Introduction to the prediction of mechanisms

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Why Do We Care?

In reactor design we need to determine

- Process chemistry
  - What reactions can lead to the desired products
  - What side reactions occur
  - What are the rates of the processes
  - Any safety issues?
- Reaction conditions
  - Temperature, pressure
  - Catalysts, solvents
- Contacting pattern
  - CSTR vs plug flow
  - Mixing issues
  - Heat transfer & pressure drop
  - Mathematical modeling

We Know How to Calculate

- Process chemistry
  - What reactions can lead to the desired products
  - What side reactions occur
  - What are the rates of the processes
  - Any safety issues?
- Reaction conditions
  - Temperature, pressure
  - Catalysts, solvents
- Contacting pattern
  - CSTR vs plug flow
  - Mixing issues
  - Heat transfer & pressure drop
  - Mathematical Modeling

This Work Gives

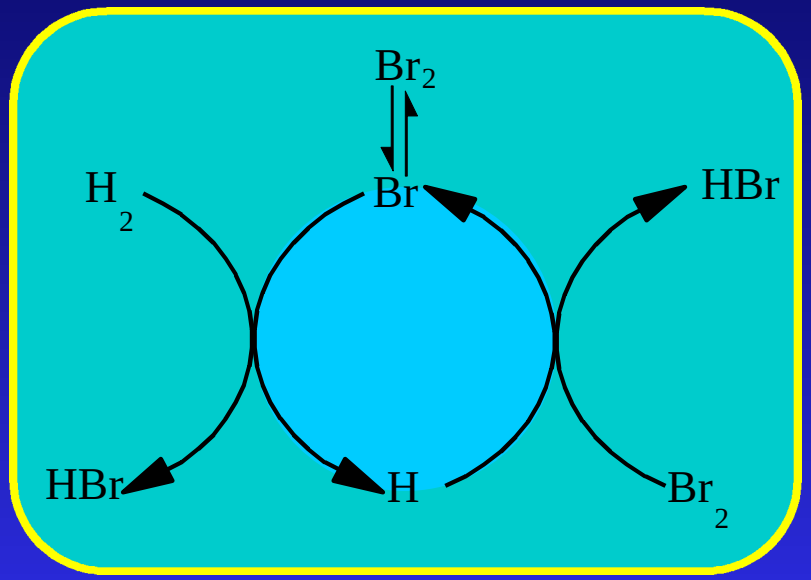
- Process chemistry
  - What reactions can lead to the desired products
  - What side reactions occur
  - What are the rates of the processes
  - Any safety issues?
- Reaction conditions
  - Temperature, pressure
  - Catalysts, solvents
- Contacting pattern
  - CSTR vs plug flow
  - Mixing issues
  - Heat transfer & pressure drop
  - Mathematical Modeling

Our Approach to Predict Process Chemistry & Conditions

- Develop rules for what reactions can happen
  - Ea < 75 kT for initiation reactions
  - Ea < 35 kT for propagation reactions
- Develop approximations for Ea
- Use the findings as a way to quantify process chemistry
- Synthesize the results for design

Rules for mechanisms: Most practical mechanisms must have

- Initiation step
  - weakest bond in reactants break
- Catalytic cycle
  - 7 generic reaction types
- Termination step



- All steps have low barriers
  - Ea < 75 kT for initiation step
  - Ea < 35 kT for propagation step

WeiTi Lee's PhD

The complete method for mechanism prediction

- Figure out what species are possible
  - Radicals
  - Reactants,Products
- Make a list of all possible reactions of those species
- Check which reactions must be included
  - Initiation reaction
  - Catalytic cycle
- Eliminate reactions which are slow

