ChemE 2200 – Chemical Kinetics Lecture 9

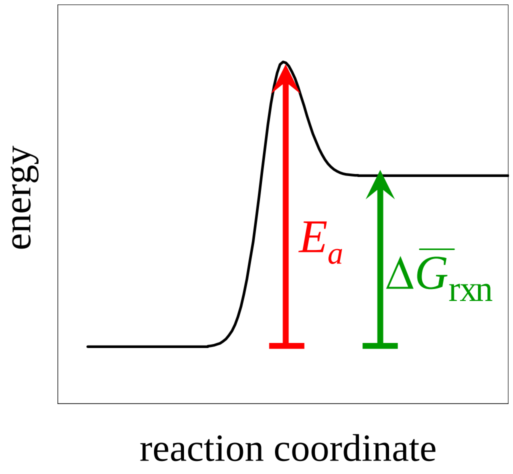
Today:

Chain Reactions:

The Rice-Herzfeld Mechanism

for the Dehydrogenation of Ethane

"How can E_a be less than $\Delta\overline{G}_{\mathrm{rxn}}$?"



Recap:

Our Goal

Given an overall reaction and its rate equation,
devise a mechanism of elementary steps, with specifications.

Example Specifications:

"Reaction 3 is the Rate-Limiting Step (RLS)."

"Steady-State Approximation on •OH."

"Pre-Equilibrium Approximation on Reaction 1."

Apply Occam's Razor:
"… as simple as possible, but no simpler." A. Einstein

Reading for Kinetics Lecture 10:

McQuarrie & Simon, Chp 15.8.

2^{nd} Prelim

Tuesday, April 15, 7:30 – 9:30 p.m.

245 and 128 Olin Hall

Covers –
Classical Thermodynamics

Covers –
- Thermodynamics Lectures 1 through 12.
- Homework Assignments 5 through 8.
- Calculation Sessions 5 through 8.

You may use a hand-written, double-sided reference sheet
and your annotated “Equations of Thermodynamics” lecture handout.

Bring a ruler or straightedge.

Our Goal

Given an overall reaction and its rate equation,
devise a mechanism of elementary steps, with specifications.

Our Plan

Gain experience through case studies.

Case Studies:

- Unimolecular Decomposition ⟵ Kinetics Lecture 8
- Chain Reactions ⟵ Today
- Photochemistry
- Polymerization
- Homogeneous Catalysis
- Heterogeneous Catalysis

Recap: Unimolecular Decomposition: The Lindemann Mechanism (1921)

$$M + F_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} F_2^* + M$$

$$F_2^* \xrightarrow{k_2} F\cdot + F\cdot$$

Assume steady-state approximation on activated complex F_2^*.

Rate Equation: $$-\frac{d[F_2]}{dt} = \frac{k_1 k_2 [F_2][M]}{k_2 + k_{-1}[M]} \approx \frac{k_1 k_2}{k_{-1}}[F_2]$$

Because $k_{-1}[M] \gg k_2$ for $P \geq 1$ atm.

For ChemE 2200, an acceptable elementary reaction is

$$F_2 \xrightarrow{k_1} F\cdot + F\cdot$$

Rate Equation: $$-\frac{d[F_2]}{dt} = k_1[F_2]$$

But $F\cdot + F\cdot \xrightarrow{k_1} F_2$ is forbidden.

Must use $M + F\cdot + F\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} F_2 + M$

