# Triplet-singlet intersection at hydrogen transfer stage in reactions of organic sulfides photooxidation

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## Abstract

Methanethiol and hydrogen sulphide photooxidation reaction pathways contain stages of hydrogen transfer, after which intersection crossing supposed to be to achieve singlet products of the reaction. While studying this stages no minimum was found at the point near reactants in the singlet state. At the same time there is a minimum in the triplet state. Moreover energy of reactants in the singlet state exceeds energy in the triplet state. That observation allows us to suppose intersection between the singlet and the triplet potencial energy surfaces at the hydrogen transfer stage. It may increase chance of the triplet-singlet transition. Calculation of the potencial energy surface profiles, sliced along with the hydrogen transfer path for both the singlet and the triplet states, performed with UB3LYP 6-311G++ (d) method of the density functional theory have showed both existence and reaction coordinate of intersection.

**Keywords:** quantum chemistry, nitrocompound, DFT, S-containing organical compound, intersection crossing, isc, sulphide

## Introducton

The mechanism of the sulphide photooxidation reaction considers [1] only questions of the radicals intercombination, but we did not focus on products of the reaction. The intermidiates of this reaction will not probably stay in the triplet state for a long time. There are some ways of the intermediates futher transformations [2]:

1. A clash with a wall that will lead to lose activity of radical
2. A reaction with other intermediates that was not observed in our work
3. The intersection crossing that will lead to change multiplicity

The third scenario may be useful for practical purposes because the last of observed triplet intermediates has a structure of stable compounds like ammonia and sulphur dioxide [3]. The possibility of the triplet-singlet conversion at last stages of photooxidation reaction will be investigated in this work using methods of quantum chemistry.

## Metodological part

To study the triplet-singlet conversion calculations of reaction paths at last process stages were performed by means of the North West Chemistry (NWChem) computational software [4]. The density functional theory UB3LYP 6-311G++(d) method was found to be suitable for this calculation for the same reasons mentioned our prevous work [1].

The scanning of PES along the reaction path is a *non*-trivial problem, that is why we used several approximations. In the first approximation only one atom is moved and in all considered cases that atom is hydrogen. All other atoms stayed frozen. The second approximation allows us to move atoms along path of the vibration with imaginary frequency for the reaction transition state. Exact reaction path can be obtained by the minimal energy path (MEP) module of NWChem [4] , but this type of calculation is not success in many cases. These approximations were compared with exact reaction path and they were shown at Fig. 1 for last stage of hydrogen transfer in hydrogen sulphide photooxidation reaction. The distance at the X axis label is the distance between nitrogen and hydrogen atoms highlighted by green at the geometry of transition state shown above curves at Fig 1.

