Theoretical study of the photochemical oxidation mechanism of S-containing organic compounds in presence of nitrocompounds

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Abstract

Nitrocompounds in the triplet states have the biradical structure, with both unpaired electrons localized on the oxygen atoms. The structure is able to participate in oxidation reactions by the radical mechanisms. We have also proposed that some molecules can catalyze the nitrocompound destruction with N=O molecules formation. We have chosen the S-containing organic compounds like H_2S, MeSH, and Me_2S as substrates for oxidations in the presence of nitrocompounds. We performed theoretical quantum chemical studies of the most possible reaction mechanisms of the oxidation reactions using DFT B3LYP 6-311G++(d) method from the Gaussian 03 program package. We calculated the PES profiles, including intermediates and transition state structures. The activation energies of all stages involved were calculated. We was able to show that MeSH molecule could dissociate to break the S-H bond. The hydrogen atoms formed immidiately find them to be added to the nitrocompound molecules. During further transformation H-atom could be abstracted from the methyl groups to form the S=C double bond. In the case of Me_2S there are no hydrohen atoms that can be easily abstracted, and oxygen atom of nitrocompound attacks the S atom to form Me_2SO has place. The last compound is able to abstract H-atom from the nitrocompound molecule and decompose to give Me_2S and OH radical.

Keywords: quantum chemistry, nitrocompound, S-containing organic compound, DFT, transition state, photochemical oxidation, reaction mechanism, triplet state

Introduction

The compounds of divalent sulfur is often not widely used in industry, on the contrary, are sometimes by-products of many industrial processes and can be a reason of a threat to the environment. Finding ways to recycle these compounds is an important task of modern chemistry. One method of processing of sulfur-containing compounds is photochemical oxidation [1], particularly in presence of nitrocompounds. The convenience of this method is caused by the wide possibilities of process control by changing the intensity of irradiation and other technological parameters. Unfortunately, the high toxicity of reactants makes it difficult to process the experimental study of this type of oxidation, but thanks to the methods of computational chemistry we can make assumptions about the possible mechanism and estimate energy of the process that can serve as a prerequisite for further experimental studies.

We used nitrous acid being one of the simplest representatives of nitrocompounds as a model oxidizing agent.

Methodological part

All calculations in this paper were performed using Gaussian 03 software package [2]. We conducted a brief comparison of methods to determine the most suitable one for our research. The tables 1 and 2 contain the results and deviations of calculated values from experimental ones. We can easily note that the deviation of the calculated geometrical parameters from the experimental ones is quite small.

Table 1: Comparison of calculated and experimental geometries for methanetiol

Method	Bond length, nm		Angle, °	Deviation, %
	S – H	S – C	H – S – C	
UHF/6-311G++	0.1363	0.1878	98.2	2.61
UB3LYP/6-311G++	0.1385	0.1901	96.7	4.10
UMP2/6-311G++	0.1384	0.1901	96.6	4.12
UPBE1PBE/6-311++	0.1382	0.1877	96.9	3.53
UB3LYP/6-311G	0.1385	0.1902	96.7	4.12
UB3LYP/3-21G++	0.1376	0.1910	96.2	4.18
Experiment [3]	0.1329	0.1818	100.3	

Table 2: Comparison of calculated and experimental geometries for dimethyl sulfide

Method	Bond length, nm	Angle, °	Deviation, %
	S – C	H – S – C	
UHF/6-311G++	0.1868	99.7	1.72
UB3LYP/6-311G++	0.1890	98.7	0.99
UMP2/6-311G++	0.1893	96.6	2.58
UPBE1PBE/6-311++	0.1868	98.5	1.22
UB3LYP/6-311G	0.1891	98.7	1.00
UB3LYP/3-21G++	0.1900	98.0	2.22
Experiment [4]	0.1802	98.9	

We could note that the best results are obtained when using the UHF/6-311G ++ to calculate geometry of methanethiol but unfortunately the method does not allow to calculate the studied system in the triplet state. Good results for both molecules are obtained by UPBE1PBE/6-311G ++, however for calculation method was chosen UB3LYP/6-311G ++ as the most accurate for dimethyl sulfide, and because of its wide use in such calculations. Furthermore, for hydrogen sulfide molecule, this method shows the best results [5].

