Creating and Harnessing Complex Reaction Networks: Application to Oxidation Chemistry

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Why Do Lubricants Fail?

- **The lubricant is used under engine operating conditions (T,P) where oxidation chemistry can occur**

- **The lubricant breaks down thermally and additives and antioxidants are consumed and/or fail**

Overall reaction

Alkane -> alcohols, acids, ketones, hydroperoxides

How Can We Reduce Tropospheric Ozone Formation?

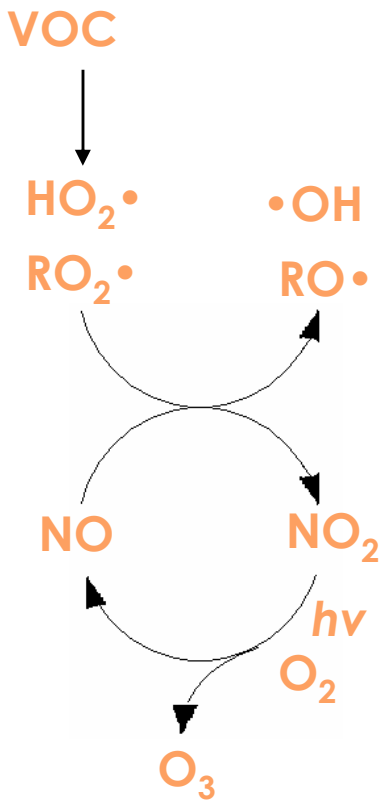
www.inrets.fr/ur/umrette/ progdetail.htm

- Emissions of volatile organic compounds from stationary and mobile sources lead to the formation of urban smog

www.inrets.fr/ur/umrette/ progdetail.htm

- Ozone poses a threat to human health

Overall reaction



How Can We Create Biofuels from Natural Resources?

www.clemson.edu/edisto/ corn/corn.htm

- **Concern over dwindling petroleum-based resources sparks exploration of alternative feedstocks**

www.timberland.com/.../ tim_ product_detail.jsp?OID=18298

- **Biochemical processes are being explored as alternatives to traditional chemical processes**

Overall reaction

biomass → polysaccharides → monosaccharides → glucose → biofuels

Common Thread: Complex Reacting Systems

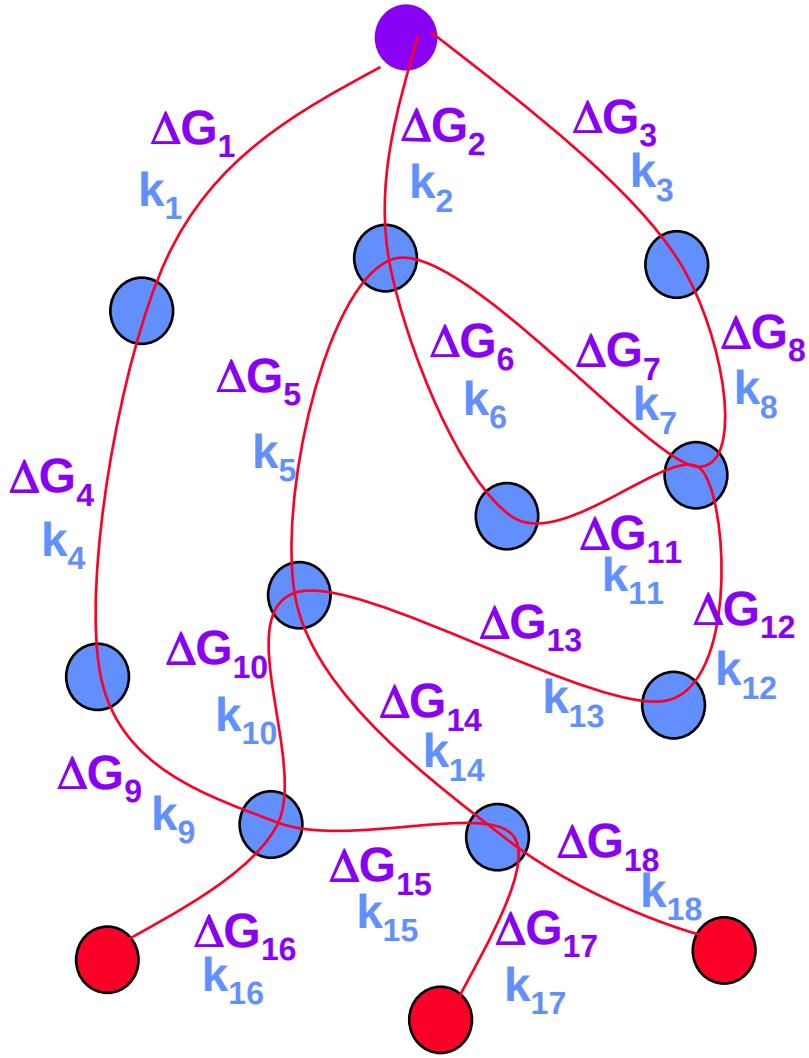
Complex systems of chemical reactions

Hundreds or thousands of reacting species comprise reaction network

Predicting system behavior requires understanding of the interplay among the components of the reaction network

Components of the Reaction Network

- **Reactants, intermediates and products**
- **Reactions**
- **Thermodynamic parameters**
- **Kinetic parameters**



Challenges for Reaction Network Development

- **Reactive intermediates have not been detected**
- **Pathways have not been elucidated experimentally**
- **Thermodynamic and kinetic parameters are unknown**
- **Reaction networks are large**
- **Construction is tedious and prone to user's bias and errors**

Computer generation of reaction networks

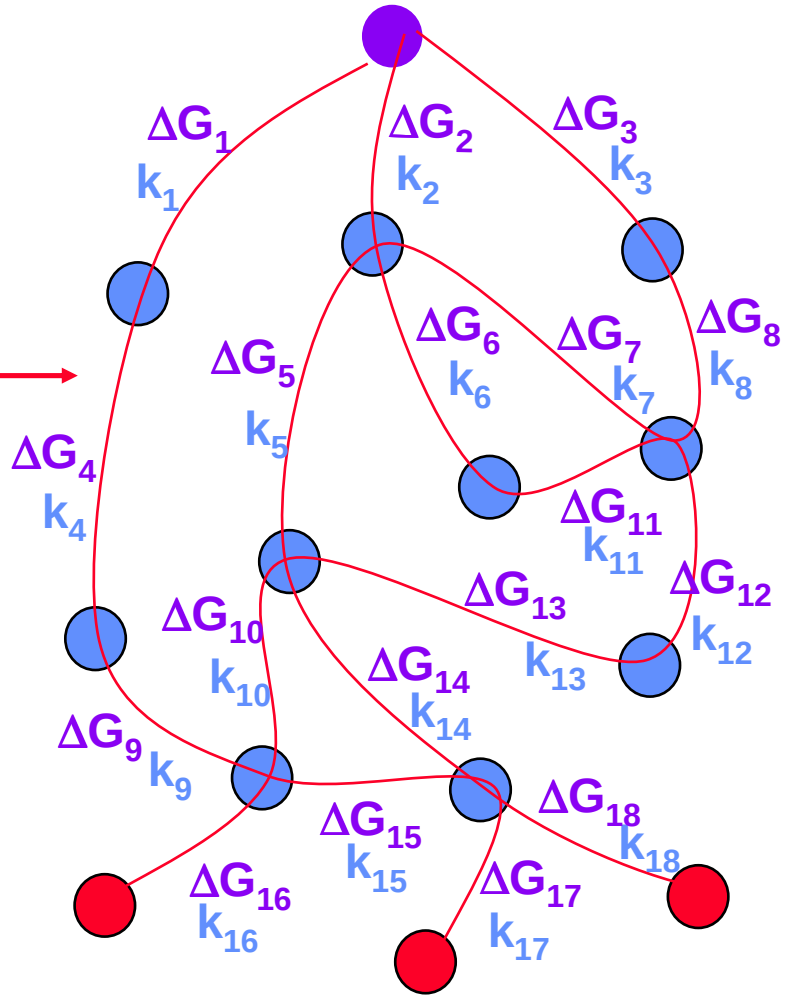
Elements of Computer Generated Reaction Networks

Reactants

Reaction Types

Reaction Rules

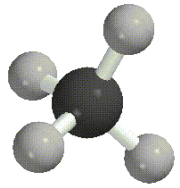
- Graph Theory
- Reaction Matrix Operations
- Connectivity Scan
- Uniqueness Determination
- Property Calculation
- Termination Criteria



Bond-Electron Representation Allows Implementation of Chemical Reaction

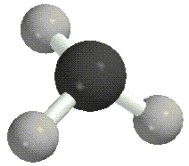
C	0	1	1	1	1
H	1	0	0	0	0
H	1	0	0	0	0
H	1	0	0	0	0
H	1	0	0	0	0

methane



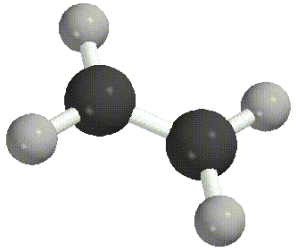
C	1	1	1	1	
H	1	0	0	0	
H	1	0	0	0	
H	1	0	0	0	

methyl radical



C	0	2	1	0	0 1
C	2	0	0	1	1 0
H	1	0	0	0	0 0
H	0	1	0	0	0 0
H	0	1	0	0	0 0
H	1	0	0	0	0 0

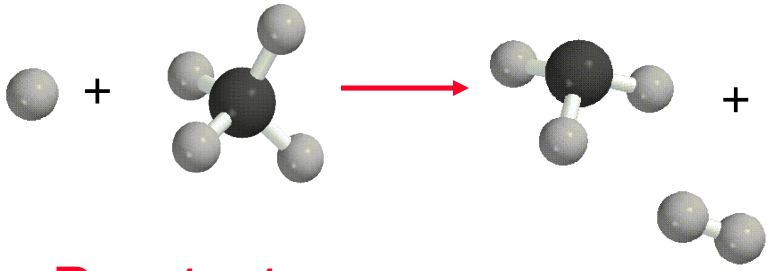
ethylene



- **ij entries denote the bond order between atoms i and j**
- **ii entries designate the number of nonbonded electrons associated with atom i**

Chemical Reaction as a Matrix Addition Operation

$$H\bullet + CH_4 \longrightarrow \bullet CH_3 + H_2$$



Reaction Operation

$$\begin{matrix} H \\ C \\ H\bullet \end{matrix}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 0 & -1 & 1 \\ -1 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix} \longrightarrow \begin{matrix} H \\ C\bullet \\ H \end{matrix}\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

Reactant Matrices

$$\begin{matrix} C \\ H \\ H \\ H \\ H \end{matrix}\begin{bmatrix} 0 & 1 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad H\bullet\begin{bmatrix} 1 \end{bmatrix}$$

Reactant Matrix

$$\begin{matrix} C \\ H \\ H \\ H \\ H \\ H \\ H\bullet \end{matrix}\begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

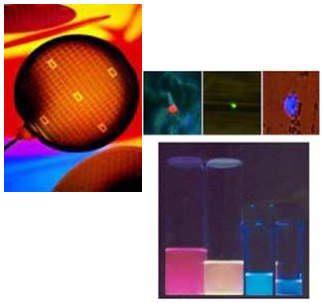
Reordered Reactant Matrix

$$\begin{matrix} H \\ C \\ H\bullet \\ H \\ H \\ H \\ H \end{matrix}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Product Matrix

$$\begin{matrix} H \\ C\bullet \\ H \\ H \\ H \\ H \\ H \end{matrix}\begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Complex Chemistry Summarized in Terms of Reaction Matrices



Lubricant degradation

9 reaction families

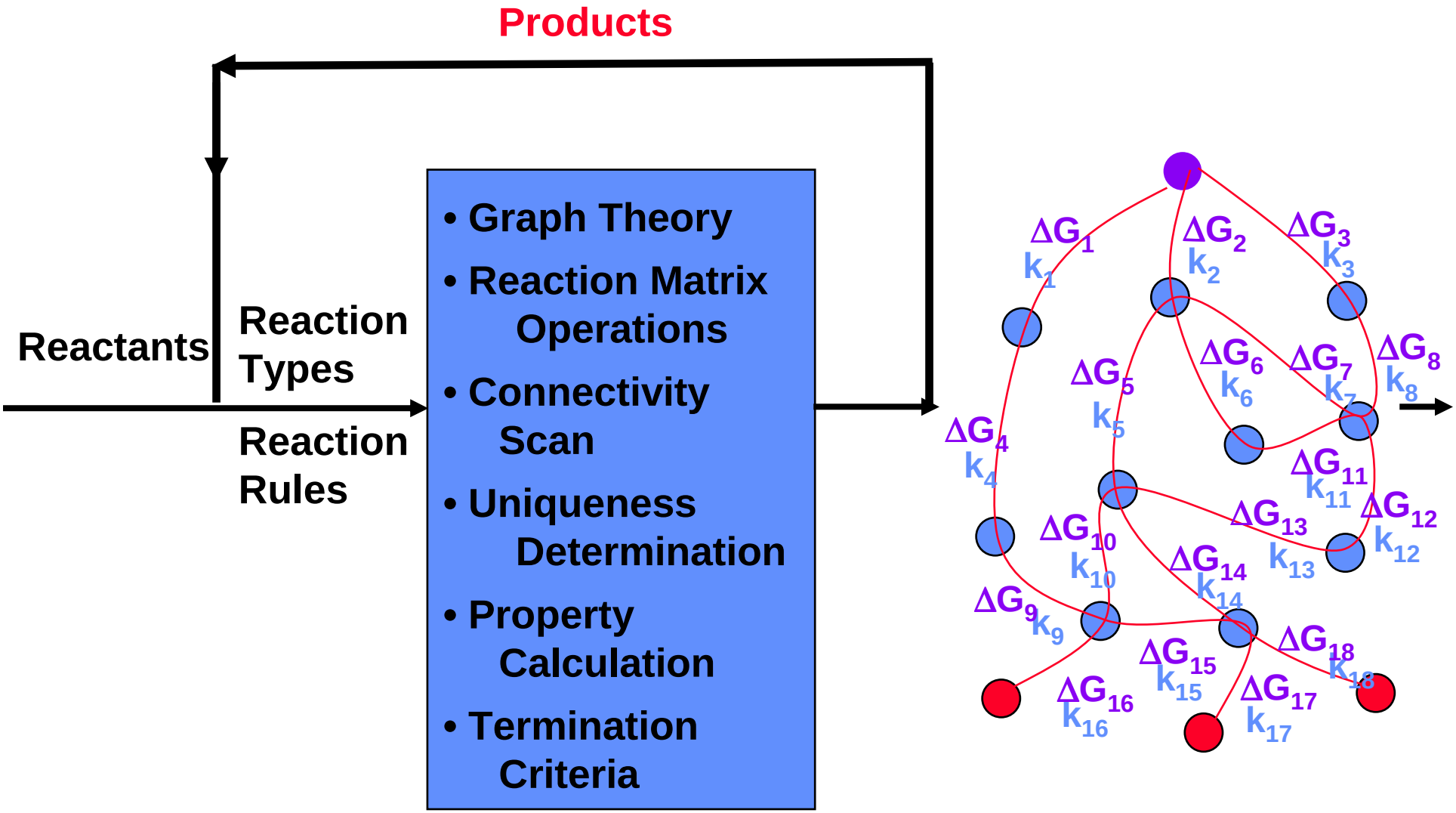
Tropospheric ozone formation

15 thermal reaction families
5 photolysis reaction families
22 small molecule reactions

