

Quantum chemical study of mechanism of reaction between nitrogen oxides with S- and N-containing compounds

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UB3Lyp/6-31g+d was used to model reaction nitro- and nitrosocompounds with sulfur oxides. Gaussian03 computer program was used to realize the study. We determined geometries and electronic structure parameters of the reactions by means of QST2 и QST3 procedures. We have found that nitroso oxides formation occurs in the course of the oxidations. The most favorable in energy was to proceeds the reactions in the triplet states. The activation energies were determined for every reaction step. The reliability of our calculations were supported by observing the only imaginary frequency. Besides we have performed the IRC calculations to recover the reaction coordinate paths.

Key words: quantum chemistry modeling, uB3Lyp, sulfur oxide, triplet state, activation energy, Gaussian03, nitroso oxide, nitrosocompound

Introduction

Important task of the modern chemical industry lays in the field of the low temperature oxidations of organic compounds including hydrocarbon substances. The great amount of the procedures was created. The most prosperous among them are photochemical methods. It was shown previously that nitrocompounds could be used as photochemical oxidants that could transfer an oxygen atom to the molecule being oxidized [1-7]. The oxygen atom transfer mechanism is of the paramount

importance. Nitrocompounds aromatics is often met in the chemical industry, and their usage in new technologies is tempting. Besides, there are great amounts of the substances produced to be used as explosives have to be recycled in the industry units. We consider quantum chemical studies of photochemical oxidations of S- and N-containing organic compounds in the presence of nitrocompounds as being very desirable and important. The work devoted to photochemical studies of the nitrocompounds and nitroso oxides reactions with substrates of different chemical nature were initiated in our group some years ago [8]. Quantum chemical studies of the transition states involved in the reactions permit to propose more correct mechanisms.

The transition state searching methodology

We determined the geometries of the transition states in the reactions under study by means of the QST2 and QST3 procedures from Gaussian03 computer program [10]. The criteria of the transition state geometry determination correctness was an occurrence of the only imaginary frequency for the system under study. Besides, we have used the reaction coordinate recovery method to check the calculation results by means of IRC method. The DFT calculations with all geometry parameters optimization in the rank of uB3LYP platform.

The first step was a choice of a method and its verification. The relevant results are shown in Table 1 and 2.

Table 1. Choice of the method to be used to calculate HNO

Method	length of bonds, nm	
	r (H-N), nm	r (N-O), nm
PM3	0.0997	0.1175
UHF/3-21G	0.1036	0.1217
uB3LYP/6-31+G(d)*	0.1064	0.1208
UB3LYP/6-311+G(d)	0.1064	0.1241
experiment [12]	0.1063	0.1211

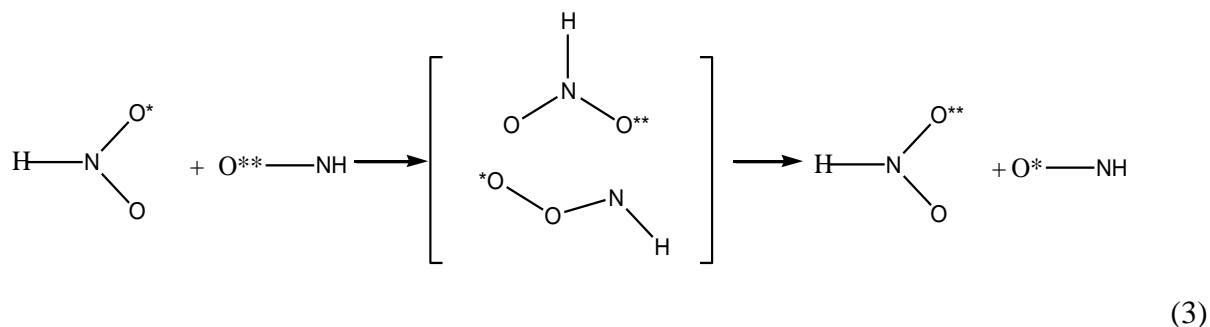
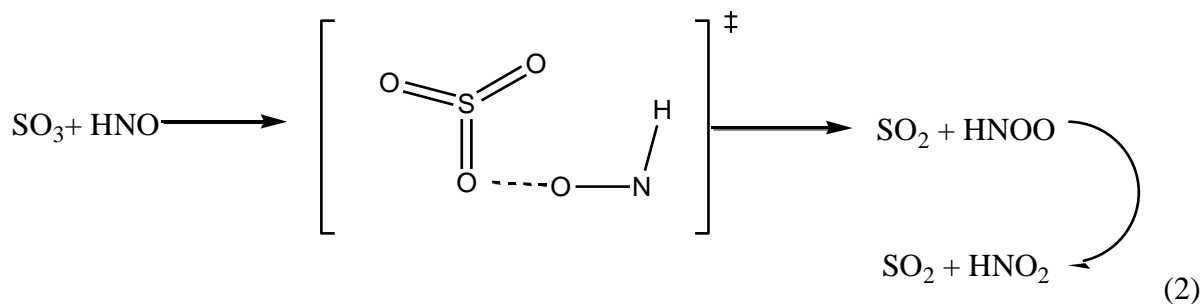
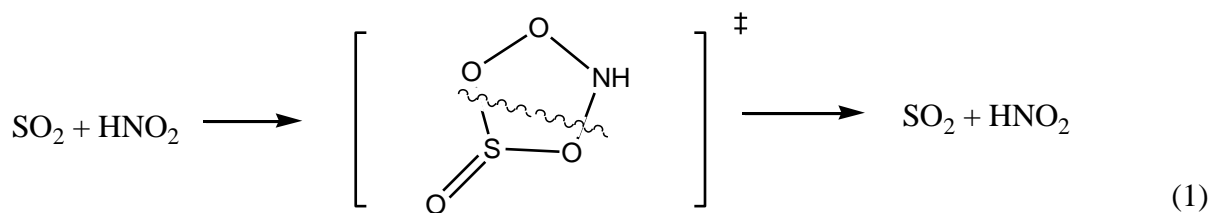
Table 2. Choice of method to calculate S-containing compounds