The Dehydrogenation of Ethane to Ethylene

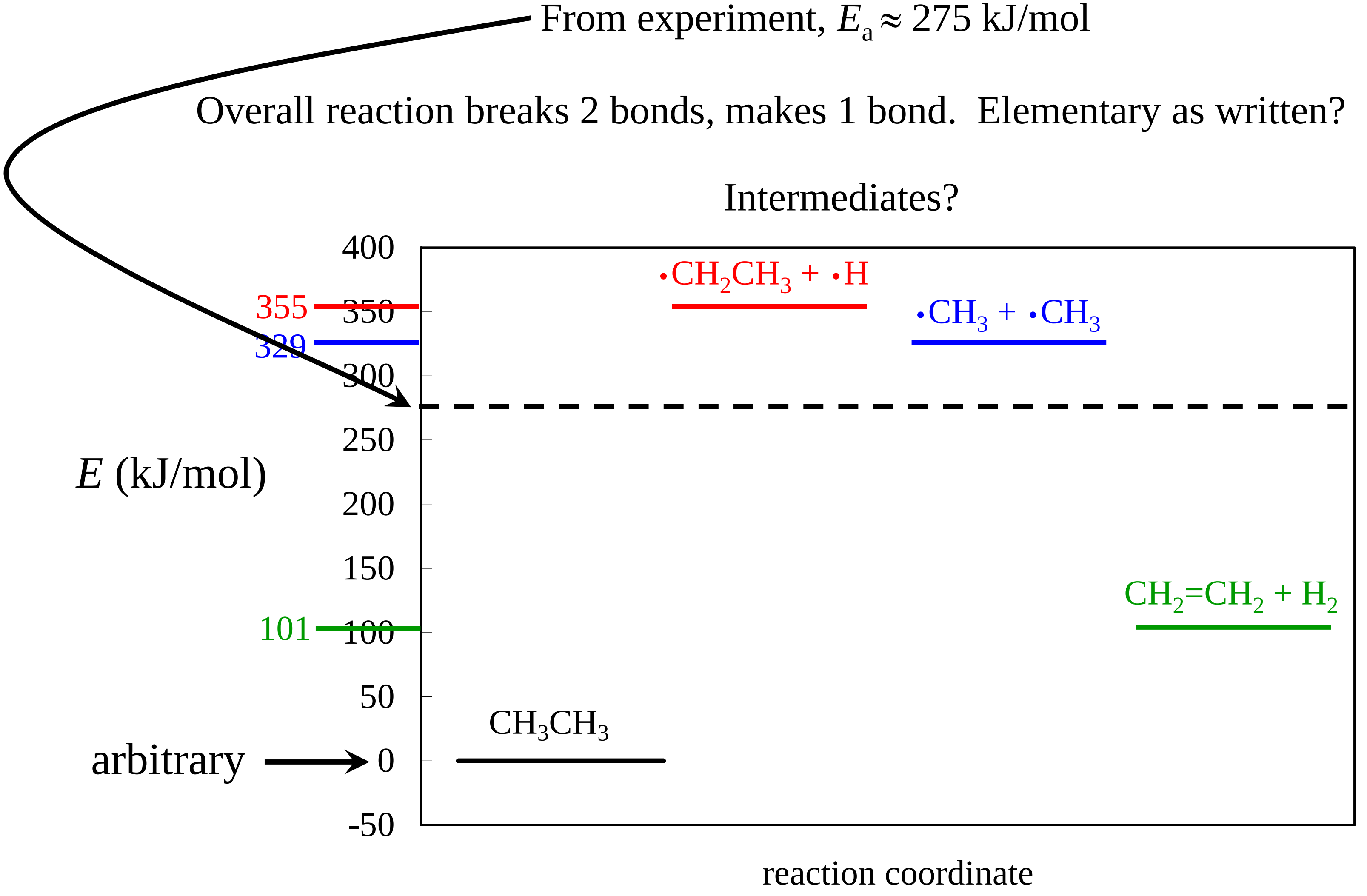
Overall Reaction: $CH_3–CH_3 \rightarrow CH_2{=}CH_2 + H_2 + CH_4$ (trace)

Observed Rate Equation: $$\frac{d[CH_2{=}CH_2]}{dt} = k[CH_3CH_3]$$

From experiment, $E_a \approx 275$ kJ/mol

Overall reaction breaks 2 bonds, makes 1 bond. Elementary as written? *Unlikely.*

Intermediates?



A trace amount of CH_4 by-product is detected. Source?

$\cdot CH_3$?

How can intermediates be at a level higher than E_a?