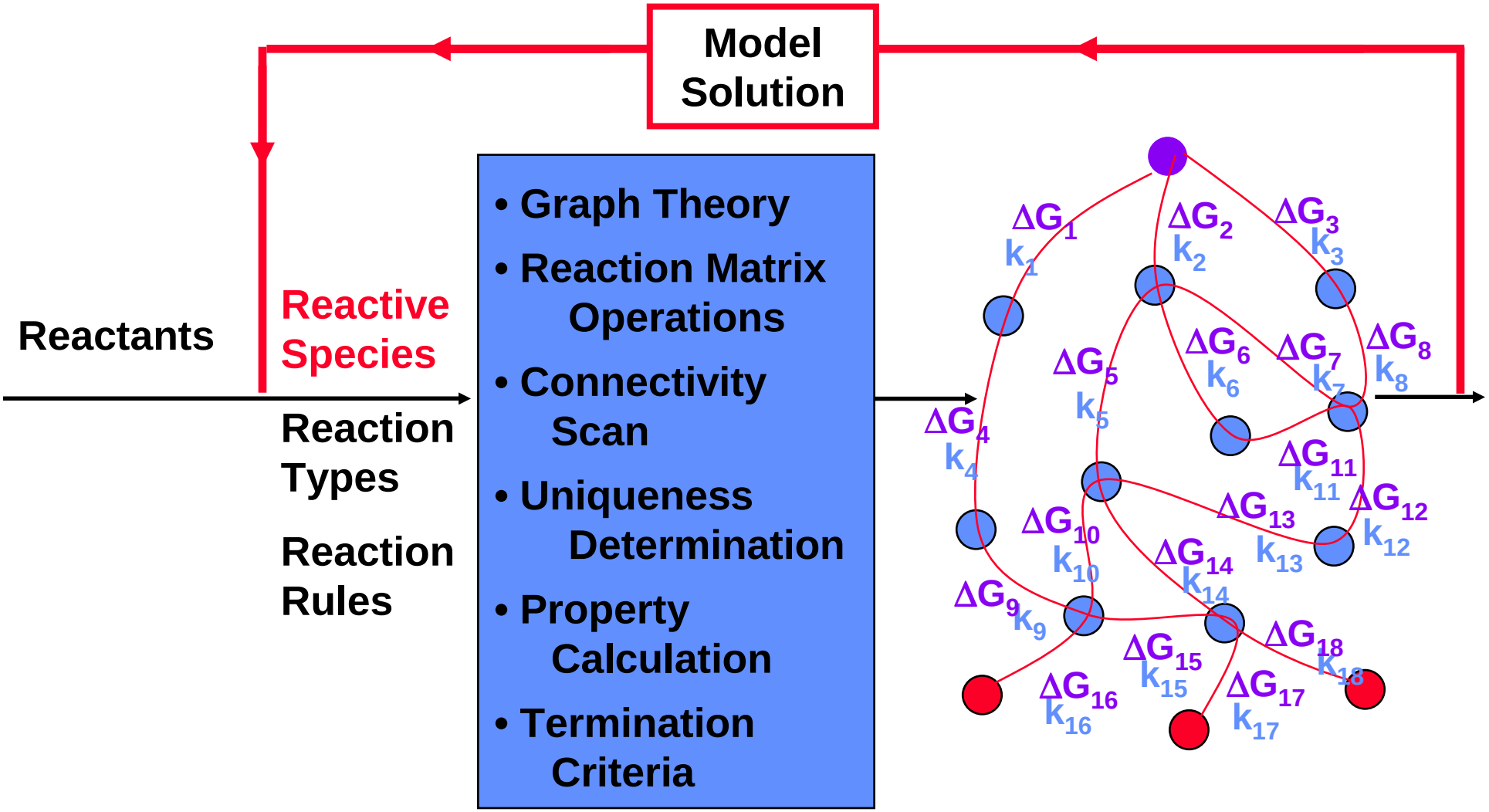
Production of biofuels from biomass

205 unique enzyme actions in KEGG database at i.j.k level

Unconstrained Network Growth



Iterative Rate-Based Network Construction



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Overall reaction

Alkane -> alcohols, acids, ketones, hydroperoxides

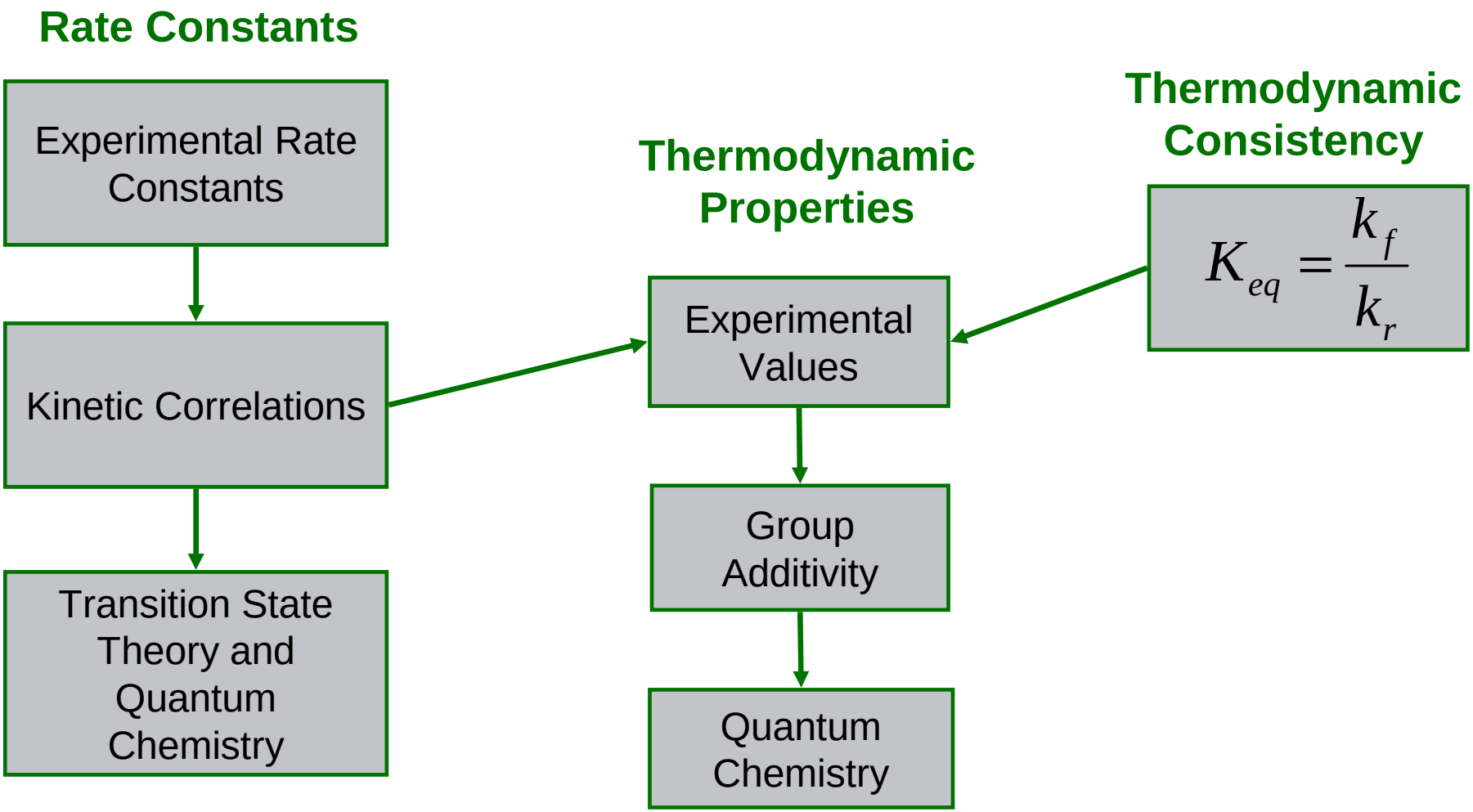
Complex Chemistry Represented by a Small Number of Reaction Families

- **Each reaction family is represented by its reaction matrix**

- **Detailed literature search revealed relevant reactions for** alkanes, aldehydes, alcohols, carboxylic acids, **and** ketones:

  - Nine **reaction families**
  - **Primary initiation, bond fission, hydroperoxide decomposition, oxygen addition, β-scission, hydrogen transfer, disproportionation, recombination and Baeyer-Villiger reaction**

The model is parameterized in a systematic fashion



L.J. Broadbelt, J. Pfaendtner, *AIChE J.*, ***51***, 2005

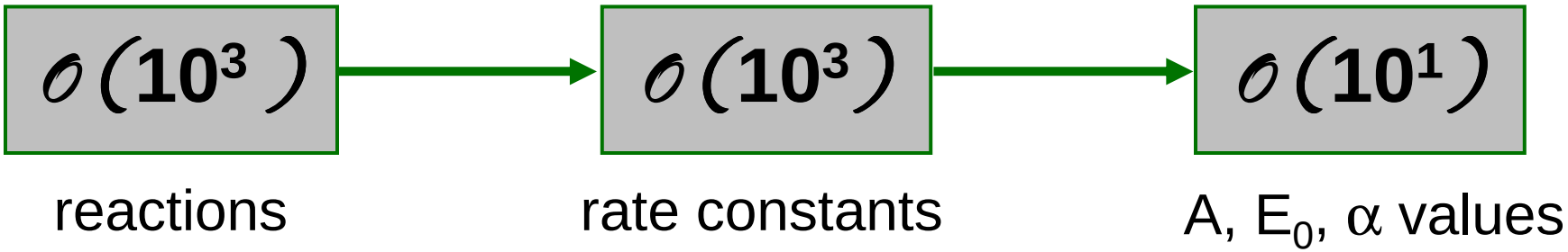
Correlations Greatly Reduce Parameterization

- **Rate constants estimated according to reaction family**
- **Correlations have 2 or 3 parameters**

$$k = Ae^{-E/RT}$$

$$E = E_o + \alpha \Delta H_{rxn}$$

The Evans-Polanyí relationship



- **Parameters regressed from experiment or found in literature or obtained from quantum chemical calculations**

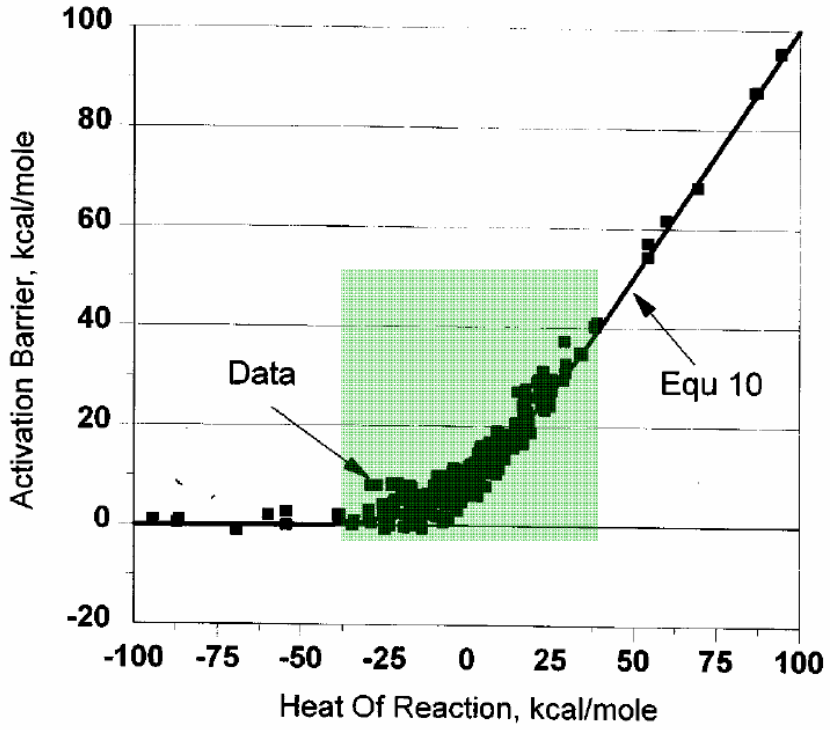
Correlations greatly reduce parameterization

- **Evans-Polanyi parameters were regressed from over 400 experimental data points for hydrogen transfer reactions**

$$E = E_o + \alpha \Delta H_{rxn}$$

$$\Delta H_{rxn} > 0 \;,\; E_a = 8 + 0.8\Delta H_{rxn}$$

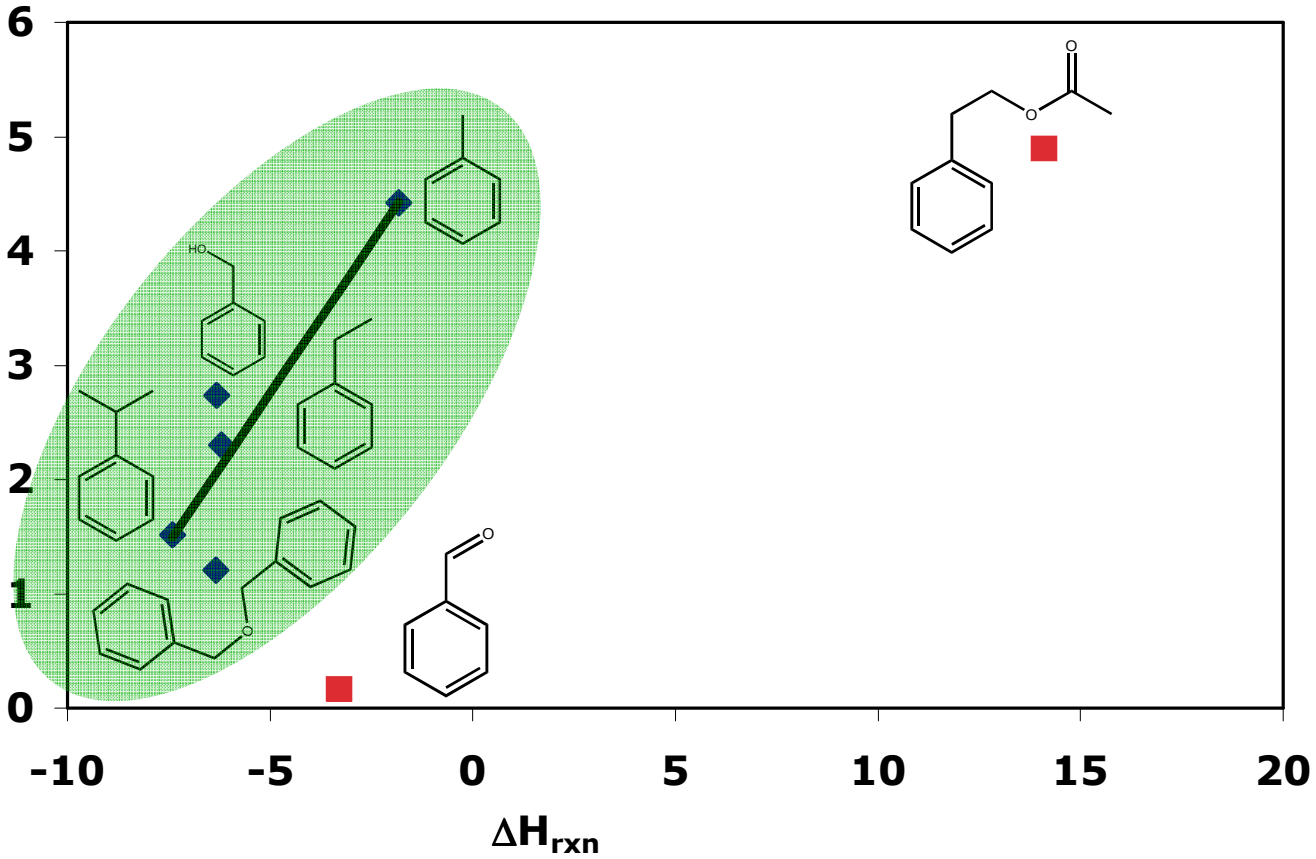
$$\Delta H_{rxn} < 0 \;,\; E_a = 8 + 0.2\Delta H_{rxn}$$