Method	length of S – O bonds, nm			
	SO ²⁻ , (S ₀)	SO ₂ , (S ₀)	SO ₃ , (S ₀)	SO, (T ₁)
MP2/6-31+G(d)	0.1550	0.1482	0.1463	0.1524
uB3LYP/6-31+G(d)*	0.1548	0.1466	0.1454	0.1516
experiment [13]	0.1523	0.1432	0.1430	0.1481

Table 1 and 2 show that uB3LYP/6-31+G(d) is the most relevant method to calculate both N – containing and S-containing compounds. We used it as the basic method in our study.

Results and discussion

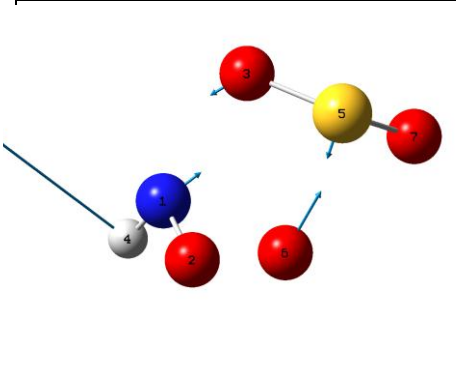
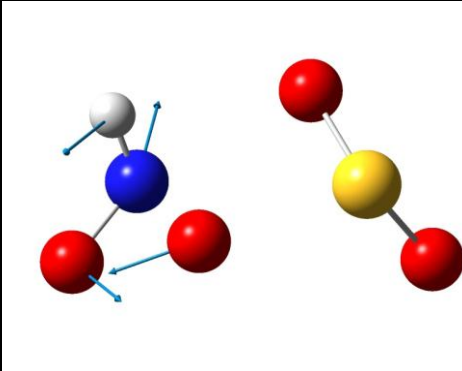
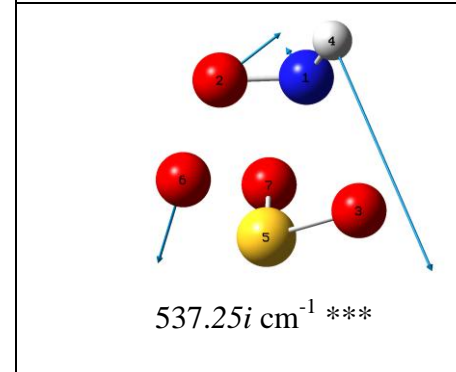
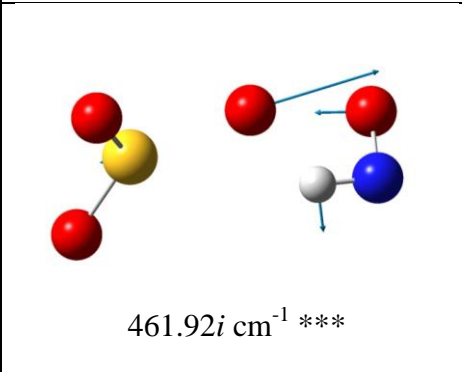
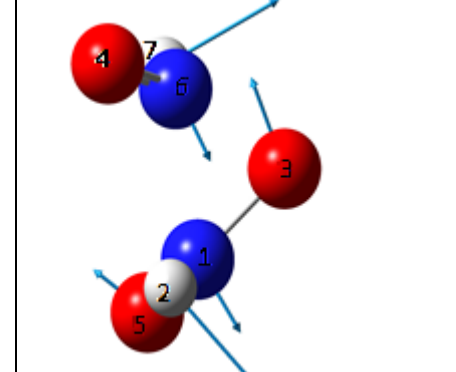
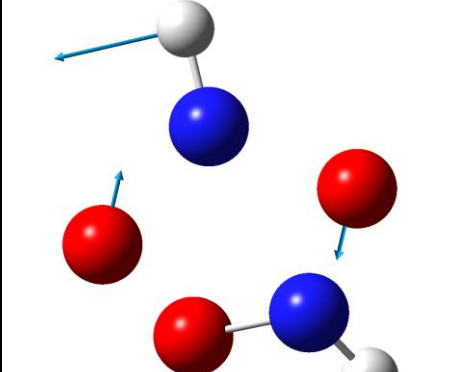
We have studied the following reactions.



