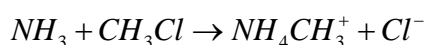


## Free Energy Change and Activation Barrier for a Menshutkin Reaction Including Effects of the Solvent

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### Overview

In this experiment, students will evaluate reaction free energies and activation free energies for a well known methyl transfer reaction in which the reactants are neutral species and the products are charged ions:



This reaction is quite endothermic in the gas-phase and exothermic in solution. The reaction proceeds through a SN2 type transition structure when in solution, but most likely a two-step process in the gas-phase. In order to correctly model the energetics of this system, one would need to take into consideration solvent effects. You will use the PCM model for solvation as implemented in Gaussian in order to calculate both the barrier and energy differences in water. You will then compare these to the computed gas-phase results and also to experimental values.

### Procedure

#### Building Molecules in CAChe

- NH<sub>3</sub>
  1. Select N atom from periodic table
  2. Click once in window
  3. Select **Beautify | Comprehensive**
  4. Save as “NH3.csf”
  
- CH<sub>3</sub>Cl
  1. Select C atom from periodic table
  2. Click once in window
  3. Select **Beautify | Comprehensive**
  4. Change one H to Cl
  5. Save as “CH3Cl.csf”
  
- NH<sub>3</sub>CH<sub>3</sub><sup>+</sup>
  1. Select C atom from periodic table
  2. Click once in window
  3. Click and drag from C to add another C
  4. Select **Beautify | Comprehensive**
  5. Change one C to N and change charge on N to +1
  6. Save as “NH3CH3.csf”

- Cl
  1. Select Cl atom from periodic table
  2. Change charge to -1
  3. Click once in window
  4. Save as “Cl.csf”
  
- NH<sub>3</sub>CH<sub>3</sub>Cl (transition structure)
  1. Select C atom from periodic table
  2. Click once in window
  3. Click and drag from C to add another C
  4. Select **Beautify | Comprehensive**
  5. Change one C to N
  6. Add Cl to opposite C by selecting Cl from periodic table and click and drag away from C
    - a. Click once on Cl, holding down Control, click on C and then N
    - b. Select **Adjust | Bond Angle**
    - c. Change Bond Angle to 180<sup>0</sup>
  7. Change bond length for C-N
    - a. Click once on C, holding down Control, Click once on N
    - b. Select **Adjust | Atom Distance**
    - c. Change Distance to 1.5
    - d. Set search from 1.4 to 2.7
  8. Change bond length for C-Cl
    - a. Click once on C, holding down Control, Click once on N
    - b. Select **Adjust | Atom Distance**
    - c. Change Distance to 1.6
    - d. Set search from 2.7 to 1.8
  9. Change angle of Hydrogens on the Carbon
    - a. Click once on H, holding down Control, Click once on the C and then on the N
    - b. Select **Adjust | Bond Angle**
    - c. Change Bond Angle to 90<sup>0</sup>
    - d. Repeat for other 2 Hydrogens
  10. Save as “TS.csf”

NOTE: These files will be the original structure files to begin each new experiment with. They will be opened and saved as a more appropriate name that distinguishes the experiment method.

### Modeling Equilibrium Structures

Follow the instructions below for each of the four equilibrium structures:

Filenames:    NH3.csf                    (replace *name* below with these)  
                   CH3Cl.csf  
                   NH3CH3.csf  
                   Cl.csf