Data and figure from Blowers P., Masel R., *AIChE J.*, ***46***, 2000

The need for specificity in kinetic correlations

Kinetic data for hydrogen transfer in aromatic-containing molecules (ROO• + RH)



Experimental data obtained from Sheldon and Kochi (1981)

The need for diversity in kinetic correlations

Options for specifying reaction families:

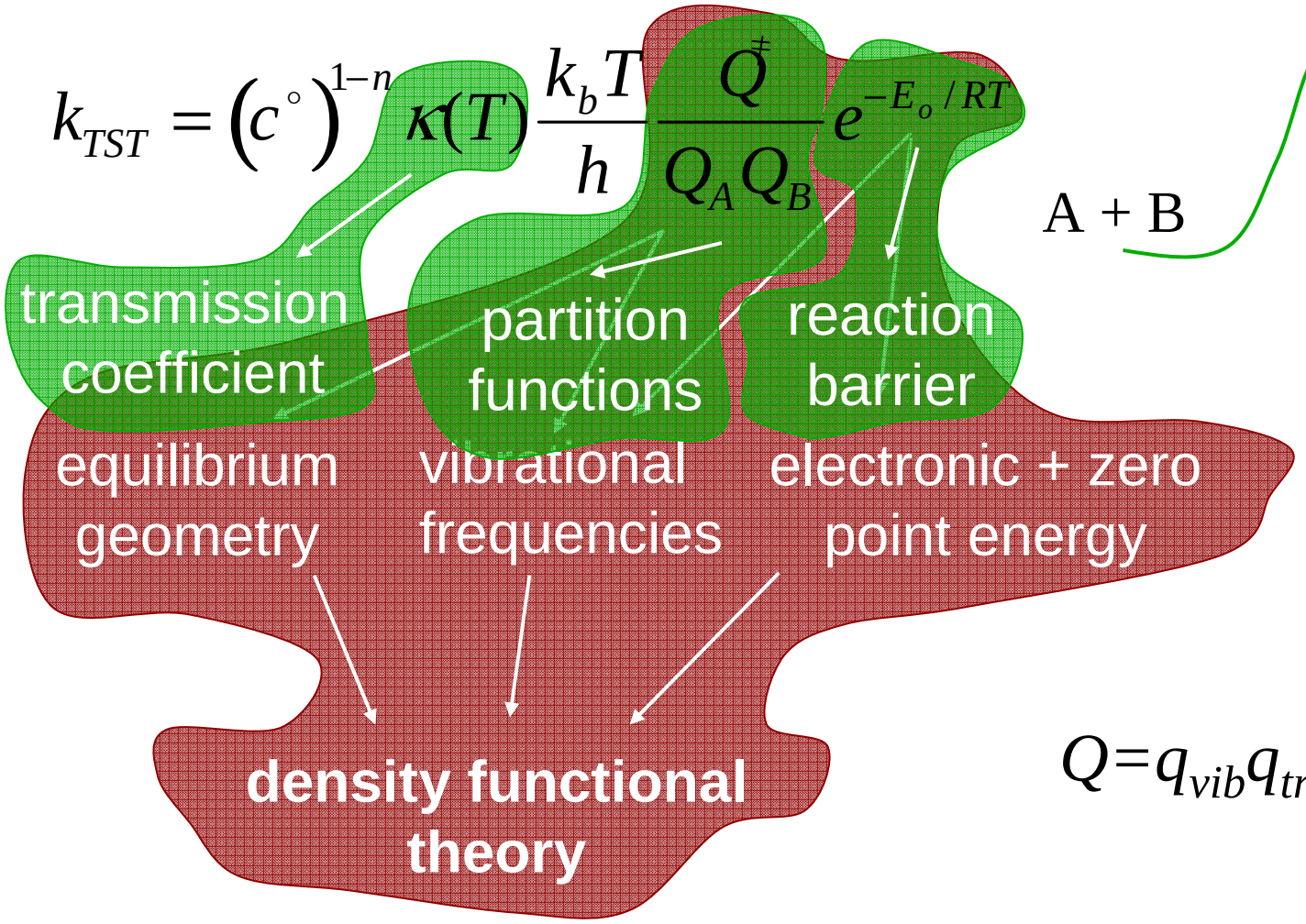
- **Specify by** radical type**:**

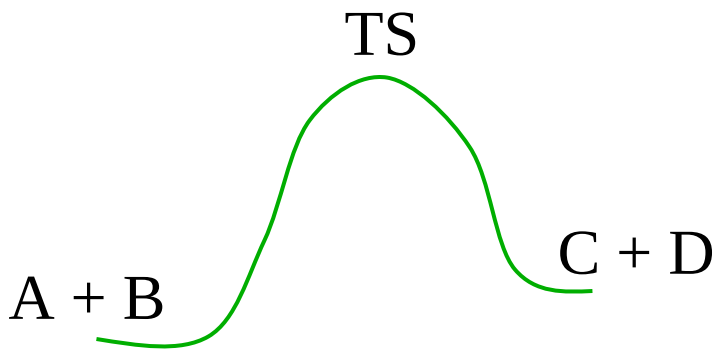
R• + R’H
RO• + R’H
ROO• + R’H
} products

- **Specify by** substrate**:**

R• + RH
R• + R’COH
R• + R’(OOH)H
} products

Kinetic properties are estimated from transition state theory

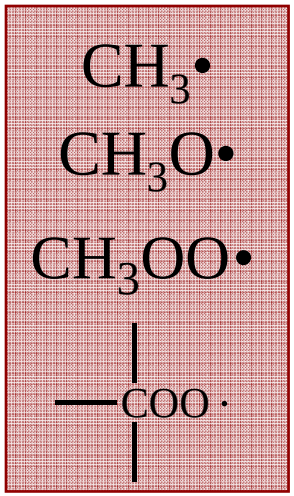




$$Q = q_{vib} q_{trans} q_{rot} q_{elec}$$

Investigate hydrogen transfer reactions using quantum chemistry

R• + R'H -> RH + R'•



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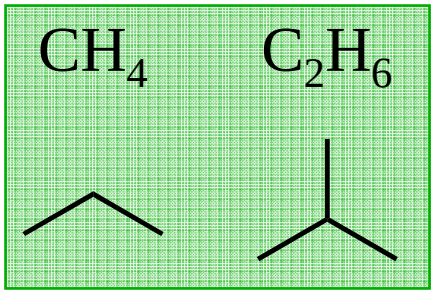


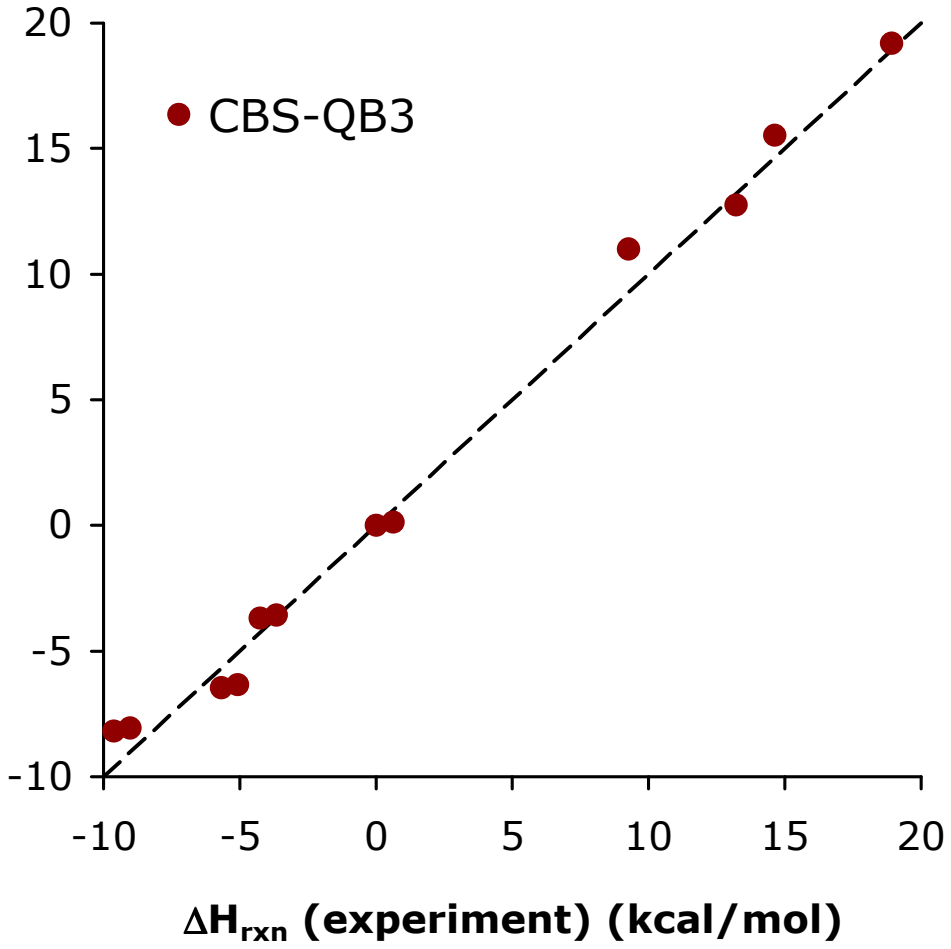
= 32 different reactions
(forward and reverse pairs)