The Dehydrogenation of Ethane to Ethylene: The Rice-Herzfeld Mechanism (1934)

Overall Reaction: $CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 + H_2 + CH_4$ (trace)

number of rxn ‘events’						
A	B	C	elementary reaction	$\Delta\overline{G}^0_{rxn}$	E_a	reaction type
1	1	1	$CH_3CH_3 \xrightarrow{k_1} \cdot CH_3 + \cdot CH_3$	+329 kJ/mol	380 kJ/mol	initiation
2	2	2	$CH_3CH_3 + \cdot CH_3 \xrightarrow{k_2} \cdot CH_2CH_3 + CH_4$	–47	51	initiation
1	3	1,000,001	$\cdot CH_2CH_3 \xrightarrow{k_3} CH_2{=}CH_2 + \cdot H$	+153	170	propagation
0	2	1,000,000	$CH_3CH_3 + \cdot H \xrightarrow{k_4} \cdot CH_2CH_3 + H_2$	–52	~40	propagation
1	1	1	$\cdot CH_2CH_3 + \cdot H \xrightarrow{k_5} CH_3CH_3$	–354	38	termination

sum of rxns 3 & 4: $CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 + H_2$

sum is consistent with overall reaction -
no radicals produced
no radicals consumed

propagation rxns

This mechanism is a *chain reaction.*

$\cdot CH_3$ is an *initiating* radical.

$\cdot CH_2CH_3$ and $\cdot H$ are *propagating* radicals.

Mechanism is consistent with the trace amount of CH_4 produced (2nd initiation reaction).

The Dehydrogenation of Ethane to Ethylene: Propagation Cycle

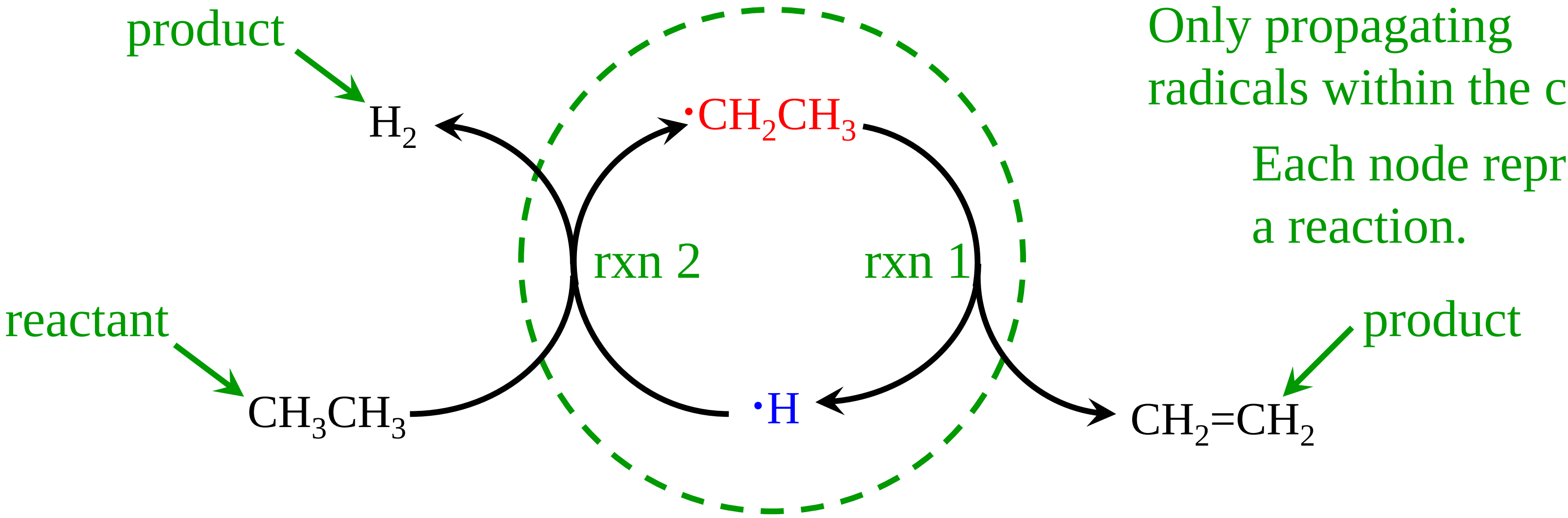
Overall Reaction: $CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 + H_2$

A useful visual is a *propagation cycle*.

