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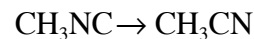
5.62 Physical Chemistry II
Spring 2008

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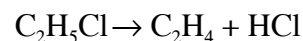
Rates of Unimolecular Reactions: RRKM

Consider a unimolecular reaction: $A \rightarrow \text{products}$

isomerization



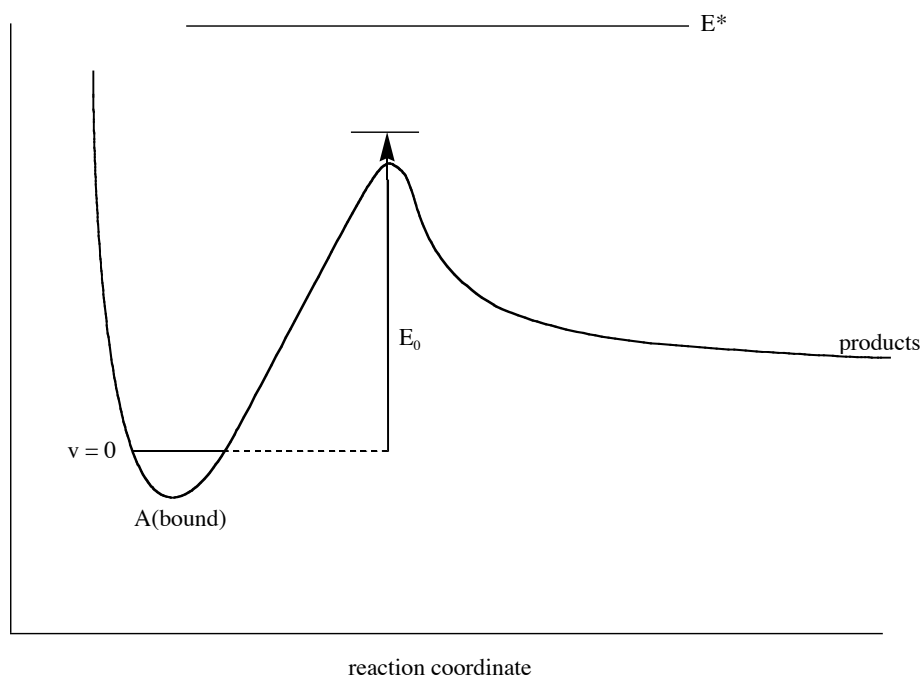
decomposition (with barrier to recombination)



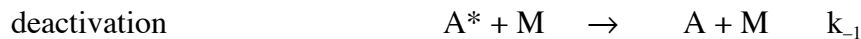
In order to occur, these reactions must overcome a barrier, E_0 . They can be activated to $E^* > E_0$ by collision, overtone pumping, infrared multiphoton excitation, optical excitation followed by Internal Conversion, or Stimulated Emission Pumping.

A molecule becomes activated, either by absorption of a photon or by a collision. The activated molecule has a *definite* E and J . If $E > E_0$, where E_0 is the energy of the zero-point-energy-dressed barrier for the *unimolecular* process:

We want to predict the rate of the reaction.



Standard mechanism (from 5.60)



irreversible decay into products $A^* \rightarrow \text{products}$ k_2

Steady state for A^*

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0$$

$$[A^*]_{ss} = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

$$\frac{d[\text{products}]}{dt} = k_{uni}[A] = k_2[A^*] = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2}$$