The first reaction is the SO_2 photochemical oxidation with nitrocompound. The oxygen atom abstraction that has place in the reaction is followed by the nitroso oxide formation. Nitrocompound in its turn goes backwards to nitrocompound. This conversation was studied in [11]. The second reaction occurs in close analogy with the preceding case including an oxygen atom abstraction and the nitro compound formation. The third reaction is the photochemical oxidation of nitroso compound by nitrocompound. Formation of nitroso oxide has place that as well as in the previous case turns into stable nitrocompound. It is worth noting that in all cases the reactions include in situ formation of nitroso oxide fragments.

In more detail the transition states are shown in Table 3.

Table 3. Transition states in the reactions studied

 <p>226.83i cm⁻¹ ***</p>	S_0^*	115.22**	 <p>878.92i cm⁻¹***</p>
	T_1^*	66.25**	
 <p>537.25i cm⁻¹ ***</p>	S_0^*	27.47**	 <p>461.92i cm⁻¹ ***</p>
	T_1^*	1.45**	
 <p>256.27i cm⁻¹ ***</p>	S_0^*	86.40**	 <p>1411.76i cm⁻¹ ***</p>
	T_1^*	1.66**	

* - multiplicity of the transition state: S_0 is the ground singlet state, T_1 is the first triplet state; ** - activation energies in kcal/mol; *** - the imaginary frequency in cm⁻¹. Arrows on the transition states picture show the active movement of atoms in the course of reactions.

We could clearly see that the most interesting peculiarity of the reaction is formation of five-membered ring containing both peroxide and oxide linkages between fragments of oxidant and substrate to be oxidized. We have previously shown that the triplet nitroso oxides can easily rearrange into the triplet nitrocompounds with very small activation barrier. The reverse process has

substantial barrier, and it seems not too take part in the oxidation reactions. And it is very interesting that it can be formed in situ in the course of oxidation reaction. We believe that this phenomenon has to be general for all reaction of the type. Fig. 1 shows the reaction coordinate typical for the reaction under studies. It can be clear illustration of the hypothesis formulated above.

