Quantum-chemical calculations of the possible formation of nitroso oxides in the course of the photooxidation reactions by nitro compounds

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Abstract.

Recently we observe the growing interest in the field of nitroso oxides being isomers of nitrocompounds. They are strong oxidizers, can eliminate singlet oxygen and generate atomic oxygen. On the base of our quantum chemical calculations we have assumed that there exists a possibility of *in situ* formation of nitroso oxide – like fragments in the course of photochemical oxidation reactions of nitrosocompounds and SO_2 by nitrocompounds. We used DFT/6-31G(d) and DFT/6-311+G(d) methods from the Gaussian-03 program package. We have performed identification of the nitroso oxide moieties by means of comparison of the calculated geometries and spectra of the reagents in the transition states with corresponding values known from experiment and/or previously made quantum chemistry calculations.

Keywords: nitroso oxide, nitrocompound, photooxidation, nitrogen-containing compound, s-containing compounds, quantum chemistry calculation, DFT, activation energy, transition state

Introduction

Recently, isomers of nitrocompounds - nitroso oxides (Fig. 1) received great interest [1-8]. These compounds are potential oxidants, sources of singlet oxygen, easily abstract hydrogen atoms, can serve as the sources of atomic oxygen. Study of nitroso oxides and their reactions are important for the correct creation of the photochemical oxidation mechanisms of large number of the N-O - containing compounds, including various photochemical reactions nitrocompounds.

The problem formulation

The main aim of our investigation is to test the following hypothesis: the photochemical reactions of the organic compounds by nitrocompounds in the triplet state often involve the in situ formation of nitroso oxides.

The transition state searching methodology

We determined the geometries of the transition states (TS) in the reactions under study by means of the QST2 and QST3 procedures from the Gaussian03 computer program package [9]. The criteria of correctness of the TS geometry determination was an existence 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 the all geometry parameters optimization were performed in the rank of the uB3LYP platform.

The first step of our study was a choice of a method of calculations and its verification for the compounds involved in the study. The relevant results are shown in Table 1 and 2.

Table 1. Choice of the method to be used to calculate geometry and other characteristics of the S - containing compounds (comparison of bond length, nm) in the triplet state

Bond	MP2/6-31+G(d)	uB3LYP/6-31+G(d)*	Experiment
SO(triplet)	0.1524	0.1516	0.1481
SO_2	0.1482	0.1466	0.1432
SO_3	0.1463	0.1454	0.1430
SO^-_2	0.1550	0.1548	0.1523

* The method of our choice

Table 2. Calculated geometrical parameters in HNO calculated by different quantum-chemical methods. Comparison with experiments

Method	r*** (H-N), nm	r (N-O), nm	r (N-O) – r (H-N), nm
PM3	0.0997	0.1175	0.0178
UHF/3-21G	0.1036	0.1217	0.0181
UMP2/6-31G(d,p)	0.1053	0.1237	0.0184
UB3LYP/6-311G(d,p)	0.1066	0.1200	0.0134
G2	0.1058	0.1236	0.0178
UB3LYP/6-311+G(d)*	0.1064	0.1241	0.0177
Experiment**	0.1063	0.1211	0.0148

** Nimlos, M. R.; Ellison, G. B. J. Phys. Chem. 1986, 90, 2574.

*** r is bond length, nm

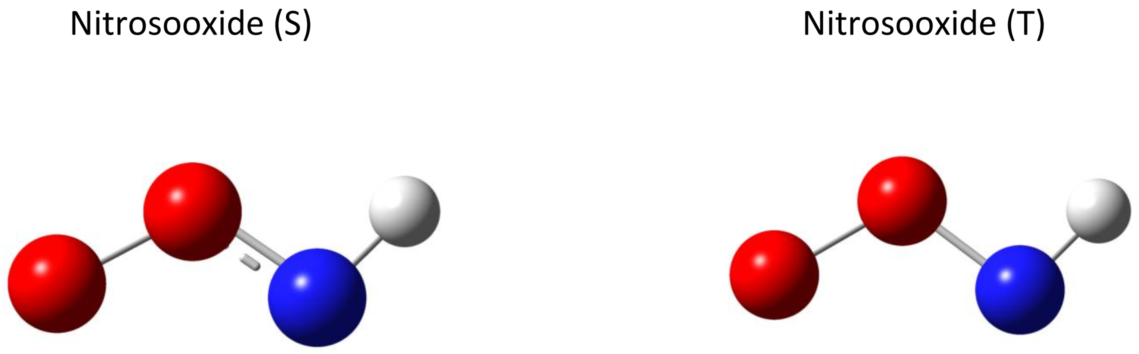
Results and discussions

Consider the possibility of the in situ nitroso oxides formation in the course of the photochemical reaction of nitro compounds with nitrosocompounds.

