The reaction of the hydrogen sulphide with the triplet nitromethane in the gas phase: the mechanism and products evaluation.

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Abstract

New reaction steps have been found for the gas phase system containing nitromethane and hydrogen sulphide molecules using the PBE/6-311++G** method. In combination with our previous results the obtained data allow us to propose the reaction mechanism as a set of the events such as the hydrogen transfer from the sulphur atom to the nitrocompound accompanied with formation of the hydrogenated nitromethane radical; and the singlet nitromethane regeneration by hydrogenated nitromethane radical reaction with the hydroxyl containing fragment. The mechanism leads to formation of the atomic sulphur and nitrosomethane as main products of the reaction. It was also predicted that the fluorescence at wavelength of 349 nm could be observed as result of the considered sulphanol and nitromethane interaction.

Keywords: nitromethane, hydrogen sulphide, sulphanol, DFT, photochemistry

1 Introduction

Many aspects of the interaction between hydrogen sulphide and nitromethane molecules in the triplet state were studied in our previous work. But obtained predictions are mostly fragmentary and hardly can be shaped into the complete description of given reaction. Some observations may be valuable in frame of the special case of reaction conditions when reactants can not freely move along the reaction system and forced to interact with their neighbours only. Such a condition is not widely spread in the real world, so there is necessity to find the mechanism that describes the nitromethane and hydrogen sulphide interaction under conditions like the gas phase that are closer to reality.

The modeling of the gas phase conditions involves one important postulate about a possibility for any molecular fragment to interact with any other molecular fragment. This postulate leads to plenty of possible reaction pathways and elemental steps. To reduce amount of steps of interest the selection bias was applied. The thermodynamic and kinetic parameters were selected as the main selection criteria. After modeling of the first reaction steps it was noticed that some of other pathways that does not meet the selection bias can be possible when increasing concentration of the intermediates formed after preforming of initial steps. So this pathways also were added to the reaction mechanism.

2 Methodology

All calculations neccessary for modeling of the reaction system were perfomed by North-West Chemistry software package. [6] For the ground state calculations and potencial energy surface (PES) scanning DFT PBE0/6-311++G** theory level was used. The excited state calculation has been performed using TD-DFT method with the same functional and basis.

For the visualization of the calculation results Gabedit [1] software was used with little bugfixes [1] in the NWChem output parsing code.

3 Results and discussion

The mechainsm evaluated starts with reaction step described before in [3]: the hydrogen transfer from the hydrogen sulphide molecule to the nitromethane molecule in the excited state. This step has an advantage before the oxygen transfer due to lower activation energy of 3.6 kcal/mol.

Full reaction mechanism in the gas phase is presented at Figure 1. Steps (1), (2) and (4) involve nitromethane molecule as a reactant and produce hydrogenated nitromethane radical which participates in steps (3), (4) and (6) to form nitrosomethane. Steps (4) and (6) can be considered as regeneration steps because their products contain nitromethane which is being excited to the triplet state can behave as a reactant for the first reaction steps again.

The step (2) involves interaction between the nitromethane molecule and HS· radical formed in the previous step. More detailed description of this step can be found in [5]. The step (2) is more likely than step (3) to be performed at early stages of the reaction due to low concentration of the hydrogenated nitromethane radical in the reaction system. But lately, when concentration of the hydrogenated nitromethane radical will be big

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[1] Improved version of Gabedit can be found at `https://github.com/xomachine/Gabedit`