Example $H_2 + Br_2 \Rightarrow 2HBr$

- Assume H, Br, H_2, Br_2, HBr only species
- Possible Initiation reactions

$H_2 + X \quad 2\,H + X$

$Br_2 + X \quad 2\,Br + X$

- Reactions of H

$H_2 + H \quad H + H_2$

$Br_2 + H \quad HBr + Br$

$HBr + H \quad H_2 + Br$

Example: $H_2 + Br_2 \Rightarrow 2HBr$ Continued

- Reactions of Br

  $Br_2 + Br \quad Br + Br_2$

  $H_2 + Br \quad HBr + H$

  $HBr + Br \quad Br_2 + H$

- Termination Reactions

  $2\,Br + X \quad Br_2 + X$

  $H + Br + X \quad HBr + X$

  $2\,H + X \quad H_2 + X$

- Impossible Reactions
  - 4 center reactions (Fl, Cl exceptions)
  - Reactions without collision partners

All Possible Reactions

$H_2 + X \quad 2\,H + X$

$Br_2 + X \quad 2\,Br + X$

$H_2 + H \quad H + H_2$

$Br_2 + H \quad HBr + Br$

$HBr + H \quad H_2 + Br$

$Br_2 + Br \quad Br + Br_2$

$H_2 + Br \quad HBr + H$

$HBr + Br \quad Br_2 + H$

$2\,Br + X \quad Br_2 + X$

$H + Br + X \quad HBr + X$

$2\,H + X \quad H_2 + X$

Rules: Must Have Initiation Reaction

$H_2 + X \rightarrow 2\,H + X$

$Br_2 + X \rightarrow 2\,Br + X$

(Need one of these)

$H_2 + H \rightarrow H + H_2$

$Br_2 + H \rightarrow HBr + Br$

$HBr + H \rightarrow H_2 + Br$

$Br_2 + Br \rightarrow Br + Br_2$

$H_2 + Br \rightarrow HBr + H$

$HBr + Br \rightarrow Br_2 + H$

$2\,Br + X \rightarrow Br_2 + X$

$H + Br + X \rightarrow HBr + X$

$2\,H + X \rightarrow H_2 + X$

Rules: Must Have Catalytic Cycle

$H_2 + X \quad 2\,H + X$

$Br_2 + X \quad 2\,Br + X$

$H_2 + H \quad H + H_2$

$Br_2 + H \quad HBr + Br$

$HBr + H \quad H_2 + Br$ (NEED)

$Br_2 + Br \quad Br + Br_2$

$H_2 + Br \quad HBr + H$

$HBr + Br \quad Br_2 + H$ (NEED)

$2\,Br + X \quad Br_2 + X$

$H + Br + X \quad HBr + X$

$2\,H + X \quad H_2 + X$

Rules: Should Have A Termination Reaction

$H_2 + X \quad 2\,H + X$

$Br_2 + X \quad 2\,Br + X$

$H_2 + H \quad H + H_2$

$Br_2 + H \quad HBr + Br$

$HBr + H \quad H_2 + Br$

$Br_2 + Br \quad Br + Br_2$

$H_2 + Br \quad HBr + H$

$HBr + Br \quad Br_2 + H$

$2\,Br + X \quad Br_2 + X$

$H + Br + X \quad HBr + X$

$2\,H + X \quad H_2 + X$

(Want one of these)

Rules: Ignore exchange reactions

$H_2 + X$	$2\ H + X$
$Br_2 + X$	$2\ Br + X$
$H_2 + H$	$H + H_2$ (Ignore)
$Br_2 + H$	$HBr + Br$
$HBr + H$	$H_2 + Br$
$Br_2 + Br$	$Br + Br_2$ (Ignore)
$H_2 + Br$	$HBr + H$
$HBr + Br$	$Br_2 + H$
$2\ Br + X$	$Br_2 + X$
$H + Br + X$	$HBr + X$
$2\ H + X$	$H_2 + X$

Rules: Initiation reaction: weakest bond breaks

$H_2 + X \quad 2\ H + X \quad$ (104 kcal/mole)

$Br_2 + X \quad 2\ Br + X \quad$ (44 kcal/mole)

$H_2 + X \quad 2\ H + X \quad$ (Ignore)

Where are we now?

