

# CEM 888 Lab/Homework

## Reaction Paths and Solvent Effects

### Wed. March 14, 2005; due March 30

This lab extends last week's study of the radical H-atom transfers by developing a picture of the reaction paths leading through the reaction. We will focus only on the unsymmetrical case, the one in which HO $\cdot$  abstracts H from CH $_4$ . There are four parts: (A) Reoptimization of the TS at the more chemically credible B3LYP/6-31G\* level; (B) calculation of the reaction path (the intrinsic reaction coordinate, or IRC) for the H-atom's motion through the reaction; (C) an exploration of how solvating this potentially polar (and polarizable) structure alters the geometry of the TS; and (D) optional extension to the higher alkanes. This latter step will entail "solvation" of the structures from (A) in low, medium, and high polarity "solvent" using SCRF methods. We will then examine the solvated TS structures and vibrational frequencies as a function of the solvent polarity. This study must be run in G98 as the B3LYP/6-31G\* method/basis set is used throughout, and reaction path and solvation methods, as used here, are only available in G98.

- A. Starting with the TS structure you obtained for HO $\cdot$  abstracting H $\cdot$  from CH $_4$  last week, you should reoptimize the TS at the B3LYP level via an input file for G98 using this command line:

```
#B3LYP/6-31G* opt=(TS,calcfc) freq
```

If you encounter failures due to the wrong number of negative eigenvalues of the hessian, you might need to make it `opt=(TS,calcfc,noeigentest)` but such jobs must be closely watched as they can wander off to never-never land very fast. An expensive, but usually successful alternative to "calcfc" is to use "calcall" which obtains an analytical hessian at every point, which means it's searching with the best possible local description of the PE surface.

Because you will also want to reuse the structural and force constant information you get, you should make a checkpoint file by including at the top of the input

```
%chk=yourfilename
```

- B. Now let's look at the IRC from the calculated TS to the two endpoints. In this case, there's not much ambiguity, but for more complex reactions, this exercise is a crucial test to identify (or confirm the identities of) the minima connected through this TS. Using your now optimized TS structure, make a job with the command line

```
#B3LYP/6-31G* geom=checkpoint irc=(calcall,maxpoints=20)
```

This will generate two sets of IRC points, following the reaction coordinate in the two directions away from the TS.

- C. Now we will solvate the TS structure you obtained in (A) using three solvents--water, acetonitrile, and dichloromethane--whose dielectric constants are 78.39, 36.64, and 8.93, respectively. The code words to use with "solvent=" are "CH $_2$ Cl $_2$ ", "acetonitrile", "water". Reoptimize the structures and obtain vibrational analyses. COPY your checkpoint file to a new name just as insurance; then you can use a new copy if you need to restart the solvation calculations. The checkpoint file is irrevocably changed by having been used in a new job. However, you can use your evolving checkpoint file to run more efficiently, if everything goes smoothly; since geometry/wavefunction changes in response to increasing "solvent polarity" tend to be small for low dielectric solvents and greater for the higher ones, it usually works best to go through the sequence in increasing polarity order (gas-phase) CH $_2$ Cl $_2$ , acetonitrile, water) rather than jumping into the water calculation from the gas-phase structure. Here is a sample command line to get you started:

```
#B3LYP/6-31G* geom=checkpoint scrf=(cpcm,solvent=CH2Cl2) opt=(ts,readfc)
```

Unfortunately, calculation of vibrational frequencies in "solvent" introduces two extra issues: (1) just adding the "freq" keyword fails because the program forgets to carry the solvation along, so you just end up with a "gas-phase" frequency job at the solvent-optimized geometry. So you need a separate frequency job after the "opt" job; here's a sample command line:

```
# B3LYP/6-31G* freq geom=checkpoint guess=read scrf=(cpcm,solvent=CH2Cl2)
```

(2) since G98 can't do analytical 2nd derivatives in "solvent," they have to be computed numerically, so this part can run a little slow. It will obtain frequencies, but trying to use "calcfc" (or worse, "call") in your optimizations above is a bust and even if you could trick it into doing them (maybe by using the "numer" keyword, for example) you would be waiting a long time. This is why it's worth it to work your way up to the higher solvent polarities using checkpointed structures, wavefunctions, and hessian matrices from the less perturbed runs.

To compute the solvent-modified  $E_a$  and  $\Delta H_{\text{reaction}}$  energies, you need endpoint energies in the appropriate "solvents." Get them using simple energy minimizations (not TS opts) for your separated species HO, CH<sub>4</sub>, H<sub>2</sub>O, and CH<sub>3</sub> and the endpoint vdW complexes HO...HCH<sub>3</sub> and HOH...CH<sub>3</sub> that you calculated in the previous problem set these reactions. Ideally you would simply modify the input file you used for your TS series to handle these six additional sets (be sure to remove the "TS"), which shouldn't take too long. You can string the jobs together with the --link1-- line if you don't want to do 6 structures x 3 solvents x 2 calcs (opt + freq) = 36 independent calculations.

- D. If you extended your efforts last time to the larger alkyl fragments (Et, I-Pr, t-Bu), you can experiment with the solvation of those TSs following the recipe above. I would recommend working up to it slowly as the bigger jobs can take a long time for the solvation calculations.

Reporting: The goal of these computational experiments is to look at the effects that solvent polarity have on TS barriers and structure. So summarize calculated geometries, energies, and vibrational frequencies of starting points, TSs, ending points, and dissociated fragments at the various levels described above. Of particular importance is to include and discuss the solvation energetics for your various structures, together with a look at the structural effects of ramping up the solvent polarity. Be sure, as in the last problem set, to include the final calculation summaries as an appendix in your report.

I know this problem set is a lot of work, but you begin to be able to see what kinds of details you can probe in thinking about a reaction's intrinsic nature and response to its environment. As with lab chemistry, a huge fraction of the work is just the process of assembling the needed reference data.