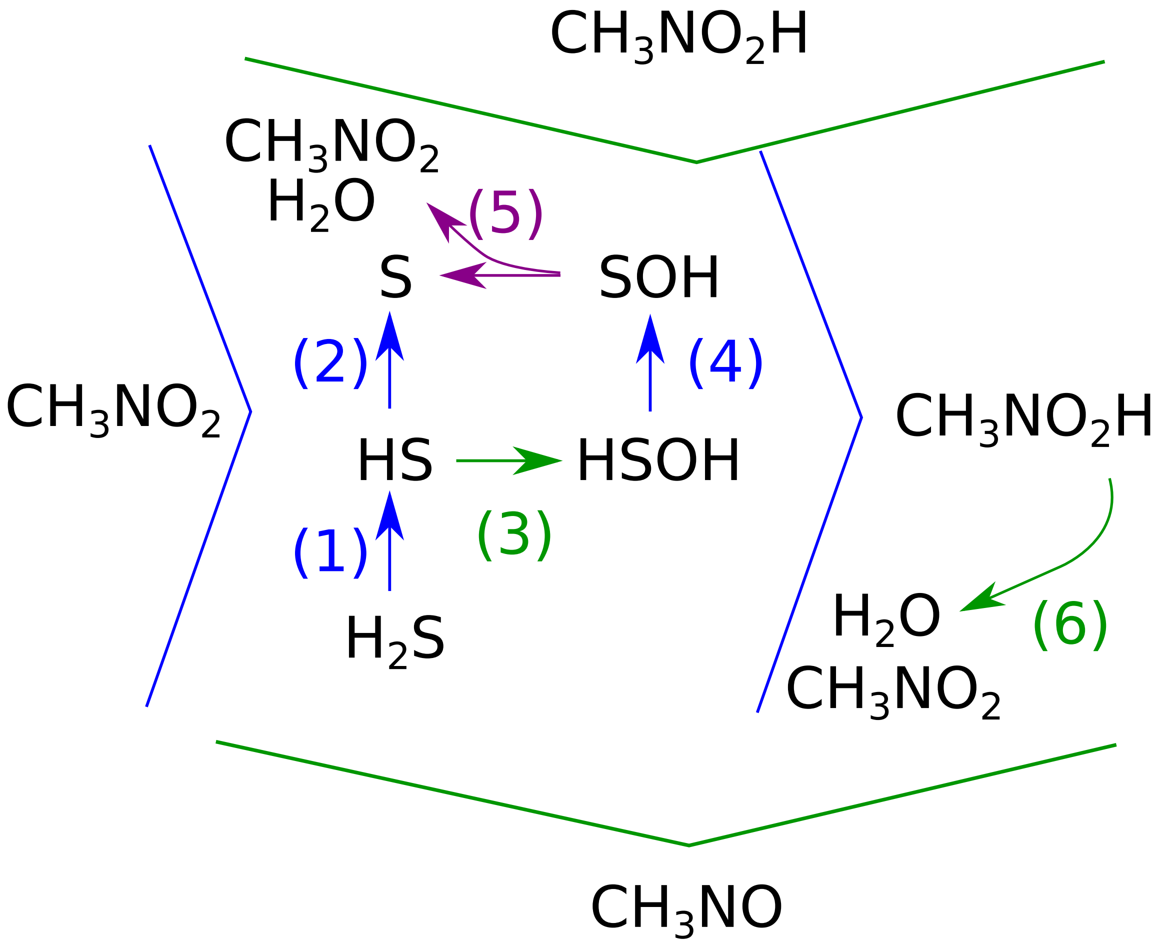
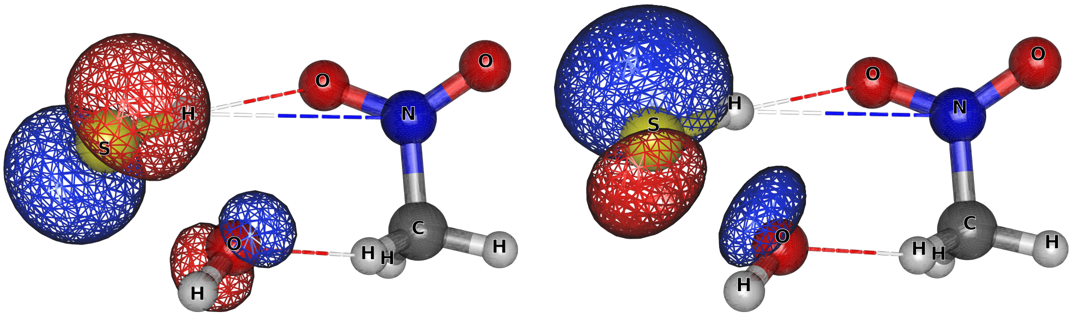