Quantum chemistry can reliably predict experimental data: *enthalpy of reaction*

R'H + ROO• → R'• + ROOH

R'H + RO• → R'• + ROH

R'H + R• → R'• + RH

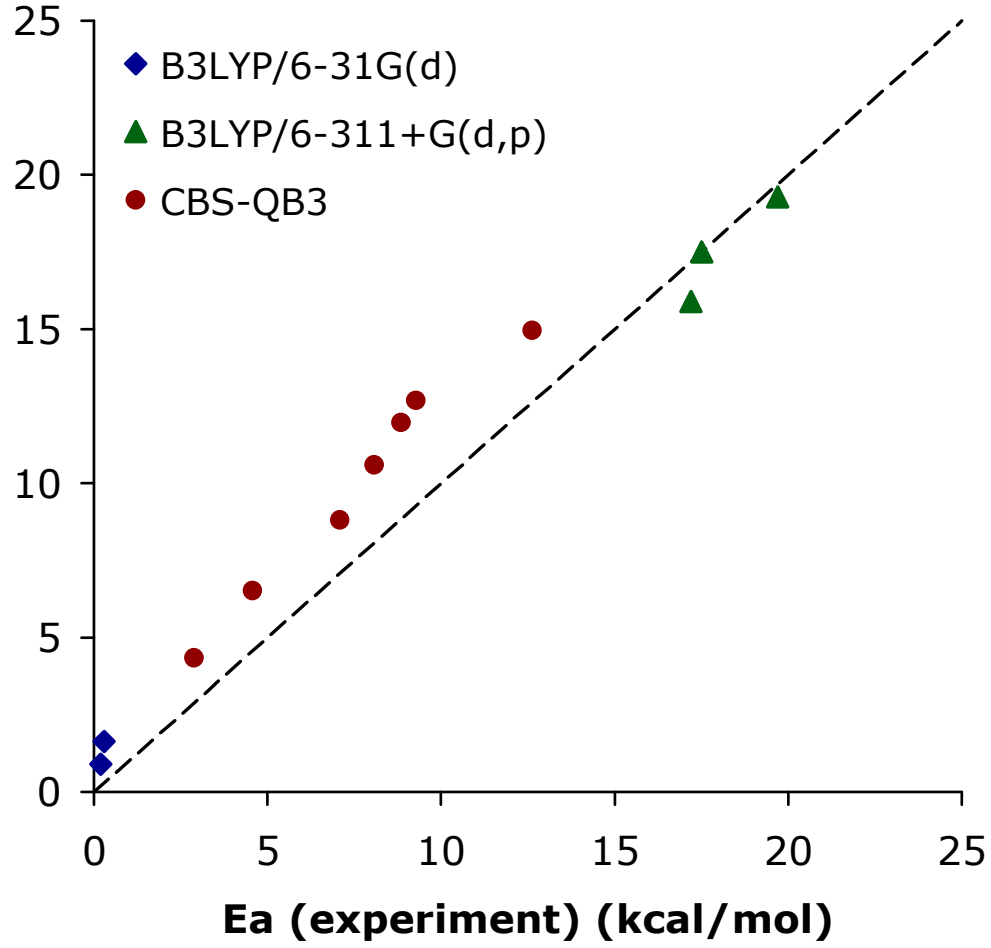


Quantum chemistry can reliably predict experimental data: *activation energy*

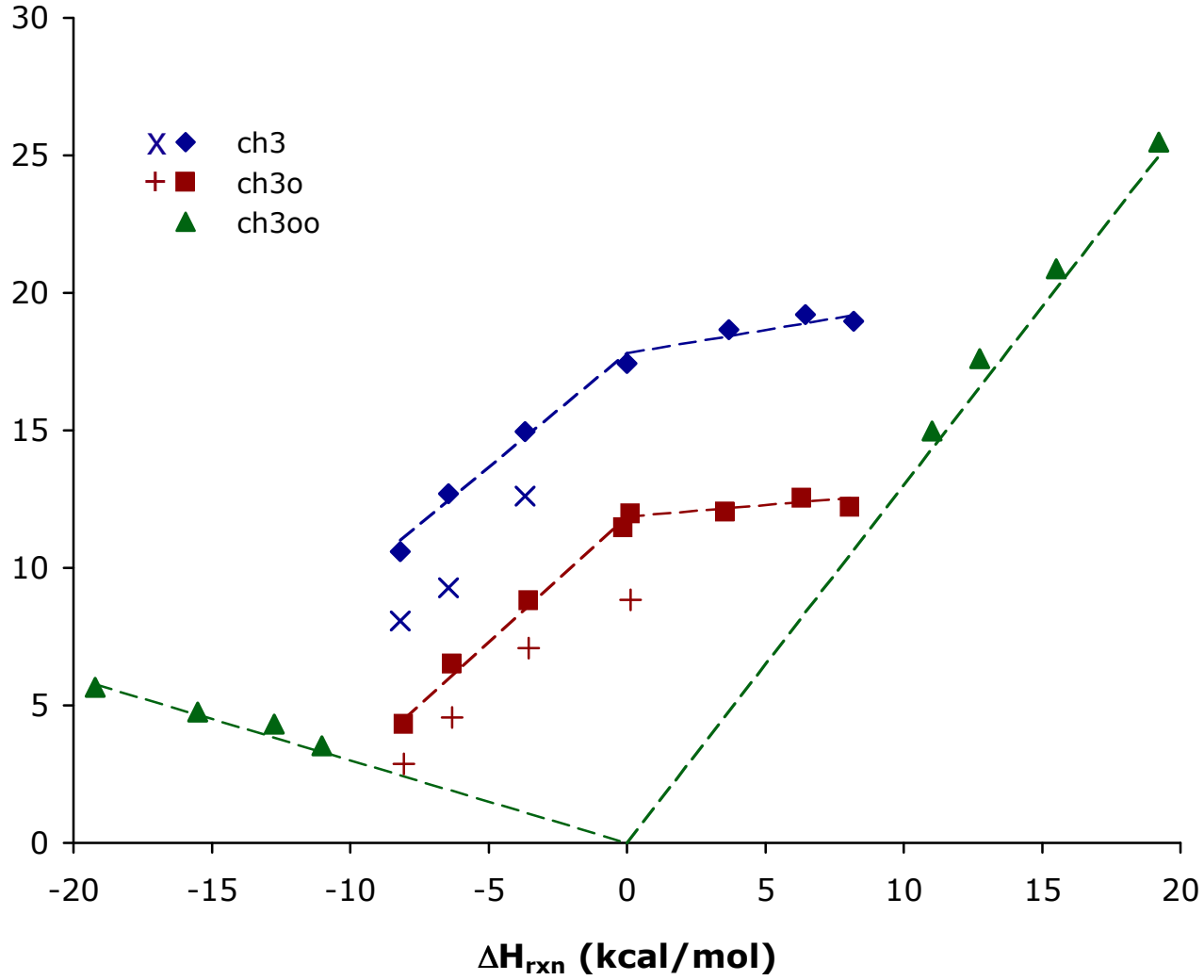
ArH + ROO• → Ar• + ROOH

ROO• → •ROOH

R'H + ROO• → R'• + ROOH

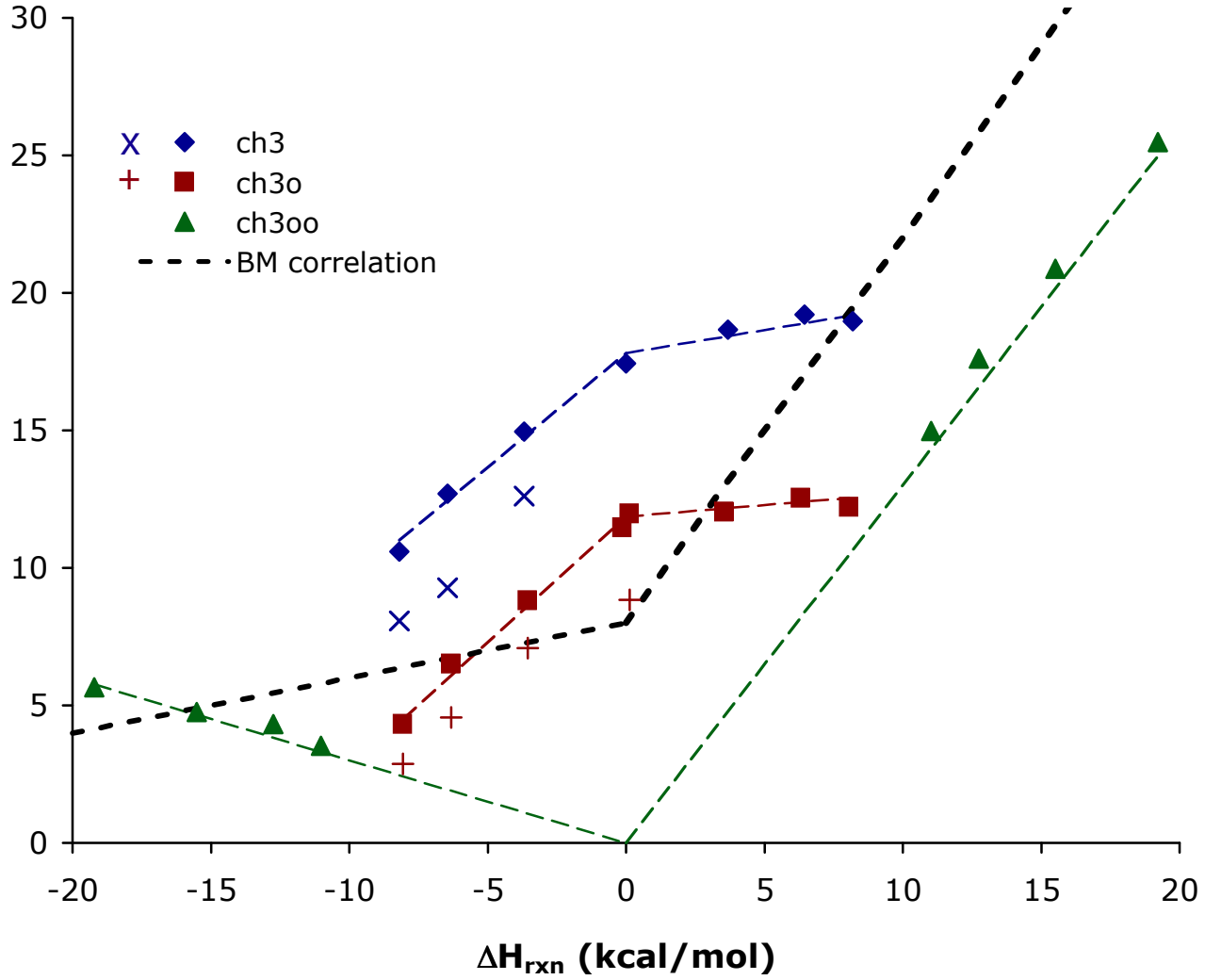


Results for bimolecular hydrogen transfer



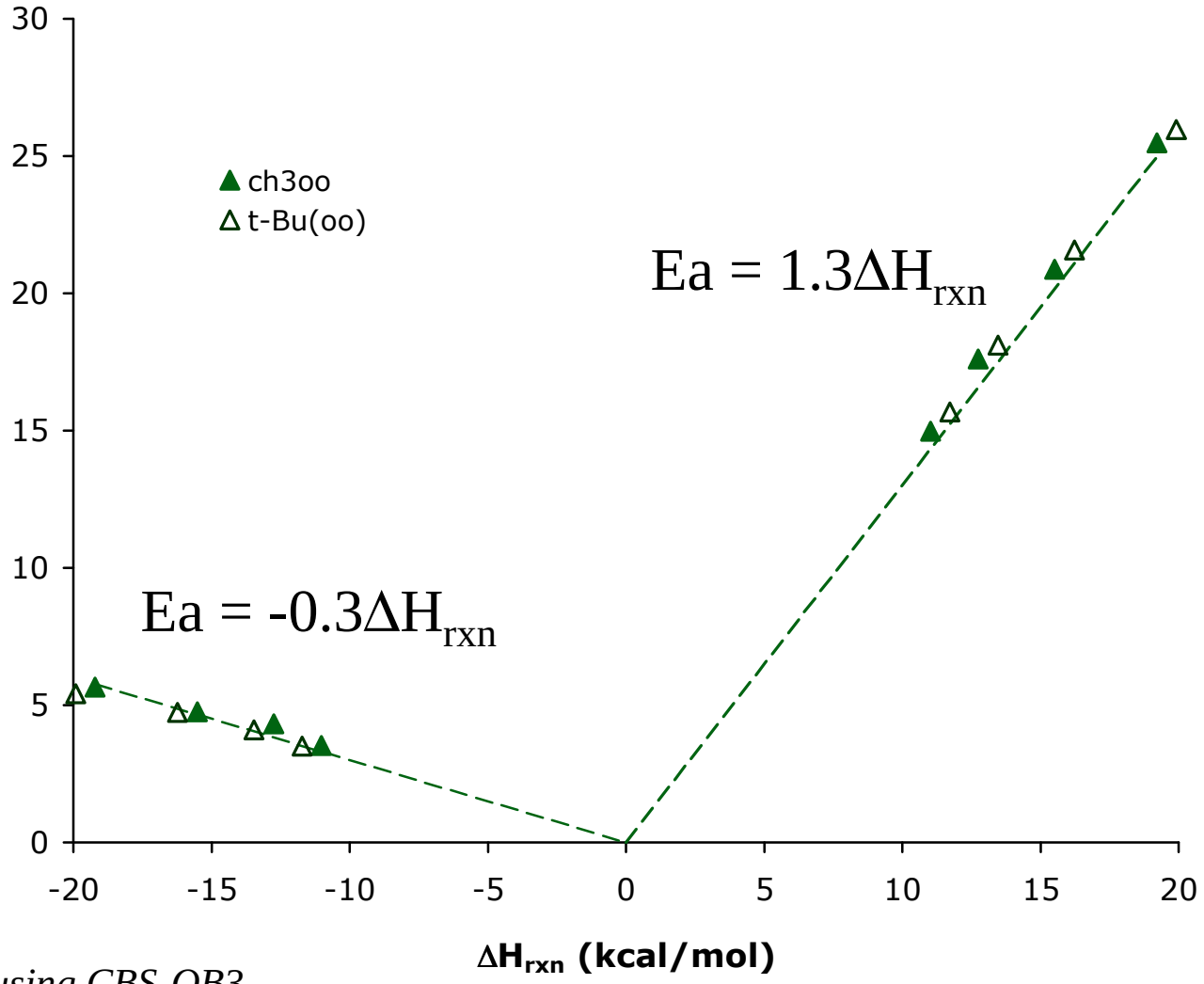
experimental data (X,+) available in NIST chemical kinetics database (http://kinetics.nist.gov)

Comparison with previous correlation



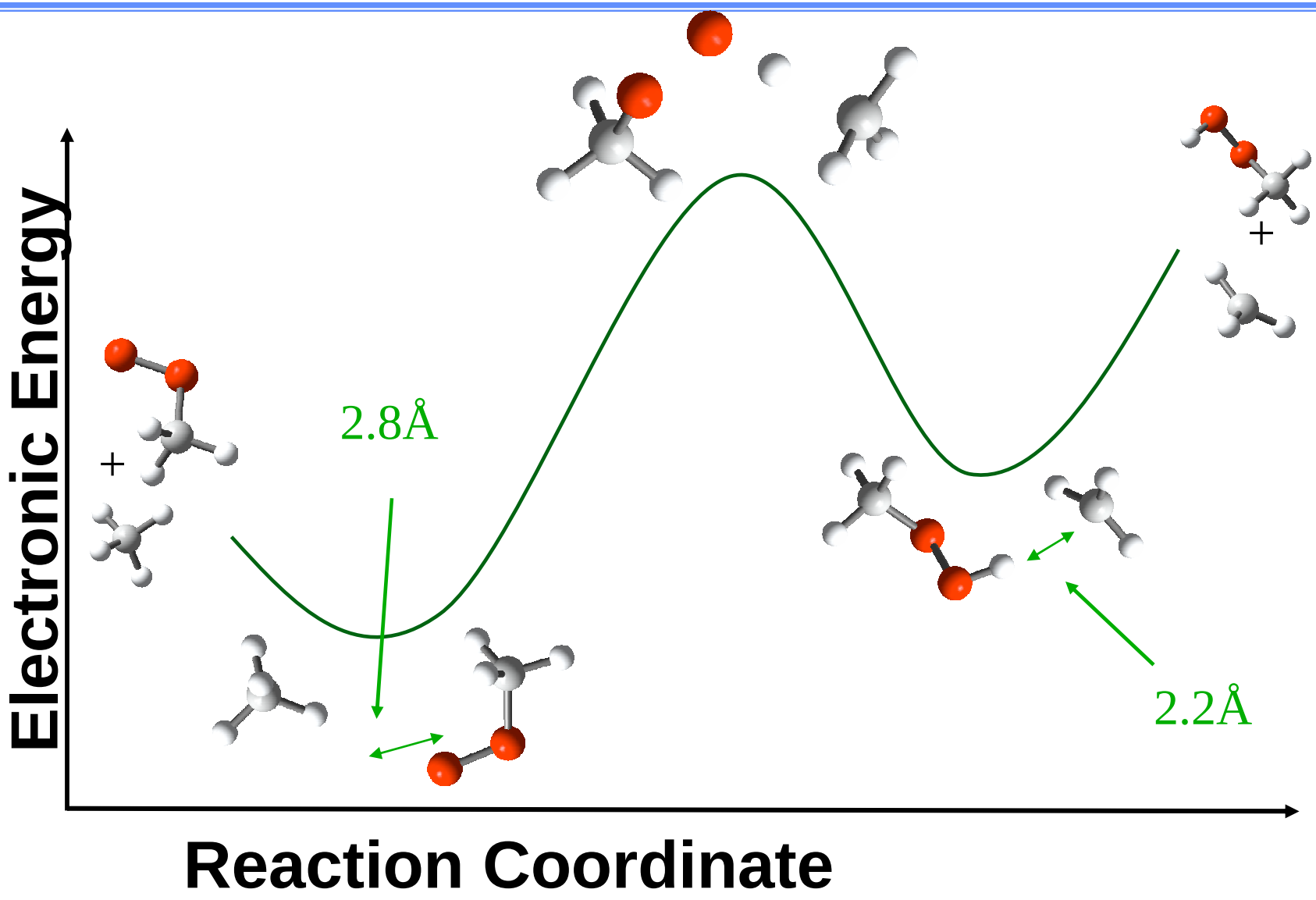
experimental activation energies (X,+) available at the NIST chemical kinetics database (http://kinetics.nist.gov)

