

“Effects of Sulfur on Fuel Nitrogen Conversion in Combustion”

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Abstract

Emission of pollutants in atmosphere is one of the big issues that researchers focus on today. The pollutants we will be focused on are NO or NO₂. In this paper we will be discussing the influence of sulfur on NO emission. This experiment is done using computational chemistry which is a field of chemistry that chemists use to solve chemistry problems. Computational chemistry will help us determine how sulfur affects the NO emission to the atmosphere. So, we will compute many reactions and run the jobs by means of computational chemistry in order to figure out which reaction is susceptible to happen after finding the changes in enthalpies of the reactions.

Introduction

Nowadays, there are many pollutants in atmosphere that are very toxic, that is why their emission needs to be controlled or reduced. They are responsible for an increase in acid rain and photochemical smog, they also increase the tropospheric ozone levels. Some of these pollutants are nitrogen oxide, dioxide and trioxide (NO, NO₂, NO₃). These NO_x have multiple origins including the NO_x from combustion, NO_x from motor vehicle exhaust and also from combustion in the engine. The NO_x is formed by reaction (bond formation) between nitrogen (N₂) and oxygen (O₂) in combustion, which is called oxidation. However, many researches try to find a way to reduce its emission or formation during combustion.

Many studies have been done on how to control the emission of NO and NO₂ into the atmosphere. According to Glarborg (2007), in combustion nitrogen fuels are oxidized to produce NO_x gases which are toxic and also represent greenhouses gases. Some studies found that, depending on the conditions under which the experiments are done, sulfur has an influence on the emission of NO_x in combustion.

Sarofim, Teare, and Tullin(1995) added NO to a gas and then burnt it, then the emission of NO₂ increased. However, when they added SO₂ the concentration of N₂O increased as well, but the concentration of NO was reduced. In this case, we can assume that the presence of sulfur in SO₂ has influenced the formation of NO.

The conditions of the experiments (combustion) also plays an important role in the control of NO_x emission. If there is more sulfur present, we can notice its effects on the NO_x emission. For example, experiment with coal will have relevant results because of the high content of sulfur in coal.

Others studies have been done regarding the influence of sulfur containing molecules on the formation of NO. Previous studies of S atoms reacting with nitrogen oxides include work on S + NO₂ by Clyne M.A.A. and Whitefield P.D. Ravichandran K., Richard W. and Fletcher T. in their paper entitled “Atmospheric reactions of vibrationally excited greenhouse gases: SH+N₂O(n, 0,0)” discussed the reaction of SH with N₂O. In their study they measured the emission by excited HSO, a product of the reaction of SH+ N₂O. They found that the rate constant of the reaction of SH+N₂O →HSO+N₂ is high meaning that the reaction is fast.

Herndon C., Froyd D., Lovejoy R., and Ravishankara A. did a study of the same chemistry as the previous group. They studied the rate of the reaction of SH with N₂O. In their study, two methods were used to detect SH radicals. The first one used a pulsed photolysis apparatus which they used to detect SH via laser-induced fluorescence and the second employed a flow tube where SH was detected via chemical ionization mass spectrometry. The first experiment they made was done using pulsed laser photolysis of H₂S to generate SH, and they found the rate constant (k₁) very small compared to the older value. Then, they measured the rate constant using another method that did not use photolysis to verify their first value of the rate

constant(k). They found that the value of the rate constant for the reaction of $\text{SH} + \text{N}_2\text{O} \rightarrow \text{HSO} + \text{N}_2$ is less than $5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. However, the group of Ravichandran K., Richard W. and Fletcher T. found the rate constant to be $k_1 = 1.3(\pm 0.14) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

My experiment consists of making reaction pathways using computational Chemistry which is based on a quantum mechanics analysis of energy changes as the molecules Collide and react. Basically, we write a possible reaction and we use computational chemistry to run some calculations in order to collect information like the changes in enthalpy of the reaction, the zero point energy, and the energy of the transition state in order to deduce the barrier. So, after collecting this information we can find out how fast the reaction proceeds.

Methodology

In our research we studied two reactions:

- 1) $\text{HS} + \text{N}_2\text{O} \rightarrow \text{HSN} + \text{NO}$
- 2) $\text{HS} + \text{N}_2\text{O} \rightarrow \text{HSO} + \text{N}_2$

From these two reactions we will try to figure out which one is exothermic because that will be the one we will focus on. We focus on the exothermic one because this reaction is fast and consequently is most likely to happen.