Figure 1: Gas phase reaction mechanism. Reaction steps marked with blue take nitromethane as a reactant and produce hydrogenated nitromethane as a product. Reaction steps marked with green use hydrogenated nitromethane as a reactant and produce nitrosomethane. The reaction step marked with purple takes the hydrogenated nitromethane as a reactant but does not produce nitrosomethane.



(a) Low energy partically occupied orbital (b) High energy partically occupied orbital

Figure 2: The orbitals with maximal spin density contribution in the ground triplet state of the nitromethane-sulphanol system. (red grid - positive, blue grid - negative.)

enough, the step (3) may become a primary way of interaction for this radicals.

Important observation was encountered during modeling of the step (4). It has been found that the state of the nitromethane-sulphanol system which it has occured after approaching of reactants to each other is not the triplet state. Assuming that the nitromethane molecule was in the triplet state before an interaction the spin density of the system should be localized at the nitrogroup. But actual spin density map in the lowest triplet state is different as it can be seen from Figure 2. There were drawn two orbitals that provided the largest contribution to spin density. It can be seen that the major part of spin density is localized at sulphanol molecule.

The excited states analysis has shown that the expected state of the system lies at 3.55 eV above the ground triplet state. It might be assumed that after the reactants approach the nitromethane-sulphanol system would be relaxed to the ground triplet state accompanied by the light emission on wavelength of 349 nm.

After the step (4) has passed nitromethane regeneration was possible through the step (5). The sulphur atom formed during this step is in the triplet state while other molecules are in the singlet state. The potencial energy surface (PES) profile of this step can be found at Figure 3. The enthalpy of the step (5) is 2.43 kcal/mol that indicates that the step is exothermic one, but the Gibbs energy has a small negative value of -0.48 kcal/mol. Despite high activation energy of this step which equals 25.8 kcal/mol it still can be considered as a possible step because the reaction system might be filled with reactants for this steps by virtue of very low activation energy of previous steps (3) and (4).

Another important point in the reaction mechanism is the step (1). It is known from literature [2; 4] that during the aromatic nitrocompound reduction the electron transfer can be observed. If the electron transfer step present in the described reaction mechanism then it could be detected through spin density transfer before reaching the saddle point in the step (1). At the Figure 4 it can be seen that the spin density at the sulphur atom at the saddle point is much smaller than the spin density at the products. So it can be concluded that the electron transfer is being performed only as being acompanied by proton transfer, in other words atom transfer is being performed without preliminary electron transfer.

Abscence of the electron transfer in the step (1) can be explained by two distinctions from the experimental conditions: the nitrocompound in the model was not aromatic and the role of a reductant played by sulphide

