Assembling Elementary Steps into Reaction Cycles

• An Ethane Pyrolysis Example
  – Commercially important process for olefins production (ethylene)
  – Main products are ethylene and hydrogen
  – Modern models need to be able to predict BTX and other byproducts as well
  – Classical illustration of Rice-Herzfeld chain mechanism

Ethane Pyrolysis Mechanism

\[ C_2H_6 \xleftarrow{\kappa} H_2 + C_2H_4 \]
\[ E^* \sim 68 \text{kcal/mol} \]
\[ n = 0.5 \rightarrow 1.5 \]

\[ C_2H_6 \xrightarrow{\alpha} 2CH_3 \cdot \]
\[ CH_3 \cdot + C_2H_6 \xrightarrow{\text{CT}} CH_4 + C_2H_5 \cdot \]
\[ C_2H_5 \cdot \xrightarrow{1} H \cdot + C_2H_4 \]
\[ H \cdot + C_2H_6 \xrightarrow{11} H_2 + C_2H_5 \cdot \]
\[ 2C_2H_5 \cdot \xrightarrow{\alpha} C_4H_{10} \]
\[ 2H \cdot \xrightarrow{\alpha} H_2 \]
\[ 2CH_3 \cdot \xrightarrow{\alpha} C_2H_6 \]
\[ C_2H_5 \cdot + H \cdot \xrightarrow{\alpha} C_2H_6 \]
\[ CH_3 \cdot + H \cdot \xrightarrow{\alpha} CH_4 \]
\[ CH_3 \cdot + C_2H_5 \cdot \xrightarrow{\alpha} C_3H_8 \]
Kinetics Analysis

\[ r_{c,\text{H}_6} = \alpha C_2H_6 + k_{c,\text{CH}_3} \cdot C_2H_6 + k_{i,\text{H} \cdot C_2H_6} - \omega H \cdot C_2H_5. \]

The object is to obtain a rate law with only observables (molecules) and parameters, using kinetics tools to eliminate the unobservables (radicals).

Kinetics Tools:
1. Steady state approximation
2. Comparison of predicted and observed products
3. Long-chain approximation

Suppose \( H + C_2H_5 \) is main termination step.
Kinetics Analysis

Suppose H + C₂H₅ is main termination step

H⁺: 0 = kₜH₂ + kᵣH · C₂H₅ - aH · C₂H₅
C₂H₅⁺: 0 = -kₜH₂ + kᵣH · C₂H₅ - aH · C₂H₅ + kᵣC₂H₅ + kᵣC₂H₅
CH₅⁺: 0 = 2αC₂H₅ - kᵣCH₅ + C₂H₅

Therefore

C₂H₅⁺: 0 = -kₜC₂H₅ + kᵣH · C₂H₅ - aH · C₂H₅ + 2αC₂H₅

Adding H° and C₂H₅⁺:

2αC₂H₅ = 2aH · C₂H₅

This is the Steady State Approximation

The creation and destruction of radicals are balanced

Substituting for H

\[ C₂H₅⁺ \equiv \frac{(α/ω)}{H} C₂H₅ \]
\[ 0 = kₜC₂H₅ + kᵣH · C₂H₅ - aH · C₂H₅ \]

becomes

\[ 0 = kₜC₂H₅ + kᵣH · C₂H₅ - aH · C₂H₅ \]
\[ kᵣC₂H₅H⁺ + αC₂H₅H⁺ = kᵣ(α/ω)C₂H₅ \]

\[ H = \frac{-α + \sqrt{α² + 4kᵣα/kᵣ}}{2kᵣ} \]
\[ ε = \frac{α}{ω} \]
\[ ε = \frac{α}{ω} \]
\[ \frac{α}{ω} \]
\[ kᵣ = \frac{1}{2} \]
\[ \frac{1}{2} \]
\[ \frac{1}{2} \]
\[ k = \sqrt{kᵣ/ω}, n = 1 \]

Long Chain Kinetics Analysis

Substituting for H⁻

\[ C₂H₅⁻ \equiv \frac{(α/ω)}{H} C₂H₅⁻ \]
\[ 0 = kₜC₂H₅⁻ + kᵣH · C₂H₅⁻ \]

provides

\[ C₂H₅⁻ \equiv \frac{kᵣH}{kₜ} C₂H₅⁻ \]

therefore

\[ H² = \frac{αkᵣ}{ρkᵣ} \]
\[ r = kᵣH · C₂H₅ = \frac{αkᵣ}{ρkᵣ} C₂H₅⁻ \]

• Repeat for H-H termination
• Repeat for C₂H₅-C₂H₅ termination
Abstraction of Reaction Cycles:

Overall Reaction

\[ A \rightarrow B + C \]

Elementary Steps

\[ A \xrightarrow{\alpha} 2 \beta \]

\[ \beta + A \xrightarrow{\mu 1} \mu + B \]

\[ \mu \xrightarrow{1} C + \beta \]

\[ 2\beta, 2\mu, \beta + \mu \xrightarrow{T.P.} \]

\( \beta, \mu \) are "in situ" catalysts in this Rice-Herzfeld cycle.