In this research, the energy optimization and frequency calculations were performed using the density functional theory (DFT) method called B3LYP which is known as one of the best method for this type of calculation. B3LYP was associated with the 6-311G** basis set. Then, from the geometry optimization and frequencies calculation we figure out the changes in enthalpy of the two reactions. I use two programs, Gaussian 09 to run my calculations and Gauss view that I use to build molecules and create my input files.

Then, we had to find the transition state for the reaction $\text{HS} + \text{N}_2\text{O} \rightarrow \text{HSO} + \text{N}_2$. So, we used the same method and basis set for accuracy purpose with `opt=(ts,calcall)` as keyword. The intrinsic reaction coordinate was then followed at the B3LYP/6-311G** level to confirm the transition state.

Results and discussion

I summarized the results for the change of enthalpy and Gibbs energy of both of my reactions in the table below: N₂OSH

Reactions	$\Delta H(298\text{K})$	$\Delta G(298\text{K})$
Reaction 1	262.6 kJ.mol ⁻¹	127.6 kJ. mol ⁻¹
Reaction 2	-376.9 kJ.mol ⁻¹	-187.4 kJ. mol ⁻¹

So, from this table we can notice that one reaction is exothermic and the other is endothermic. In our research, we are focused the exothermic reaction which is $\text{HS} + \text{N}_2\text{O} \rightarrow \text{HSO} + \text{N}_2$, because this is the one that can most likely happen. Also, we need to mention that these calculations of ΔH include the zero point energy (ZPE).

Below is the graph of our reaction showing the structures of the reactants, transition state and the products. Our reactants are N₂O and SH, at the transition state we observed that oxygen and sulfur are closer and the products are N₂ and HSO. We can see that the activation energy is 86.2 kJ/mol. In the product, we see that SH gets completely bonded to oxygen.

Graph of reaction (reactants, transition state and products)

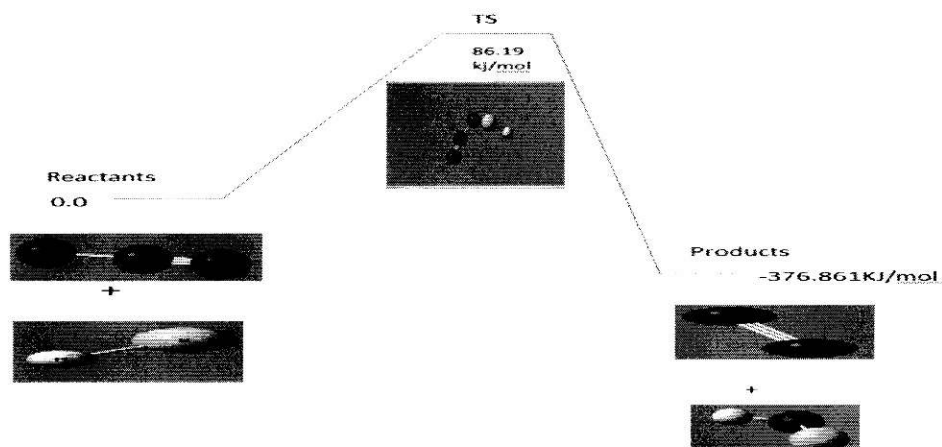


Figure 1

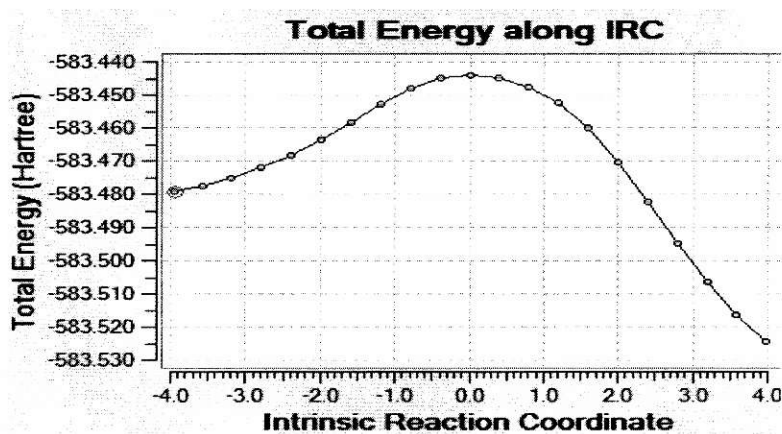


Figure 2

The tables below represent the coordinates of our different molecules including the reactants, transition state and products.

