

Kinetics 5.68 Assignment 2

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1 Background

1.1 Introduction

The calculations performed below were performed using a combination of PSI4[4] and Arkane, which is a part of the RMG software suite developed at MIT[3]. PSI4 was used to optimize the reactant, product, and transition state geometry, while Arkane was used to calculate the thermodynamic and kinetic parameters for the species involved.

1.2 Methods

Density functional theory (DFT) was utilized in the PSI4 calculations, using the B3LYP density functional and the 631g(d,p) basis set. DFT reduces the solution of the energy of a particular molecule or transition state to a function of, partially, the electron density. This allows a solution to the total energy to be found without requiring a solution to the many-electron wavefunction. DFT also implicitly uses the Born-Oppenheimer approximation. The rigid rotor harmonic oscillator (RRHO) assumption is also employed, which approximates that the rotation and vibration as separable, allowing us to decouple the rotational and vibrational energies and perform the following calculation for the partition function:

$$q = q_{trans}q_{rot}q_{vib}q_{elec}q_{nuc}$$

q = partition function for molecule

q_x = translation, rotation, vibration, electronic, or nuclear partition function

The electronic partition functions is often approximated as the energy of the lowest excited energy level. The nuclear partition function, for most chemical reactions, can be approximated as 1.

The partition functions can be used to calculate the equilibrium constant for each molecule, by taking the ratio of the partition function(s) of the products to the reactants. Rate constants are calculated by determining the modified

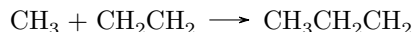
partition function of the transition state. for the modified partition function, we have one degree of freedom removed from our equation due to the freezing of our complex on a set reaction path (i.e. our path through the saddle point).

The pipeline for calculating the equilibrium constants and the reaction rates was as follows:

- in PSI4:
 - optimize the molecule to find the equilibrium geometry
 - compute the initial Hessian to get the first derivative of the potential well of our molecule/transition state
- in Arkane
 - feed the output from our PSI4 computations for each molecule and transition state into Arkane. This includes our atom energies and x-y-z geometries for the molecules/transition states.

2 Methyl Radical Reaction

The following reaction was analyzed using psi4 and arkane:



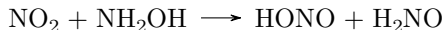
The following equilibrium constants and the reaction rates were calculated, and are shown below (units are in m^3 , mol, and s):

Rate/ K_c	Calculated Value	Literature Value[2]
Forward Rate (300K)	9.257	0.8112
Reverse Rate (300K)	4.912E-10	7.926E-10
Equilibrium Constant (300K)	1.884E10	N/A
Ratio of Methyl to Propyl radical (300K)	1.546E15	N/A
Forward Rate (1000K)	6.313E4	6850
Reverse Rate (1000K)	5.120E6	2.004E6
Equilibrium Constant (1000K)	1.233E-2	N/A
Ratio of Methyl to Propyl radical (1000K)	3373	N/A

There is quite a large discrepancy between the forward experimental rates and the literature values. In the arkane input, we did not calculate optical isomers or external symmetry for the molecules/TSS involved, and we did not explore additional transition states that exist due to the rotation of the methyl group. we also used a relatively cheap basis set, and we might have greater accuracy with a better set.

3 Hydroxylamine reaction

The following reaction was analyzed using psi4 and arkane:



The following equilibrium constants and the reaction rates were calculated, and are shown below (units are in m^3 , mol, and s):

Rate/ K_c	Calculated Value	Literature Value[1]
Forward Rate (300K)	1.155	3.4
Reverse Rate (300K)	1.354E-3	N/A
Equilibrium Constant (300K)	85.27	N/A
Forward Rate (1000K)	2976	N/A
Reverse Rate (1000K)	319.5	N/A
Equilibrium Constant (1000K)	9.315	N/A

Literature values were difficult to find for the experimental equilibrium constant and reaction rates, so unfortunately only the forward rate constant at 300k could be compared. For the forward rate, the estimate is off by a factor of 2, which could be due to the fact that we did not calculate optical isomers or external symmetry for the molecules/TSSs involved. Again, we also used a relatively cheap basis set, and we might have greater accuracy with a better set.

References

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