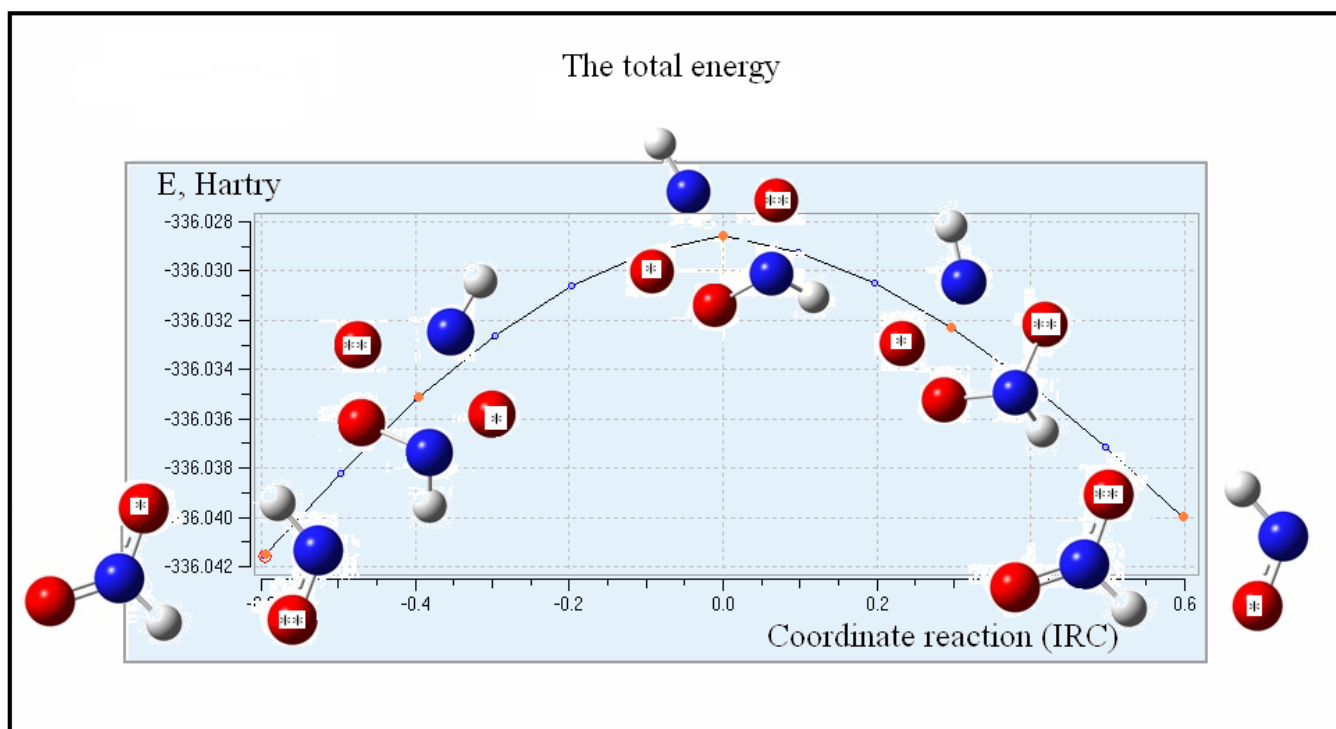
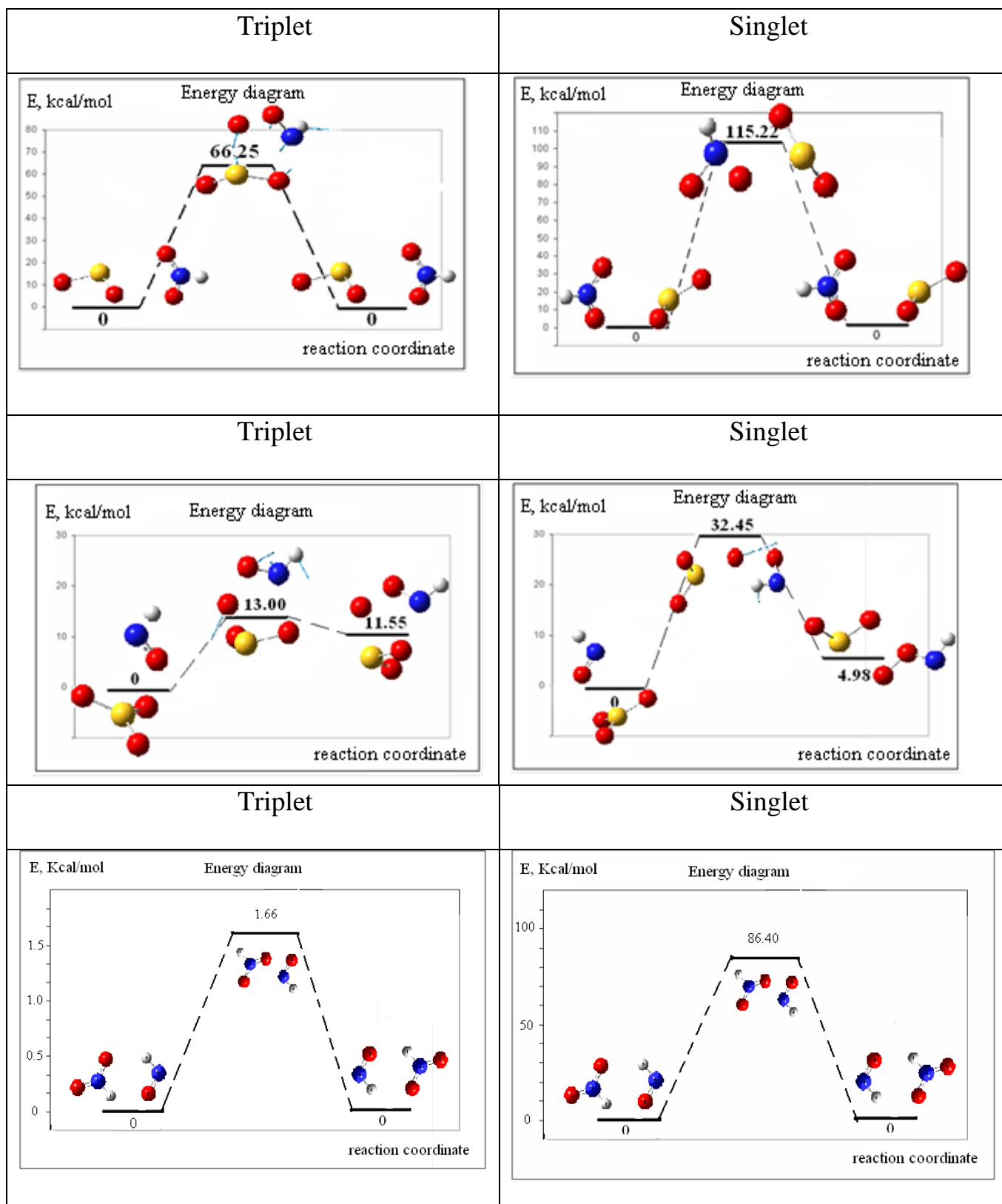


