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

$$C_2H_6 \overset{K}{\longleftrightarrow} H_2 + C_2H_4$$

$$E^* \sim 68 kcal/mol$$

$$n = 0.5 \rightarrow 1.5$$

$$C_2H_6 \xrightarrow{\alpha} 2CH_3\cdot$$

$$CH_3\cdot + C_2H_6 \xrightarrow{CT} CH_4 + C_2H_5\cdot$$

$$C_2H_5\cdot \xrightarrow{1} H\cdot + C_2H_4$$

$$H\cdot + C_2H_6 \xrightarrow{11} H_2 + C_2H_5\cdot$$

$$2C_2H_5\cdot \xrightarrow{\omega} C_4H_{10}$$

$$2H\cdot \xrightarrow{\omega} H_2$$

$$2CH_3\cdot \xrightarrow{\omega} C_2H_6$$

$$C_2H_5\cdot + H\cdot \xrightarrow{\omega} C_2H_6$$

$$CH_3\cdot + H\cdot \xrightarrow{\omega} CH_4$$

$$CH_3\cdot + C_2H_5\cdot \xrightarrow{\omega} C_3H_8$$

Kinetics Analysis

$$r_{C_2H_6} = \alpha C_2H_6 + k_{CT}CH_3 \cdot C_2H_6 + k_{11}H \cdot C_2H_6 - \omega H \cdot C_2H_5 \cdot$$

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

Kinetics Analysis

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Kinetics Tools:

1. Steady state approximation $dH \cdot / dt = dC_2H_5 \cdot / dt = dCH_3 \cdot / dt = 0$
2. Comparison of predicted and observed products: CH_4 minor
3. Long-chain approximation: H_2 and C_2H_4 major products

$$r_{C_2H_6} = \alpha C_2H_6 + k_{11}H \cdot C_2H_6 - \omega H \cdot C_2H_5 \cdot$$

Suppose H + C_2H_5 is main termination step

Kinetics Analysis

Suppose H + C_2H_5 is main termination step

H·: $0 = k_1 C_2H_5 \cdot - k_{11} H \cdot C_2H_6 - \omega H \cdot C_2H_5 \cdot$

C_2H_5·: $0 = -k_1 C_2H_5 \cdot + k_{11} H \cdot C_2H_6 - \omega H \cdot C_2H_5 \cdot + k_{CT} CH_3 \cdot C_2H_6$

CH_3·: $0 = 2\alpha C_2H_6 - k_{CT} CH_3 \cdot C_2H_6$

Therefore

C_2H_5·: $0 = -k_1 C_2H_5 \cdot + k_{11} H \cdot C_2H_6 - \omega H \cdot C_2H_5 \cdot + 2\alpha C_2H_6$

Adding H· and C_2H_5·:

$2\alpha C_2H_6 = 2\omega H \cdot C_2H_5 \cdot$

This is the Steady State Approximation

The creation and destruction of radicals are balanced

Substituting for H·

$$C_2H_5 \cdot = \frac{(\alpha/\omega)}{H \cdot} C_2H_6$$

$0 = k_1 C_2H_5 \cdot - k_{11} H \cdot C_2H_6 - \omega H \cdot C_2H_5 \cdot$

becomes

$$0 = k_1 \frac{(\alpha/\omega)}{H \cdot} C_2H_6 - k_{11} H \cdot C_2H_6 - \omega H \cdot \frac{(\alpha/\omega)}{H \cdot} C_2H_6$$

$$k_{11} C_2H_6 H \cdot^2 + \alpha C_2H_6 H \cdot - k_1 (\alpha/\omega) C_2H_6$$

$$H \cdot = \frac{-\alpha \pm \sqrt{\alpha^2 + 4k_{11}\alpha k_1/\omega}}{2k_{11}}$$

$$r_{C_2H_6} = \alpha C_2H_6 + k_{11} H \cdot C_2H_6$$

$$r_{C_2H_6} = \alpha C_2H_6 + k_{11} \frac{-\alpha \pm \sqrt{\alpha^2 + 4k_{11}\alpha k_1/\omega}}{2k_{11}} C_2H_6$$

$$\alpha^2 << 4k_{11}\alpha k_1/\omega$$

$$r_{C_2H_6} = \alpha C_2H_6 + \frac{-\alpha + \sqrt{4k_{11}\alpha k_1/\omega}}{2} C_2H_6$$