1. Open the “*name.csf*” file.
  - a. **File | Save As** “*name\_PM5gas.csf*”
  - b. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: optimized geometry
    - iii. Using: PM5 geometry
  - c. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: IR transitions
    - iii. Using: MOPAC PM5 FORCE
  - d. Record the Free Energy for 298 K.
    - i. Select **Analyze | Chemical Properties Spreadsheet**.
    - ii. Then select the Thermodynamic Info tab at the bottom of the window.  
The Free Energy (energy\_au) is found here. Record the value for 298.
2. Open the “*name.csf*” file.
  - a. **File | Save As** “*name\_PM5water.csf*”
  - b. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: optimized geometry
    - iii. Using: PM5 geometry in water
  - c. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: IR transitions
    - iii. Using: MOPAC PM5 FORCE
  - d. Record the Free Energy as before.
3. Open “*name.csf*” file.
  - a. **File | Save As** “*name\_B3LYPgas.csf*”
  - b. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: optimized geometry
    - iii. Using: Gaussian B3LYP 6-31G(d)
  - c. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: IR transitions
    - iii. Using: Gaussian B3LYP 6-31G(d) at current geometry
  - d. Record the Free energy as before.
4. Open “*name.csf*” file.
  - a. **File | Save As** “*name\_B3LYPwater.csf*”
  - b. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: optimized geometry
    - iii. Using: Gaussian B3LYP 6-31G(d) in water
  - c. Select **Experiment | New**
    - i. Property of: chemical sample
    - ii. Property: IR transitions
    - iii. Using: Gaussian User-Defined Model in Gas

1. Select Edit
2. Double click on Run Gaussian Using Sample 1
  - a. Make sure Calculation Type is set to Vibrational Spectra
  - b. Set density functional method to B3LYP
  - c. Set basis set to 6-31G(d)
  - d. Under simulate solvent, method: PCM; solvent: water.
- d. Record the Free Energy as before.

After completing these steps on all the equilibrium structures, you now should have 16 Free energy values in all (4 for each):

1. Gas-Phase PM5
2. Solvated PM5
3. Gas-Phase B3LYP
4. Solvated B3LYP

### **Modeling the Transition Structure**

1. Open "TS.csf"
2. **File | Save As** "TS\_PM5.csf"
3. Select **Experiment | New**
  - i. Property of: reaction and transition states
  - ii. Property: map reaction
  - iii. Using: PM5 reaction coordinate (two labels)
  - iv. Click Start. Wait until the State option reports Done.
4. A window will open with a potential energy surface. A small window with your molecule will appear next to it.
5. Rotate the potential energy surface so that the curve looks like the energy diagram of the reaction. Make sure the reactants are on the left and products are on the right. Is this reaction endothermic or exothermic in the gas phase? Should the transition structure look more like the reactants or more like the products?
6. Next repeat steps 1 through 5, but this time use PM5 in water as the model. The results should look much different. We will use this to help construct a transition structure search in Gaussian.
7. In the potential energy surface window, switch to the select tool. Click in the region you would expect to find a transition state. The window on the right will display the structure of the molecule at that point on the surface.
8. Select the window with the transition state molecule displayed to make it active. Select **Edit | Copy**. Go to **File | New**. Select **Edit | Paste**. Save as "TS new."
9. Select **Experiment | New**
  - i. Property of: reaction and transition states
  - ii. Property: refine transition state
  - iii. Using: PM5 transition state geometry in water
  - iv. Click Start. Wait until the State option reports Done.

You have just obtained the transition structure using the PM5 Theory including the effects of the solvent. The next step will refine this structure using Gaussian.