Scan of the potential energy surface profile was carried out in the triplet state due to the following plan. At first, the optimization of the geometry and energy calculation for the reagents and expected products of elementary reaction steps were performed. At second, the optimal energy of the transition state was determined by QST2 method starting from the initial and resultant geometries for the reaction under study. All of calculated structure corresponded to the only imagionary frequency. At third, to verify the correctness of the calculations of the transition state structure we recovered the reaction coordinates for all reactions studied.

Results and Discussion

Hydrogen sulfide

During scanning of the potential energy surfaces there were found two possible reaction paths of the photochemical oxidation of hydrogen sulfide with nitrous acid. One of the ways was described in detail in our previous work [5]. The first step of it is shown in Fig. 1.

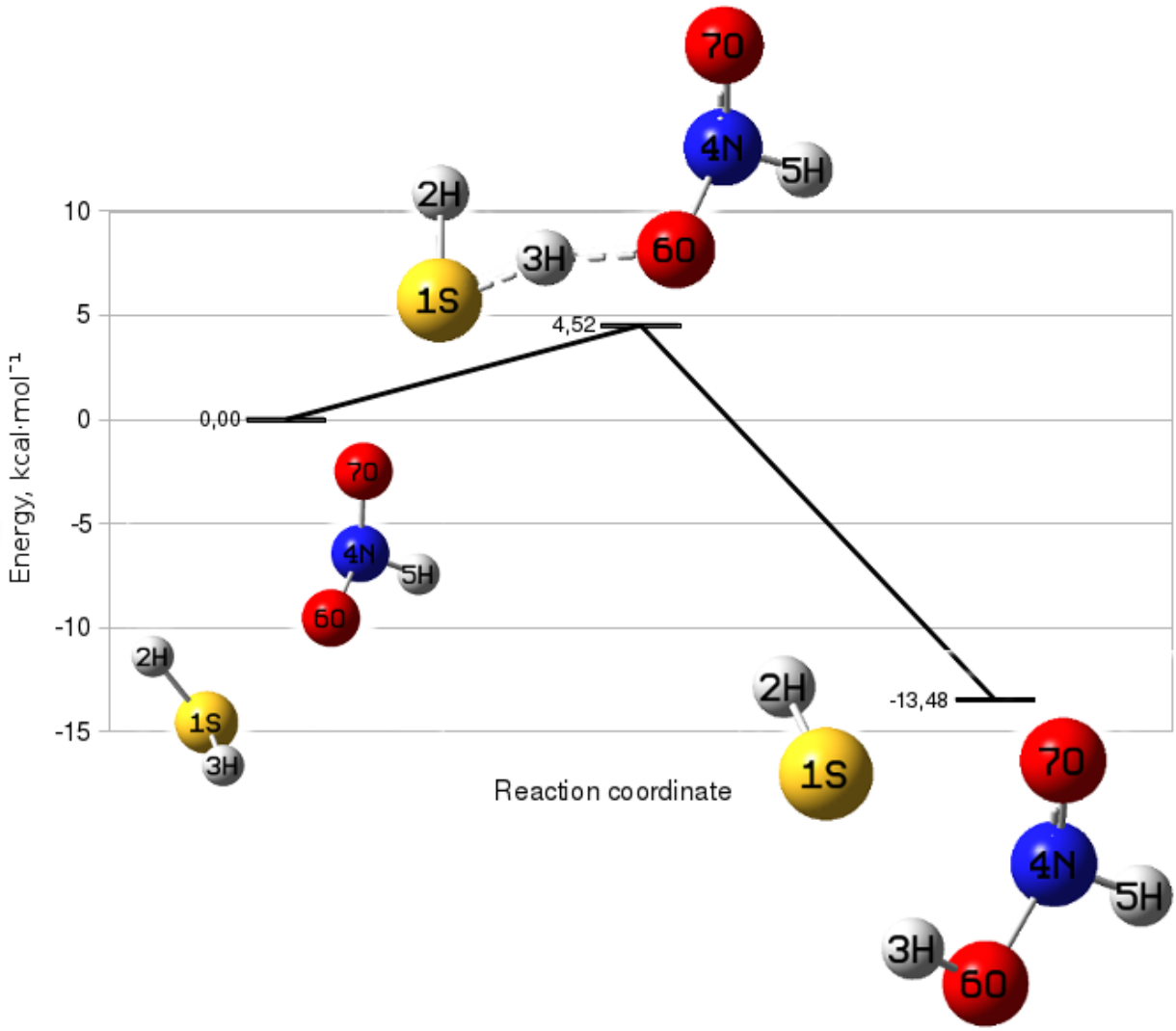

Fig. 1: The first step in the process of photochemical oxidation of hydrogen sulfide by HNO_2 with abstraction of the hydrogen atom

As one can see from the Fig. 1 the first step of the reaction is an abstraction of hydrogen atom from hydrogen sulfide to form HS• and HN (O•)OH radicals, there being a coupling between an orbital containing an unpaired electron at an oxygen atom in the HN(O•)OH radical and p-AO of

nitrogen. The latter was concluded from the spin density distribution for the product of the first step shown in Table 3. The process of hydrogen abstraction requires small activation energy only of 4.52 kcal mol^{-1}.

Table 3: Spin densities in HS and HNOOH system

Atom number	Atom	Spin density
1	S	0.9585
2	H	-0.0207
3	H	-0.0231
4	N	0.4490
5	H	0.0056
6	O	0.1207
7	O	0.5100

Alternative reaction path of the first stage consists of addition of oxygen atom to a molecule of hydrogen sulfide, as is shown in Fig. 2.

