New reaction pathways of the hydrogen sulphide photooxidation initiated by nitromethane

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Abstract

The quantum chemistry study of the hydrogen sulphide photooxidation process in gas phase was performed using density functional theory at the PBE0 6-311++G(d, p) theory level. It was found new perspective reaction pathways. One of them provides a possibility of partial nitromethane regeneration accompanied by nitroso-methane and water formation from radical product of hydrogen addition to nitromethane. This radical product can be obtained in many reaction stages, including new one leading to formation of new reaction product being atomic sulphur. Analysis of thermodynamic and kinetic parameters at standart laboratory conditions (298.15 K, 101325 Pa) showed a high probability for mentioned stages to be performed due to low activation energy and negative Gibbs energy. Negative enthalpy causes newly found stages to be exothermic.

Keywords: DFT, photochemistry, hydrogen sulphide, photooxidation, nitrocompounds

Introduction

The hydrogen sulphide photooxidation mechanism discribed in [1] does not considering interactions between molecular fragments on different stages of reaction. Such interactions can lead to many new reaction pathways and of course they may occur in real gas phase system. A quantity of branches in the reaction path should reviewed in this approach is huge and poses a problem. Observation a few amount of stages leading to useful products or important intermediants allow to avoid the problem by decreasing number of nessesery calculations. There are described only stages that lead to regeneration of oxidant and formation of oxidated sulphur product.

Methodology

The PBE0/6-311++G(d,p) level of theory shows good results for the compounds in question [1] and is used for further studies. All calculations were performed using North-West Chemistry software [2]. Search of new stages was done by the following way. First of all the possible interaction table was formed. The table presents a intermediates and reactants at headers of rows and columns. Each cell of table contains information about products of molecular fragments interaction represented in corresponding row and column. New rows and columns were added to the table when there is a product that is not present in the table. Activation energy, enthalpy and Gibbs energy of each stage were calculated using corrections obtained from vibration frequencies calculation at 101 325 Pa and 278.15 K.

Results and discussion

Nitromethane interaction with intermediates

A first and obvious way is an interaction of both oxidizing agent and intermediates involved into the reaction. So the $\cdot SH$ radical fragment when it clashes with nitromethane molecule can be oxidized to atomic sulphur biradical by hydrogen transfer to nithromethane molecule. A potential energy surface (PES) profile of the stage is shown at Fig. 1.

