

Answers to Homework Set 9

From lecture 34: What is the rate constant at 298 K for a unimolecular reaction that has a free-energy of activation of 21 kcal mol<sup>-1</sup>? Now, rearrange eq. 34-4 so that all terms involving the variables  $t$  and  $[A]$  are on opposite sides of the equation. Integrate both sides from the starting point  $t = 0$ ,  $[A] = [A]_0$  to  $t = t'$ ,  $[A] = [A]_{t'}$  to obtain an expression for the concentration  $[A]_{t'}$  relative to the starting concentration  $[A]_0$  at any time  $t'$ . Using this equation, what is the half-life (the time required for  $[A]_{t'}$  to equal  $\frac{1}{2}[A]_0$ ) for a unimolecular reaction as a function of the rate constant  $k$ ? What is the half-life for the specific case of the unimolecular reaction having a free energy of activation of 21 kcal mol<sup>-1</sup> (which is about right for rotation about the C-N bond in an amide, for instance)?

We must evaluate

$$k = \frac{k_B T}{h} e^{-(G_{TS} - G_A)/RT}$$

for  $\Delta G = 21$  in units of kcal mol<sup>-1</sup>. In that case, we must express  $R$  in units of kcal mol<sup>-1</sup> K<sup>-1</sup> and our exponential is

$$e^{-(21)/(0.0019872 \times 298)} = 3.96 \times 10^{-16}$$

and we have

$$k = \frac{k_B T}{h} \times 3.96 \times 10^{-16}$$

using  $k_B = 1.3806 \times 10^{-23}$  J K<sup>-1</sup>,  $T = 298$  K, and  $h = 6.626 \times 10^{-34}$  J s, we derive  $2.46 \times 10^{-3}$  s<sup>-1</sup>.

The requested rearrangement of eq. 34-4 gives

$$-\frac{d[A]}{[A]} = k dt$$

If we integrate both sides over the indicated limits we have

$$\begin{aligned}
 -\int_{[A]_0}^{[A]_{t'}} \frac{d[A]}{[A]} &= k \int_0^{t'} dt \\
 -\ln([A]) \Big|_{[A]_0}^{[A]_{t'}} &= kt \Big|_0^{t'} \\
 \ln\left(\frac{[A]_0}{[A]_{t'}}\right) &= kt' \quad \left\{ \text{note } \ln\left(\frac{[A]_0}{[A]_{t'}}\right) = \ln([A]_0) - \ln([A]_{t'}) \right\}
 \end{aligned}$$

solving for the half-life time at which  $[A]_{t'} = \frac{1}{2}[A]_0$  we have

$$\begin{aligned}
 \ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right) &= kt' \\
 \ln 2 &= kt' \\
 \frac{\ln 2}{k} &= t'
 \end{aligned}$$

So, independent of starting concentration, the half life of a unimolecular reaction is the natural logarithm of 2 divided by the rate constant  $k$ . For the particular case of, say, an amide rotation having a barrier of 21 kcal mol<sup>-1</sup>, we can use the rate constant derived above to predict a half life of 282 seconds, or a bit less than 5 minutes.

From lecture 35:

Use the virial theorem (described in the solved homework of Lecture 16) to prove that since H<sub>2</sub> is bound (i.e., is lower in energy than two separated H atoms) then the kinetic energy of the electrons in H<sub>2</sub> must be greater than it is in two separated H atoms.

For any system we have

$$E = T + V$$

where  $E$  is the total energy,  $T$  is the kinetic energy, and  $V$  is the potential energy. For electronic structure problems, the virial theorem says that

$$V = -(2T)$$

If we make this substitution above, we have

$$E = -T$$

So, if total energy goes down (becomes more negative), then kinetic energy must increase. Since bonding is a situation where energy goes down, the point is proven.

Q.E.D.