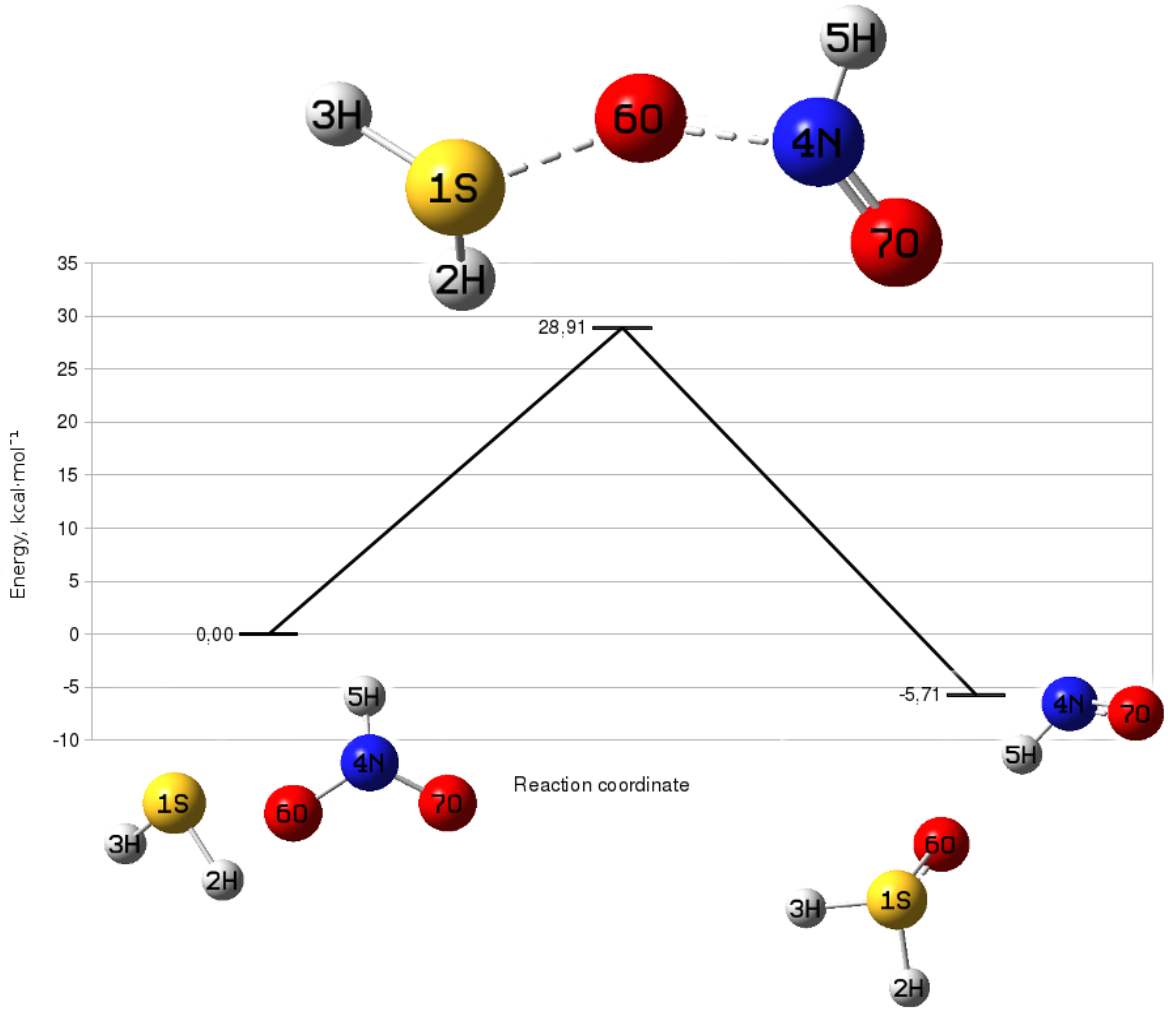

Fig. 2: The first stage of the photochemical oxidation of hydrogen sulfide by nitrous acid with the oxygen atom transfer

This reaction path requires more activation energy because probably of the complexity of moving such a heavy atom as oxygen.

Methanetiol

In the triplet state methanethiol dissociates to give H • and CH_3S • radicals [6]. In the presence of nitrous acid H• radical adds to the oxygen of nitrous acid. As shown in Fig.3 further progress of the reaction is possible through the transfer of OH groups to form CH_3SOH.

