School on Kinetics and Dynamics of Chemical Reactions

Hydrogen abstraction reactions from ethanol (Practical Session)

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In this example we are going to study the H abstraction from ethanol by atomic hydrogen. There are three possible channels for this reaction:

$CH_3CH_2OH + H \rightarrow CH_3CHOH + H_2$ (Ra)
$CH_3CH_2OH + H \rightarrow CH_2CH_2OH + H_2$ (Rb)
$CH_3CH_2OH + H \rightarrow CH_3CH_2O + H_2$ (Rc)

Follow these steps:

1. Load the following modules: `module load cesga/2020 pilgrim/2021.5`

2. Go to the working directory: `EtOH`. This directory has two subdirectories: `/UDATA` and `/4-PLG-RST`; the former has all stationary points, while the latter contains the precomputed minimum energy paths.

3. `pilgrim --gather` transforms the electronic structure files inside `/UDATA` into files that can be used by Pilgrim.

4. `pilgrim --input` gives you access to an interactive menu to generate Pilgrim's input files.

5. After typing `pilgrim --input`:

a) `ls struc` lists all structures included en `/UDATA`.

b) To include the enantiomer of a given structure, just change the weight from unity to two. In the case of ethanol the weight of structure 001 can be changed by using `mod struc EtOH` and then `weight(001) = 2`. The same needs to be applied to transition states TSB and TSC that have structures with C1 symmetry. For instance, to change the weight of all structures with C1 symmetry, first we exit by writting `..` or `exit` in the command line, then we write `mod struc TSB`, and finally we write `weight(all) = 2`

c) `add temp 300 500 1000 2000` for performing calculations at T = 300, 500, 1000, and 2000 K. The temperatures are listed in `pif.temp`

d) The chemical reactions are added by typing:
```
add chem Ra: EtOH + H --> TSA --> H2 + PA
add chem Rb: EtOH + H --> TSB --> H2 + PB
add chem Rc: EtOH + H --> TSC --> H2 + PC
```
The resulting reactions can be listed with ls chem. This information is stored in `pif.chem`

e) By writing `add path` we indicate that we want to compute the minimum energy path (MEP) for the reactions. The program lists the interval in which the reaction coordinate is going to be computed for the three channels `[sbw,sfw]`, which is `[-0.500,0.500]` by default. We have precomputed the MEPs for the tree channels in the interval `[-2.000,2.000]`, so we have to modify the values of `sbw` and `sfw`. It can be done by

writing `..` or `exit` in the command line, then typing `mod path`, and finally writing `sbw = -2` and `sfw = 2`. This information is stored in `pif.path`

f) To exit the menu type `..` or `exit` in the command line

g) Notice that a file called `pif.calcs` is also created to indicate the electronic structure level at which we want to perform the MEP. In this case, everything has been precomputed at the HF/STO-3G level. However, in general this file needs to be modified by the user.

6. `pilgrim --pfn` generates the translational, rotational, vibrational and electronic partition functions of each stationary point. The information is kept in the directory `/3-PLG-OUTPUT`

7. `pilgrim --path` builds the MEP and calculates the variational and tunneling transmission coefficients (using the zero- and small-curvature approximations) at each of the selected temperatures. This information is stored in `/3-PLG-OUTPUT`.

8. `pilgrim --rcons` calculates the multi-structural transition state theory (MS-TST) rate constants, the multi-structural canonical variational transition state theory with small-curvature tunneling corrections (MS-CVT/SCT), and the multi-path canonical variational transition state theory with small-curvature tunneling corrections (MP-CVT/SCT). This information is stored in `/3-PLG-OUTPUT`.

9. It is now possible to run a kinetic Monte-Carlo (KMC) simulation. We enter the menu by typing `pilgrim --input` and write `add kmc Habs`, where `Habs` is the name of our KMC calculation. We exit the menu and the file `pif.kmc` is created.

10. We edit the file and change the rate constants that should be used by KMC from `tst` to `mpcvtsct`. Notice that rate constants obtained from the Ra reaction channel should be multiply by 2 [because there are two hydrogen atoms that can be abstracted but the resulting transition states are configurational (not conformational)]. Therefore, we substitute `k(Ra)` by `k(Ra)*2`. We change the variable `timeunits` to seconds (`s`). We assume an excess of ethanol molecules, so we change the population of ethanol to 1×10^{14} molecules and that of hydrogen radicals to 1×10^{6} molecules. To run the KMC simulation, just type `pilgrim --kmc`. The results are stored in `/3-PLG-OUTPUT`.

11. The user can analyze individual sets of data within the output. The syntax is shown by typing `pilgrim --help` summary. For instance, to list the TST thermal rate constants of reaction Ra, we use `pilgrim --summary rcons tst Ra`