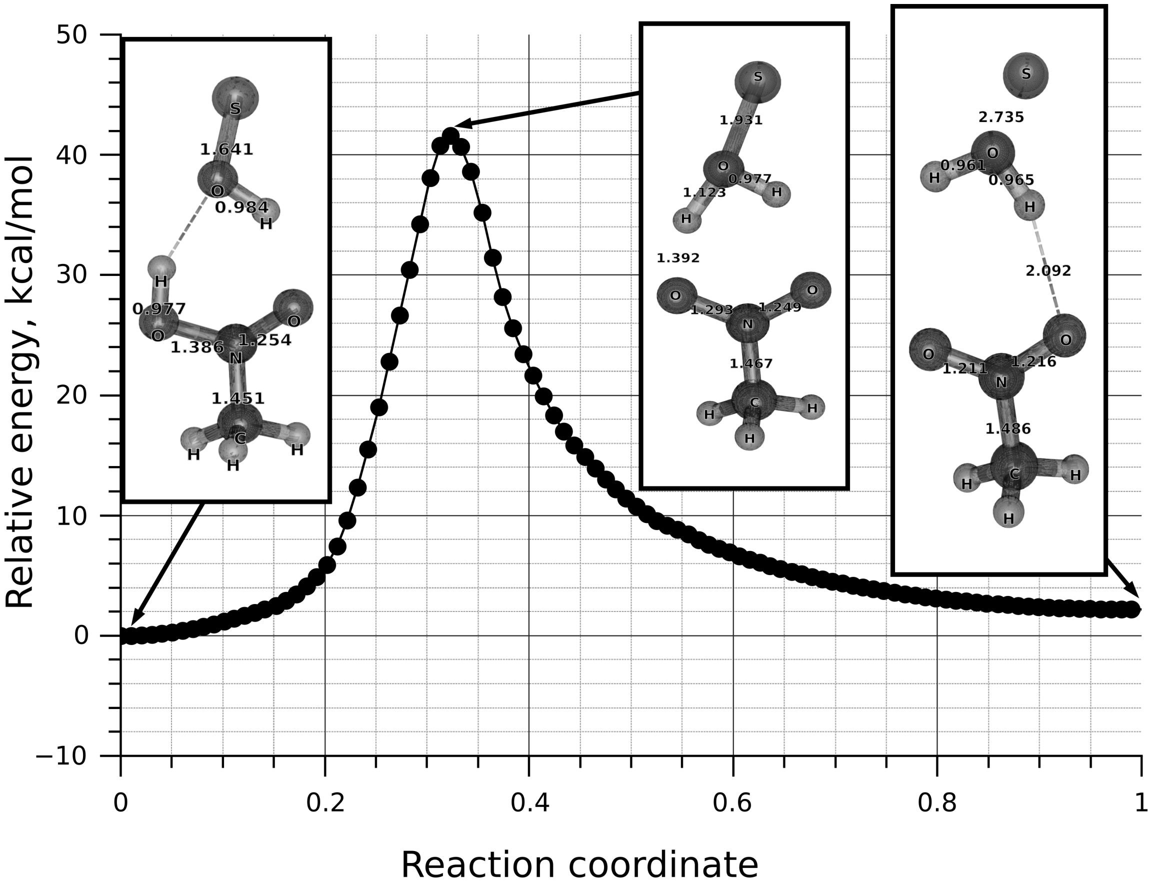
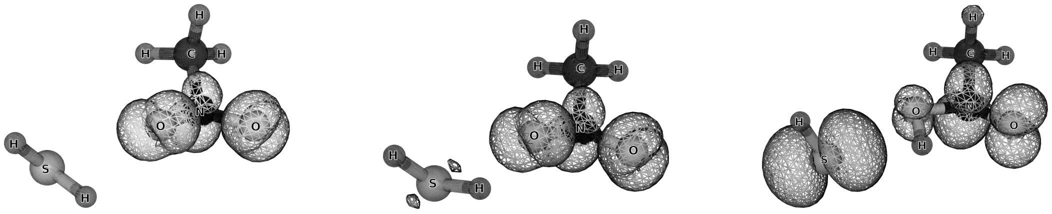


Figure 3: Potencial energy surface (PES) profile and key geometries of the step (5). (Interatomic distances shown in angstroms)



(a) Reactants (b) Transition state (c) Products

Figure 4: Spin density distribution in the nitromethane-hydrogen sulphide system at step (1).

instead of amine in the original experiment. Nevertheless the search for a reason of abscence of the electron transfer will be continued in our next studies.

4 Conclusion

The mechanism of the nitromethane and hydrogen sulphide interaction in the gas phase developed leads to formation of atomic sulphur in the triplet state, nitrosomethane in the triplet state and water. Products predicted may not be the final products of the reaction but their formation in the reaction system is highly possible. The charge transfer observed for aromatic nitrocompounds in experiment was not predicted for nitromethane by quantum chemistry modeling. The prediction of fluorescence during the reaction is based on assumption of the system relaxation before interaction which is not reliable enough by itself so it requires further experimental check.

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