ROO• + R'H: Contrathermodynamic behavior



Results calculated using CBS-QB3

Reaction coordinate following reveals loosely bound adducts



Hydrogen transfer specified according to sub-families

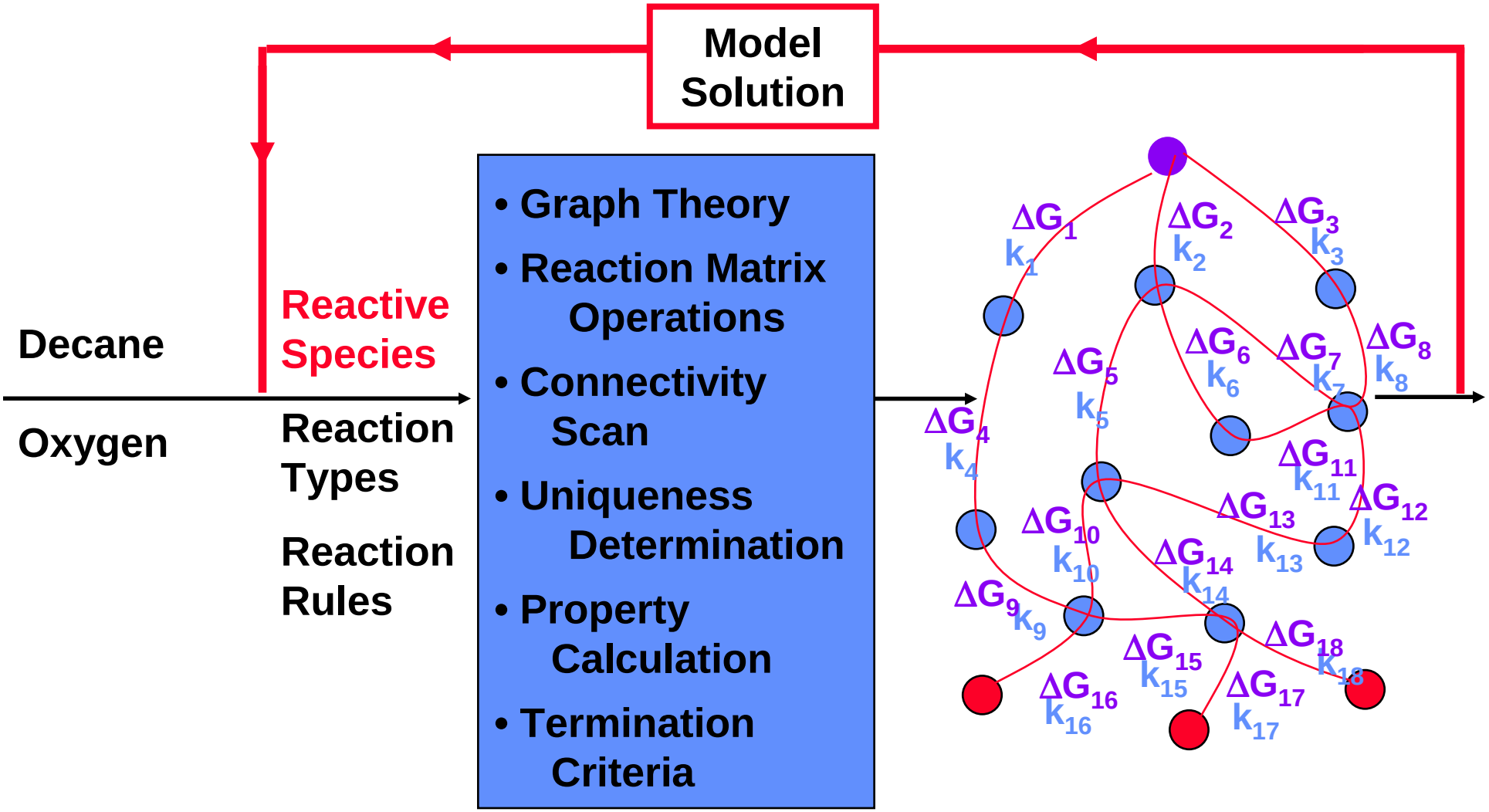
- **Oxidation of alkanes involves hundreds or thousands of hydrogen transfer reactions**
  - **< 1% experimentally available**
- **Evans-Polanyi parameters were regressed from quantum chemistry calculations**

$$E_a = E_o + \alpha \Delta H_{rxn}$$

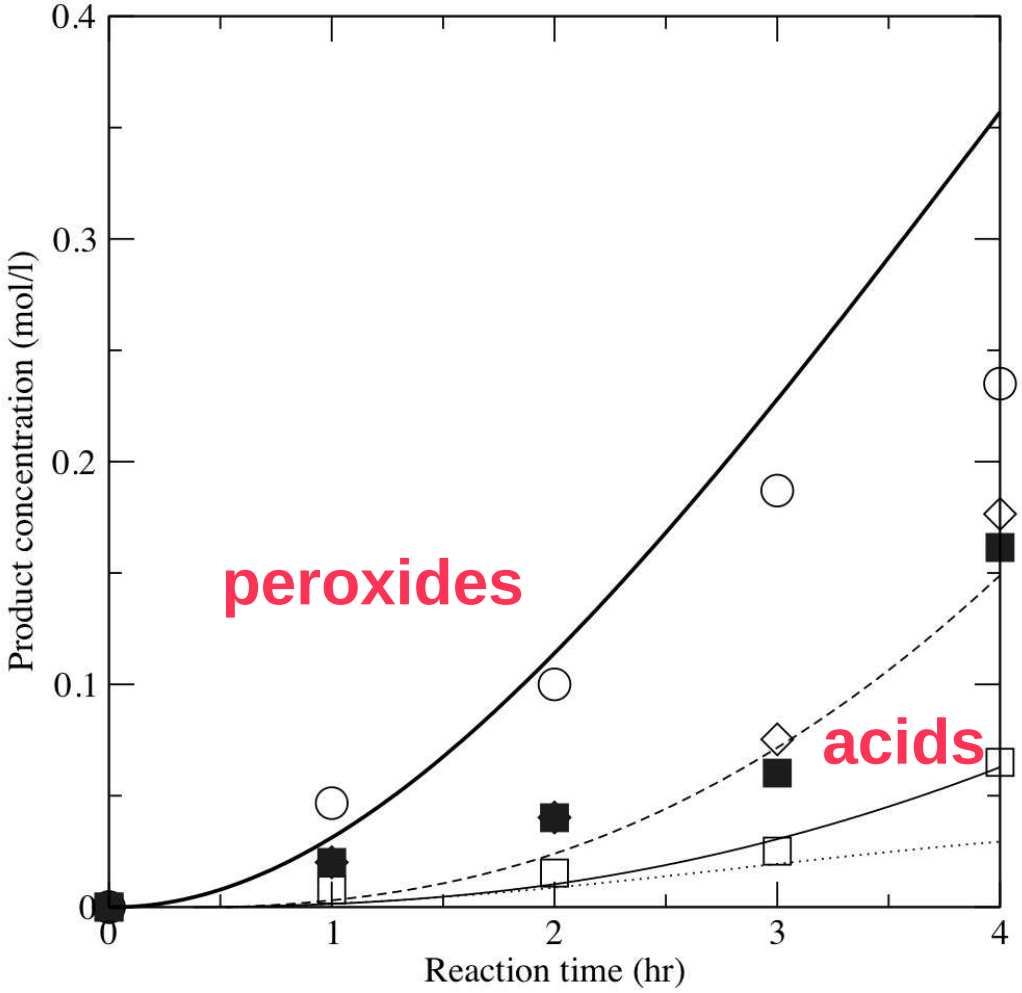
Six separate correlations:

1. RO• + R'H
2. ROO• + R'H
3. ROO• + R(CO)H (aldehydes)
4. ROO• + HCOOH (ketone forming)
5. R• + RC(O)R' (ketone consuming)
6. R• + R'H "everything else"

Iterative Rate-Based Network Construction



Application to decane autoxidation - prediction



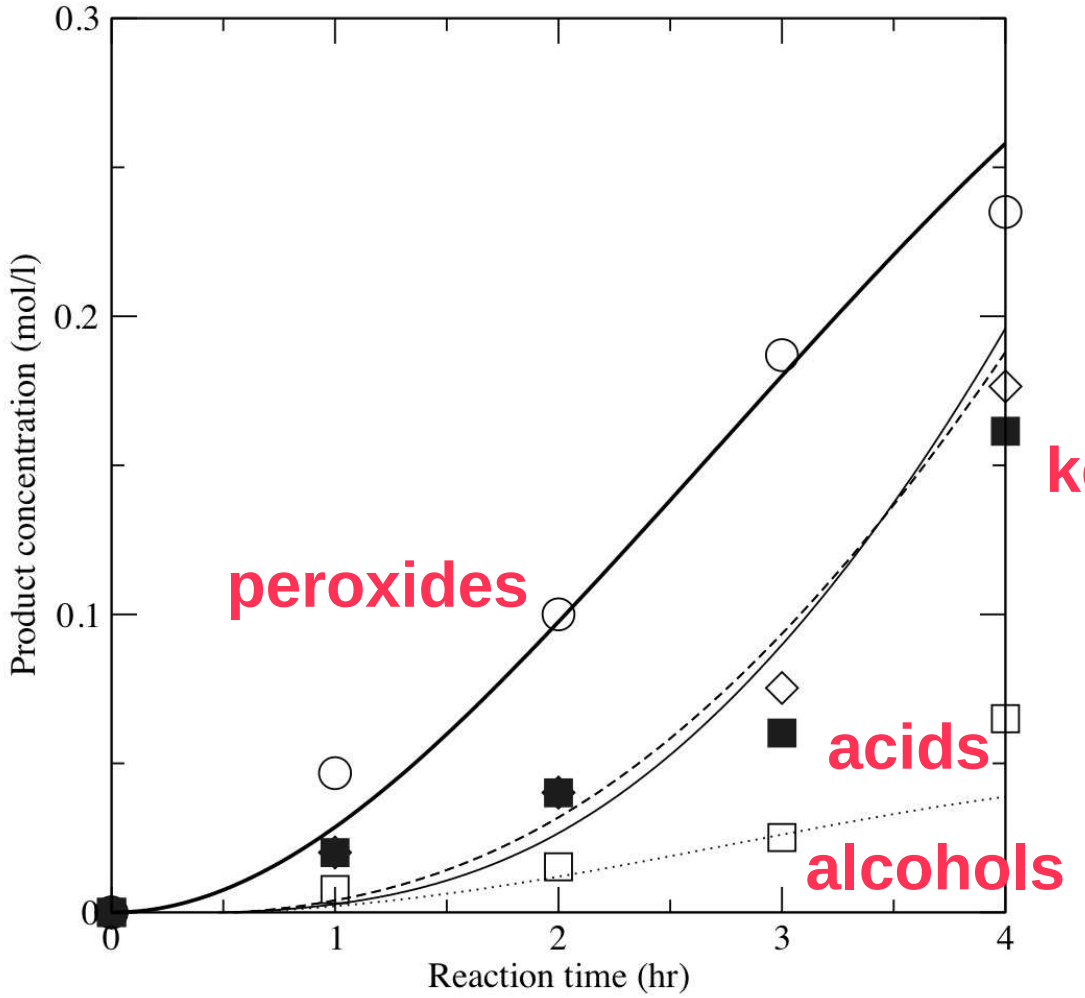
Model info:

1. 259 species, 5663 rxns - 423 K
2. 45 {A, E_o, α values} and branching ratio for disproportionation
3. **Pure prediction**

The model agrees reasonably well with experiment

Data from A. Syroezhko, V. Potekhin, and V Proskuryakov, *J. Appl. Chem. USSR.*, ***46***, 1970

Refinement of decane autoxidation



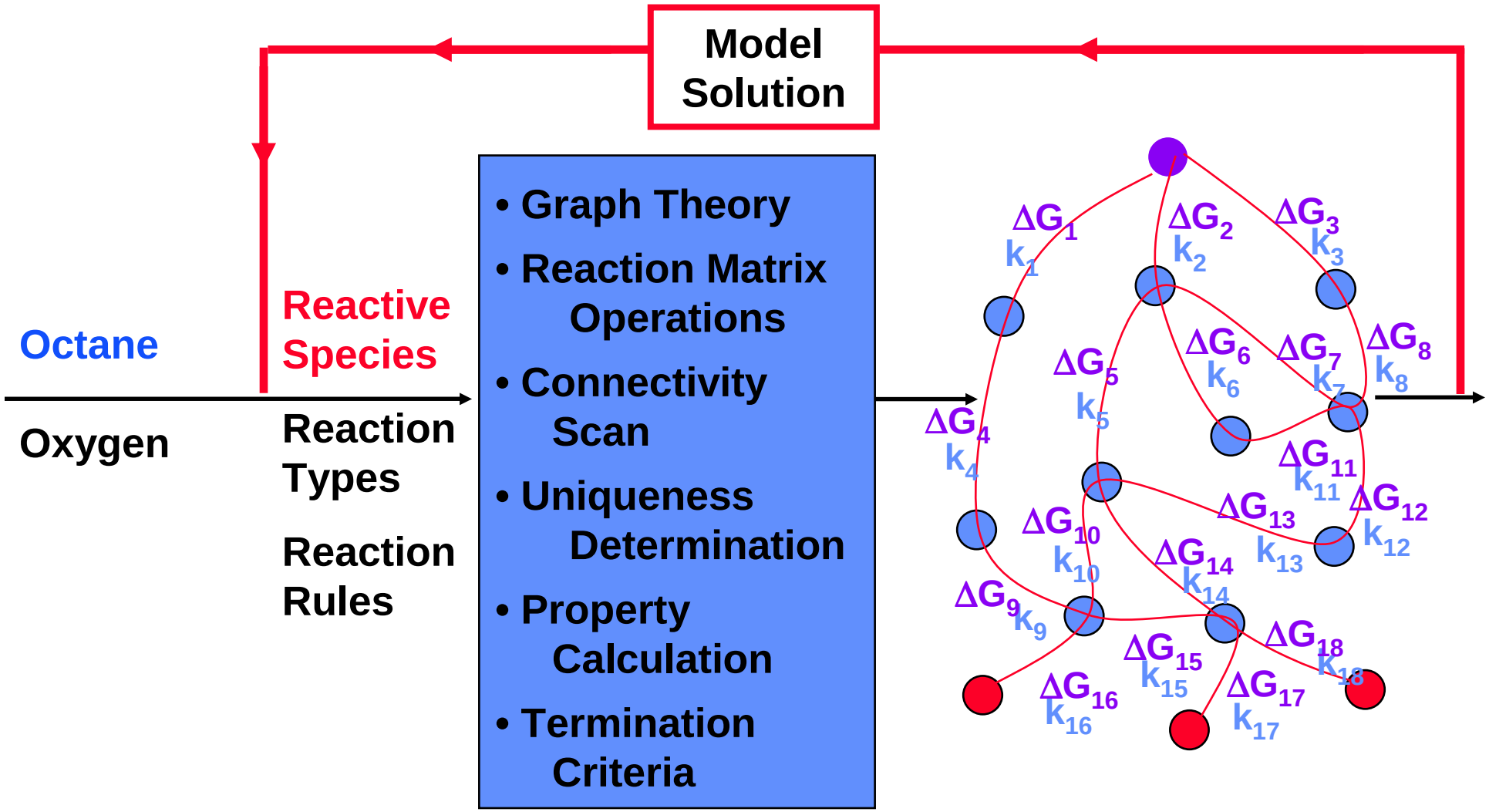
Model info:

1. 259 species, 5663 rxns - 423 K
2. 45 {A, E_o, α values} and branching ratio for disproportionation
3. **Three parameters optimized against this data**

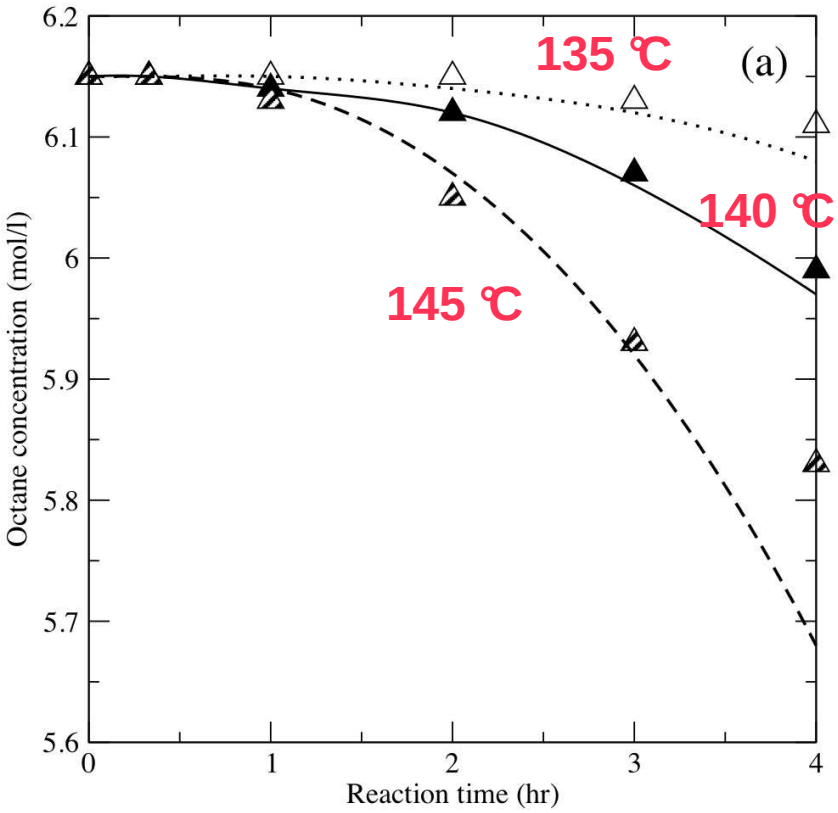
The model agrees very well with experiment