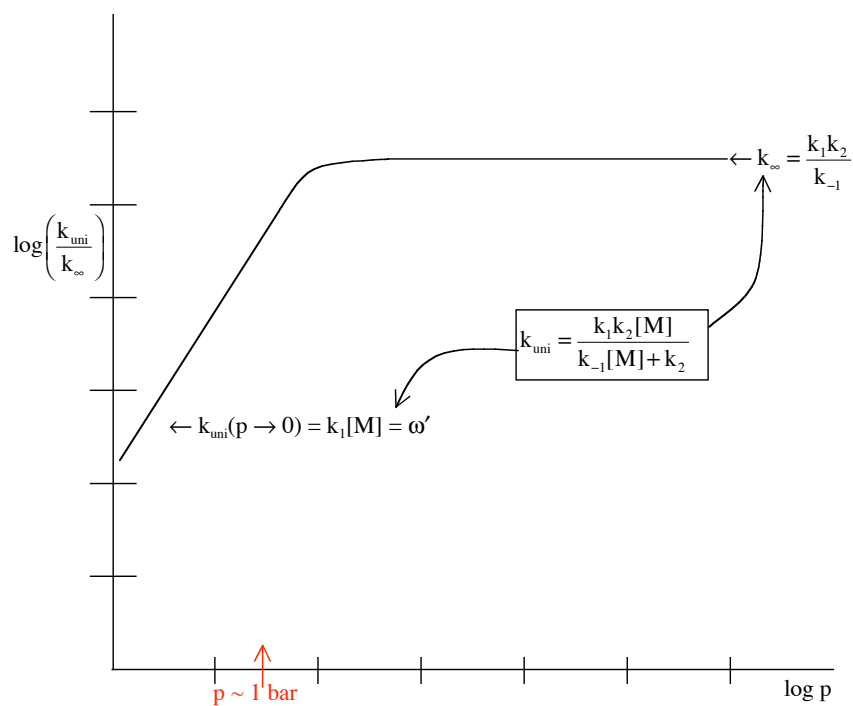
$$\therefore k_{uni} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2} = \frac{k_1 k_2 / k_{-1}}{1 + k_2 / (k_{-1}[M])}$$

use this form of k_{uni} below

“Unimolecular” rate is actually pressure-dependent.

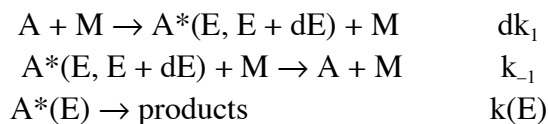
$$k_{uni}(p \rightarrow \infty) \equiv k_{\infty} = \frac{k_1 k_2}{k_{-1}}$$

$$k_{uni}(p \rightarrow 0) = k_1[M] \equiv \omega' \quad (\text{a collision frequency})$$



But A^* really is produced in a distribution of energies of activation and k_2 will be E-

dependent. We will have to integrate over E.

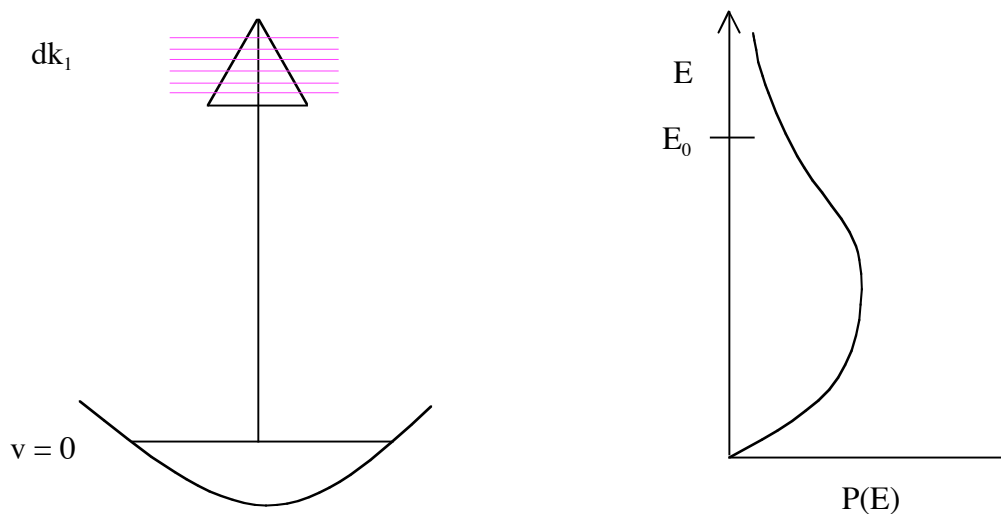


Assume that k_{-1} is *not* E-dependent. Thus

$$dk_{\text{uni}}(E, E + dE) = \frac{(k_2(E)/k_{-1})dk_1}{1 + k_2(E)/(k_{-1}[M])}$$

$$k_{\text{uni}} = \int_{E_0}^{\infty} \frac{k_2(E)(dk_1/k_{-1})}{1 + k_2(E)/(k_{-1}[M])}$$

The k_{-1} relaxation converts the E, E + dE region of activated states into a steady-state distribution of states P(E).