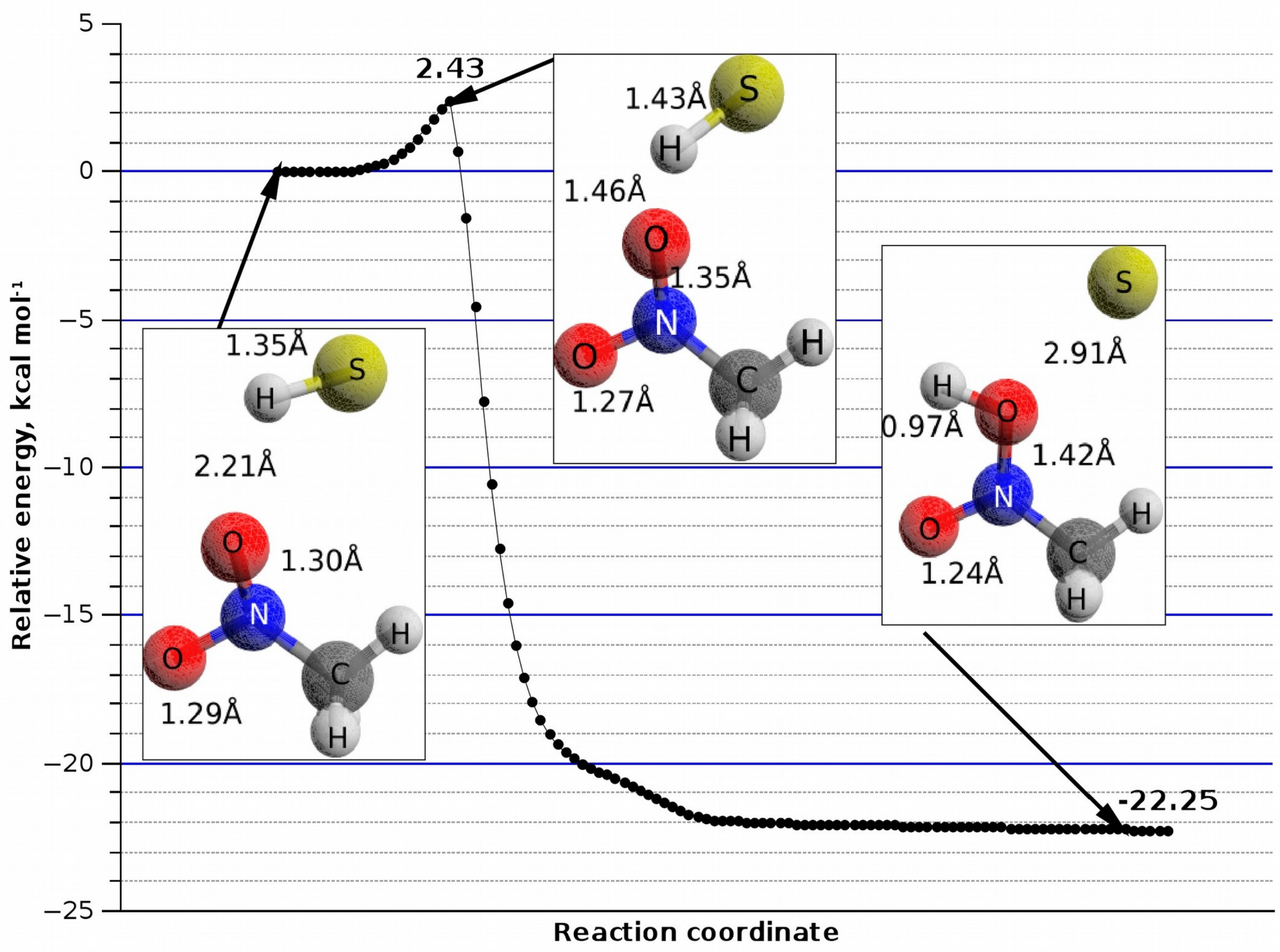

Fig. 1: PES profile of the atomic sulphur formation stage. Distances shown are lengths of (N-O), (S-H) and (O-H) bonds and the minimal distance between molecular fragments.

The calculation showed that such interaction is possible only if total spin multiplicity of the system equals 4. Energetic parameters with corresponding corrections of the reaction can be found in Table 1.

Another hydrogen transfer stage to nitromethane is a hydrogen atom abstraction from *HSO* radical can be also performed in the quartet system state. Corresponding PES profile is shown at Fig. 2.