Consider the two propagation reactions:

$$\cdot CH_2CH_3 \xrightarrow{k_3} CH_2{=}CH_2 + \cdot H$$

$$CH_3CH_3 + \cdot H \xrightarrow{k_4} \cdot CH_2CH_3 + H_2$$



product

H_2

$\cdot CH_2CH_3$

rxn 2

rxn 1

reactant

CH_3CH_3

$\cdot H$

$CH_2{=}CH_2$

product

Only propagating
radicals within the cycle

Each node represents
a reaction.

Overall mass balance consistent
with overall reaction:
only reactants in,
only products out.

The Dehydrogenation of Ethane to Ethylene: Analysis

Overall Reaction: $CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 + H_2$

$$
\begin{array}{rcll}
CH_3CH_3 & \xrightarrow{k_1} & \cdot CH_3 + \cdot CH_3 & \text{initiation} \\
CH_3CH_3 + \cdot CH_3 & \xrightarrow{k_2} & \cdot CH_2CH_3 + CH_4 & \text{initiation} \\
\cdot CH_2CH_3 & \xrightarrow{k_3} & CH_2{=}CH_2 + \cdot H & \text{propagation} \\
CH_3CH_3 + \cdot H & \xrightarrow{k_4} & \cdot CH_2CH_3 + H_2 & \text{propagation} \\
\cdot CH_2CH_3 + \cdot H & \xrightarrow{k_5} & CH_3CH_3 & \text{termination}
\end{array}
$$

From propagation reaction 1: $\dfrac{d[CH_2{=}CH_2]}{dt} = k_3[\cdot CH_2CH_3]$

Assume steady state on the total number of radicals. This yields two useful relations.

1. rate of initiation rxn(s) = rate of termination rxn(s)

$$
\left(\frac{d[\cdot CH_3]}{dt}\right)_{\text{rxn 1}} = \left(\frac{d[\cdot CH_2CH_3]}{dt}\right)_{\text{rxn 2}} = -\left(\frac{d\big([\cdot CH_2CH_3]+[\cdot H]\big)}{dt}\right)_{\text{rxn 5}}
$$

$$
2k_1[CH_3CH_3] = k_2[CH_3CH_3][\cdot CH_3] = 2k_5[\cdot CH_2CH_3][\cdot H]
$$

The Dehydrogenation of Ethane to Ethylene: Analysis

Overall Reaction: $CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 + H_2$

$$CH_3CH_3 \xrightarrow{k_1} \cdot CH_3 + \cdot CH_3 \qquad \text{initiation}$$

$$CH_3CH_3 + \cdot CH_3 \xrightarrow{k_2} \cdot CH_2CH_3 + CH_4 \qquad \text{initiation}$$

$$\cdot CH_2CH_3 \xrightarrow{k_3} CH_2{=}CH_2 + \cdot H \qquad \text{propagation}$$

$$CH_3CH_3 + \cdot H \xrightarrow{k_4} \cdot CH_2CH_3 + H_2 \qquad \text{propagation}$$

$$\cdot CH_2CH_3 + \cdot H \xrightarrow{k_5} CH_3CH_3 \qquad \text{termination}$$

From propagation reaction 1: $\dfrac{d[CH_2{=}CH_2]}{dt} = k_3[\cdot CH_2CH_3]$

Assume steady state on the total number of radicals. This yields two useful relations.