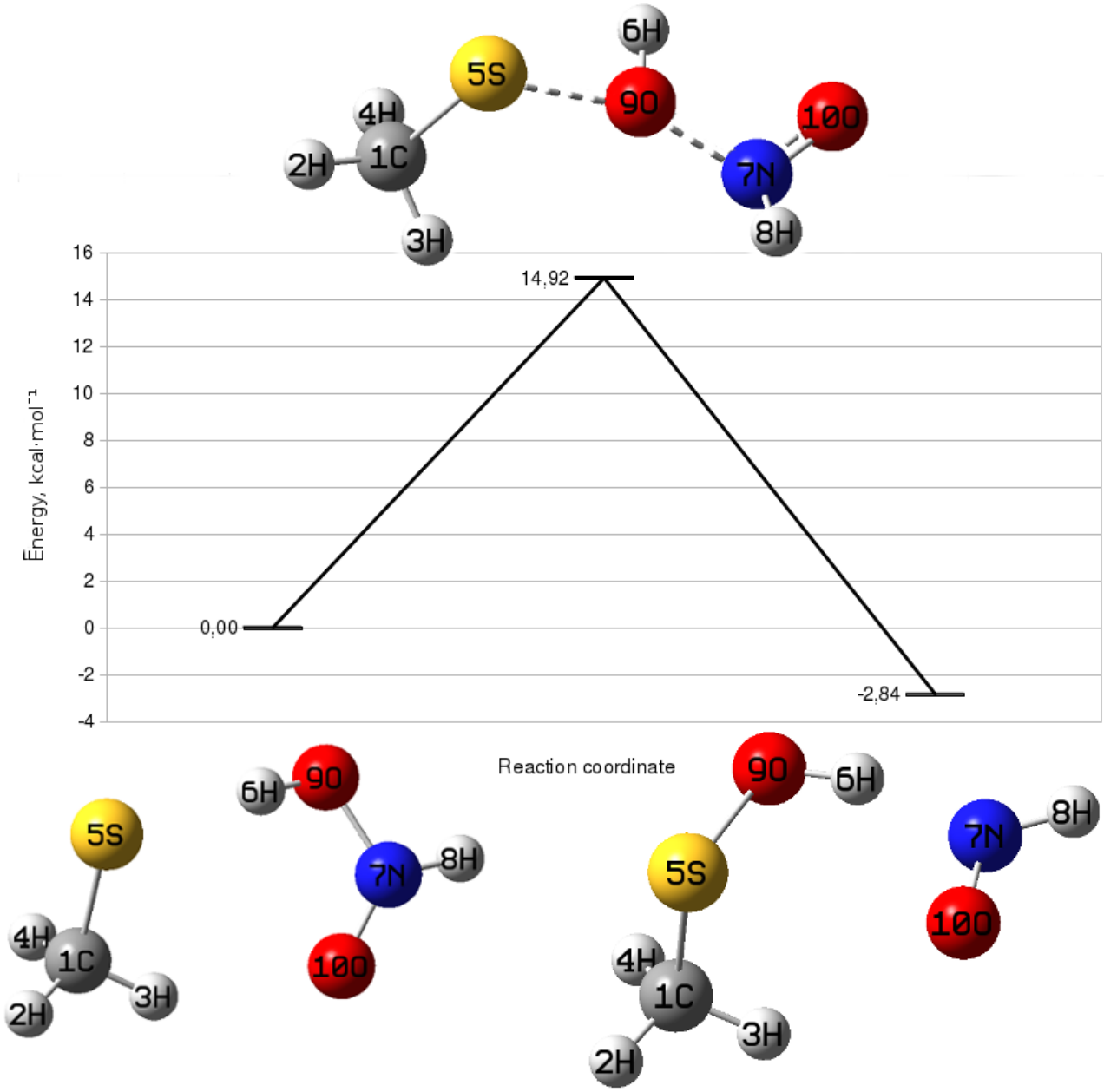

Fig. 3: The first stage of the methanethiol photochemical oxidation in the presence of HNO_2

This stage has the activation energy of 14.92 kcal mol^{-1} and a negative change in enthalpy indicating the exothermic process realization.

Dimethyl sulfide

Dimethyl sulfide in the presence of nitrous acid in the triplet state can add an oxygen atom, as shown in Fig. 4.

