A Systematic Study of Radical Addition Reactions to Substituted Benzenes and the Reverse $\beta$-Scission Reactions

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Aromatic molecules play an important role in pyrolysis chemistry

- Molecular weight grows chemistry
  - Source for carbon black
  - Coking of reactors
  - Sooting in combustion systems

Light fractions from oil or NGL
  - Ethane
  - Propane
  - Naphtha

Steaming cracking

Base Chemicals
  - Ethene
  - Propene
  - Butadiene
  - Aromatics

Pilot steam cracker
Thermochemical Conversion Of Biomass => Aromatics

- Thermochemical conversion of biomass produces large amounts of aromatic products
- Subsequent chemistry has a significant impact on the product quality (bio-oils)
- Large amounts of benzene and toluene at higher temperatures has been related to initial pool of aromatics
Addition-Elimination Reactions Are Important in (subst.) Syringol Pyrolysis

Flash vacuum pyrolysis experiments indicate importance of addition/elimination chemistry (Britt et al. J. Org. Chem. 2000, 65, 1376-1389)

Possible/likely mechanism involves H,CH₃ addition; note: 30% of the products

Kinetic modeling of biomass pyrolysis Radical requires the inclusion of addition reactions to aromatic species and their reverse reactions.
Long-Term Objective: Let Computers Create the Models

Conditions
- Reactants
- T
- P
- Reaction time
- Reactor model
- Termination criteria

Automated Mech Gen. (RMG or Genesys)

Reaction mechanism
- complete
- consistent
- error free
- quickly generated

Thermo databases (Group Additivity)

kinetic databases (Group Additivity)

GAV/NNI for
- 143 closed-shell subst. benzenes
- > 300 radicals

G4BAC - GA

Closed-shell

![Molecular structure]

![Bar chart]

Number of Molecules

$\Delta H^0$ [kJmol$^{-1}$]
Long-Term Objective: Let Computers Create the Models

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- T
- P
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Reaction mechanism
- complete
- consistent
- error free
- quickly generated

Automated Mech Gen. (RMG or Genesys)

Thermo databases (Group Additivity)
kinetic databases (Group Additivity)

24 GAV/NNI for
- 104 C₆-cyclic radicals

CBS-QB3^{BAC} – GA

\[ \Delta H^{298} \text{[kJ/mol]} \]
Long-Term Objective: Let Computers Create the Models

Conditions
- Reactants
- T
- P
- Reaction time
- Reactor model
- Termination criteria

Automated Mech Gen. (RMG or Genesys)

Reaction mechanism
- complete
- consistent
- error free
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Thermo databases (Group Additivity)

Kinetic databases (Group Additivity)

Thermo:
\[ y = \sum_{i} (n_i \cdot GAV_{y,i}) + \sum_{j} (n_j \cdot NNI_{y,j}) \]

Kinetics:
- database for kinetics Group Additivity parameters (\(\Delta GAV^0\)) is incomplete

One of the missing reaction families is

Objective of this study:
1. Systematic investigation of reaction family
2. Impact of X, Y, Z on reactivity
3. Will \(\Delta GAV^0\) approach work?
Group Additivity To Predict Rate Parameters

\[ k_{TST} = n_e \cdot \frac{k_BT}{h} \cdot \left( \frac{RT}{p} \right)^{\Delta n} \cdot e^{-(\Delta_{\hat{H}} - T\Delta_{\hat{S}})/RT} = n_e \cdot \tilde{k} \quad ; \quad n_e = \frac{n_{\text{opt},\hat{H}}}{\prod_j n_{\text{opt},j}} \cdot \frac{\prod_j \sigma_{\text{react}}}{\sigma_{\hat{H}}} \]

\[ E_a(T) = RT^2 \cdot \frac{\partial \ln(k)}{\partial T} = \Delta_{\hat{H}} + (1 + \Delta n)RT \]

\[ \tilde{A}(T) = \frac{k_BT}{h} \cdot \left( \frac{RT}{p} \right)^{\Delta n} \cdot e^{\frac{\Delta_{\hat{S}}}{\tilde{R}}} \cdot e^{1+\Delta n} \]

GAV is well-known to work for H, S, Cp

\[ \Rightarrow \text{Similar GA approach must work for } E_a, \tilde{A} \]

Introducing a reference reactions finally leads to

\[ E_a(T) = E_{a,\text{ref}}(T) + \sum_{i=1}^{3} \Delta GAV_{\text{ref}_Ea,T}(R_i) + \sum_{j=1}^{N} \Delta NNI_{Ea,T,j}^{0} \]

\[ \log_1 \tilde{A}(T) = \log_1 \tilde{A}_{\text{ref}}(T) + \sum_{i=1}^{3} \Delta GAV_{\log\tilde{A},T}(R_i) + \sum_{j=1}^{N} \Delta NNI_{\log\tilde{A},T,j}^{0} \]

**R_2 variations**

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\[ R_1, R_2, R_3 => \Delta GAV^{0} \]

\[ X_i, Y_j, Z_k => \Delta NNI^{0} \]
Methodology

QM calcs CBS-QB3 level

Geometry Frequencies Electronic Energy
Hindrance potentials for internal rotors (B3LYP/6-31G(d)