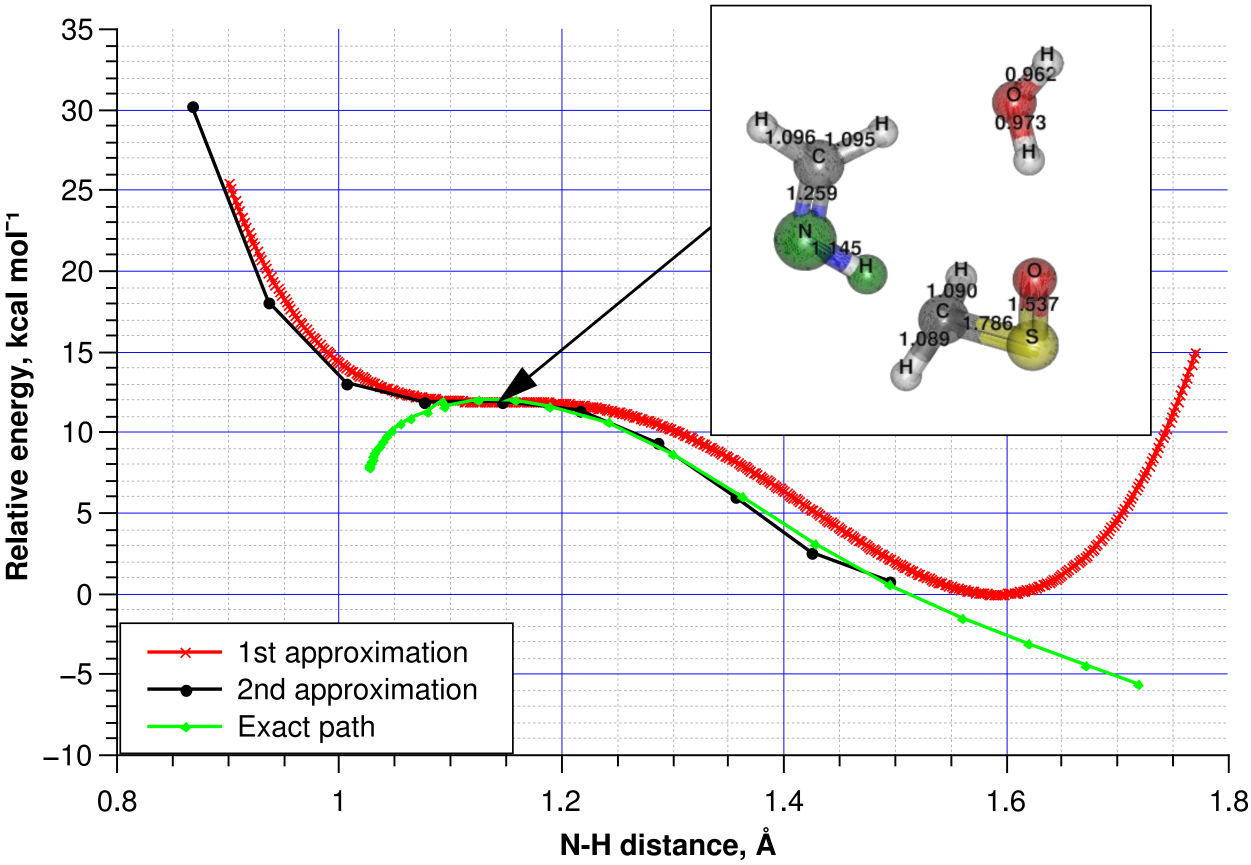

*Fig. 1: Comparsion between curves obtained from the approximations and the minimal energy path search*

At the Fig. 1 it is shown that curves of reaction path obtained by using the above-mentioned approximation looks similiar with exact reaction path curve near the transition state point and along with the right branch of curves. The difference at the left branch was caused by addition of new degree of freedom that separates two intermediates after hydrogen transfer and will not be taken into consideration. So we used the first approximation for futher calculation because it takes much less time and allows us to figure out a form of PES profile with enough precision.

## Methylamine and sulphur dioxide

The triplet and the singlet PES profiles plotted for hydrogen transfer in methylamine and sulphur dioxide formation are shown at Fig. 2. The distance between hydrogen and nitrogen is a distance between highlighted by green atoms on the intersection point geometry is shown at Fig 2.