$$r_{C_2H_6} = \frac{\alpha}{2} C_2H_6 + \sqrt{k_{11}\alpha k_1/\omega}\, C_2H_6$$

$$\alpha << \sqrt{k_{11}\alpha k_1/\omega}$$

$$k = \sqrt{k_{11}\alpha k_1/\omega}, \; n = 1$$

Long Chain Kinetics Analysis

Substituting for H·

$$C_2H_5 \cdot = \frac{(\alpha/\omega)}{H \cdot} C_2H_6$$

$$0 = k_1 C_2H_5 \cdot - k_{11} H \cdot C_2H_6$$

provides

$$C_2H_5 \cdot = \frac{k_{11} H \cdot}{k_1} C_2H_6$$

therefore

$$H^2 \cdot = \frac{\alpha k_1}{\omega k_{11}}$$

$$r = k_{11} H \cdot C_2H_6 = \sqrt{\frac{\alpha k_1 k_{11}}{\omega}} C_2H_6$$

- Repeat for H-H termination
- Repeat for C_2H_5-C_2H_5 termination

Abstraction of Reaction Cycles:

Overall Reaction $A \rightarrow B + C$

Elementary Steps

$A \xrightarrow{\alpha} 2\beta$

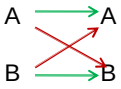
$\beta + A \xrightarrow{11} \mu + B$

$\mu \xrightarrow{1} C + \beta$

$2\beta,\ 2\mu,\ \beta + \mu \xrightarrow{\omega}$ T.P.

β, μ are "in situ" catalysts in this Rice-Herzfeld cycle.

The Simplification of Statistical Termination



Cross Termination Twice as Likely As Self Termination

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

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

$$LCA: k_{11}\beta A = k_1\mu$$

$$\alpha A = \omega\beta^2(1 + \frac{2k_{11}A}{k_1} + (\frac{k_{11}A^2}{k_1})) = \omega\beta^2(1 + \frac{k_{11}A}{k_1})^2$$

$$r = k_{11}\beta A = \frac{k_{11}A^{3/2}(\alpha/\omega)^{1/2}}{\left(1 + \frac{2k_{11}A}{k_1} + \frac{k_{11}A^2}{k_1}\right)^{1/2}} = \frac{k_{11}A^{3/2}(\alpha/\omega)^{1/2}}{1 + \frac{k_{11}A}{k_1}}$$

Ethane Pyrolysis and NetGen

790 *Ind. Eng. Chem. Res.* 1994, 33, 790–799

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 reactant/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

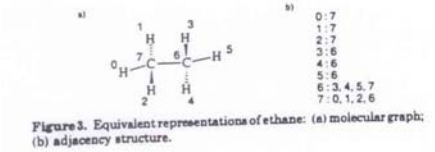


Figure 3. Equivalent representations of ethane: (a) molecular graph; (b) adjacency structure.

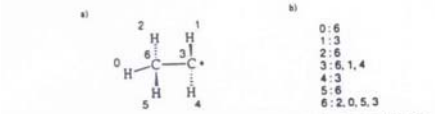


Figure 4. Radical species can also be represented in terms of (a) the molecular graph and (b) the adjacency structure.

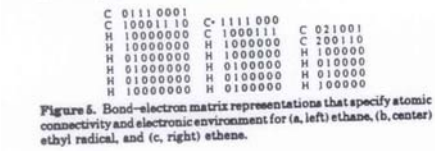


Figure 5. Bond–electron matrix representations that specify atomic connectivity and electronic environment for (a, left) ethane, (b, center) ethyl radical, and (c, right) ethene.

Reactions as Matrices

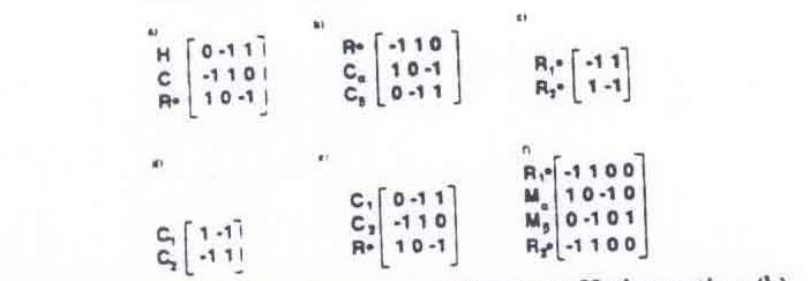


Figure 6. Reaction matrix representation for (a) H-abstraction, (b) β-scission, (c) recombination, (d) bond fission, (e) radical addition, and (f) disproportionation.

