounds rather easily undergo the intersystem crossing (*isc*) [2]. Since nitroso oxides and nitro compounds are isomers, it is interesting to explore the possibility of *isc* and for niroso oxides. Fig. 8 shows the location of the energy levels for HNOO. It can easily be seen that the main level is T_1. Then there are disposed S_0, T_2 and S_1 levels. The proximity of T_2 and S_0 levels is estimated as 5 kcal/mol. Thus, *isc* can occur for both nitro compounds and nitroso oxide.

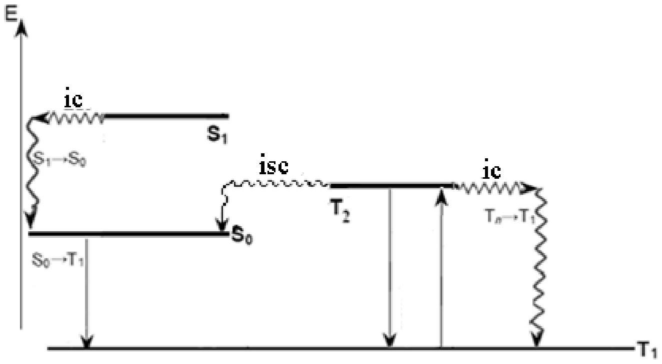


Fig. 8 Distribution of energy levels in HNOO ($T_1<S_0<T_2<S_1$). *isc* - intersystem crossing, *ic* - internal conversion.

Table 9: Energy levels in HNO_2 и HNOO

level	HNO_2	HNOO(*trans*)
	Energy levels, kcal/mol	
S_0	0	27.42
T_1	44.99	0
T_2	82.33	32.63
S_1	110.56	116.77

Conclusions

1. The mechanism of the propylene and ethylene photochemical oxidation into epoxide by nitro compounds in the singlet and triplet states was studied. The oxidation takes place in two stages:

a) formation of the biradical complex;

b) collapse of the complex into the epoxy and nitroso compounds.

It is shown that all three mechanisms of the reactions are of the same type.

2. The mechanisms of the reactions of nitro compounds with sulfur-containing compounds on the example of reactions $SO_2 + RNO_2^{**} \leftrightarrow SO_2^{*} + RNO_2^{*}$ и $SO_3 + RNO \leftrightarrow SO_2 + RNOO \rightarrow SO_2 + RNO_2$ by uB3LYP/6-31+G(d) was also studied. It was established that the reactions occur in the triplet state.

3. A common feature of the mechanisms of studied reactions is the transfer of an oxygen atom from the nitro compound to oxidizing substances.

4. It is shown the proximity of the energy levels of the triplet and singlet states in nitro and nitroso compounds.

5. It is suggested the formation of *in situ* nitroso oxide - like fragments in the transition states in the photochemical oxidation of nitroso compounds and sulfur-containing compounds in the presence of nitro compounds.

References.

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