$Br_2 + X$	$2\ Br + X$	(Need)
$Br_2 + H$	$HBr + Br$	(Need)
$H_2 + Br$	$HBr + H$	(Need)

$HBr + Br$	$Br_2 + H$	
$HBr + H$	$H_2 + Br$	
$2\ Br + X$	$Br_2 + X$	(Need)
$H + Br + X$	$HBr + X$	
$2\ H + X$	$H_2 + X$	

Rules for other reactions

- All steps have low barriers
  - Ea < 75 kT for initiation step
  - Ea < 35 kT for propagation step
  - Ea < 40 kT for side reaction
- Can calculate minimum temperature for the reaction
- Include any other steps which follow the rules

Polanyi Relationship To Estimate Activation Barriers

Polanyi relationship

$$E_a = E_a^o + \gamma_p \Delta H_r$$

2 parameter equation

"If someone claims to have a general correlation for reaction rates the prudent engineer should be suspicious"
L.D. Schmidt, 1998

Blowers-Masel Equation

Bond Dissociation Energy

Heat of reaction

$$E_a = \frac{(2w_o + \Delta H_r)(V_P - 2w_o + \Delta H_r)^2}{V_p^{\,2} - 4w_o^{\,2} + \Delta H_r^{\,2}}$$

1 parameter equation

Parameter related to intrinsic barrier

Gives Reasonable Results

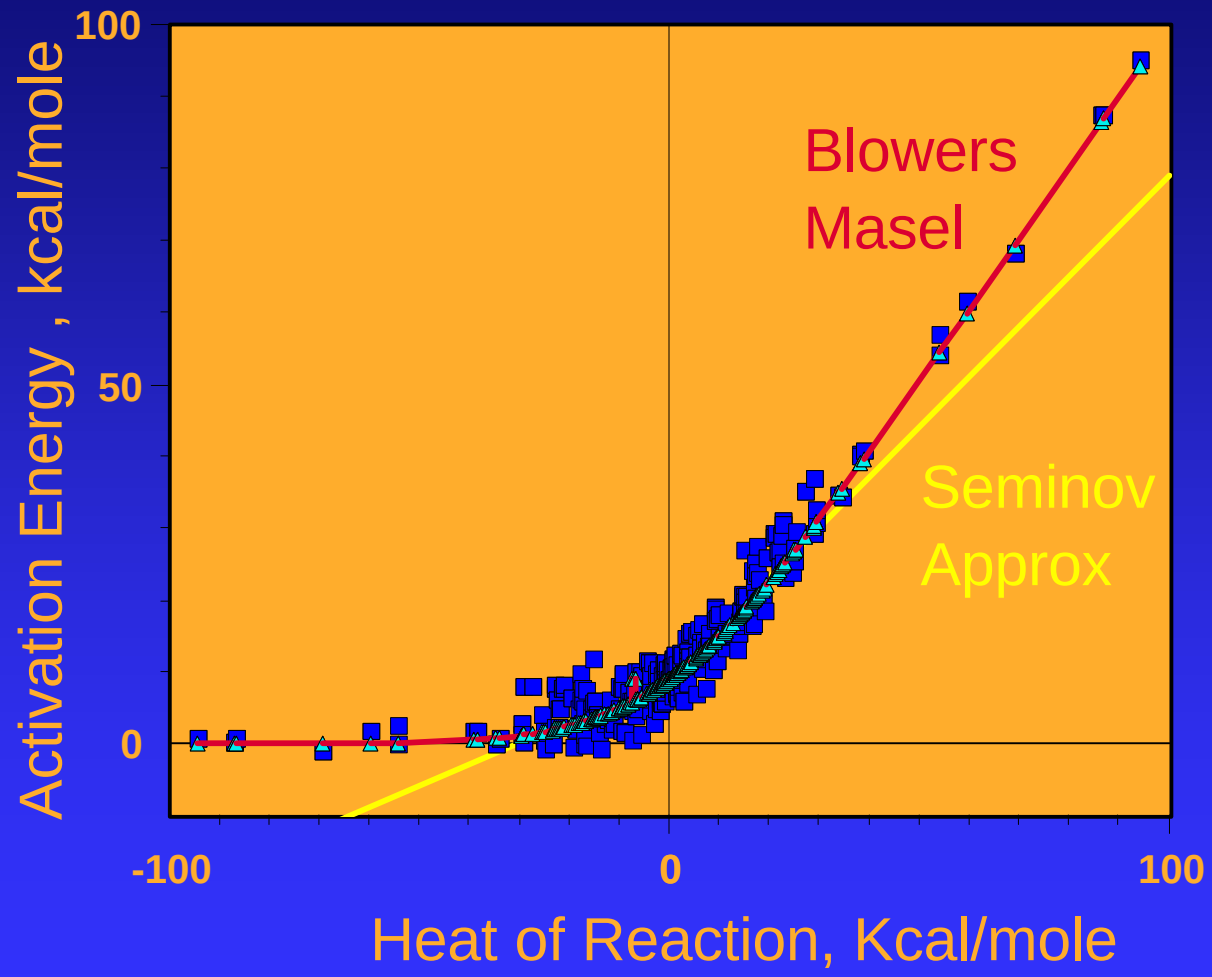


Table of Parameters

Table 5.4 Intrinsic barriers and transfer.
Coefficients for different types of reaction of neutral species.

Reaction	Example	Actual kcal/mole	E_A^o to assume when predicting mechanisms kcal/mole	Actual γ_P	γ_P to assume when predicting mechanisms
Simple bond scission	AB+X→A+B+X X=a collision partner	0-1	1	1.0	1.0
Recombination	A+B+X→AB+X X=a collision partner	0-1	1	0.0	1.0