Just relative energies needed => no BAC

Statistical Mech. Atomization Method

$\Delta^+ H^0$, $S^0$ and $cp(T)$
NASA polynomials
all internal rotors replaced

TSTdG Eckart tunneling

Arrhenius expressions

$k(T)$

$\Delta G^+$

$\Delta f H^0$, $S^0$ and $cp(T)$

$k(T) = \chi(T) \cdot \frac{k_B T}{h} \cdot \left( \frac{RT}{p} \right)^{\Delta n - 1} \cdot e^{-\frac{\Delta G^+}{RT}}$

Single event rate coefficient $\tilde{k}$:

$k_{TST} = n_e \cdot \tilde{k}$; $n_e = \frac{n_{opt,\pm}}{\prod_{j=1}^{n_{react}} \frac{n_{opt,j}}{\sigma_j}} \cdot \frac{\prod_{j=1}^{n_{react}} \sigma_j}{\sigma_\pm}$

Methodology chosen to be consistent with previous work of this lab
Intuition: reactivity should depend on X,Y,Z

But only X is involved in bond breaking/making
Y, Z only indirectly (non-nearest neighbor interaction NNI) involved

\[ E_a(T) = E_{a,ref}(T) + \sum_{i=1}^{3} \Delta GAV_{Ea,T}(R_i) \]
\[ \log_1 \tilde{\alpha}(T) = \log_1 \tilde{\alpha}_{ref}(T) + \sum_{i=1}^{3} \Delta GAV_{log\tilde{\alpha},T}(R_i) \]

Expectation is that “X” affects reactivity most

Suitable reference reaction for carbon-centered radical addition would be

\[ \text{CH}_3 + \text{benzene or CH}_3 + \text{toluene} \]
How does the type of the adding radical (X) change the reactivity?
\[ X + \text{PhH} \]

\[ \text{H} + \text{Benzene} \rightarrow \text{cyclohexadienyl} \]

*Graph showing single event rate coefficient vs. \(1/T\) with various data points and labels.*

- Nicovich 1984
- Gordon 1978
- Hoyermann 1975
- Ackermann 1990
- Berho 1999
- Mebel 1997 (calc)
- Baulch 1992 (review)
X + PhH; X = Alkyl

C-centered radicals are > factor 100 slower than H

Surprise: HCO and even resonantly stabilized radicals react similar than alkyl radicals
X + PhH; X = Alkyl

- The PES are different but the entrance barriers are similar for this group of C-centered radicals.
- Addition reactions group reasonably well.
X + PhH; X = Vinylic Radicals

X = H
"Alkyll"
C=C●
CC=C●
C₂C=C●
C=CC=C●
C=C●C
C=CC=C●
2-MePh●
2,6Me₂Ph●
X + PhH: fully oxidized C-centered Radicals

\[ + \quad \text{X = H} \]

"Alkyl"
"Vinyl"
\[ C\dot{=}O\text{OH} \]
\[ C\dot{=}O\text{OMe} \]
$X + \text{PhH}: \text{Allylic Radicals}$

$X = H$

"Alkyl"
"Vinyl"
"C(=O)OR"

$C=CC\cdot$
$CC=CC\cdot$
$C=CC\cdotC$
$C=CC\cdotC2$
X + PhH: Propargylic Radicals

X = H
"Alkyl"
"Vinyl"
"C•(=O)OR"
"p-allyl"
"s,t-Allyl"
C#CC•
CC#CC•
C#CC+CC
C#CC•C2
X + PhH: X = Benzylic Radicals

X = H
"Alkyl"
"Vinyl"
"C(=O)OR"
"allyl"
"propargyl"
PhC•
PhC•C (- -)
PhC•C₂ (...)
X + PhH: X = Allenenic Radials

\[ + \]

- H
- "Alkyl"
- "Vinyl"
- "C\(\cdot(=O)OR\)"
- "allyl"
- "propargyl"
- "benzyl"
- "C=C=C\(\cdot\)"

**Graph:**

- Single event rate coefficient (\(\text{cm}^3\text{mol}^{-1}\text{s}^{-1}\))
- \(10^3 \frac{1}{T} \text{K}^{-1}\)

**Equation:**

\[
\text{rate} = k \times \left( \frac{1}{T} \right)^n
\]
$X + \text{PhH}$

$X =$

"Alkyl"
"Vinyl"
"C\(=\text{O}\)OR"
"allyl"
"propargyl"
"benzyl"
"Allenyl"
X + PhH: O-centered radicals

\[
\begin{align*}
\text{C} & \quad + \quad \text{X} \\
\rightarrow \\
\text{X} & \quad \text{H}
\end{align*}
\]

- **X =**
  - H
  - "Alkyl"
  - "Vinyl"
  - "C\(\bullet(=O)OR""
  - "allyl"
  - "propargyl"
  - "benzyl"
  - "Allenyl"
  - OH