Generating Reactions on the Computer

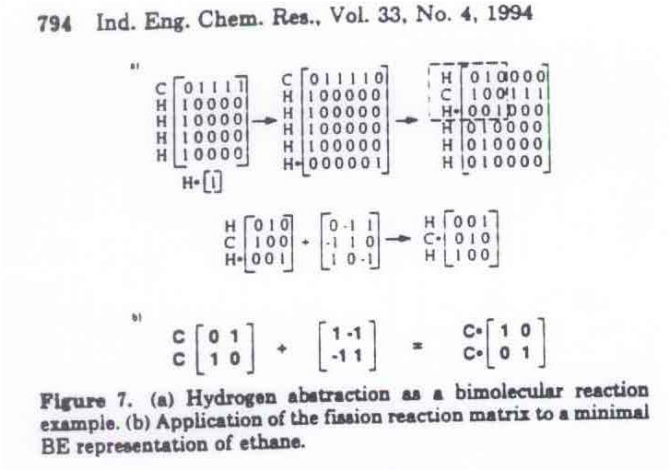


Figure 7. (a) Hydrogen abstraction as a bimolecular reaction example. (b) Application of the fission reaction matrix to a minimal BE representation of ethane.

Machine Mimicking Human Logic

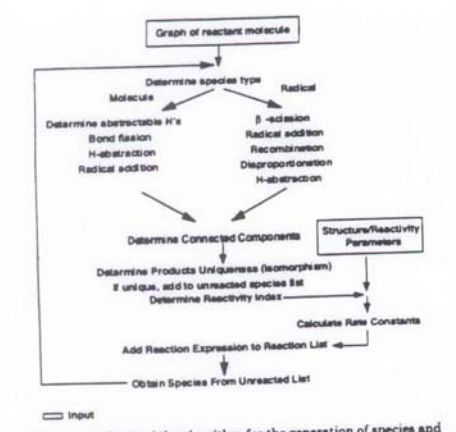
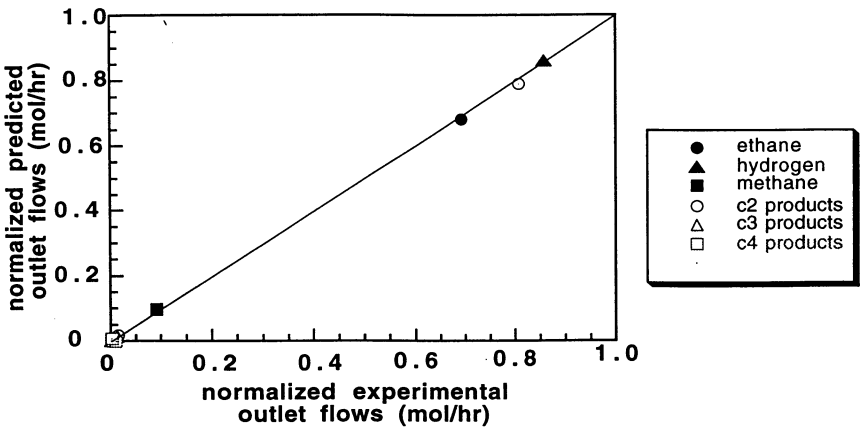


Figure 11. Logic of the algorithm for the generation of species and the assembly of the reaction mechanism.

NetGen Output: The Ethane Pyrolysis Mechanism

Figure 12. (a) Generated unique reaction mechanism species. (b) Sample output for pyrolysis of ethane constrained by initiation of species with no more than two carbon atoms. (c) Component definitions with their associated heat of formation values.