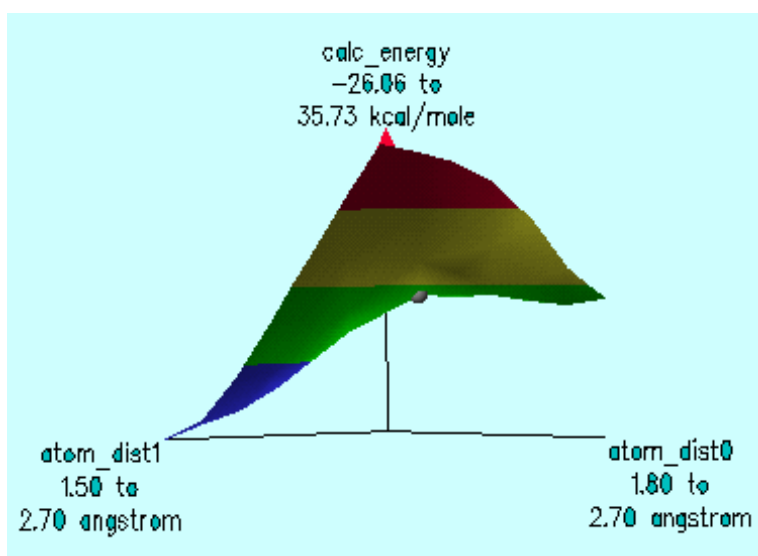
10. Select **Experiment | New**
  - i. Property of: reaction and transition states
  - ii. Property: refine transition state
  - iii. Using: Gaussian User-Defined Model in Gas Phase
11. Select Edit
12. Double click on Run Gaussian Using Sample 1
  - i. Make sure Calculation Type is set to Transition State Search
  - ii. Set density functional method to B3LYP
  - iii. Set basis set to 6-31G(d)
  - iv. Under simulate solvent set: method to PCM, solvent to water
  - v. Under File I/O and Extra Keywords
    1. Delete "IOP(1/11=1)"
13. Click Start. Wait until the State option reports Done.
14. Record the Free Energy as before.

## Analysis

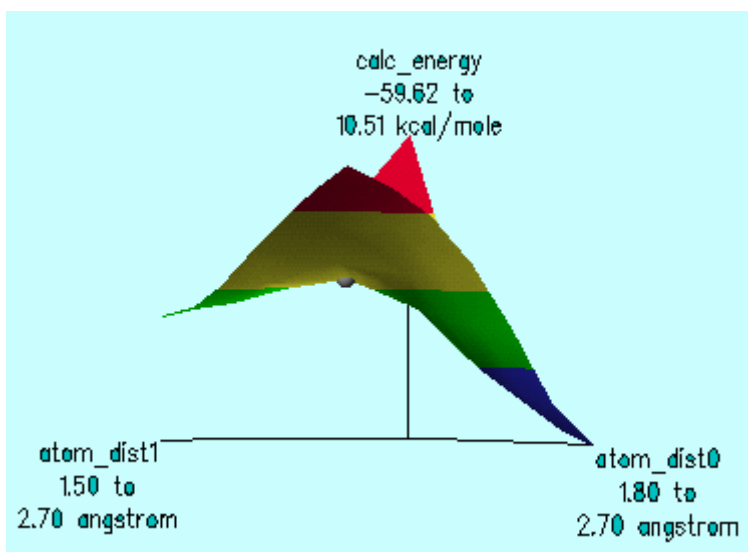
Collect together all of your Free Energy values and by subtracting reactant energies from product energies, create a summary table showing the change in free energy for the reaction as computed using the four models (PM5 gas, PM5 in water, B3LYP gas, and B3LYP in water). Now compute the activation energy for the reaction in solution using the Gaussian data in water alone (transition structure energy minus reactants). Compare your values to the experimental results that your instructor can provide.

## Instructor's Notes

Here are screen shots of the potential energy surfaces that the students will produce:



GAS-PHASE PM5 Surface



PM5 surface in water

The gas-phase surface shows the possibility of a transition structure very late in the reaction, but attempts to refine this structure using Gaussian would probably fail. It is more likely that the gas-phase reaction occurs by a two-step process. The PM5 surface in water is probably more realistic and can be used as a starting point for Gaussian calculations. PM5 energetics for the difference between reactants and products is quite good in this case. The activation energy and PES is less accurate than the B3LYP results. This makes sense because semi-empirical methods are largely parameterized for equilibrium structures and not transition structures.

Energetics of Menshutkin Reaction [kcal/mol]		
	$\Delta G_{\text{reaction}}$	$\Delta G_{\text{activation}}$
<i>Gas-phase</i>		
PM5	118	29
B3LYP	126	<i>unknown</i>
Expt <sup>1</sup>	110	<i>unknown</i>
<i>In Water</i>		
PM5	-28	13
B3LYP	-15	20
Expt <sup>1</sup>	-30	24

<sup>1</sup>Experiment involves CH<sub>3</sub>I not CH<sub>3</sub>Cl

## References

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