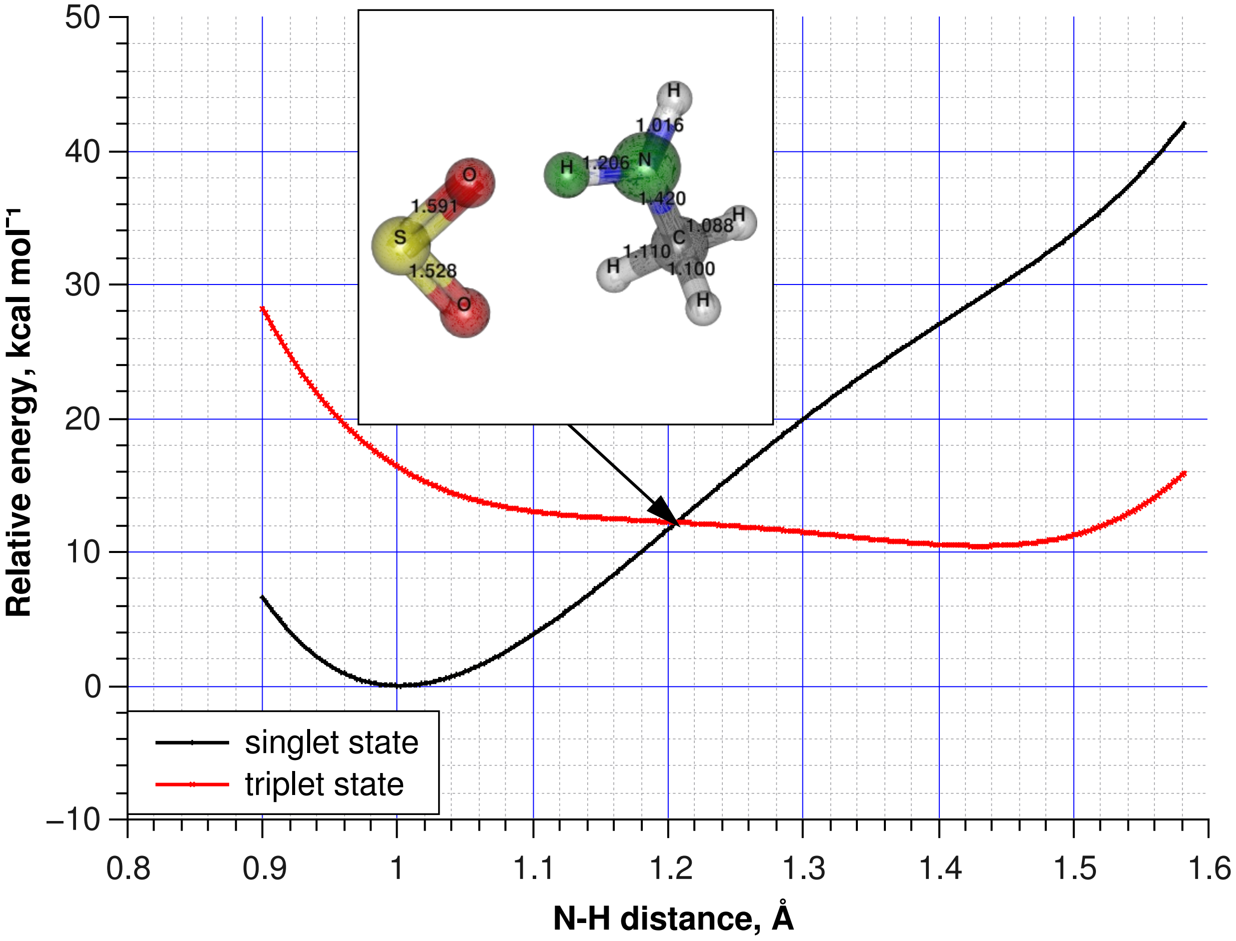

*Fig. 2: The triplet and singlet PES profiles for the hydrogen atom transfer in methylamine and sulphur dioxide formation*

The intersection between the singlet and the triplet PES profiles occurs when the distance between hydrogen and nitrogen becomes about 1.206 Å. In products formation process, reactants cross the intersection and after that they may change their multiplicity to the singlet state [5], [6]. The stage of products formation has low activation energy in both directions, that means that reaction system will move forward and backward crossing the intersection until change multiplicity.

## Methanimine and sulphinilmethane

In case of methanimine and sulphinilmethane there is no intersection found using first approximation. So, we used MEP procedure to obtain exact reaction path in the triplet state and calculated energy for obtained the singlet state geometries. Resulting PES profiles was shown at Fig. 3.