Exothermic atom transfer reaction	R x + R^1 → R + x-R^1 x = an atom	8-16	12	0.2 to 0.6	0.3
Endothermic atom transfer reaction	R- x + R→R + x-R^1 x=an atom	8-16	12	0.4 to 0.8	0.7
Ligand transfer reaction to hydrogen	H+R-R^1 → HR + R^1	40-50	45	0.4 to 0.6	0.5
Other ligand transfer reactions	x + R-R^1 → xR+ R^1 x=an atom	50 or more	50	0.3 to 0.7	0.5

Where are we now?

$Br_2 + X$	$2\ Br + X$	(Need)
$Br_2 + H$	$HBr + Br$	(Need)
$H_2 + Br$	$HBr + H$	(Need)

$HBr + Br$	$Br_2 + H$	(Ea=7 kcal/mole)
$HBr + H$	$H_2 + Br$	(Ea=43 kcal/mole)
$2\ Br + X$	$Br_2 + X$	(Need)
$H + Br + X$	$HBr + X$	
$2\ H + X$	$H_2 + X$	

Rules for other reactions

- All steps have low barriers
  - Ea < 75 kT for initiation step
  - Ea < 35 kT for propagation step
  - Ea < 40 kT for side reaction
- Can calculate minimum temperature for the reaction
- Include any other steps which follow the rules

More Complex Cases: Additional Reactions

Other classes of reactions

- Ligand Transfer Reactions
- Beta-scissions
- Association Reactions
- Addition Reactions
- Disproportionations
- Isomerization Reactions (5-center)

All the same rules apply

More Complex Examples: Need To Reduce Number Of Species Considered

Simplified Method

- Find a feasible initiation step
- Find all feasible reactions of radicals produced in initiation step
- Continue generating reactions until I get to desired products
- Make sure reaction follows rules