2. rate of propagation rxn 1 = rate of propagation rxn 2 = …

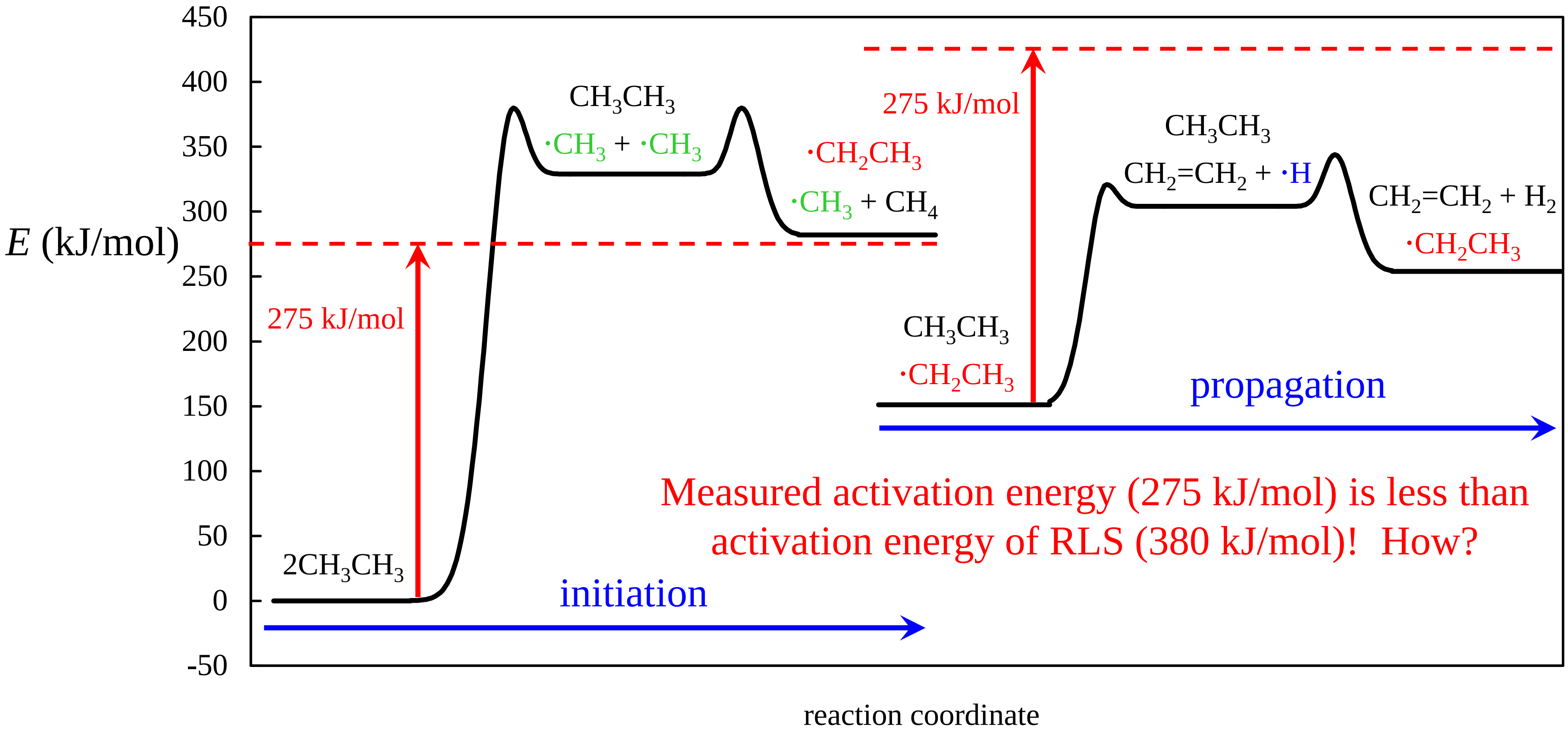
$$k_3[\cdot CH_2CH_3] = k_4[CH_3CH_3][\cdot H]$$

The two equations yield the rate equation: $$\frac{d[CH_2{=}CH_2]}{dt} = \left(\frac{\overset{\text{initiation}}{k_1}\overbrace{k_3 k_4}^{\text{propagation}}}{\underset{\text{termination}}{k_5}}\right)^{1/2}[CH_3CH_3]$$

Important Features of Chain Reactions - 1

Overall Reaction: $CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 + H_2$

From experiment, $E_a \approx 275$ kJ/mol



Measured activation energy (275 kJ/mol) is less than activation energy of RLS (380 kJ/mol)! How?