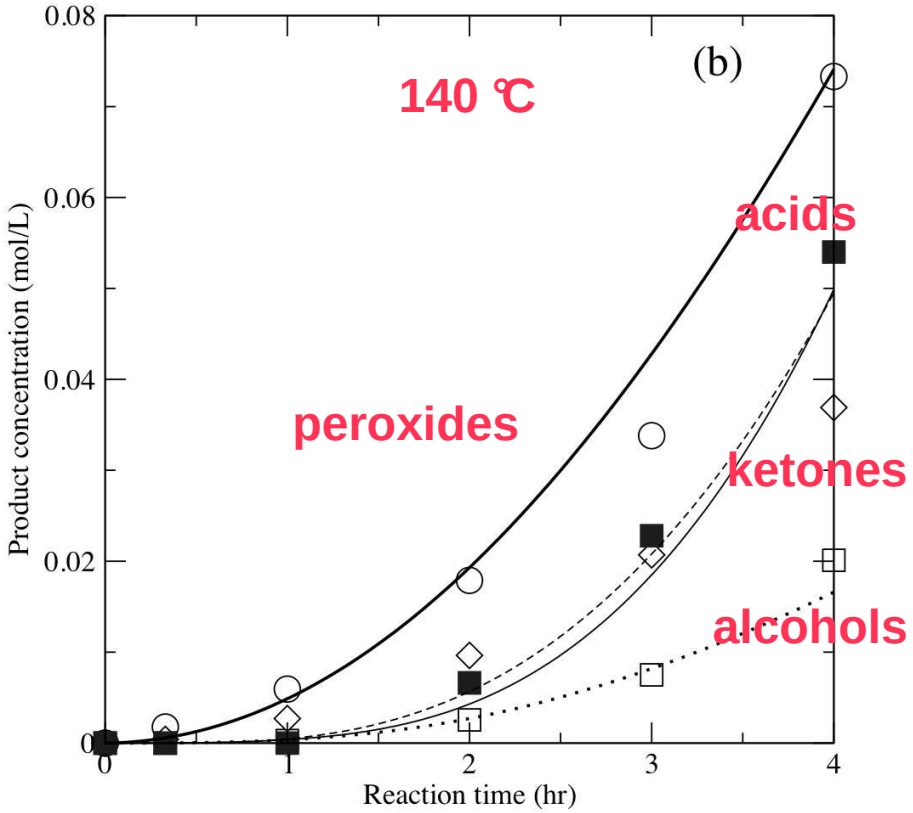
Data from A. Syroezhko, V. Potekhin, and V Proskuryakov, *J. Appl. Chem. USSR.*, ***46***, 1970

Iterative Rate-Based Network Construction



Prediction of octane autoxidation



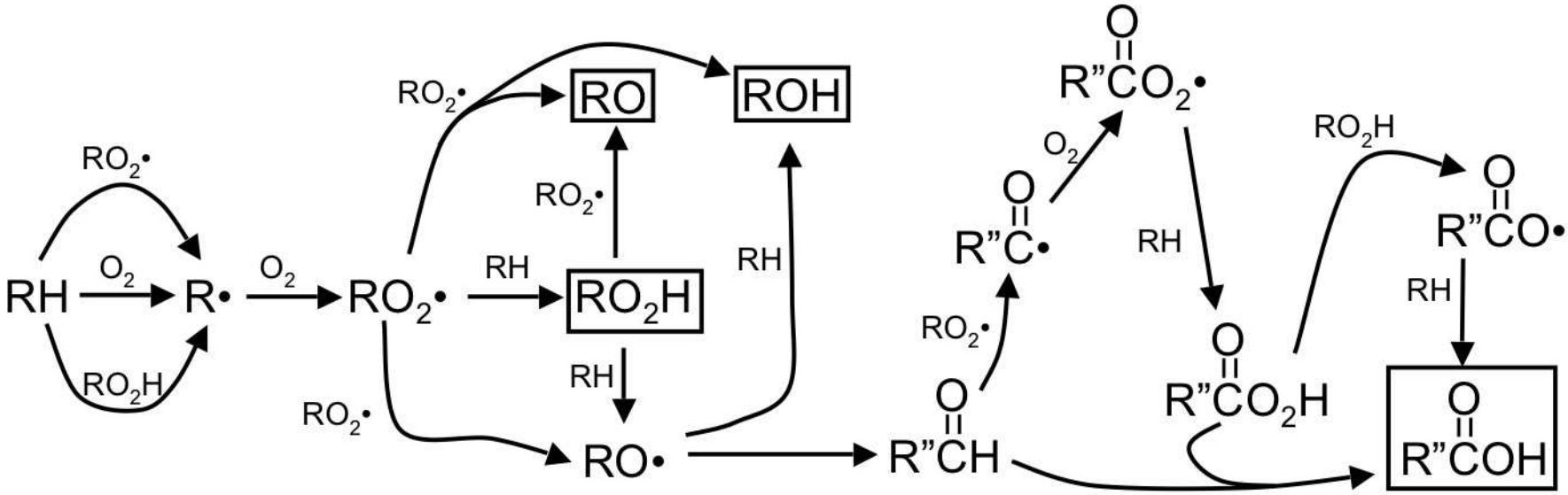


121 species, 1811 rxns

No parameters optimized against this data

Data from F. Garcia-Ochoa et al., *Ind. Eng. Chem. Res.*, ***28***, 1989

Insight into dominant reaction pathways



How Can We Reduce Tropospheric Ozone Formation?

www.inrets.fr/ur/umrette/ progdetail.htm

- Emissions of volatile organic compounds from stationary and mobile sources lead to the formation of urban smog

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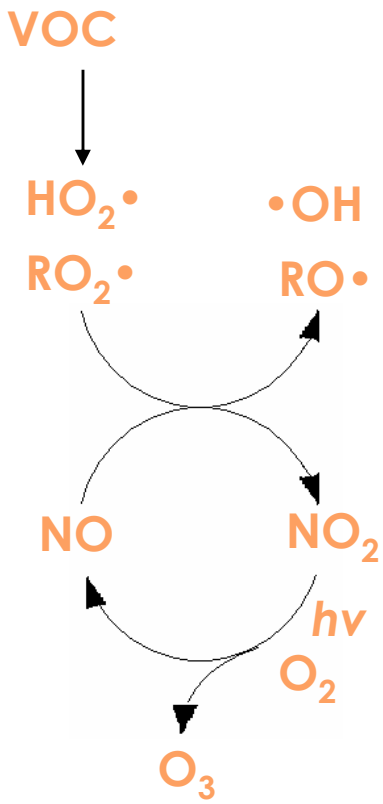
- Ozone poses a threat to human health

Overall reaction



Complex Chemistry Summarized in Terms of Reaction Matrices

Tropospheric ozone formation

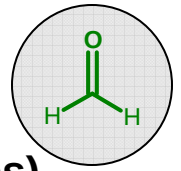
15 thermal reaction families
5 photolysis reaction families
22 small molecule reactions

Reaction Families

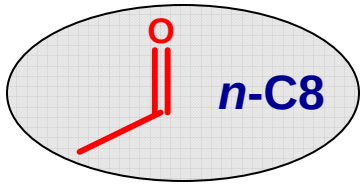
Initiation	Bond Fission	RXYR → RX• + RY•
Propagation	Oxygen Addition	$\bullet CH_3 + O_2 \rightarrow CH_3OO\bullet$
	Peroxy & NO Radical Reaction	$CH_3OO\bullet + \bullet NO \rightarrow CH_3O\bullet + \bullet NO_2$
	Oxygen Disproportionation	$C_2H_5OO\bullet + CH_3O\bullet \rightarrow C_2H_5O\bullet + \bullet CH_3 + O_2$
	Carbon Radical & Oxygen Reaction	$\bullet CH_2CH_3 + O_2 \rightarrow C_2H_4 + HOO\bullet$
	Radical Addition	$R\bullet + C_2H_4 \rightarrow \bullet CH_2CH_2R$
	Alkoxy Radical & Oxygen Reaction	$CH_3O\bullet + O_2 \rightarrow HCHO + HOO\bullet$
	β-Scission	$C_2H_5O\bullet \rightarrow \bullet CH_3 + HCHO$
	One-Five Radical Shift	$n\text{-}C_4H_9O\bullet \rightarrow \bullet C_4H_8OH$
	Hydrogen Abstraction	$R\bullet + CH_4 \rightarrow RH + \bullet CH_3$
Termination	Radical Recombination	$\bullet R_1 + \bullet R_2 \rightarrow R_1R_2$
	Peroxy Radical Disproportionation	$2\ CH_3OO\bullet \rightarrow HCHO + CH_3OH + O_2$
	Peroxy Radical Recombination	$2\ CH_3OO\bullet \rightarrow CH_3OOCH_3 + O_2$
	Peroxy & NO Radical Recombination	$CH_3OO\bullet + \bullet NO \rightarrow CH_3ONO_2$
	Alkoxy Radical & NO_x Reaction	$CH_3O\bullet + \bullet NO \rightarrow HCHO + HNO$
		$HCHO + h\nu \rightarrow CO + H_2$
Photolysis	Decarbonylation	$HCHO + h\nu \rightarrow H\bullet + \bullet CHO$
	Norrish Type I	$R_1CH_2CH_2CH_2COR_2 + h\nu \rightarrow R_1CHCH_2 + R_2COCH_3$
	Norrish Type II	
	N-O Bond Breakage	$R_1ONR_2 + h\nu \rightarrow R_1O\bullet + R_2N\bullet$
	O-O Bond Breakage	$R_1OOR_2 + h\nu \rightarrow R_1O\bullet + R_2O\bullet$

Experimental Systems Modeled

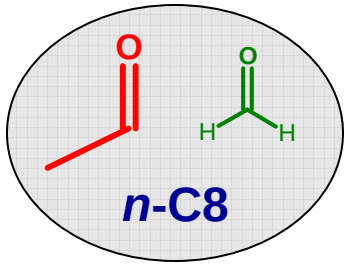
- **Formaldehyde**
  - Indoor chamber **(ETC, ~4 m^3)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, Nitrates)**
  - Outdoor chamber **(~300 m^3)**
    - **Exposed to natural sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, NO_2)**



- **Acetaldehyde and n-Octane Mixture**
  - **Indoor chamber (DTC)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species (CH_3CHO, nC8, O_3, NO, Nitrates, PAN, HCHO)**



- **Acetaldehyde, Formaldehyde and n-Octane Mixture**
  - **Indoor chamber (XTC)**
    - **Xenon light source to mimic sunlight**
    - **Monitor major reactant and product species (HCHO, CH_3CHO, O_3, NO, Nitrates, PAN)**



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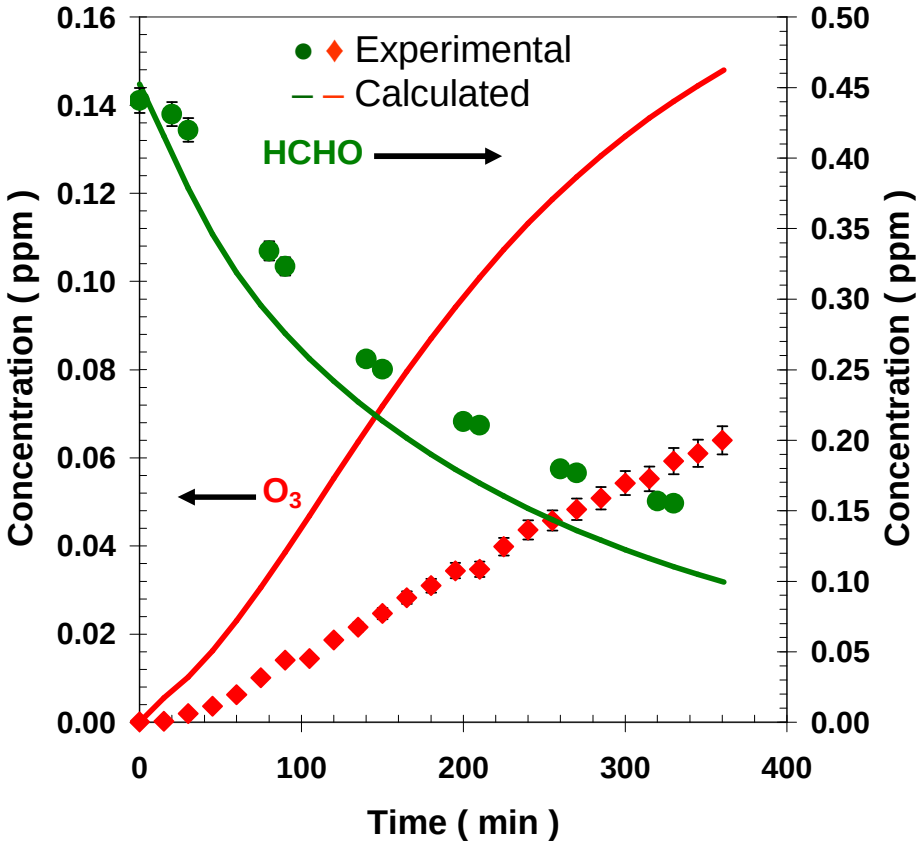
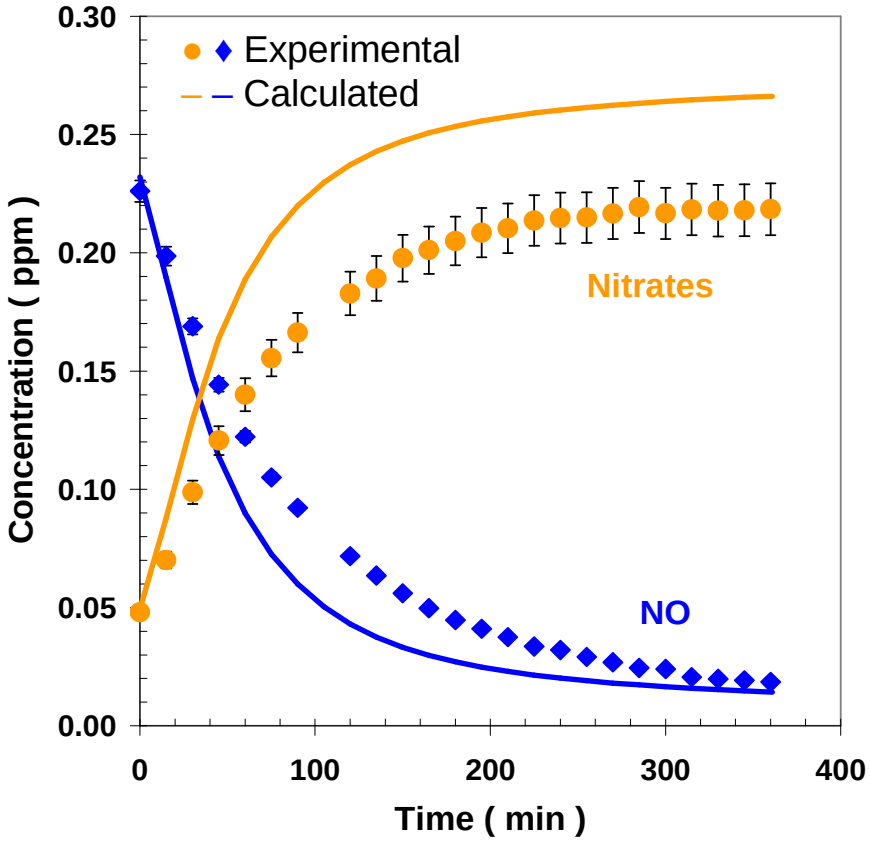
http://airchem.sph.unc.edu/Research/Facilities/UNCChamber/default.htm#tomap