Light Gas Thermal Cracking Model Predictions

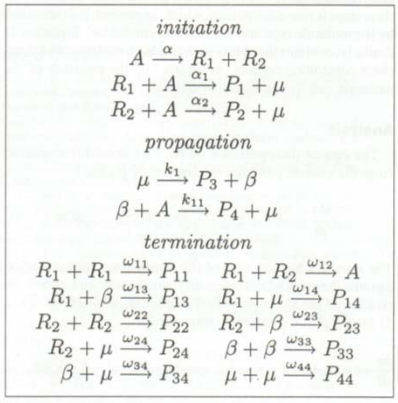


A Simple Approximation

- 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



initiation

$$A \xrightarrow{\alpha} R_1 + R_2$$
$$R_1 + A \xrightarrow{\alpha_1} P_1 + \mu$$
$$R_2 + A \xrightarrow{\alpha_2} P_2 + \mu$$

propagation

$$\mu \xrightarrow{k_1} P_3 + \beta$$
$$\beta + A \xrightarrow{k_{11}} P_4 + \mu$$

termination

$$R_1 + R_1 \xrightarrow{\omega_{11}} P_{11} \qquad R_1 + R_2 \xrightarrow{\omega_{12}} A$$
$$R_1 + \beta \xrightarrow{\omega_{13}} P_{13} \qquad R_1 + \mu \xrightarrow{\omega_{14}} P_{14}$$
$$R_2 + R_2 \xrightarrow{\omega_{22}} P_{22} \qquad R_2 + \beta \xrightarrow{\omega_{23}} P_{23}$$
$$R_2 + \mu \xrightarrow{\omega_{24}} P_{24} \qquad \beta + \beta \xrightarrow{\omega_{33}} P_{33}$$
$$\beta + \mu \xrightarrow{\omega_{34}} P_{34} \qquad \mu + \mu \xrightarrow{\omega_{44}} P_{44}$$

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

Analysis

Full Solution with Statistical Termination:

$$-\frac{dA}{dt} = \alpha A + \alpha_1 A R_1 + \alpha_2 A R_2 + k_{11} A\beta - \omega_{12} R_1 R_2 \qquad (3)$$

$$\frac{d\mu}{dt} \approx 0 \approx k_{11} A\beta - k_1 \mu + \alpha_1 A R_1 + \alpha_2 A R_2 - 2\omega_{33}\mu^2 - \sum_{j \neq 3} \omega_{3j} \mu R_j \qquad (4)$$

$$\frac{d\beta}{dt} \approx 0 \approx -k_{11} A\beta + k_1 \mu - 2\omega_{44}\beta^2 - \sum_{j \neq 4} \omega_{4j} \beta R_j \qquad (5)$$

$$R_T = \left(\frac{\alpha A}{\omega}\right)^{1/2} \qquad (6)$$

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

Full Solution

$$-\frac{dA}{dt}=\alpha A+\frac{\alpha_1\alpha A^2}{2(\omega\alpha A)^{1/2}+\alpha_1 A}+\frac{\alpha_2\alpha A^2}{2(\omega\alpha A)^{1/2}+\alpha_2 A}-\frac{2\omega\alpha^2 A^2}{[2(\omega\alpha A)^{1/2}+\alpha_1 A][2(\omega\alpha A)^{1/2}+\alpha_2 A]}+\frac{k_1 k_{11} A\left(\frac{\alpha A}{\omega}\right)^{1/2}[(\alpha_1+\alpha_2)A(\omega\alpha A)^{1/2}+\alpha_1\alpha_2 A^2]}{[k_1+k_{11}A+2(\omega\alpha A)^{1/2}][2(\omega\alpha A)^{1/2}+\alpha_1 A][2(\omega\alpha A)^{1/2}+\alpha_2 A]} \quad (8)$$

Long Chain Solution

$$k_{11}A\beta=k_1\mu \quad (9)$$

$$r_{LC}=\frac{k_{11}\left(\frac{\alpha A}{\omega}\right)^{1/2}}{1+\frac{k_{11}A}{k_1}} \quad (10)$$

Approximate Solution

$$r_{AP} = r_i + r_{LC}$$

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

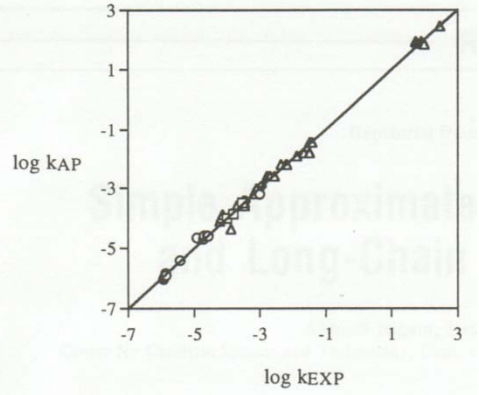


Figure 2. Comparison of approximate apparent first-order rate constant with experimental values.
□ dibenzylether, △ ethane, ○ bibenzyl, ◇ benzylphenylamine.