$$\frac{d[CH_2{=}CH_2]}{dt} = \left(\frac{k_1 k_3 k_4}{k_5}\right)^{1/2} [CH_3CH_3]$$

$$k_{\text{overall}} = \left(\frac{k_1 k_3 k_4}{k_5}\right)^{1/2} = \left(\frac{A_1 e^{-E_{a,1}/RT} A_3 e^{-E_{a,3}/RT} A_4 e^{-E_{a,4}/RT}}{A_5 e^{-E_{a,5}/RT}}\right)^{1/2}$$

$$k_{\text{overall}} = \left(\frac{A_1 A_3 A_4}{A_5}\right)^{1/2} \exp\left(\frac{\tfrac{1}{2}(E_{a,1} + E_{a,3} + E_{a,4} - E_{a,5})}{RT}\right)$$

$$E_{\text{a,overall}} = \tfrac{1}{2}(E_{a,1} + E_{a,3} + E_{a,4} - E_{a,5}) = \tfrac{1}{2}(380 + 170 + 40 - 38) = 276 \text{ kJ/mol}$$

Important Features of Chain Reactions - 2

Overall Reaction: $CH_3\text{–}CH_3 \rightarrow CH_2\text{=}CH_2 + H_2$

$$\begin{array}{rcll}
CH_3CH_3 & \xrightarrow{k_1} & \cdot CH_3 + \cdot CH_3 & \text{initiation} \\
CH_3CH_3 + \cdot CH_3 & \xrightarrow{k_2} & \cdot CH_2CH_3 + CH_4 & \text{initiation} \\
\cdot CH_2CH_3 & \xrightarrow{k_3} & CH_2\text{=}CH_2 + \cdot H & \text{propagation} \\
CH_3CH_3 + \cdot H & \xrightarrow{k_4} & \cdot CH_2CH_3 + H_2 & \text{propagation} \\
\cdot CH_2CH_3 + \cdot H & \xrightarrow{k_5} & CH_3CH_3 & \text{termination}
\end{array}$$

We assumed rate of initiation rxn(s) = rate of termination rxn(s) *Is this realistic?*

$$2k_1[CH_3CH_3] \overset{?}{=} k_5[\cdot CH_2CH_3][\cdot H]$$

$$E_{a,1} = 380 \text{ kJ/mol} \qquad E_{a,5} = 38 \text{ kJ/mol}$$

$$e^{-E_{a,1}/RT} = 10^{-33} \text{ at 600K} \qquad e^{-E_{a,5}/RT} = 5\times 10^{-4} \text{ at 600K}$$

The key is that $[\cdot CH_2CH_3]$ and $[\cdot H]$ are miniscule.

Assume $[\cdot CH_2CH_3] \approx [\cdot H]$

$$\Rightarrow [\cdot H] = \left(\frac{2k_1}{k_5}\right)^{1/2}[CH_3CH_3]^{1/2} \approx 10^{-15}[CH_3CH_3]^{1/2} \text{ at 600K}$$

Important Features of Chain Reactions - 3

Overall Reaction: $CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 + H_2$

$$\begin{array}{rcll}
CH_3CH_3 & \xrightarrow{k_1} & \cdot CH_3 + \cdot CH_3 & \text{initiation} \\
CH_3CH_3 + \cdot CH_3 & \xrightarrow{k_2} & \cdot CH_2CH_3 + CH_4 & \text{initiation} \\
\cdot CH_2CH_3 & \xrightarrow{k_3} & CH_2{=}CH_2 + \cdot H & \text{propagation} \\
CH_3CH_3 + \cdot H & \xrightarrow{k_4} & \cdot CH_2CH_3 + H_2 & \text{propagation} \\
\cdot CH_2CH_3 + \cdot H & \xrightarrow{k_5} & CH_3CH_3 & \text{termination}
\end{array}$$

We assumed steady state on the total number of radicals.

Apply the steady-state approximation to a specific radical?

$$\frac{d[\cdot CH_2CH_3]}{dt} = 0 = k_2[CH_3CH_3][\cdot CH_3] - k_3[\cdot CH_2CH_3] + k_4[CH_3CH_3][\cdot H] - k_5[\cdot CH_2CH_3][\cdot H]$$

relative rates: 2 1,000,001 1,000,000 1 ≈ 0

The assumption is valid, but less useful than …

rate of initiation = rate of termination $\Rightarrow$ $k_2[CH_3CH_3][\cdot CH_3] = 2k_5[\cdot CH_2CH_3][\cdot H]$

rate of propagation rxn 1 = rate of propagation rxn 2 $\Rightarrow$ $k_3[\cdot CH_2CH_3] = k_4[CH_3CH_3][\cdot H]$

