Gaussian Homework

Advanced Reaction Engineering

September 4, 2013

Each group of 2-3 students are assigned one reaction for parts 1-4. We will be using the B3LYP method and 6-31G basis in Gaussian for all calculations.
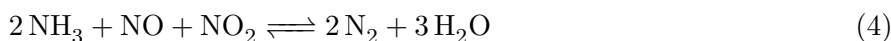
Part 1

NO Oxidation

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2 \tag{1}$$

Ammonia Oxidation

$$4\,NH_3 + 3\,O_2 \rightleftharpoons 2\,N_2 + 6\,H_2O \tag{2}$$

NO Selective Catalytic Reduction

$$4\,NH_3 + 4\,NO + O_2 \rightleftharpoons 4\,N_2 + 6\,H_2O \tag{3}$$

NO/NO$_2$ Selective Catalytic Reduction

$$2\,NH_3 + NO + NO_2 \rightleftharpoons 2\,N_2 + 3\,H_2O \tag{4}$$

1. For your assigned reaction perform an optimization+frequency calculation for each reaction species. A default temperature of 298 K will be used by Gaussian to compute the free energy, it is also possible to specify a different temperature. Record the energy, enthalpy, and gibbs free energy at 298K for each species and report these in a table.

2. Pick one of the gas species in your reaction. Take a picture of the optimized molecule and record any bond distances and angles on the picture. Also save an image of the molecule's IR spectra. Look up experimentally computed spectra and bond distances for the molecule. How do the calculated distances and spectra compare?

3. From your calculations in part 1 compute your reaction energy, enthalpy, and Gibb's free energy of reaction at 298K. Look up experimental data for your reaction. How well does the reaction energy compare to experimental data?

4. What is the equilibrium constant for your reaction? What does this tell you?

Part 2

5. Figure 1 contains the transition state geometry for

$$H_2NNO \longrightarrow TS_1 \longrightarrow HNNOH$$
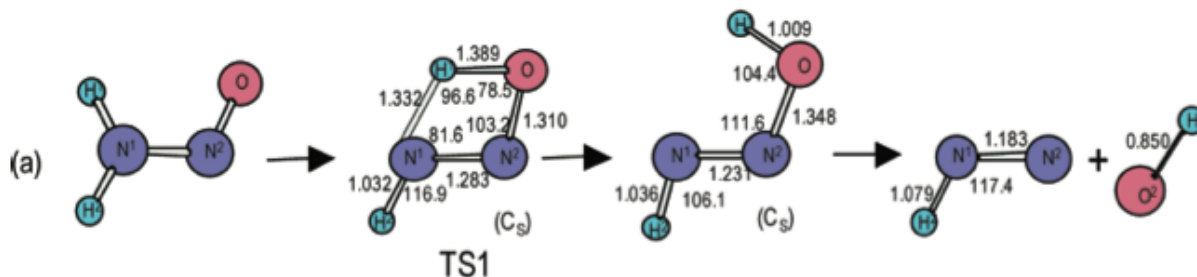
Do an opt+freq calculation for H$_2$NNO.

Figure 1: Sun, D., Schneider, W. F., & Adams, J. B. (2004). Molecular Origins of Selectivity in the Reduction of NOx by NH3 - The Journal of Physical Chemistry A (ACS Publications).

6. Build the TS1 geometry in Gaussian using the given information to make your initial guess structure (it is planar). Instead of doing a regular optimization we are going to try and find the transition state, which is a saddle in potential energy space rather than a minima. To perform this calculation change the entry in the Optimize To box from "Minimum" to "TS (Berny)". You will also need to change the Calculate Force Constants box to once. Run the calculation.

7. From the log files for the transition state and the reactant report the electronic and free energies.

8. Compute a free energy of activation at 298 K, $\Delta G^{\ddagger}$, by subtracting the the reactant free energy from the transition state free energy.

9. Calculate a rate constant at 298 K for this reaction.

10. Open the .log file of your transition state in Gaussian. Change the job type to IRC (Intrinsic Reaction Coordinate). This will link the transition state with its respective reactant and product. In the guess tab change to default. If anything is written in the additional keywords box delete it and hit update. Run the calculation.

11. Open the .log file for your IRC calculation after it finishes. To see the energy for going from reactant to the TS and then to the product open "IRC/Pathway" in the results menu. Take a picture of the product, reactant, and transition state along the IRC, and also the energy pathway.