

Assignment #12 (Due Wed. April 21)

1. Using the accompanying diagram (Report the value you use for the energy barrier) and the equation from lecture calculate the Transition State Theory rate constant for the conversion of the boat form of cyclohexane to the chair form at (NOTE: Assume $\Delta E = \Delta G$):

- i. 100K
- ii. 300K
- iii. 600K
- iv. 1200K

From figure estimated barrier to be 7.333kcal/mol

$$k^{TST} = \frac{k_b T}{h} e^{-\frac{\Delta G^\ddagger}{k_b T}} \approx \frac{k_b T}{h} e^{-\frac{E_a}{k_b T}}$$

$$k^{TST} = \frac{(1.38 E - 23 J / K)(T)}{6.626 E - 34 J s} e^{-\frac{(7.333 kcal / mol)(41)}{}} \quad (1.3)$$

T	k
100	0.000192659
200	40062.57572
300	28257672.51
400	817011660.2
500	6468895657
600	26574961516
700	74675385145
800	1.65002E+11
900	3.09979E+11
1000	5.19091E+11
1100	7.98728E+11
1200	1.15254E+12

2. In PCModel:
- a. Build the boat form of cyclohexane (Choose 'Rings')
 - i. Choose 'Query' and click on 4 adjacent carbons then anywhere on the screen to display the dihedral.
 - b. Goto 'Compute' then 'Dynam'
 - i. Change the number of steps to 5000 and the initial temperature and bath temperature to 100 K.
 - ii. Run the molecular dynamics simulation

1. Observe any structural changes/dihedral angle changes during the run. Does the boat appear to convert to the chair at any time?

The chair has a dihedral angle of $\sim 56^\circ$ so this is what we will try and observe.

NO.

2. Erase the final structure ('Edit' then 'Erase')

- iii. Repeat the molecular dynamics simulation for 300, 600 and 1200K and note the temperature at which the conversion "readily" takes place.

At 300K it did convert to the chair once. Subsequent runs showed no conversion.

At 600K observed conversion after ~ 2000 fs and chair-boat conversion toward end of run. Subsequent runs showed similar behavior.

At 1200K most readily converted between two forms.

3.

- a. Assuming the rate constants in 1a tell us how many conversions take place per second compute how long between conversions at each temperature?

$K^{\text{TST}}(100\text{K})=1.9\text{e-}4$ /s, period = $1/k = 5263$ s between conversions

$K^{\text{TST}}(300\text{K})=4.01\text{e}4$ /s, period = $2.5\text{e-}5$ s between conversions

$K^{\text{TST}}(600\text{K})=2.66\text{e}10$ /s, period = $3.76\text{e-}11$ s between conversions or roughly 37,000 fs between conversions

$K^{\text{TST}}(1200\text{K})=1.15\text{e}12$ /s, period = $8.70\text{e-}13$ s or ~ 900 fs between conversions

- b. Would we observe the transition at lower temperatures by increasing the total simulation time? Explain.

Eventually, yes as the rate is a product of the frequency of attempts and the probability of success (exponential factor). However, we will have to wait on the order of $5.263\text{e}18$ fs for this to occur at 100K for instance.