The Simplification of Statistical Termination

Cross Termination Twice as Likely As Self Termination

\[ \alpha A = \omega_{\beta A} \beta^2 + \omega_{\mu A} \beta \mu + \omega_{\alpha} \mu^2 \]

\[ \alpha A = \omega(\beta^2 + 2\beta \mu + \mu^2) = \omega(\beta + \mu)^2 \]

\[ LCA: k_{11} \beta A = k_{1} \mu \]

\[ \alpha A = \omega \beta^2 (1 + \frac{2k_{11} A}{k_{1}} + \frac{(k_{11} A^2)}{k_{1}}) = \omega \beta^2 (1 + \frac{k_{11} A}{k_{1}})^2 \]

\[ r = k_{11} \beta A = \frac{k_{11} A^{3/2} (\alpha / \omega)^{1/2}}{\left(1 + \frac{2k_{11} A}{k_{1}} + \frac{k_{11} A^2}{k_{1}}\right)^{1/2}} = \frac{k_{11} A^{3/2} (\alpha / \omega)^{1/2}}{1 + \frac{k_{11} A}{k_{1}}} \]
Ethane Pyrolysis and NetGen

Computer Generated Pyrolysis Modeling: On-the-Fly Generation of Species, Reactions, and Rates

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The development of an integrated system for the computer generation of kinetic models is described. Required input is the structure of the reactants, the reaction rules, and the parameters of a structure/property kinetics correlation. The algorithm transforms this information into reaction/product relationships, i.e., the reaction network, species properties, rate constants, and the FORTRAN code corresponding to the governing species balance equations, and offers a solution capability. Graph theory is exploited to represent the constituent atoms of a molecule to allow determination of species uniqueness, implement chemical reactions, and identify reaction products. Special attention was devoted to improved algorithm efficiencies, the handling of ring systems, and “on-the-fly” quantum chemical calculations. This general approach is described in using ethane and cyclohexane pyrolysis case studies. The increase in the number of equations and number of components for ethane pyrolysis was exponential with the carbon number of allowed species.

Molecules as Graphs

![Graphs of Molecules](image)

Figure 1: Equivalent representations of ethane: (a) molecular graph; (b) adjacency structure.

Figure 2: Radical species can also be represented in terms of (a) the molecular graph and (b) the adjacency structure.

Figure 3: Bond-electron matrix representations that specify atomic connectivity and electronic environment for (a) ethylene, (b) center alkyl radical, and (c, right) ethene.
Reactions as Matrices

Generating Reactions on the Computer
Machine Mimicking Human Logic

NetGen Output: The Ethane Pyrolysis Mechanism
A Simple Approximation

- The LCA provides an analytically tractable solution
- All chain lengths may not be high (long)
- For short chains, fission step may control
- Investigate the approximation:

\[ r_i + r_{LCA} \approx r_{exact} \]
RH Construct for Approximate Solution

![Diagram](image)

Figure 1. Organization of pyrolysis elementary steps into the Rice Herfeld chain formalism.

Analysis

Full Solution with Statistical Termination:

\[
\frac{dA}{dt} = \alpha A + \alpha_1 AR_1 + \alpha_2 AR_2 + k_{12} A \beta - \omega_{13} R_1 R_2 \tag{3}
\]

\[
\frac{d\mu}{dt} = 0 = k_{11} A \beta - k_{13} \mu + \alpha_1 AR_1 + \alpha_2 AR_2 - 2\omega_{13} \mu^2 - \sum_{j \neq 3} \omega_{ij} \mu R_j \tag{4}
\]

\[
\frac{d\beta}{dt} = 0 = -k_{11} A \beta + k_{13} \mu - 2\omega_{13} \beta^2 - \sum_{j \neq 4} \omega_{ij} \beta R_j \tag{5}
\]

\[
R_T = \left( \frac{\alpha A}{\omega} \right)^{1/2} \tag{6}
\]

\[
2\omega_j R_j^2 + \sum_{j \neq i} \omega_{ij} R_i R_j = 2\omega \left( \sum_j R_j \right) R_i = 2\omega R_T R_i = [2(\omega \alpha A)^{1/2} R_i] \tag{7}
\]
Full Solution

\[ \frac{dA}{dt} = \alpha A + \frac{\alpha_1 \alpha A^2}{2(\omega \alpha A)^{1/2} + \alpha_1 A} + \frac{\alpha_2 \alpha A^2}{2(\omega \alpha A)^{1/2} + \beta_2 A} \]

\[ \frac{2\omega \alpha^2 A^2}{2(\omega \alpha A)^{1/2} + \alpha_1 A}[2(\omega \alpha A)^{1/2} + \beta_2 A] \]

\[ k_1 k_{11} A \left( \frac{\alpha A}{\omega} \right)^{1/2} \]

\[ (\alpha_1 + \alpha_2) A (\omega \alpha A)^{1/2} + \alpha_1 \alpha_2 A^2 \]

\[ + \frac{k_1 + k_{11} A + 2(\omega \alpha A)^{1/2}[2(\omega \alpha A)^{1/2} + \alpha_1 A][2(\omega \alpha A)^{1/2} + \beta_2 A]}{2(\omega \alpha A)^{1/2} + \alpha_1 A}[2(\omega \alpha A)^{1/2} + \beta_2 A] \]

(8)

Long Chain Solution

\[ k_{11} \beta = k_{11} \mu \]

(9)

\[ k_{11} \left( \frac{\alpha A}{\omega} \right)^{1/2} \]

\[ r_{LC} = \frac{k_{11} A}{1 + \frac{k_{11} A}{k_1}} \]

(10)
Approximate Solution

\[ r_{AP} = r_1 + r_{LC} \]

\[ r_{AP} = 3\alpha A + \frac{k_{11} \left( \frac{\alpha A}{\omega} \right)^{1/2}}{1 + \frac{k_{11}A}{k_1}} \]

Figure 2. Comparison of approximate apparent first-order rate constant with experimental values.

- ○ Dibenzylether, • ethane, ◦ dibenzyl, ◇ benzylphenylamine.