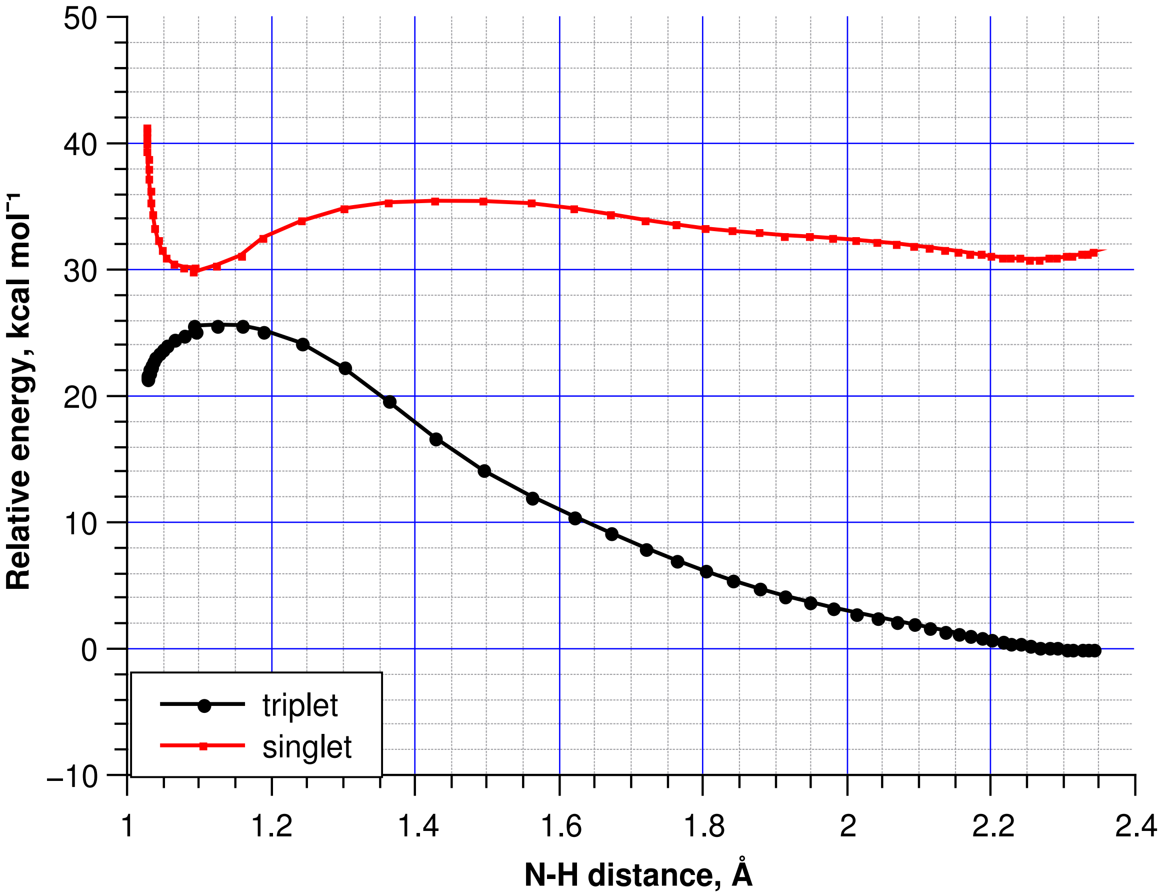

*Fig. 3: The triplet and singlet PES profiles plotted for the hydrogen atom transfer in methanimine and sulphinilmethane*

Indeed the MEP procedure has showed us that the triplet and singlet PES have no intersection along the hydrogen atom transfer reaction path. Moreover the singlet PES profile exceeds the triplet PES profile by energy, that means that these products are more stable in the triplet state and not liable to change multiplicity spontaneously.

## Dimethylamine and sulphur dioxide

For the case of dimethylamine and sulphur dioxide in the first approximation we obtained PES profiles shown at Fig. 4.