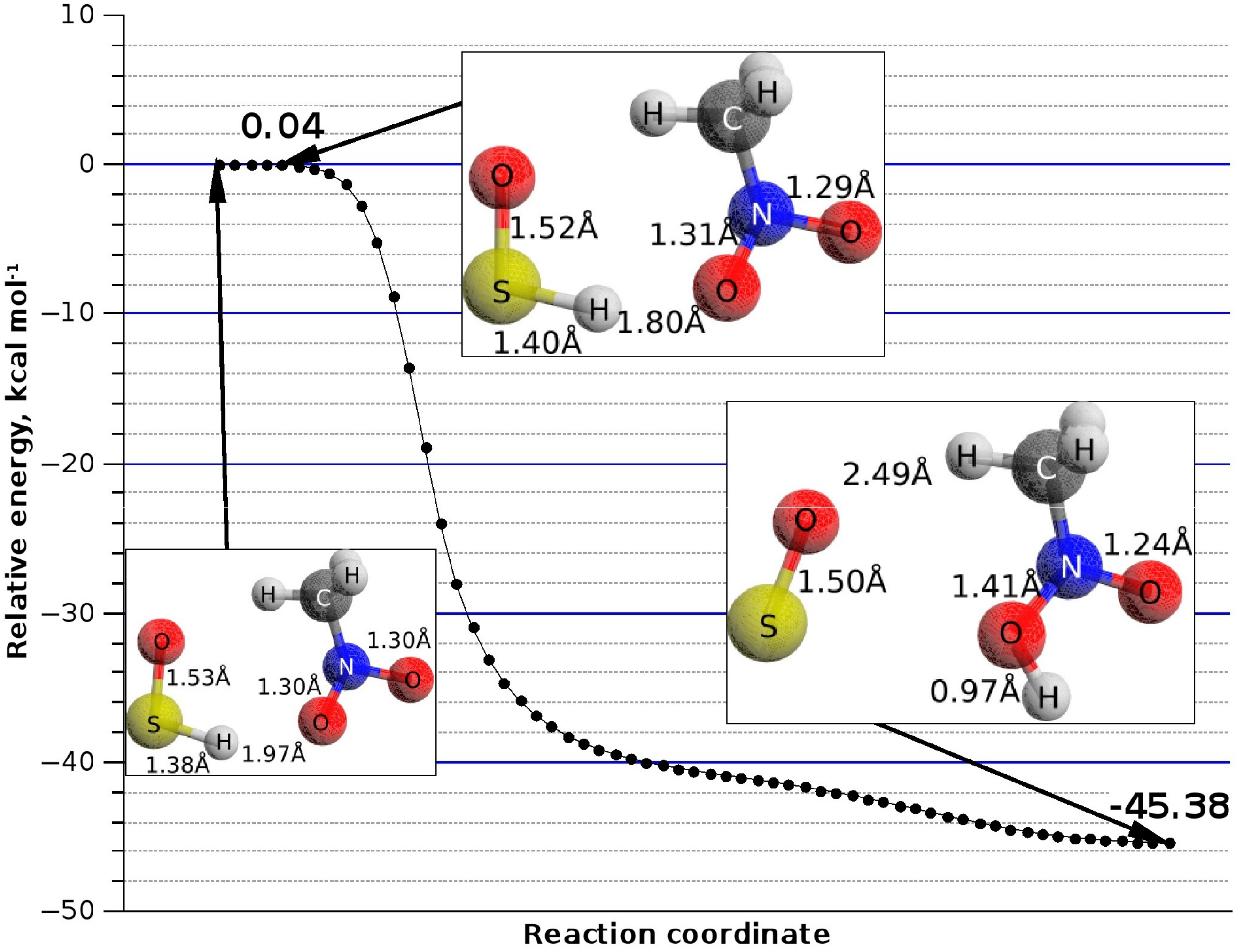

Fig. 2: The PES profile of the SO formation stage. Distances shown are (O-H), (N-O), (S-O) and (S-H) bond lengths and the minimal distance between molecular fragments.

This stage has the extremely low activation energy and it imposes a problem to obtain activation energy value taking into account zero point corrections: resulting value appears below zero. Values of Gibbs energy and enthalpy can be found in Table 1. The *SO* molecule formed in triplet state and it may probably be oxidized into SO_2. A possibility of this way will be considered in our further work. The sulphur monooxide molecule can also undergo dimerization [3] or oxidation into sulphur dioxide by ozone [4] if monooxide becomes singlet.

A nitromethane molecule being in the triplet state can abstract hydrogen from *HSOH* intermediate as well. The hydrogen transfers from the sulphur atom to an oxygen atom of nithromethane. Such interaction proceeds a bit harder than previously considered one due to higher activation energy but the energy is low enough to perform the interaction at the standart laboratory conditions. The PES profile of the stage is shown at Fig. 3.