$$\mathrm{HNO} + \mathrm{HNO} \leftrightarrow \mathrm{HNO}^{*} + \mathrm{HNO}_2^{**} \qquad (1)$$

When simulating the reaction, as well as similar ones we have noticed that the TS geometry in the reaction contained fragments that could be identified as a nitroso oxide moiety. Upon further study of the geometry as well as the IR spectra of transients we revealed the similarities in the structure and the frequencies of vibrations of the respective groups of atoms in the TS and in nitroso oxides.

The geometries of the TS in the nitroso oxides were compared with the geometries of nitroso oxides optimized to find the energy minima. The calculation was performed using the Gaussian 03w method UB3LYP/6-311 G (d)*. The results are shown in Table 3.


Nitrosooxide (S)

Nitrosooxide (T)

Fig. 1. Nitroso oxides in the singlet and triplet state

The possibility of occurrence of reaction 1 can be estimated by its activation energy which is in accordance with Table 4 for the triplet state of the participants is of 1.66 kcal mol^{-1} and 86.40 kcal mol^{-1} for the singlet state. Fig. 2 shows the TS itself where one can easily find the nitroso oxide fragment. A comparison of its geometrical parameters optimized for minimum of energy revealed that we could see also the same nitroso fragments in the TS and in the shown in the table 3.

Table 3. Table of calculated parameters of nitroso oxides iand vibrations in the singlet and triplet states

Method	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

Table 4. The activation energy of the reaction of nitro compounds with nitroso compounds

Electronic state	activation energy, Ea, kcal mol^{-1}
S_0	86.40
T_1	1.66

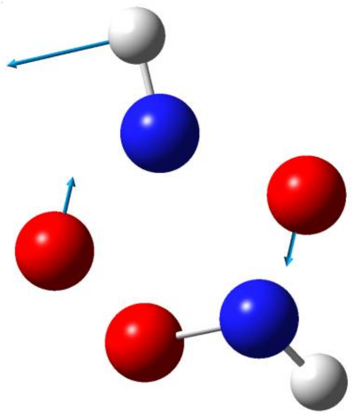


Fig. 2. Transition state having a negative frequency of 1411.76*i* cm^{-1}. Arrows are the vectors of displacement of the atoms.

Table 5 Comparison of geometrical parameters and IR spectra of nitroso oxide fragment in the TS with the optimized geometry of nitroso oxides in the triplet states

	HNOO(in TS)	HNOO (molecule of nitroso oxide)
O-O, nm	0.1436	0.1368
N-O, nm	0.1421	0.1369
ν(N-O), cm^{-1}	893.16	829.42
ν(O-O), cm^{-1}	788.89	1061.11

Based on the table 5 one can conclude that the nitroso oxide geometry practically coincides with the geometry of nitroso oxide fragment in the TS. It is important to note coincidence of the vibration frequencies of groups of atoms N-O 829.42 and 893.16 cm^{-1}, respectively. For groups of atoms O-O there is no coincidence of the vibration frequencies. This is apparently caused by the fact that nitroso oxide moiety is altered by the rest part of the TS state molecule. IR - spectra are shown in Fig. 3-7.

