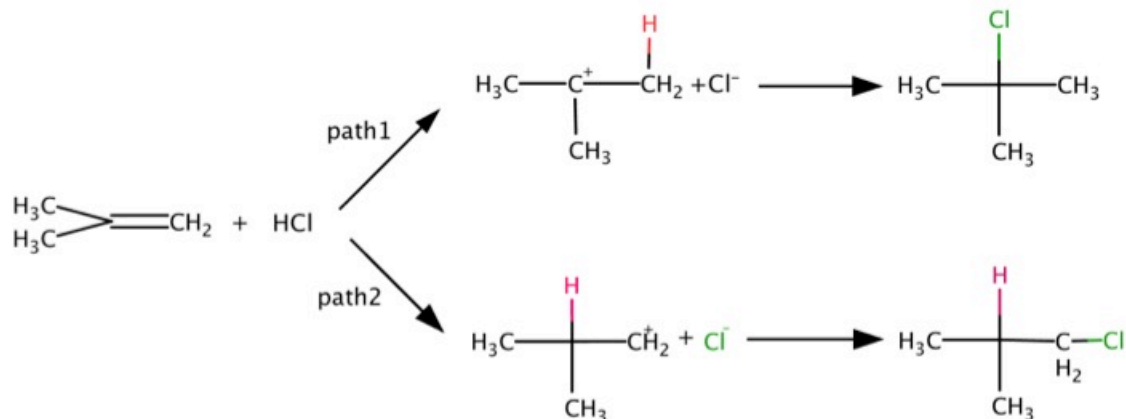


## Homework Assignment 4

Due @ 11:59pm Thursday 23th April by email [serdal@nyu.edu](mailto:serdal@nyu.edu) or to ERB 114

1. Water is one of the most intriguing molecules and has been the subject of many modeling studies. There are many water models for Molecular mechanics studies are using. SPC, TIP3P and TIP5P are among the many.
  - a. Find the parameters for this water models and calculate dipole moment and total energy of a single water molecule in vacuum for these models (energy unit kcal/mole).
  - b. Calculate the dipole moment and total energy from Ab-initio calculations using the methods: PM3, Restricted Hartree Fock with basis sets STO-3G and 6-31G(d, p). Compare your results with section a. Also compare your results with experiments for the dipole moment measurements in the gas phase.
  - c. Using the keyword *freq* calculate the IR spectra using the three Quantum methods given in b and compare your results for each vibrational mode and frequency. Don't forget to scale your energies for a fair comparison. Draw each vibrational mode with arrows using Avogadro for 6-31G(d, p). Compare your results for vibrational modes with experiments.
2. We will study the mechanism of electrophilic addition of Hydrogen-chloride to 2-methylpropene. The proposed reaction with two intermediate states and two different products are shown below. The first path leads to 2-chloro-2-methylpropane while the second path leads to 1-chloro-2-methylpropane.



- Calculate the energy of the Reactant, Intermediates and Products for the two paths using MMFF94s force field in Avogadro.
- Using the intermediate structures from MMFF94s perform minimization using Gaussian program with Hartree Fock Method with 6-31G(d, p) Basis set. Report the SCF energy for both intermediates. Which one is more likely to happen?
- Using population analysis (pop=Reg) keyword in your input calculate the electrostatic potentials and plot for the two intermediates using Avogadro. Also report the Mulliken charges for both carbocation at the intermediate states. From the point charges can you predict which intermediate is more likely for the  $\text{Cl}^-$  to attack?
- Calculate the minimized energies of the reactant and the intermediates and the products using Gaussian with the method and basis set in b. Convert energies to kcal/mole and compare energies with MM calculations. How good are MM estimates. Also calculate the relative populations of each final products at room temperature  $T=300\text{K}$ . (Hint:  $1\text{Hartree} = 4.3597482 \times 10^{-18} \text{ J}$  and  $627.509 \text{ kcal/mol}$ )
- Using the freq keyword in Gaussian calculate the thermochemical properties of the reactant, intermediates and products. Tabulate Enthalpy, Entropy and Free energy for each species.
- The rate of a chemical reaction in its simplest form is given by Arrhenius equation:

$$k = A \exp(-E_a / RT)$$

where, A is called the pre-factor and is in units of the overall rate of reaction.  $E_a$  is the activation energy or the minimum energy needed to climb the energy barrier to transition state  $E_a = E^* - E_0$  and  $E_0$  is the grand state energy of the reactant. Assuming the pre-factor to be the

same in two paths what is the ratio of the rate of path 1 to the rate of path2 ( $k_1/k_2$ )? (Use only Quantum calculations in this question)

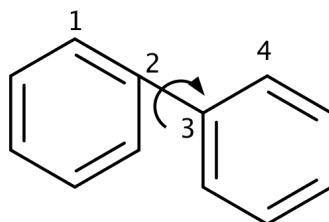
- g. A more accurate way of calculating the chemical rate is using Eyring equation, which is based on the transition state theory. The rate of a chemical reaction is:

$$k = \frac{k_B T}{c^n h} \exp(-\Delta G^* / RT)$$

where,  $c$  is the concentration with an exponent changing with the order of the reaction. For example if the reaction is a first order reaction  $n=1$ .  $\Delta G^*$  is the Gibbs Free Energy of activation  $\Delta G^* = G^* - G_0$ ,  $k_B$  is the Boltzmann constant,  $h$  is the Planck's constant and  $R$  is the gas constant,  $R = N_A k_B$ .

How do we know if it is first order or not?

Calculate the rate of the forward chemical reactions for each pathway at 1Molar solution and  $T=300K$ . Which reaction is faster? Which final product is more stable? Does it agree with your organic chemistry knowledge? (Hint: Markovnikov rule?)



3. We are studying the conformational transition of phenyl-phenyl ring.
- Create biphenyl molecule by Avogadro and minimize the structure. Show the minimized structure and report the dihedral angle between the phenyl rings (between atom indices 1,2,3 and 4.) Also report the minimum energy value. All by using MMF94s.
  - Optimize the structure using Gaussian with basis set 6-31G(p,d). Show the minimized geometry together with the dihedral angle and energy (in kcal/mole).
  - Using the Scan option in Gaussian, calculate the Potential Energy Surface for the dihedral angle for points  $[-180:180]$  with increments of 10 degrees. Check each point for energy convergence before

reporting. Ignore the points that did not converge or give infinity as energy value. Plot energy as a function of dihedral angle.

- d. Calculate the probability distribution of dihedral angle distributions in  $T=270\text{K}$ ,  $300\text{K}$  and  $400\text{K}$  and plot on a same graph for comparison. Discuss how it is changing.
- e. Plot the average torsional angle as a function of Temperature for  $T=270\text{K}$  to  $400\text{K}$  with  $dT=1\text{K}$ . How is your result for  $300\text{K}$  compares with your minimized geometry value? How does it compare with experiments?

*(Every question is 0.4 pts)*