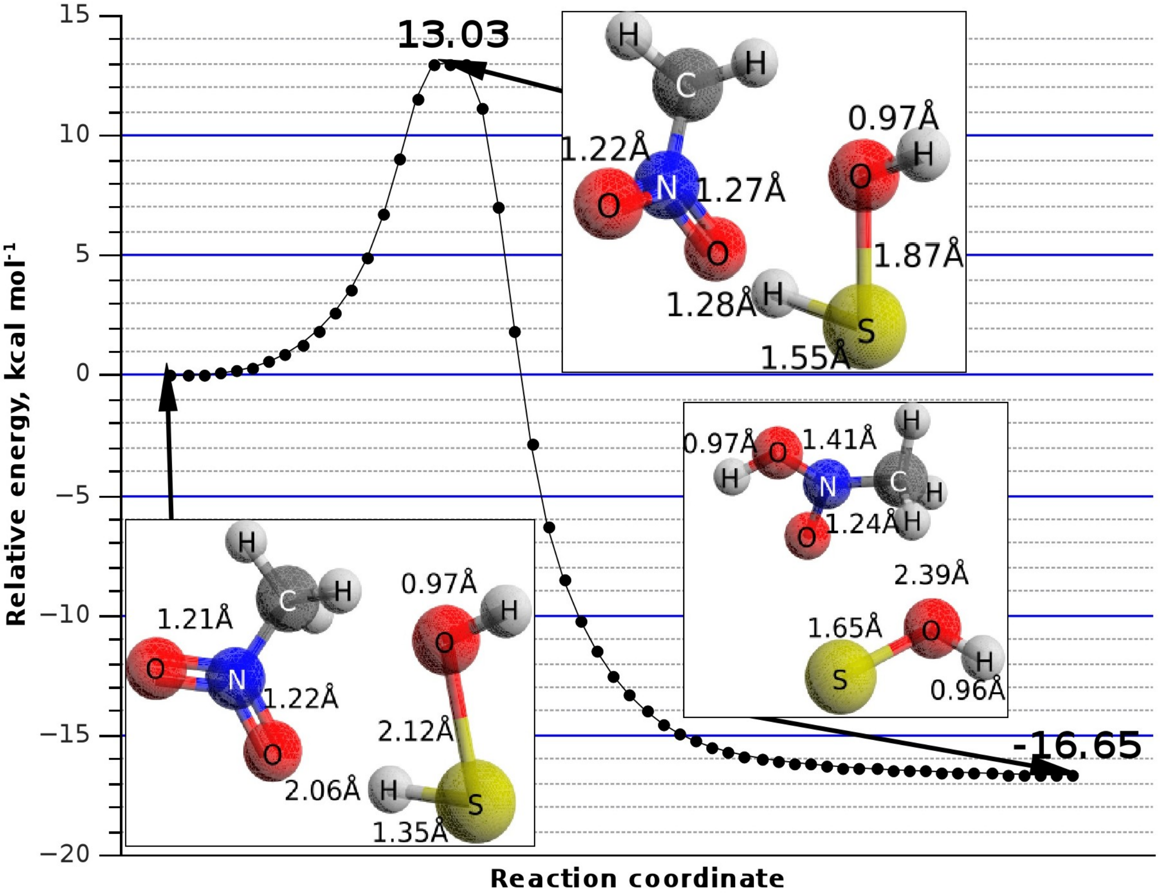

Fig. 3: The PES profile of the SOH formation stage. Distances shown are (O-H), (N-O), (S-O) and (S-H) bond lengths and the minimal distance between molecular fragments.

The energy parameters of this and all mentioned before stages with nessesary corrections are shown at Table 1. The stages are thermodynamicaly permitted in the choosen conditions and they all have high probabilities to perform due to low activation energy. Such type of interaction can be prevailing in the reaction system especially on early stages when concentration of nitromethane is high.

Table 1: Energetic parameters of nitromethane interactions with various intermediates.

Intermediate	Enthalpy, kcal mol^{-1}	Gibbs energy, kcal mol^{-1}	Activation energy, kcal mol^{-1}
HS	-13.9	-17.2	6.2
HSO	-44.5	-44.9	N/A
HSOH	-13.2	-15.3	11.3

Nitromethane regeneration

After all considered nitromethane interactions there is formed a product of hydrogen addition to nitromethane. We considered futher destiny of the product and we found a way of its utilization with acompanied formation of nitromethane molecule. The scheme of interaction leading to this way is shown at Fig. 4.