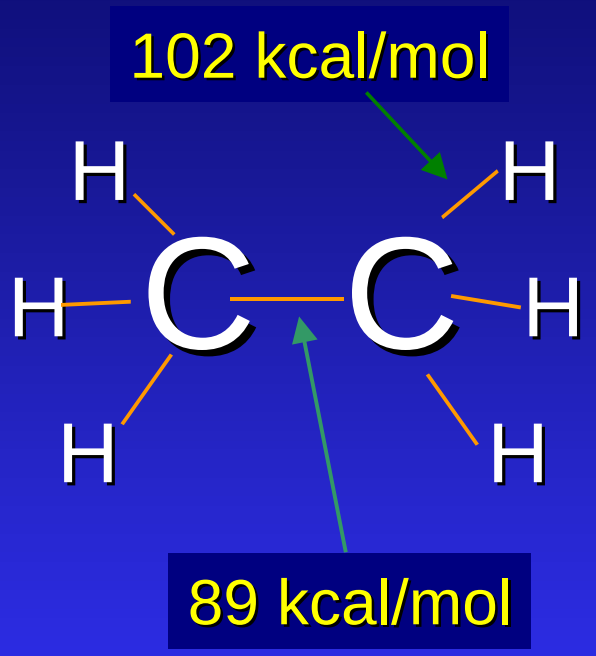
Automated mechanism generation

Example: $CH_3CH_3 \Rightarrow H_2C{=}CH_2 + H_2$

- Steps
- Find a feasible initiation step
- Find all feasible reactions of radicals produced in initiation step
- Continue generating reactions until I get to desired products
- Make sure reaction follows rules

Automated mechanism generation

Initiation step: weakest bond breaks in the reactants



Initiation step is

$$CH_3CH_3 + X \xrightarrow{1} 2 \cdot CH_3 \cdot + X$$

Possible mechanism for

$CH_3CH_3 \Rightarrow H_2C{=}CH_2 + H_2$

$$CH_3CH_3 + X \xrightarrow{1} 2 \bullet CH_3 + X$$

$$\bullet CH_3 + CH_3CH_3 \xrightarrow{2} CH_4 + \bullet CH_2CH_3$$

$$\bullet CH_2CH_3 + X \xrightarrow{3} CH_2{=}CH_2 + H\bullet + X$$

$$H\bullet + CH_3CH_3 \xrightarrow{4} H_2 + \bullet CH_2CH_3$$

$$2\,CH_3\bullet + X \xrightarrow{5} CH_3CH_3$$

Does the Mechanism Fit All of the Rules?

$$CH_3CH_3 + X \xrightarrow{1} 2 \bullet CH_3 + X$$

$$\bullet CH_3 + CH_3CH_3 \xrightarrow{2} CH_4 + \bullet CH_2CH_3$$

$$\bullet CH_2CH_3 + X \xrightarrow{3} CH_2{=}CH_2 + H\bullet + X$$

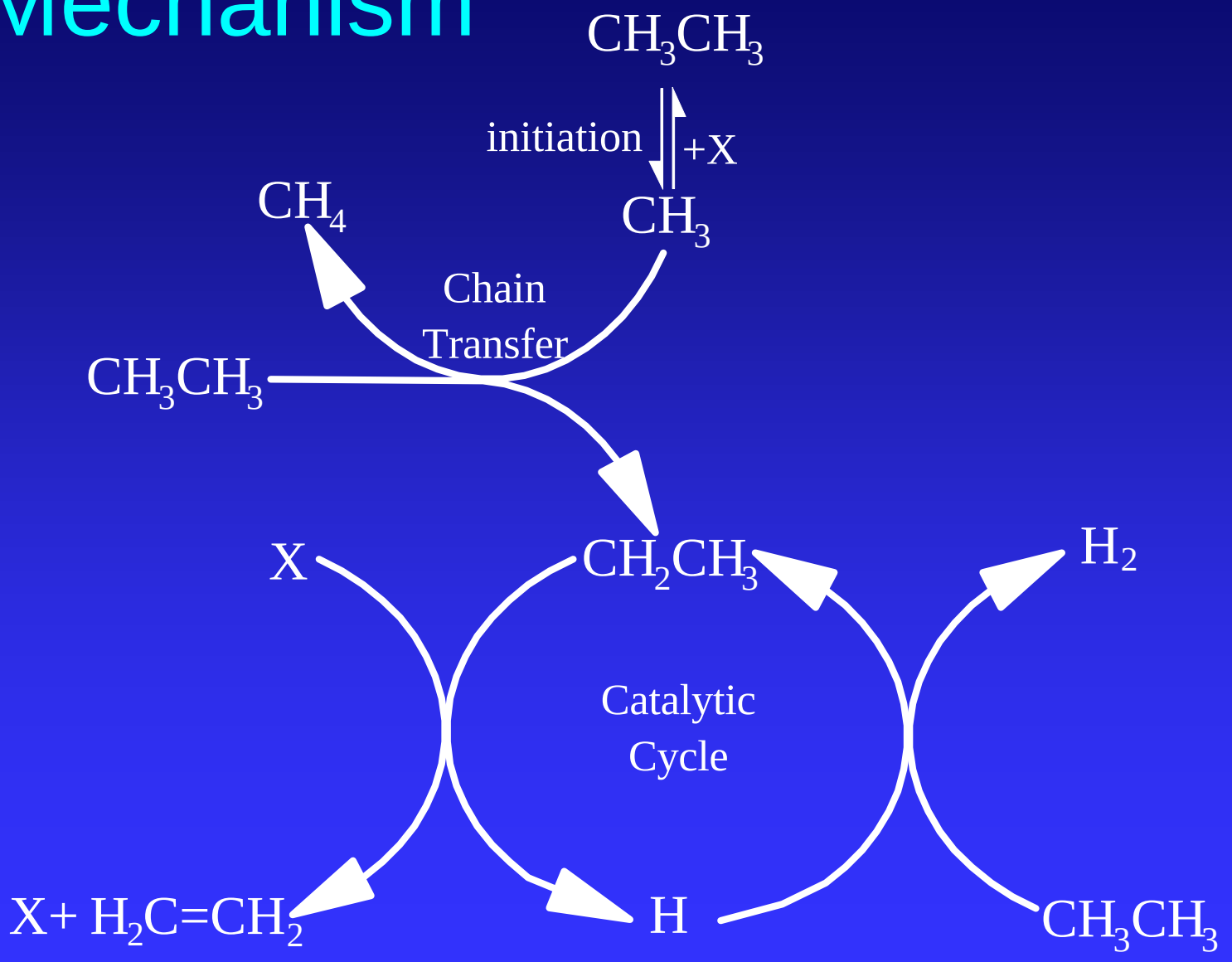
$$H\bullet + CH_3CH_3 \xrightarrow{4} H_2 + \bullet CH_2CH_3$$