Formaldehyde Indoor Chamber Results

- **All concentrations agree well with experimental data**
- **Trends are captured**
- No fitting of parameters

Mechanism
38 species
148 reactions
$1x10^{-4}$ threshold

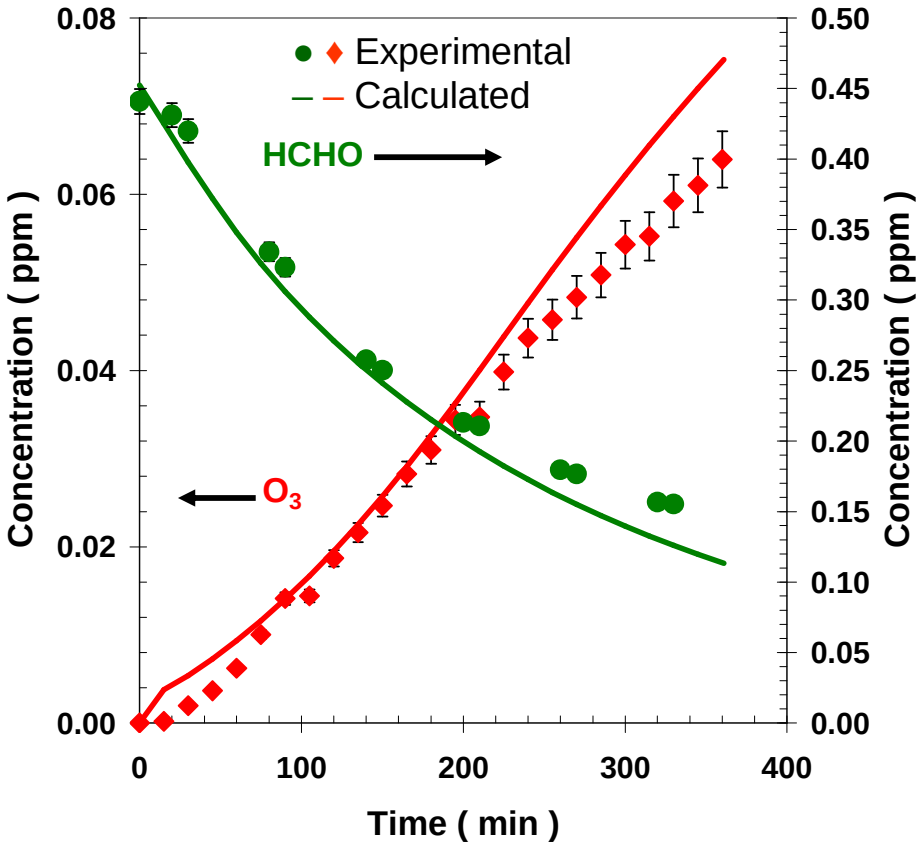


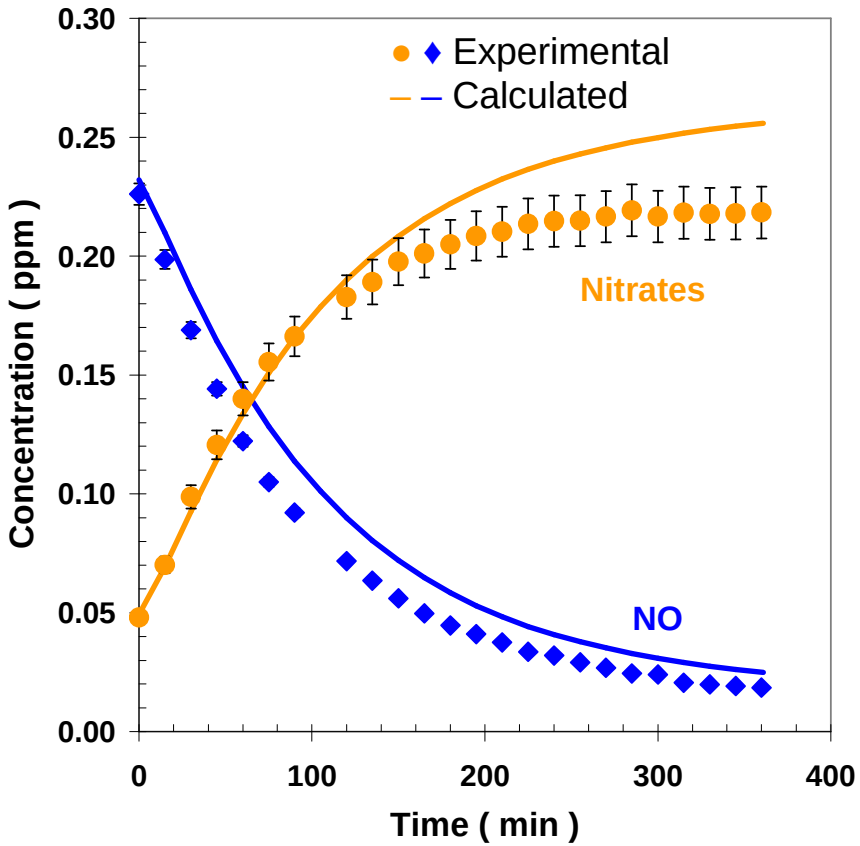


Optimization of Rate Parameters for Formaldehyde Indoor Chamber

- **Optimize parameters to which the model is most sensitive**
- **All concentrations agree well with experimental data**

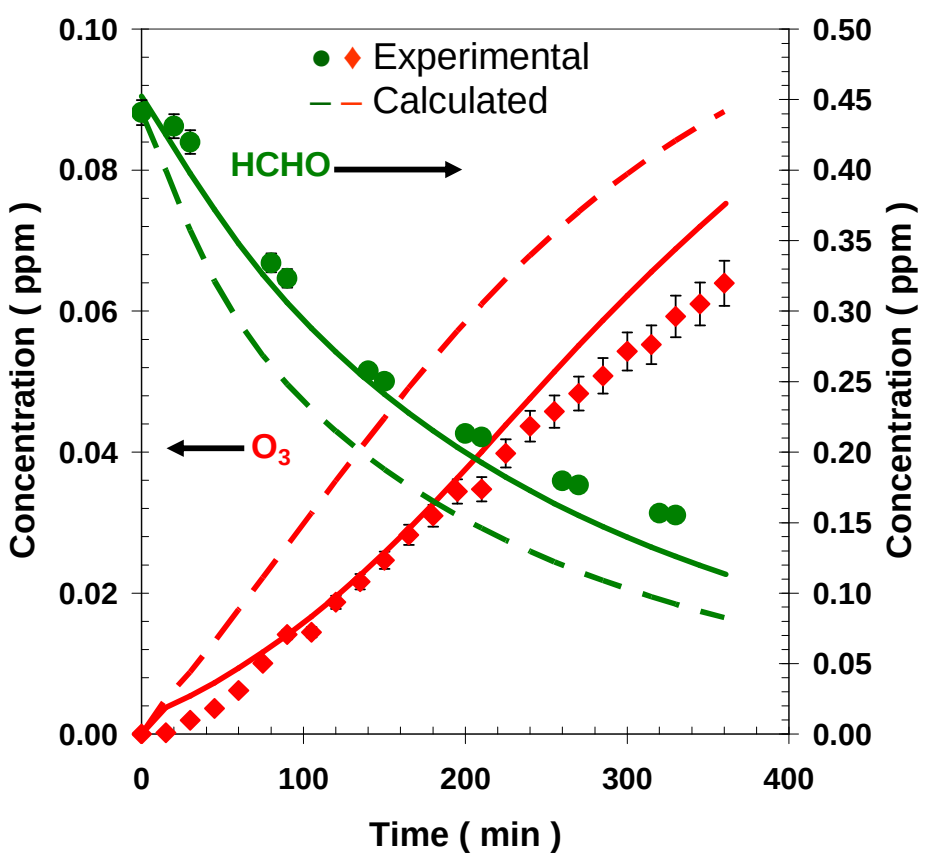
Optimized
1 reaction family A

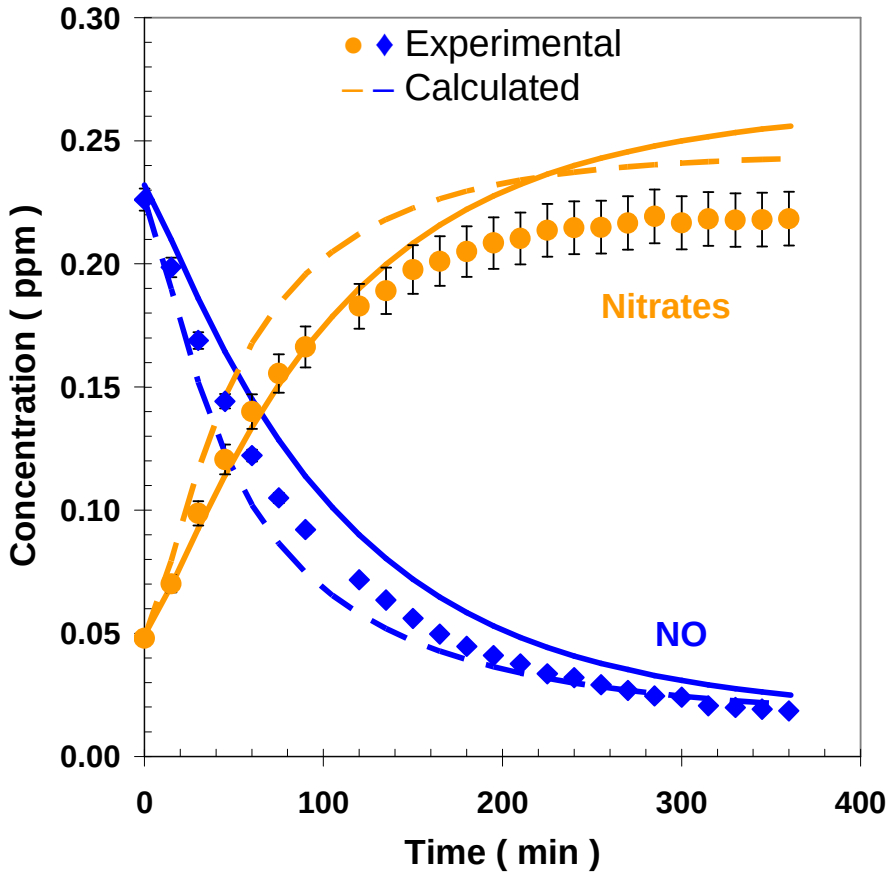




Comparison to a Lumped Model

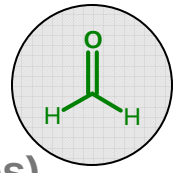
- Dashed lines are results from the SAPRC99 software by Carter
- Explicit model is more accurate than the lumped structure model





Experimental Systems Modeled

- **Formaldehyde**
  - Indoor chamber **(ITC, ~4 m^3)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, Nitrates)**
  - Outdoor chamber **(~300 m^3)**
    - **Exposed to natural sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, NO_2)**



- **Acetaldehyde and n-Octane Mixture**
  - **Indoor chamber (DTC)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species**
    - **(CH_3CHO, nC8, O_3, NO, Nitrates, PAN, HCHO)**

- **Acetaldehyde, Formaldehyde and n-Octane Mixture**
  - **Indoor chamber (XTC)**
    - **Xenon light source to mimic sunlight**
    - **Monitor major reactant and product species ($HCHO$, CH_3CHO, O_3, NO, Nitrates, PAN)**

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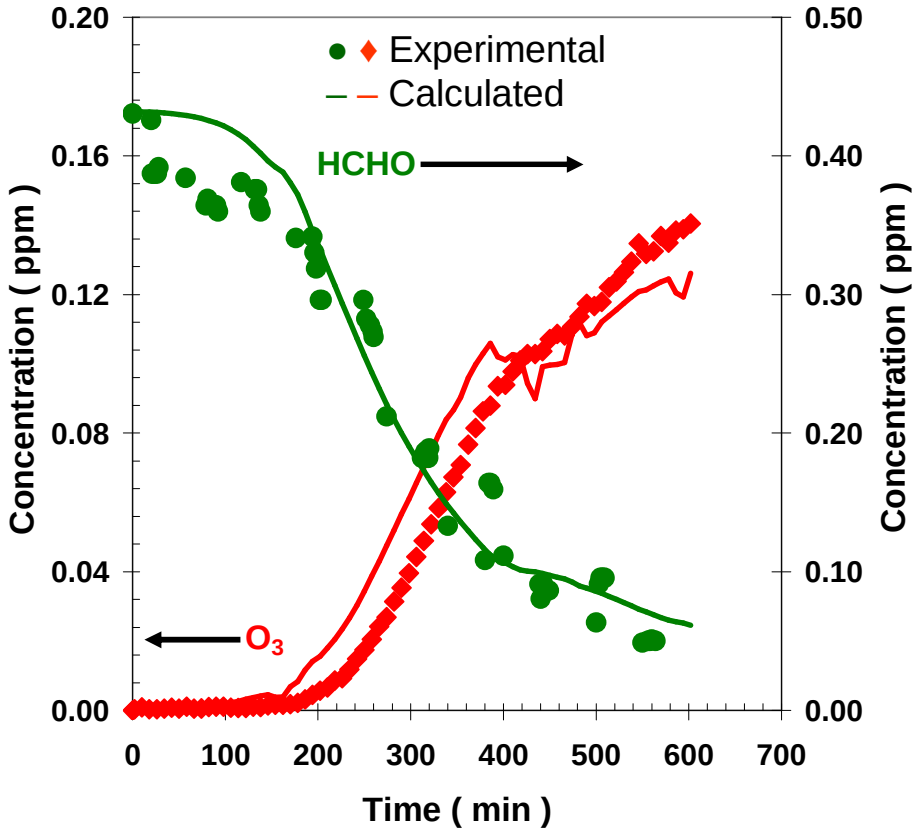
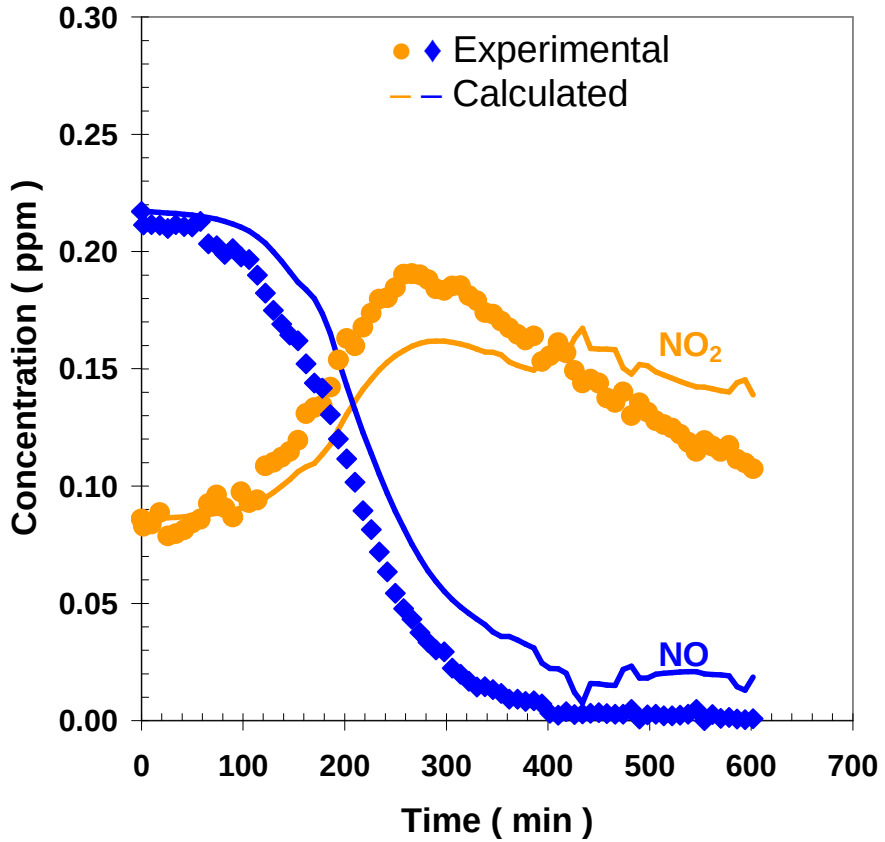
Indoor Chamber Parameters Applied to Outdoor Chamber