Replace dk_1/k_{-1} by $P(E)dE$ and replace $k_{-1}[M]$ (the deactivation frequency) by ω (different from $k_{\text{uni}}(p \rightarrow 0) \equiv \omega'$).

$$k_{\text{uni}} = \int_{E_0}^{\infty} dE \frac{k_2(E)p(E)}{1 + k_2(E)/\omega}$$

but since $k_2(E) = 0$ for $E < E_0$

$$k_{\text{uni}} = \int_0^{\infty} dE \frac{k_2(E)p(E)}{1 + k_2(E)/\omega}$$

At high pressure $\omega \rightarrow \infty$ and the integrand simplifies to

$$k_{\infty} = \int dE k_2(E)p(E)$$

How do we compute $k_2(E)$? **RRKM.**

Non-Lecture

Some notation.

$$E = E_+ + E_0 + E_{\text{active}}$$

E is total energy, E_0 is the energy of barrier (zero-point dressed), E_+ is the amount of energy not in the active mode, and E_{active} is the amount of above-barrier energy in the active mode.

We are doing a microcanonical calculation so we want to know how many energy levels there are at total energy E where $E_{\text{active}} \geq 0$, $W^{\ddagger}(E)$.

We want to compare this total number of states that will react to the total density of states at energy E . This ratio

$$\frac{W^{\ddagger}(E)}{\rho(E)}$$

has units $[\#]/[\#/E]$. If we divide by h , we get a quantity that has units of t^{-1} . $\frac{W^{\ddagger}(E)}{h\rho(E)}$ has the correct units for a unimolecular rate constant. Why h^{-1} ?

$$W^{\ddagger}(E) = \int_{E_+=0}^{E_+=E-E_0} dE_+ \rho^{\ddagger}(E_+)$$

When $E_+ = 0$, all of the energy is in the active mode. When $E_+ = E - E_0$, $E_{\text{active}} = 0$ thus there is no extra energy in the active mode. $\rho^{\ddagger}(E_+)$ is the density of states when there is energy E_+ in the $n - 1$ stable modes.

Thus we need to compute $\rho^{\ddagger}(E_+)$ and then integrate it to obtain $W^{\ddagger}(E)$. We also need to know $\rho(E)$.

A Simple model.

Assume all modes, including the active one, have the same frequency, ν .

There are s modes. s is an integer

$$E = jh\nu \quad j \text{ is an integer} \quad (\text{total energy})$$

$E_0 = mh\nu$ m is an integer (energy required in active mode to get over barrier)

want : $\frac{\text{probability that special oscillator has } \geq m \text{ quanta}}{\text{total \# of ways of distributing } j \text{ quanta}}$

How many ways can j indistinguishable quanta be distributed into s indistinguishable modes? Represent problem by dots \bullet and partitions $|$.

one \bullet for each quantum,
need j indistinguishable \bullet 's

for partitions between s modes, $|$,
need $s-1$ indistinguishable partitions

From combinatorics, we know

$$\Omega(j,s) = \frac{(j+s-1)!}{j!(s-1)!}$$

This is the number of energy states at $E = jh\nu$, thus

$$\rho(E(j))dE = \Omega(j,s)dj$$

$$\rho(E(j)) = \frac{dj}{dE} \Omega(j,s).$$

We want to derive both $W(E)$ and $\rho(E)$ from $\Omega(j,s)$. First we compute $W(E)$, which is a total number of states at or below E obtained by integrating the density of states

$$W(E) = \int_0^E dE' \rho(E')$$

thus

$$\rho(E) = \frac{dW}{dE} = \frac{dW}{dj} \frac{dj}{dE} = \Omega(j,s) \frac{dj}{dE}$$

$$\boxed{\frac{dW}{dj} = \Omega(j,s) = \frac{(j+s-1)!}{j!(s-1)!}}$$

Also, since $E = jh\nu$, $\frac{dj}{dE} = \frac{1}{h\nu}$.