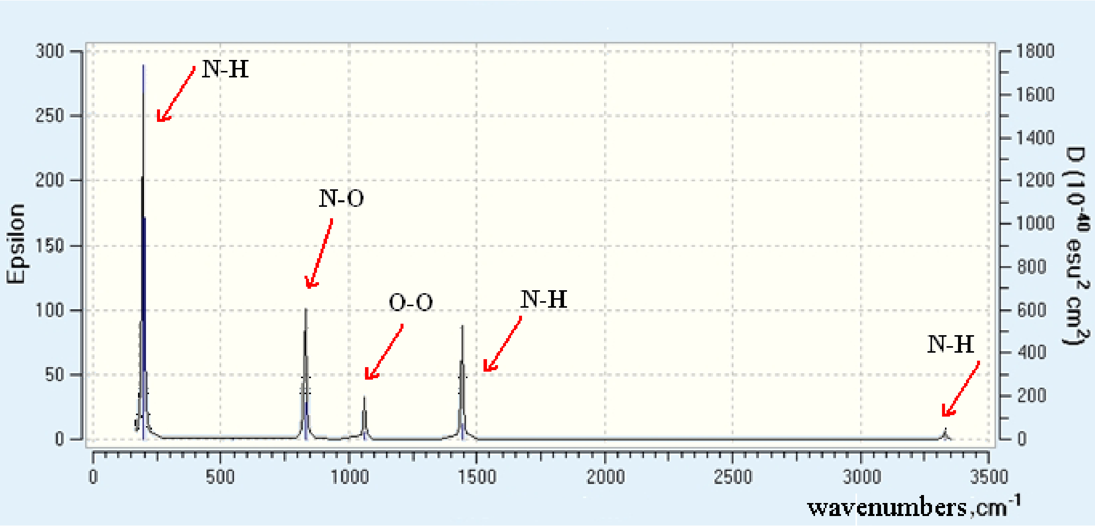


Fig. 3. IR spectrum of the nitroso oxide molecule HNOO (T)

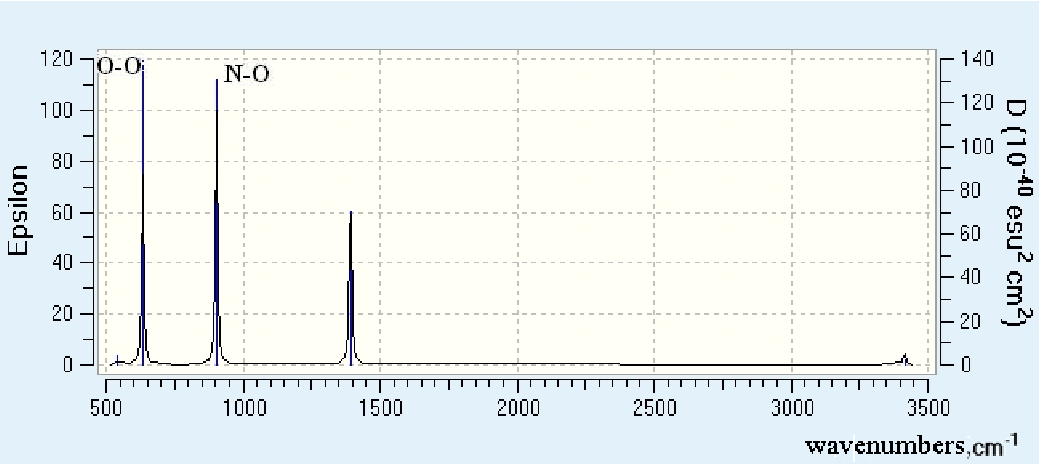


Fig. 4. IR spectrum of the HNOO (T) transition state

Consider the possibility of nitroso oxides in situ formation on the reaction of nitromethane with a sulfur oxide (II). The activation energy for the above reaction according to Table 6 for the triplet and singlet state of the participants is of 33.31 and 49.52 kcal mol^{-1} respectively.

Table 6 Activation energies the reaction of nitromethane with sulfur dioxide (II)

Electronic state	activation energy, E_a, kcal mol^{-1}
S_0	49.52
T_1	33.31

Fig. 5 shows the TS, where one could easily see nitroso oxide fragment.

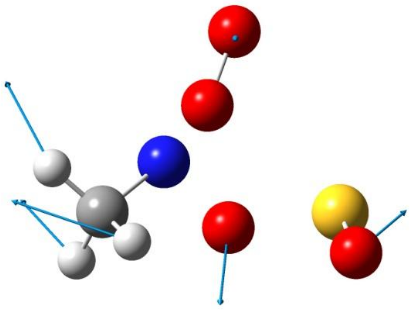


Fig. 5. The transition state of reaction of nitromethane with a sulfur oxide (II), with the value of the imaginary frequency of 110.98*i* cm^{-1}.

A comparison of its optimized geometrical parameters for ones for nitroso oxide itself is given in Table 7. Comparison of the geometric parameters and IR spectra of nitroso oxide in the TS with an optimized energy in the triplet states.

	CH_3NOO(in TS)	CH_3NOO (molecule of nitroso oxide)
O-O, nm	0.1346	0.1375
N-O, nm	0.1590	0.1535
v(N-O), cm^{-1}	585.90	664.83
v(O-O), cm^{-1}	1023.92	1016.56

From the table 7, the geometry of nitroso oxide is almost identical to the geometry nitroso oxide fragment in the TS. Also there is a match in the vibration frequencies of N-O bond of 664.83 and 585.90 cm^{-1}, respectively, and O-O bond of 1016.56 and 1023.92 cm^{-1}. IR - spectra are shown in Fig. 6 and 7.