Input orientation of the transition state molecule:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	1.256225	0.182402	0.021523
2	7	1.949807	-0.698415	-0.018069
3	8	0.493871	1.095949	0.063395
4	16	-1.600917	-0.318843	-0.073064
5	1	-1.604399	-0.115303	1.262863

- **E(RB3LYP) in Hartree** = -475.543081304
- **Frequencies(cm^{-1}):** 435.0722, 594.606, 656.4212, 760.8459, 901.0212, 929.7628, 1757.8565, 3280.9152, 3338.7289,

Input orientation for nitrous oxide (N_2O)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.000000	0.000000	0.035892
2	7	0	0.000000	0.000000	1.162147
3	8	0	0.000000	0.000000	2.345961

- **E(RB3LYP) in Hartree** = -184.713284354
- **Frequencies (cm^{-1}):** -3.2994, -3.2994, 0.0004, 0.0009, 0.0009, 608.1066, 608.1066, 1336.9536 2355.1007.

Input orientation for SH

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	0.000000	0.000000	-0.021598
2	1	0	0.000000	0.000000	1.331598

- **E(UB3LYP) in Hartree** = -398.772115042
- **Frequencies(cm^{-1}):** -0.0057 -0.0047 -0.0029 60.7034 63.7140 2661.7728

Input orientation for HSO(hydrogen, sulfur and oxygen)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-0.084291	0.000000	-0.584596
2	16	0	0.456532	0.000000	1.515922
3	8	0	0.762252	0.000000	-0.116727

- **E(UB3LYP) in Hartree** = -474.001557782
- **Frequencies (cm^{-1}):** 810.4575, 1157.5805, 3757.5016, -64.2945, -45.6466, -38.7296 0.0014, 0.0015, 0.0028, 810.4577, 1157.5813, 3757.5016.

Input orientation for dinitrogen (N₂)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.000000	0.000000	-0.001721
2	7	0	0.000000	0.000000	1.093721

- **E(RB3LYP) in Hartree = -109.555930156**
- **Frequencies (cm⁻¹): -7.0264 -7.0264 -0.0006 -0.0006 0.0005, 2447.5326**

Input orientation for HSN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-0.116433	0.000000	-0.634178
2	16	0	0.474457	0.000000	1.431413
3	7	0	0.776469	0.000000	-0.118435

- **E(RB3LYP) in Hartree = -453.507385916.**
- **Frequencies (cm⁻¹): -11.0389, -1.5899, 0.0014, 0.0050, 0.0050, 32.6152, 1059.5615, 1233.5778, 3299.7728.**

Input orientation for NO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.000000	0.000000	-0.043757
2	8	0	0.000000	0.000000	1.104557

- **E(RB3LYP) in Hartree = -129.926702176**
- **Frequencies (cm⁻¹): -0.0005 0.0005 0.0006 17.9898 22.0165 1988.4446**

Conclusion

The protection of the environment from pollution is one of the main concerns today. That is why studies will always be done order to improve our environmental air. The main goal of my research is to find a way to reduce pollutants especially NO_x . So, in my research I am using sulfur to see if it can reduce the emission of NO_x . My research was done using computational chemistry.

In my research, I have been using B3LYP/6-311G** for calculations of geometry optimization and frequency. Also, the same basis set with the keyword `opt=(ts,calcall)` was used to figure out the transition. However, we tried the QST2 keyword but it did not work, so we used `opt=(ts,calcall)` instead. Further, we run an IRC calculation to confirm our transition state which worked well. Then, from the transition state we figured out the activation energy. However, the goal of this study is to see how sulfur can affect the nitrogen oxide emission. The figure 1 show the three steps reactants, transition state and product. From this graph we can notice how sulfur is getting closer to oxygen and finally get bonded to the oxygen leaving nitrogen dioxide alone. This is just a part of the research we are doing, so further works can be done in addition to what we already did. For example , the next step for this study can be to get improved energies for the molecules at the geometries I already have, by using more advanced methods such as "coupled cluster" theory, typically denoted CCSD(T), with basis sets larger than the 6-311G(d,p) I have used so far. After that one, I could compute the reaction rate through the transition state I discovered, using "Transition State Theory" sometimes called "Activated Complex Theory". Then, from the enthalpy for the transition state that yields the activation enthalpy, and the

geometry and frequencies can be used to calculate the activation entropy, in order to get the Gibbs energy of activation that in turn yields the rate constant.

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