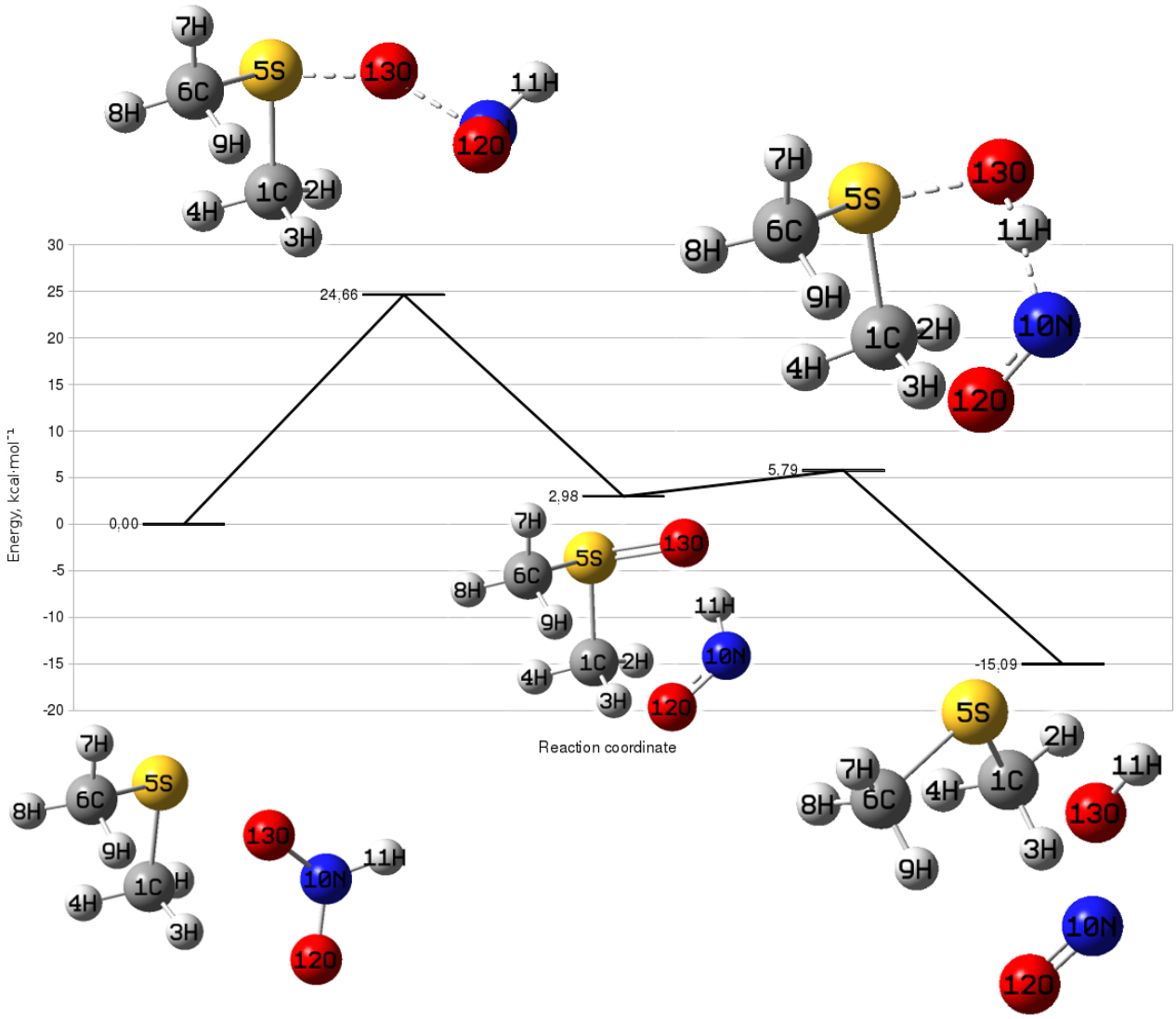

Fig. 4: The first two stages of the photochemical oxidation of dimethyl sulfide in the presence of nitrous acid.

The first stage of the reaction is characterized by a positive change in enthalpy, hence it is endothermic. It is very likely that the oxidation does not stop at this stage. The next stage of the process has very low activation energy of only 2.81 kcal mol^{-1}. As a result, the second stage of the reaction gives fairly stable radical •OH. The reaction can proceed further but this part of reaction path will be discussed in our next works.

Conclusions

This paper describes the probable mechanisms of the first stages of photochemical interaction of hydrogen sulfide, methanethiol and dimethyl sulfide with HNO_2. They have been studied by means of quantum-chemical calculations in the frame of Gaussian 03 program. In the case of hydrogen sulfide there are two reaction paths observed. The first one includes abstraction of a hydrogen atom from a molecule of hydrogen sulfide, and the second one is based on transfer of the oxygen atom of nitrous acid molecule to the sulphur atom of hydrogen sulphide molecule. The second path of the reaction is not available for methanethiol, as a consequence of the spontaneous elimination of hydrogen atom in the course of transition to the triplet state. Dimethyl sulfide in its turn can only add an oxygen atom.

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