Note:
- OH forms a pre-complex with benzene
  - the barrier is below the reactants
  - \(vTST\) for complex formation step still needs to be done
  - current rate coefficients not reliable
X + PhH: O-centered radicals

\[ \text{[Diagram of chemical reaction]} \]

\[ \text{X} = \text{H} \]

- "Alkyl"
- "Vinyl"
- "C(=O)OR"
- "allyl"
- "propargyl"
- "benzyl"
- "Allenyl"

\[ \text{OH} \]
\[ \text{CH}_3\text{O}^{-} \]

Note:
- Almost no interaction with the aromatic ring
- Rate coefficient should be okay
X + PhH : O-centered radicals

X = H
"Alkyl"
"Vinyl"
"C•(=O)OR"
"allyl"
"propargyl"
"benzyl"
"Allenyl"

OH
CH₃O•
C=CO•
X + PhH : O-centered radicals

Resonantly stabilized O-centered radicals are among the least reactive ones

X = H
   "Alkyl"
   "Vinyl"
   "C\((=O)OR\)"
   "allyl"
   "propargyl"
   "benzyl"
   "Allenyl"

OH
CH\(_3\)O•
C=CO•
PhO•
X + PhCH₃: H and C-centered Radicals

Same observations for addition to toluene.
X + PhCH₃: plus O-centered Radicals

ICCK, Ghent, 28.06-02.07.2015
**X + PhCH₃ : Evans-Polanyi Plot**

- Wide range of heats of reaction and activation energies
- Loss of aromaticity leads to high endothermicity for resonantly stabilized radicals despite cyclohexadienyl resonance
- Low activation energies of OH and RO• oxygenated radicals
- Vinoxy radicals roughly in line with C-centered radicals

Nature of X clearly influences the reactivity
β-Scission of Substituted Cyclohexadienyl Radicals

- H and CH₃ are slowly released
- CH₃ and C₂H₅ differ clearly
- OH release is faster than alkyl
- C-O bond breaks easier in β-scission reactions than C-C
- Allyl vs vinoxy supports conclusion that C-O bond breaks easily
- No steric effect for alkoxy radicals
β-Scission of Substituted Cyclohexadienyl Radials

Toluene case confirms a strong steric impact on β-scission kinetics:
=> Branched substituents are more quickly released

Diagram:
- benzyl
- propargyl
- alkyl
- vinyl
The roles of Y and Z

How important are Y and Z for the reactivity?
Rate Coefficients Depend Little On Y

\[
y + H \rightarrow \text{Y leads to different C}_b \text{ GAV groups in reactant}
\]

Observations:
1. As expected, rather small changes in reactivity
2. Rate coefficients for same reactant type (GAV) fall together
3. Deviations for factor 2 is within uncertainty of calculations
4. Y = H and Ph are special:
   
   CBS-QB3 has problems with phenyl radical

\[
x \times 10^{-3} 1/T [K^{-1}]
\]

\[
\text{Single event } k_{\text{addition}} \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}]
\]

- blue: Cb-(C)
- red: Cb-(O)
- green: Cb-(Cd)
- orange: Cb-(CO)
- brown: Cb-(Cb)
- black: Cb-(H)
β-Scission Barriers Independent Of Most Y-Substituent

- β-scission barriers for Y = H, CH₃, C•CHO are very similar
β-Scission Barriers Independent Of Most Y-Substituent

- β-scission barriers for Y = H, CH₃, C•CHO are very similar
- CHO substituent has slightly lower barrier because of resonance stabilization
Very narrow range in $E_a$ (1000K)

Small range in $\Delta_{R}{H}_{298}$ values range is comparable with earlier discussed substituent effects

Oxygenated Y might alter reactivity somewhat due to H bonds.

Similar data obtained for CH$_3$
Rate Coefficient Depend Little On Z

- At relevant temperatures, reactivity differences are not significant
- Radical addition reaction to subst. benzenes is mainly affected by the adding radical
- Note: polarized radicals and substituents not considered
Same trend in $\Delta R H_{298}$
Higher values for ethylene expected
+ stability gain due to aromaticity in benzene cannot be compensated by resonance stabilization of cyclohexadienyl radical

Same trend in $E_a$
Higher barriers for benzene correlate with lower exothermicity (Evans-Polanyi)
Conclusions

- A systematic study of radical addition to substituted benzenes and the reverse reaction was performed at the CBS-QB3 level of theory.

- The reactivity is mainly determined by the adding (or leaving) radical.

- For the radicals considered, the activation energies vary by ~ 100 kJ/mol and the heats of reactions by some 200 kJ/mol.

- Substituents at the ipso, ortho, meta or para positions influence the reactivity very little.

- The $\Delta G^0$ methodology can easily be applied (with one major contribution) and thus this reaction family can easily be implemented into automated mechanism generation codes.

- The $\beta$-scission reactions releasing H and CH$_3$ from cyclohexadienyl radicals are slower compared to most other radicals. Combined with the fact that H and CH$_3$ radicals are generally readily available in pyrolysis reactions, this explains the observation that substituted monocyclic aromatic species are converted with time to benzene and toluene.
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