So what is $W(E)$? Demonstrate that

$W(j) = \frac{(j+s)!}{j!s!}$ by showing that $\frac{dW}{dj}$ has the required value.

$$\begin{aligned} \frac{dW}{dj} &= \frac{W(j) - W(j-1)}{j - (j-1)} = \frac{W(j) - W(j-1)}{1} \quad \left(\begin{array}{l} \text{definition of} \\ \text{derivative} \end{array} \right) \\ &= \frac{(j+s)!}{j!s!} - \frac{(j+s-1)!}{(j-1)!s!} \\ &= \frac{(j+s)! - j(j+s-1)!}{j!s!} \\ &= \frac{(j+s)(j+s-1)! - j(j+s-1)!}{j!s!} \\ &= \frac{s(j+s-1)!}{j!s!} = \frac{(j+s-1)!}{j!(s-1)!} = \Omega(j,s) \end{aligned}$$

so all is well!

Now, use this simple model to compute $k(E) = \frac{W^\dagger(E)}{h\rho(E)}$.

Need m quanta in active mode, thus $j-m$ quanta in $s-1$ inactive modes.

s-1 modes
j-m quanta

$$W^\dagger(E) = \frac{(j-m+s-1)!}{(j-m)!(s-1)!}$$

s modes
j quanta

Now compare to j quanta in all s modes:

$$\rho(E) = \frac{1}{h\nu} \frac{(j+s-1)!}{j!(s-1)!}$$

$$k(E) = \frac{W^\dagger(E)}{h\rho(E)} = \nu \frac{(j-m+s-1)! j!}{(j-m)!(j+s-1)!} = \nu f(j, m, s)$$

≈ 1 in limit $j \gg m, j \gg s$

$k(E)$ is slower than the constant vibrational frequency for all modes, by the simple factor $f(j, m, s)$.

In the limit $s \gg j$ and $j-m \approx 1$ (near threshold),

$$k(E) \rightarrow \nu \frac{s! j!}{1!(s+m)!} \approx \nu \frac{j!}{s^{j-1}} \ll \nu$$

Improvements

all modes not equal frequency

Classical E

$$\text{Rabinovitch} \quad W^\ddagger(E) = \frac{(E + aE_{z.p.})^s}{s! \prod_{i=1}^s h\nu_i}$$

a is an empirical fudge factor

$$a = 1 - \beta w(E/E_z)$$

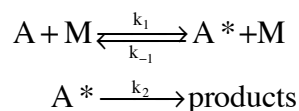
$$\beta = \frac{s-1}{s} \frac{\langle v^2 \rangle}{\langle v \rangle^2}$$

$$w = \left[5.00 \left(\frac{E}{E_z} \right) + 2.73 \left(\frac{E}{E_z} \right)^{1/2} + 3.51 \right]^{-1} \quad 0.1 < \frac{E}{E_z} < 1$$

$$w = \exp \left[-2.4191 \left(\frac{E}{E_z} \right)^{1/4} \right] \quad 1 < \frac{E}{E_z} < 8$$

Better Still: Beyer-Swineheart, Even better: direct count

Return to problem of computing $k_{\text{uni}}(T)$ from $k_{\text{uni}}(E, J)$.



Note that the energy in the activated complex is $E^\ddagger = E^* - E_0 = E_{\text{vib}} + E_{\text{rot}} - E_0$

$$k_{\text{uni}} = \int_0^\infty \frac{k_2(E^*)P(E^*)}{1 + k_2(E^*)/\omega} dE^*$$

$$E^* = E_{\text{vib}} + E_{\text{rot}}$$

$$P(E^*) = P(E_{\text{vib}})P(E_{\text{rot}}) = \frac{\rho(E_{\text{vib}})e^{-E_{\text{vib}}/kT}}{q_{\text{vib}}^*, A^*} \frac{\rho(E_{\text{rot}})e^{-E_{\text{rot}}/kT}}{q_{\text{rot}}^*, A^*}$$

$$k_{\text{uni}} = \int_0^\infty \int_0^\infty \frac{k_2(E_{\text{vib}} + E_{\text{rot}})P(E_{\text{vib}})P(E_{\text{rot}})}{1 + k_2(E_{\text{vib}} + E_{\text{rot}})/\omega} dE_{\text{vib}} dE_{\text{rot}}$$

Now evaluate $k_2(E_{\text{vib}} + E_{\text{rot}})$.