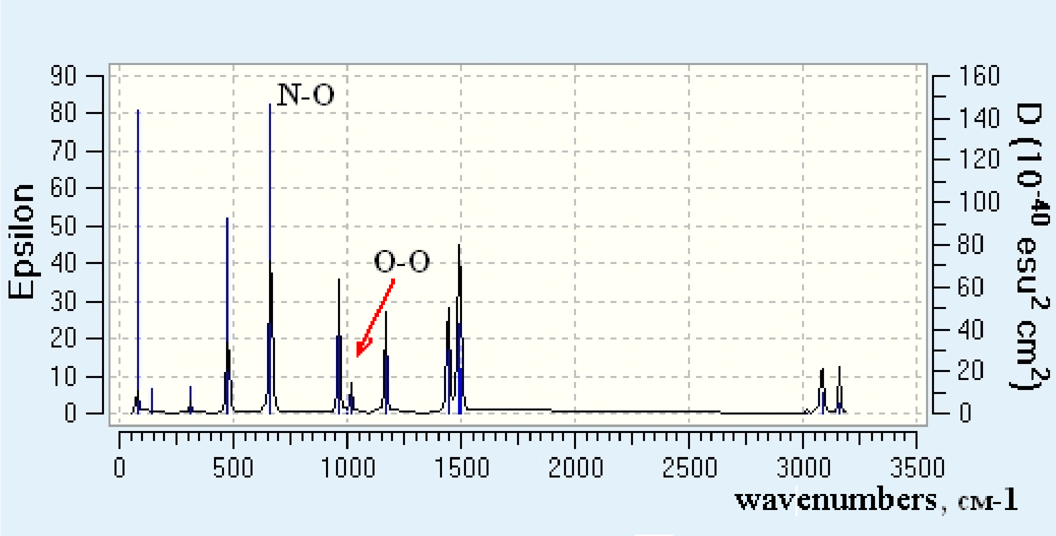


Fig. 6. IR spectrum of a molecule nitroso CH_3NOO (T) in the transition state

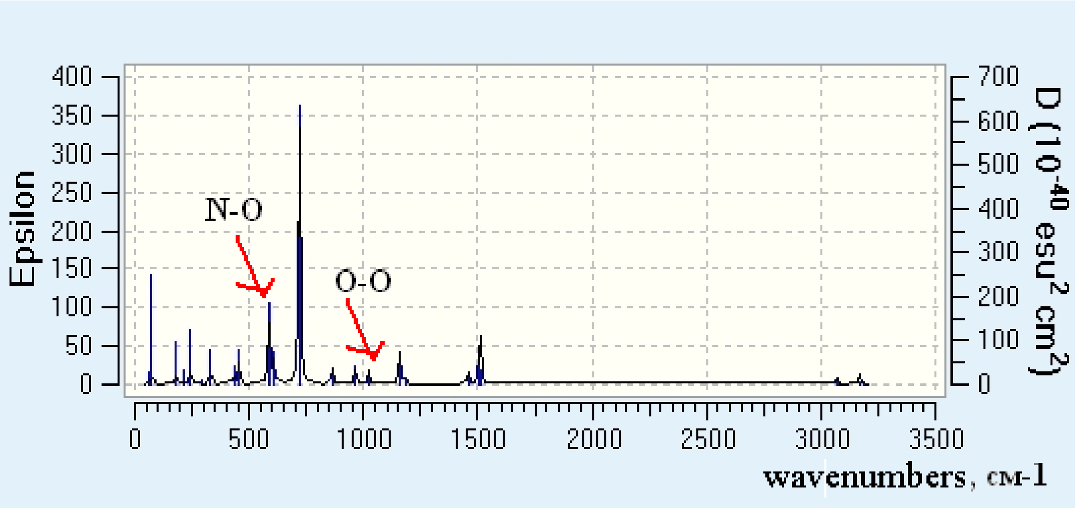


Fig. 7. IR spectrum of the nitroso oxide CH_3NOO (T)

Conclusions

Based on the data obtained we can state that the reactions occur mainly in the triplet states by the oxygen atom transfer; they proceed via TS with the nitroso oxide predominantly in the triplet state; the geometries of the nitroso oxide fragments in the transition states are close to the corresponding geometries of the nitroso oxides themselves; the structure of the transition states are essentially independent of substituents.

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