Rates of Unimolecular Reactions: RRKM Theory

Unimolecular Reactions

Detailed theoretical treatments are available for bimolecular (A+BC) reactions:
- Simple gas-kinetic collision theory
- Transition-state (absolute rate) theory
- Complete classical or quantum-mechanical reactive scattering calculations

What about unimolecular reactions (A→products) such as:
- Isomerization, e.g. CH₃NC → CH₃CN
- Decomposition, e.g. C₂H₅Cl → C₂H₄ + HCl

Theoretical treatment of unimolecular reactions is microcanonical transition-state theory

Excite A to A* (with energy E*)

If E* > E₀, A* → products

How does A acquire energy E*?

1. By collisions, A+M→A*
2. “Overtone pumping”, A+hν → A*
3. “Multiphoton excitation”, A+nhν (IR) → A*
4. Stimulated-emission pumping
(Optical pumping methods such as 2-4 were suggested by Perrin in 1919, but could not be realized until lasers became available)

“Classic” thermal activation mechanism for unimolecular reactions (Lindemann and Hinshelwood)

\[ A + M \rightarrow A^* + M \quad k_1 \]
\[ A^* + M \rightarrow A + M \quad k_{-1} \]
\[ A^* \rightarrow \text{products} \quad k_2 \]

Making steady-state assumptions on \( A^* \) (review your 5.60 notes!) yields:

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

\[
\frac{d[\text{products}]}{dt} = k_{uni}[A] = k_2[A^*] = \frac{k_1k_2[A][M]}{k_{-1}[M] + k_2}
\]

So the “unimolecular” rate constant is in fact pressure-dependent:

There really is a distribution of energies:
\[ A + M \rightarrow A^* (E, E+dE) + M \quad \text{dk1} \]
\[ A^*(E, E+dE) + M \rightarrow A + M \quad k_1 \]
\[ A^*(E) \rightarrow \text{products} \quad k(E) \]

Using same steady-state treatment as before,

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

\[ k_{uni} = \int_{E_0}^{\infty} k(E) \left[ \frac{dk_1}{k_{-1}} \right] \frac{1}{1 + k(E)/k_{-1}[M]} \]

\[ k_{uni} = \int_{E_0}^{\infty} k(E)p(E)dE \quad \frac{1}{1 + k(E)/\omega} \quad \text{where w is deactivating collision frequency} \]

(assume that all excess energy removed in one collision)

\[ = \int_{0}^{\infty} k(E)p(E)dE \quad \frac{1}{1 + k(E)/\omega} \quad \text{(because k(E) = 0, for E<E_0)} \]

Can we find k(E)?

YES - thanks to RRKM Theory
(O.K. Rice, H.C. Ramsperger, L.S. Kassel, and R.A. Marcus)

Assume \( A^* \rightarrow A^\dagger \) by converting some of \( E^* \) into potential energy \( E_0 \)

The remainder if \( E^\dagger \) (vib, rot)

\[ k(E) = \frac{1}{h} \frac{G(E^\dagger)}{N(E_{vib})} \]
\( G(E^\dagger) = \text{number of states in transition state with } E^\dagger = E^\dagger_{\text{vib}} + E^\dagger_{\text{rot}} \)

\( N(E_{\text{vib}}) = \text{density of states in } A^* \text{ with } E_{\text{vib}} = E^* \)

Then

\[
k_{\text{uni}} = \int_0^\infty k(E)p(E)dE \quad 1 + k(E)/\omega
\]

\[
= \int_0^\infty \int_0^\infty \frac{k(E_v + E_r)p(E_v)p(E_r)dE_vdE_r}{1 + k(E_v + E_r)/\omega}
\]

The distributions are

\[
p(E_v) = \frac{N(E_v)e^{-E_v/k_BT}}{q_{\text{vib}}^A}
\]

\[
p(E_r) = \frac{N(E_r)e^{-E_r/k_BT}}{q_{\text{rot}}^A}
\]

\[
k_{\text{uni}} = \frac{1}{\hbar q_{\text{vib}}^A q_{\text{rot}}^A} \int_0^\infty \int_0^\infty \frac{G(E^\dagger)N(E_r)e^{-(E_v + E_r)/k_BT}dE_vdE_r}{1 + k(E_v + E_r)/\omega}
\]

Transform energy scale to

\( E^\dagger = E^* - E_0 = E_v + E_r - E_0 \):

\[
k_{\text{uni}} = \frac{1}{\hbar q_{\text{vib}}^A q_{\text{rot}}^A} e^{-E_0/k_BT} \int_0^\infty \int_0^\infty \frac{G(E^\dagger)e^{-E_v^\dagger + E_r^\dagger/k_BT}dE_v^\dagger dE_r^\dagger}{1 + k(E_v^\dagger + E_r^\dagger)/\omega}
\]

Take limit as \( \omega \to \infty \) (high pressure, \( k_{\text{uni}} \to k_\infty \)): 
\[ k_\infty = \frac{1}{h q_{vib}^A q_{rot}^A} e^{-E_0/k_B T} \int_0^\infty N(E_r^+) e^{-E_r^+/k_B T} dE_r^+ \int_0^\infty G(E^+) e^{-E^+/k_B T} dE_v^+ \]

So

\[ k_\infty = \frac{k_B T}{h} q_r^+ q_{vib}^\ast e^{-E_0/k_B T} \]

**Summary of Unimolecular Rate Theory**

\[ k_{uni} = \int_0^\infty \frac{k(E) p(E) dE}{1 + k(E) / \omega}; \quad \omega = k_1[M] = Z_{AM} \]

\[ k(E) = \frac{1}{h N(E_{vib})} G(E^+); \quad E^+ = E - E_0 \]

\[ p(E) = \text{Boltzmann distribution}; \quad N(E) e^{-E/k_B T} / q \]

gives:

\[ k_\infty = \frac{k_B T}{h} q_r^+ q_{vib}^\ast e^{-E_0/k_B T} \]

That is, \( k_\infty \) has the form of a transition state theory rate constant:

RRKM theory is a microcanonical transition state theory

To get finer detail, such as \( k_{uni} \) in the fall-off region:

1. Need density of states \( N(E) \)
2. Replace \( k(E) \) with \( P(E,E') \)
3. "non-RRKM" behavior may be possible?
4. See recent textbooks such as W. Frost "Unimolecular Reactions" (Cambridge U.P., 2003) or Gilbert & Smith, "Theory of Unimolecular and Recombination Reactions" (Blackwell, 1990)