The quantum-chemical method selection for modeling of photochemical oxidation of sulfides by organic nitrocompounds

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Abstract: The search for the optimal level of theory has been performed to achieve the best correspondence of calculated values and experimental results for further quantum-chemical modeling of systems composed from sulfides and organic nitrocompounds in the triplet state. The reaction: $HS + NO_2 \rightarrow HSO + NO$ was selected as the model reaction. The standard enthalpy of this reaction calculated theoretically was compared with its experimental value known from literature. Such theories as DFT, UHF and ROHF and the following basis sets: 6-31++G**, 6-311++G**, aug-cc-pVDZ, were used for computations. XC functionals for DFT calculations are the following: b3lyp, bhlyp, pbe0, xpbe96_cpbe96.

Keywords: the triplet state, nitrocompound, sulfide, photochemistry, photooxidation, DFT, UHF, ROHF

Introduction

Hydrogen sulfide is one of the most common waste products of industrial chemical synthesis. At the moment there are no ways of useful utilization of hydrogen sulfide and its derivatives. The reason of this situation is that there are no experimental base that can be used to produce useful industrial ways of sulfur wastes utilization for its future reuse.

According to some literature information[1] it can be shown that organic nitrocompounds can interact to oxidize sulfur compounds in the triplet state as a result of a light irradiation. It is very difficult to conduct such experiments to study this phenomenon more directly, but we can computationally simulate all these reactions and make some conclusions.

The aim of this research is to find the most suitable level of theory for future quantum-chemical calculations of the reactions described above.

Results and Discussion

To achieve our aim we should find a reaction in which sulfur-containing molecule will interact with nitrogroup in an organic compound. Fortunately, we found information concerning the following reaction[2]:

$$HS\cdot + NO_2 \rightarrow HSO\cdot + NO$$

The standard enthalpy of this reaction is $\Delta H_f°_{298} = -26$ kcal·mol^{-1}. Then we calculated the standard enthalpy of the initial and the final states of this system and compared its difference with the standard enthalpy of the reaction. Results are shown in Table 1.

Table 1. Calculations results.

Method (and XC functional for DFT)	Basis set	$\Delta H_f°_{298}$, kcal·mol^{-1}	Theoretical deviation, kcal·mol^{-1}
DFT (b3lyp)	6-31++G**	-13.544	-12.456
	6-311++G**	-16.324	-9.676
	aug-cc-pVDZ	-13.587	-12.413
DFT (pbe0)	6-31++G**	-12.343	-13.657
	6-311++G**	-12.121	-13.879
	aug-cc-pVDZ	-13.445	-12.555
DFT (xpbe96_cpbe96)	6-31++G**	-8.742	-17.258
	6-311++G**	-9.088	-16.912
	aug-cc-pVDZ	-9.210	-16.790
DFT (bhlyp)	6-31++G**	unconverged	–
	6-311++G**	-20.265	-5.735
	aug-cc-pVDZ	unconverged	–
UHF	6-31++G**	-39.298	13.298
	6-311++G**	-37.802	11.802
	aug-cc-pVDZ	-38.318	12.318
ROHF	6-31++G**	-31.156	5.156
	6-311++G**	-30.645	4.645
	aug-cc-pVDZ	-29.731	3.731

All computations were performed by using North-West Chemistry software package[3].

First we should pay attention to the opposite signs of theoretical deviation values of DFT and HF methods calculation results. We can suppose that it is occurred because of difference in computation mechanism of these methods. But someone would have a question: if atoms of the system are located correctly according to the reaction formula. To verify this we can look at the Figure 1:

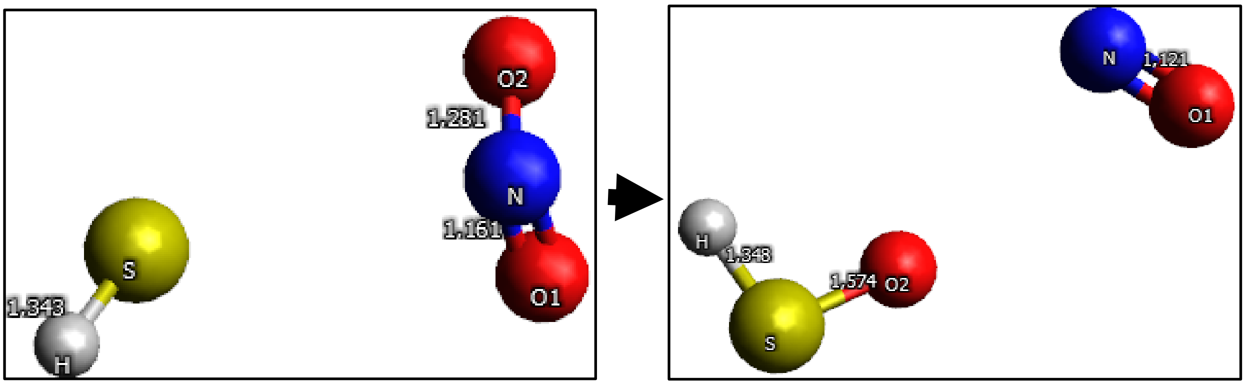

Figure 1. The initial and the final states of the system. Visualizations are made by using Avogadro software[4].

No doubts, system geometry is correct.

Now, let us examine the results in more details. The half of DFT (bhlyp, xpbe96_cpbe96) method calculation results are extremely unacceptable. For xpbe96_cpbe96 XC functional the error is about 17 kcal·mol^{-1}, for bhlyp the 2/3 of results are failed to converge but despite this the 6-311++G** basis set brought us one of the least theoretical error in this research: -5.735 kcal·mol^{-1} which is almost equal to the same values of ROHF's.

Another part of DFT functionals (b3lyp, pbe0) is more acceptable than results described above but still is not eligible for our aim. Also we can notice very interesting trend: all the unrestricted methods calculations in this research (this part of DFT's and UHF) have close in absolute value theoretical errors (~12–13 kcal·mol^{-1}), this fact is a strong argument for ineligibility of unrestricted methods using in modeling of such open-shell systems in the triplet state.

According to the information in the last row of Table 1, computations based on ROHF method are expectedly much more useful than any other computations performed during this research. Its theoretical error value is about 4-5 kcal·mol^{-1}. But its accuracy is not enough for complete quantum-chemical modeling of our system and all similar systems.

Conclusions

These results (Table 1) are quite unexpected. Theoretical deviation minimum of calculations is about 12 kcal·mol^{-1} in absolute value for DFT and UHF and about 3 kcal·mol^{-1} for ROHF. Hence we can conclude that such methods as DFT, UHF and ROHF are not eligible for computation of the open-shell systems composed from sulfides and organic nitrocompounds. So, it is necessary to continue our research with use of more accurate methods.

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