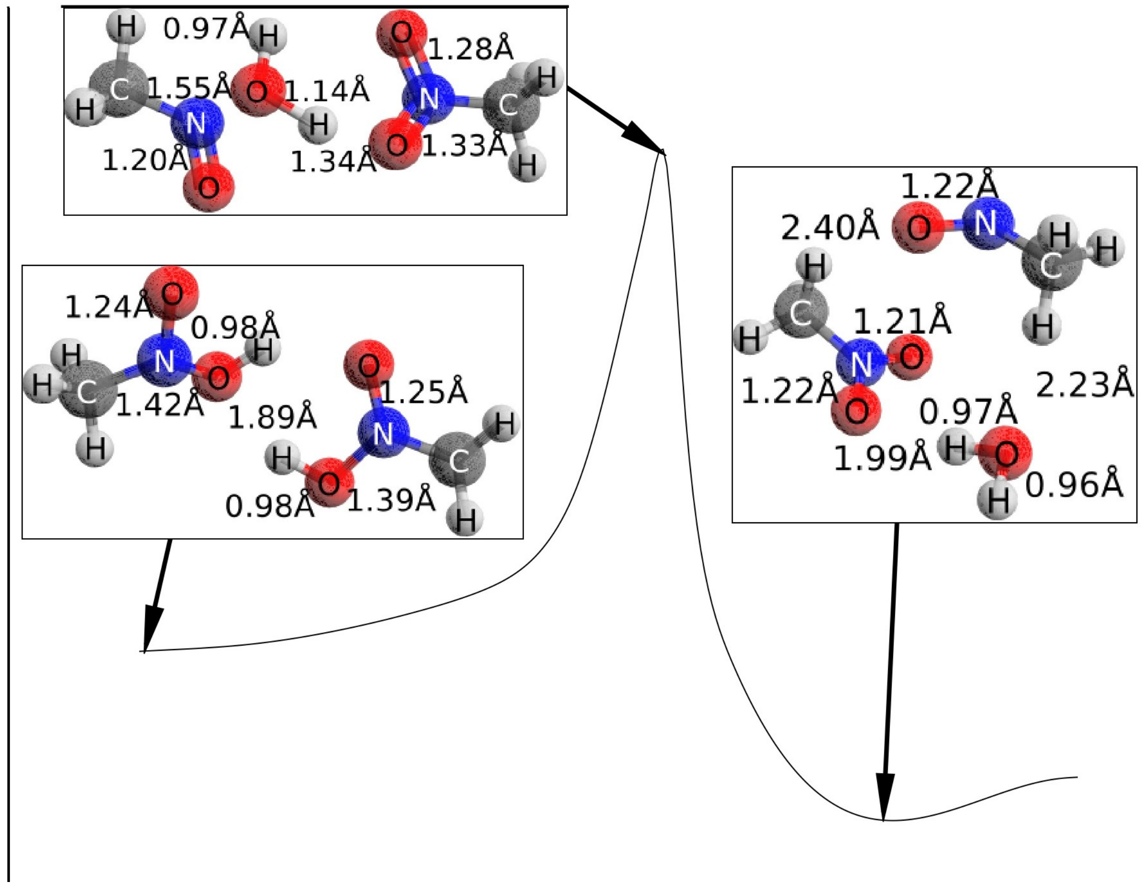

Fig. 4: The scheme of the nithromethane regeneration stage. Distances shown are (O-H) and (N-O) bond lengths and minimal distances between molecular fragments. Curve is nominal.

The regeneration reaction is allowed thermodinamicaly because of Gibbs energy equals to -22.7 kcal mol^{-1}. Activation energy of the stage is 24.96 kcal mol^{-1} and its enthalpy equals to -18.79 kcal mol^{-1}. Activation energy obtained is lower than obtained in [1] for other way of the nitromethane hydrogen addition product consumpion that causes considered stage will be more preferable interaction for the product. Spin density analysis showed nitromethane formed at the stage in the singlet state while nitrosomethane's multiplicity equals 3.

Conclusion

We have found new reaction ways showing a possibility of the nitromethane regeneration during the hydrogen sulphide photooxidation reaction. Regeneration of nitromethane may reduce amount of nitrogen-containing products of reaction as well as nitromethane consumption. Also, newly found stages may reduce amount of reaction steps needed to achieve the final products.

Reference

[1] D. A. Fomichev and S. V. Zelentsov, "Theoretical study of photochemical oxidation of organic sulfides and hydrogen sulfide in the presence of nitro compounds," *High Energy Chem.*, vol. 49, no. 2, pp. 104–110, Mar. 2015.

[2] M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, and W. A. de Jong, "NWChem: A comprehensive and scalable open-source solution for large scale molecular simulations," *Comput. Phys. Commun.*, vol. 181, no. 9, pp. 1477–1489, Sep. 2010.

[3] N. N. Greenwood and A. Earnshaw, *Chemistry of the elements*, 2nd ed. Oxford ; Boston: Butterworth-Heinemann, 1997.

[4] R. L. Benner and D. H. Stedman, "Chemical Mechanism and Efficiency of the Sulfur Chemiluminescence Detector," *Appl. Spectrosc.*, vol. 48, no. 7, pp. 848–851, Jul. 1994.