Fig. 1 Reaction coordinate determined by the IRC method

Activation parameters of the reactions are shown in Table 4.

Table 4. Activation parameters of the reactions $\text{SO}_2^* + \text{HNO}_2^{**} \leftrightarrow \text{SO}_2^{**} + \text{HNO}_2^*$ and $\text{NO} \leftrightarrow \text{SO}_2 + \text{HNOO}$. All energies are given in kcal/mol.



From the data in the table 4 we can conclude that the oxidation reaction can have place in the triplet state and close to be impossible for the oxidations in the singlet ground states.

We have studied the spin density distribution in the transition states of the reaction under study. The corresponding data are shown in the Table 5.

Table 5. Spin density distribution on the atoms in the transition state in the reaction $\text{HNO}_2 + \text{HNO}^* \leftrightarrow \text{HNO} + \text{HNO}^*\text{O}$ in the triplet state

Number of atom	Atom	Spin density
1	N	-0.0130
2	H	-0.0012
3	O	0.5355
4	O	-0.0029
5	O	0.4216
6	N	0.9902
7	H	0.0698

Numbers of atoms are shown on the Table 3.

Spin density distribution on the atoms in the transition state in the reaction $\text{SO}_3 + \text{HNO}^* \leftrightarrow \text{SO}_2 + \text{HNO}^*\text{O}$ in the triplet state

Number of atom	Atom	Spin density
1	N	0.8494
2	O	0.2029
3	O	0.7284
4	H	0.0098
5	S	0.0342
6	O	0.2873
7	O	0.0436

Spin density distribution on the atoms in the transition state in the reaction
 $\text{SO}_2 + \text{HNO}_2^* \leftrightarrow \text{SO}_2 + \text{HNO}_2^*$ in the triplet state

Number of atom	Atom	Spin density
1	N	1.0047
2	O	0.2800
3	O	0.5702
4	H	0.0004
5	S	-0.0480
6	O	0.5134
7	O	-0.3208

From the results we can conclude that the reaction could be considered as involving biradical nitroso oxide fragment formed in situ.

Conclusions

We have shown that the oxidation of nitroso compounds and sulfur oxides proceeds mainly in the triplet state by oxygen atom transfer. They include in situ formation of nitroso oxides fragments. Preliminary studies have shown that the transition state structures are only slightly influenced by substituents in the reagents. The most probable mechanism includes redistribution of chemical bonds (mainly N-O) in the five-membered ring with the nitroso oxide moiety.

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