$$2\,CH_3\bullet + X \xrightarrow{5} CH_3CH_3$$

Procedure:

Diagram the mechanism, estimate the activation barrier for each step and ask whether the mechanism follows the rules

Solution I: Diagram Mechanism



Solution II: Estimate activation barriers

ΔH_f (CH_2CH_3) =28.4 kcal/mole

$$CH_3\bullet + CH_3CH_3 \rightarrow CH_4 + \bullet CH_2CH_3$$

First Estimate heat of reaction

ΔH_f (CH_3CH_3) = -20.0 kcal/mole

ΔH_f ($CH_3\bullet$) = +34.8kcal/mole

ΔH_f (CH_4) = -17.9 kcal/mole

ΔH_f ($\bullet CH_2CH_3$) = +28.4 kcal/mole

Data from NIST Webbook

Therefore

ΔH_r = -17.9 +28.4 -34.8 -(-20.0) = -4.3 kcal/mole

Next Use Blowers -Masel to Estimate Activation Barrier

E_A= 8.7 kcal/mol

Is that a low enough activation energy?

- All steps must satisfy
  - Ea < 75 kT for initiation step
  - Ea < 35 kT for propagation step
- Energy low enough if temperature high enough

Can Calculate feasible process temperatures!

Does Another Reaction Occur?

$$H\bullet + CH_3CH_3 \xrightarrow{6} CH_4 + CH_3\bullet$$

E_A =37.48 Kcal/mole

Step does not satisfy criterion at 500K: rate negligible

Satisfies criterion at 700K

What Are Side Reactions?

- Seven generic reaction types
- All steps must satisfy
  - Ea < 70 kT for initiation step
  - Ea < 35 kT for propagation step
- Find other steps that satisfy constraints

Bridge to catalysis

- Rules also work on metal surfaces
- Blowers-Masel works On Metals
  - Assume a possible catalyst (try all metals)
  - Heat of reaction changes because catalyst binds intermediates
  - Calculate temperature where all criterion satisfied
  - Lowest temp is best catalyst - need to also check side reactions
- Does not work on acid catalysts
  - need new rate laws

Summary

- Can predict mechanisms
- Can predict process temperatures
- Can use results to predict catalysts