- **All concentrations agree reasonably well with experimental data**
- No adjustment in parameters

Mechanism
Same as indoor chamber with different photolysis rates

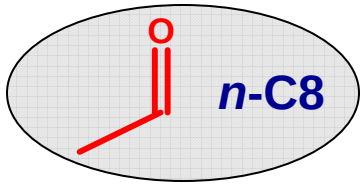




Experimental Systems Modeled

- **Formaldehyde**
  - Indoor chamber **(ITC, ~4 m^3)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, Nitrates)**
  - Outdoor chamber **(~300 m^3)**
    - **Exposed to natural sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, NO_2)**

- **Acetaldehyde and n-Octane Mixture**
  - **Indoor chamber (DTC)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species**
    - **(CH_3CHO, nC8, O_3, NO, Nitrates, PAN, HCHO)**



- **Acetaldehyde, Formaldehyde and n-Octane Mixture**
  - **Indoor chamber (XTC)**
    - **Xenon light source to mimic sunlight**
    - **Monitor major reactant and product species (HCHO, CH_3CHO, O_3, NO, Nitrates, PAN)**

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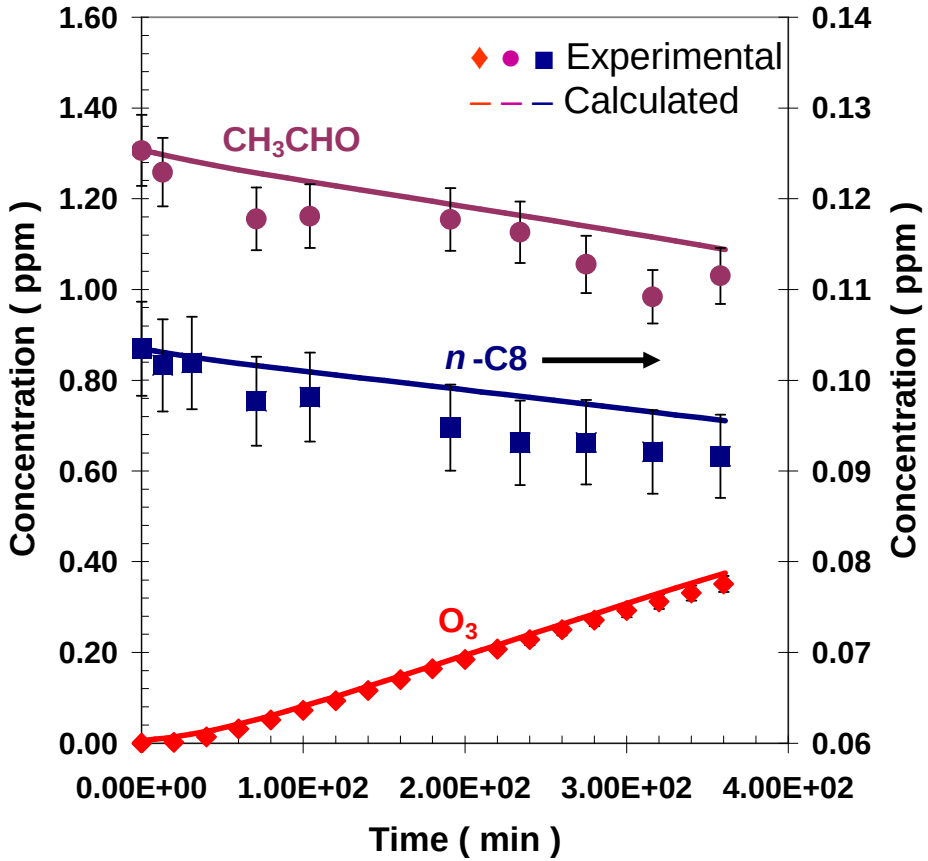
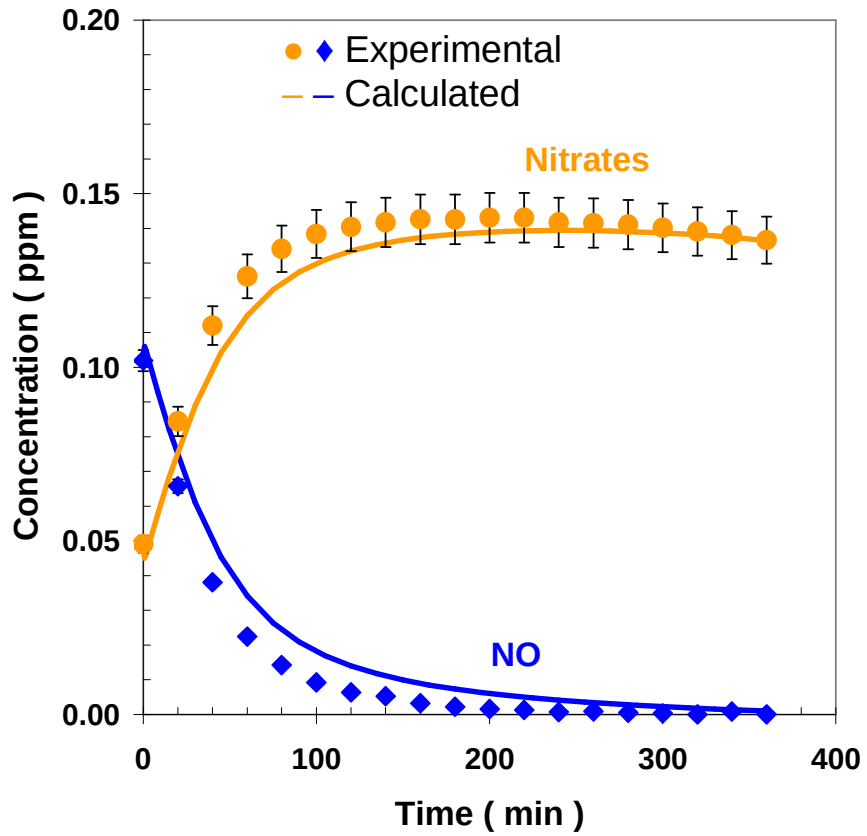
Acetaldehyde-n-Octane Indoor Chamber Results

- **Apply the parameters from the optimized formaldehyde model**
- **Trends are all captured very well**
- No adjustment in parameters

Mechanism
305 species
4555 reactions
$1x10^{-4}$ threshold



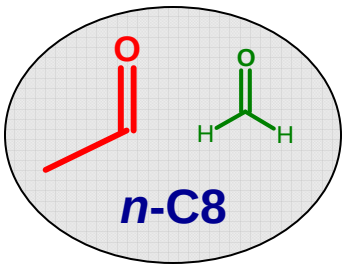


Experimental Systems Modeled

- **Formaldehyde**
  - Indoor chamber **(ITC, ~4 m^3)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, Nitrates)**
  - Outdoor chamber **(~300 m^3)**
    - **Exposed to natural sunlight**
    - **Monitor major reactant and product species (HCHO, O_3, NO, NO_2)**

- **Acetaldehyde and n-Octane Mixture**
  - **Indoor chamber (DTC)**
    - **Blacklight to mimic sunlight**
    - **Monitor major reactant and product species**
    - **(CH_3CHO, nC8, O_3, NO, Nitrates, PAN, HCHO)**

- **Acetaldehyde, Formaldehyde and n-Octane Mixture**
  - **Indoor chamber (XTC)**
    - **Xenon light source to mimic sunlight**
    - **Monitor major reactant and product species (HCHO, CH_3CHO, O_3, NO, Nitrates, PAN)**



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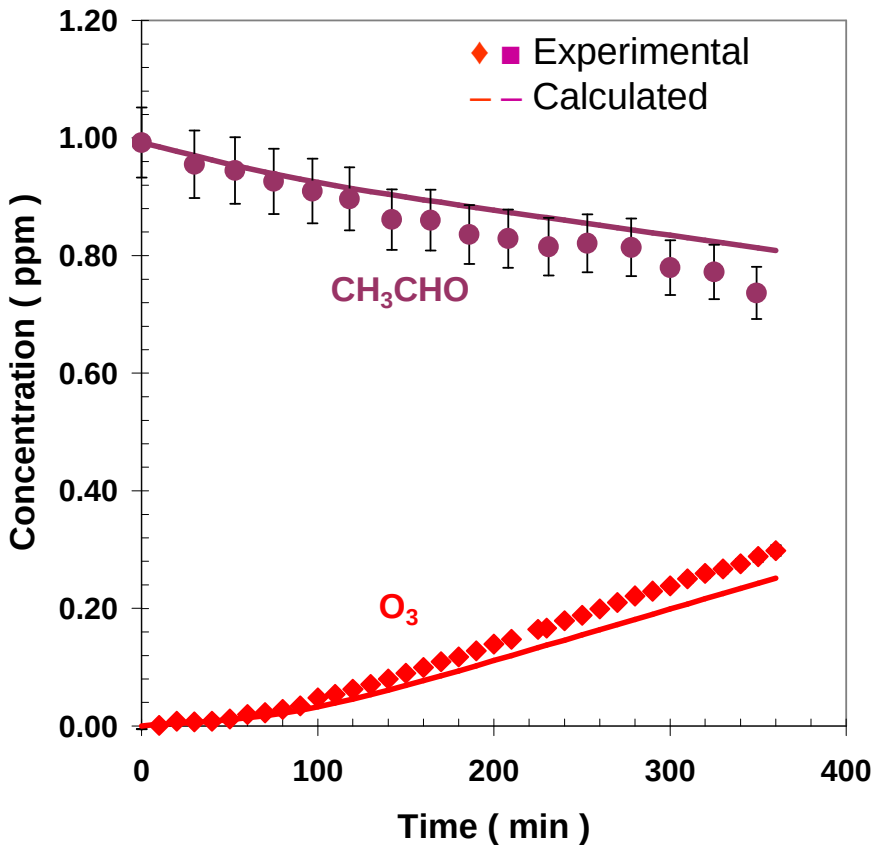
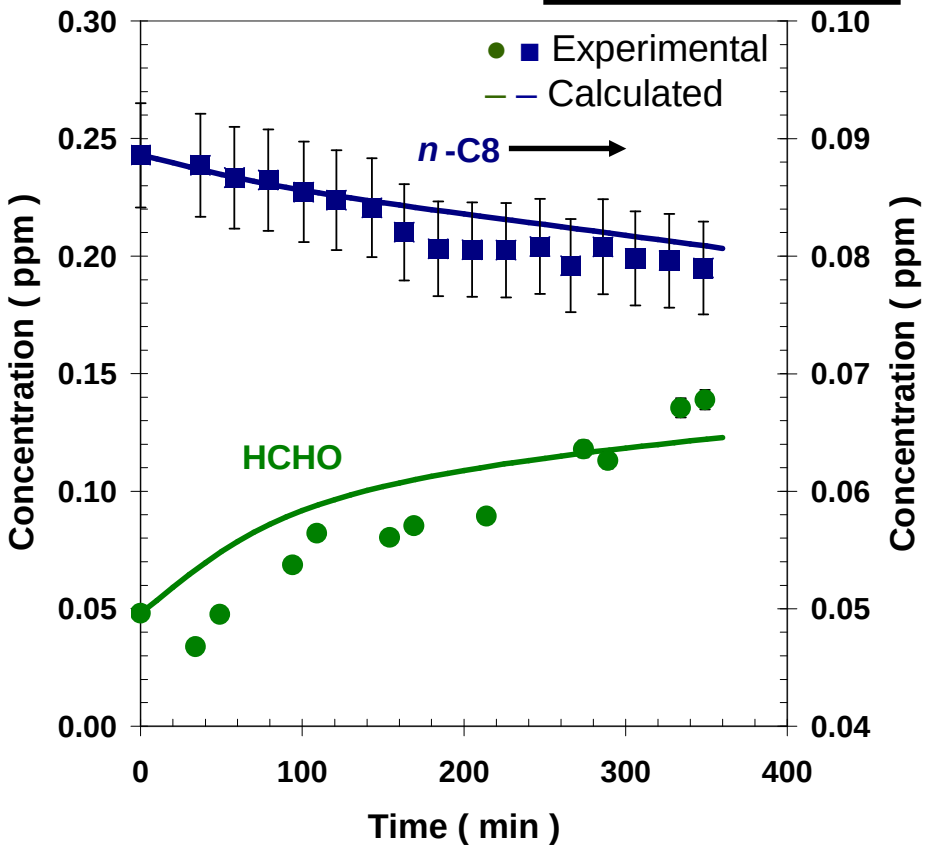
Formaldehyde-Acetaldehyde-*n*-Octane Indoor Chamber Results

- **Same mechanism used as in the acetaldehyde-*n*-octane model**
- **NO and nitrates are not shown here but equally well modeled**
- No adjustment in parameters

Mechanism
305 species
4555 reactions
$1x10^{-4}$ threshold





Accomplishments

- Reaction families **and** kinetic correlations **for condensed-phase hydrocarbon autoxidation and atmospheric oxidation of volatile organic compounds**
- **Incorporation of** oxidation chemistry **into automated mechanism generation framework**
- **Creation of** reaction mechanisms **which quantitatively describe degradation of model lubricants and tropospheric ozone formation**

Acknowledgments

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EUROKIN