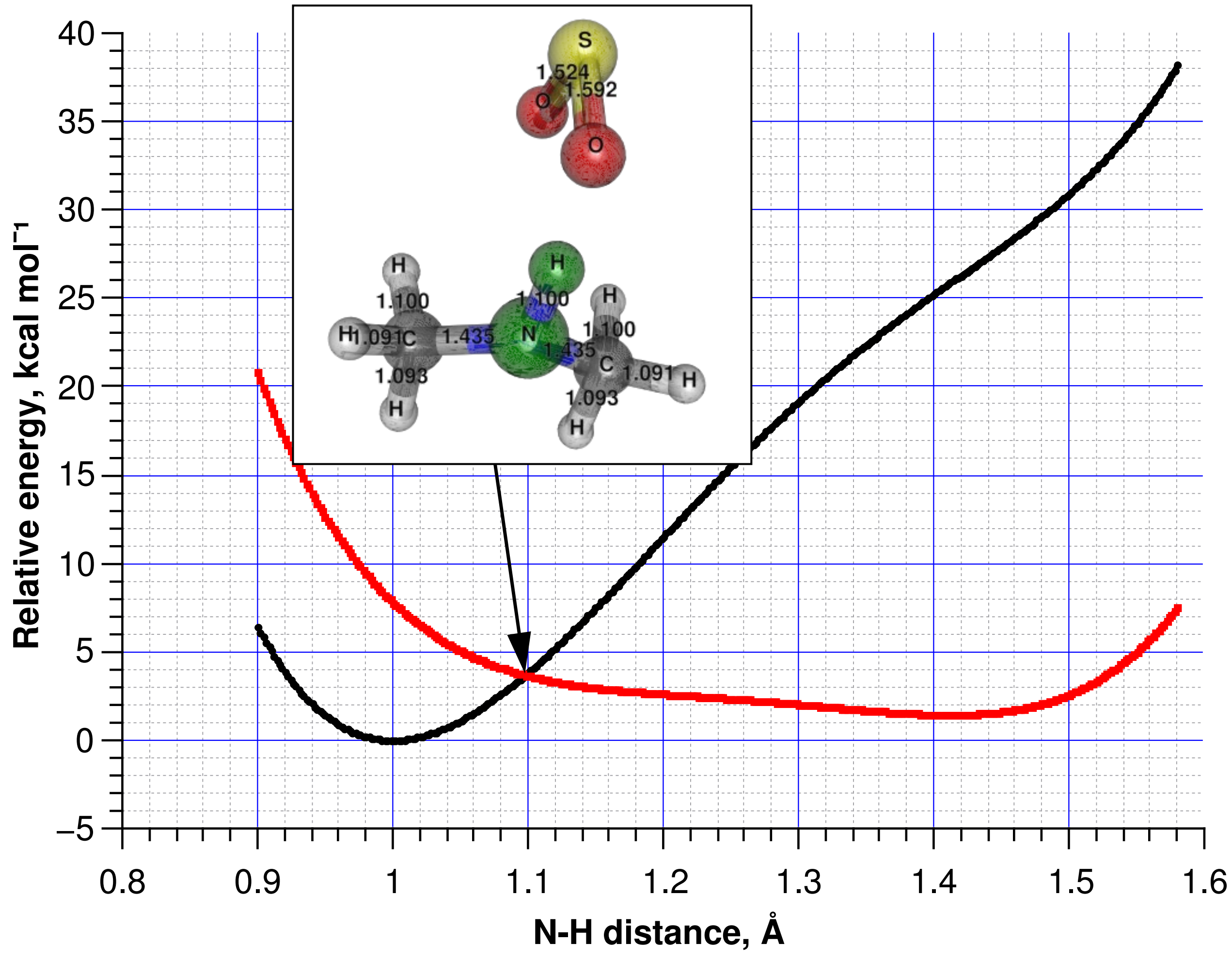

*Fig. 4: The triplet and singlet PES profiles for the hydrogen transfer in dimethylamine and sulphur dioxide formation*

There is an intersection at the geometry at N-H bond length of about 1.098 Å. Taking into account that the optimal N-H bond length for dimethylamine is 1.019 Å [7] , we can expect that the reaction system will cross the point of intersection when going down to the products valley. Unfortunately the MEP procedure fails when goes to this direction, and we can not be sure about achieving the point of intersection at this moment.

## Conclusion

Summarizing all cases considered in this work we can predict the chances of formation of disscussed products in the singlet state. We showed that methanimine and sulphinilmethane have a low chance to be formated during photooxidation of methanetiol by nitromethane. In contrast to the prevous case the chance of sulphur dioxide and dimethylamine formation looks high but for more accurate estimate an additional investigation is required because intersection point is far from the transition state of reaction and the used approximation gives a bad results for this kind of points.

Methylamine and sulphur dioxide also have a high chance to be gotten in the singlet state and in this case the estimation is more accurate.

## Acknowledgment

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