Another Chain Reaction

Overall Reaction: $CH_3{-}C(O){-}CH_3 \rightarrow CH_2{=}CO + CH_4 + CO + CH_3CH_3$ (trace)

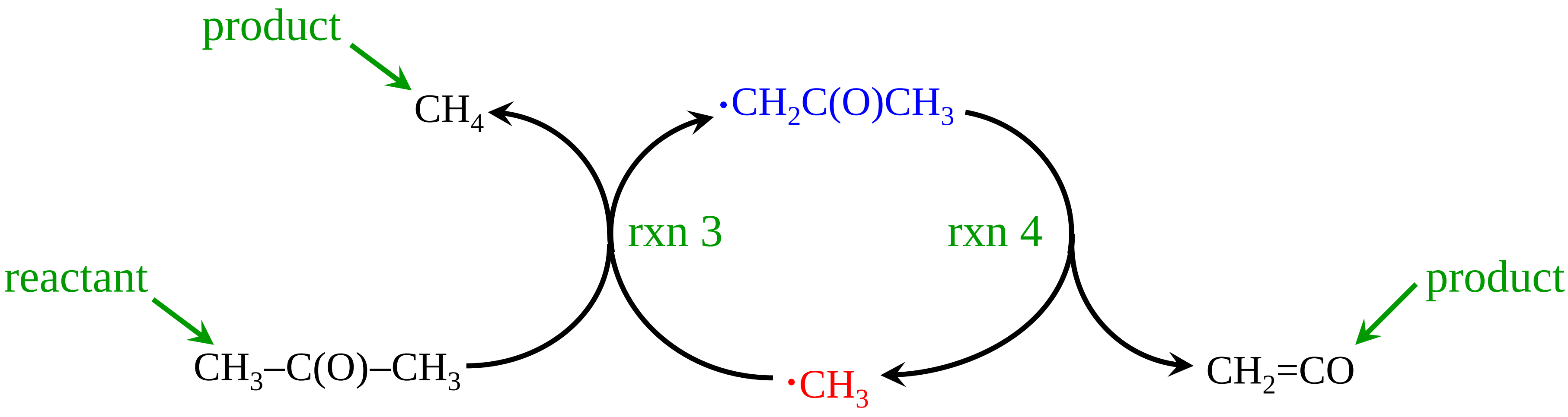
$CH_3{-}C(O){-}CH_3 \xrightarrow{k_1} \cdot CH_3 + CH_3CO\cdot$ initiation

$CH_3CO\cdot \xrightarrow{k_2} \cdot CH_3 + CO$ initiation

$CH_3{-}C(O){-}CH_3 + \cdot CH_3 \xrightarrow{k_3} CH_4 + \cdot CH_2{-}C(O){-}CH_3$ propagation

$\cdot CH_2{-}C(O){-}CH_3 \xrightarrow{k_4} CH_2{=}CO + \cdot CH_3$ propagation

$\cdot CH_3 + \cdot CH_3 \xrightarrow{k_5} CH_3CH_3$ termination



“*The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VI. The Mechanism of Some Chain Reactions,*” Francis Rice and Karl Herzfeld,
J. Am. Chem. Soc. **56**, 284 (1934).

Summary of Chain Reactions (to date)

All chain reactions comprise …

At least one initiation reaction

At least two propagation reactions

At least one termination reaction

Propagation cycles are useful visuals with …

Closed internal loops with only propagating radicals and intermediates within the loops.

Reactants entering the loops from the periphery.

Products and by-products leaving the loops to the periphery.

There are two key assumptions for chain reactions:

1. The rate radicals are created in the initiation reaction(s)
   equals the rate radicals are consumed in the termination reaction(s)

   If multiple initiation reactions, must determine if reactions are in series or in parallel.

   If multiple termination reactions, must determine if reactions are in series or in parallel.

   The termination reaction need not eliminate all propagating radicals. The termination reaction need only remove two propagating radicals such as two $\cdot CH_2CH_3$ radicals.

2. The rate of propagation rxn 1 = rate of propagation rxn 2 = …