WE START WITH YES.

TUNNELING, ROAMING, AND OLIGOMERIZATION KINETICS OF CRIEGEE INTERMEDIATES ELUCIDATED THROUGH THEORY AND EXPERIMENT


Dec. 7, 2022

UC Davis
UNIMOLECULAR DISSOCIATION RATES
ENERGY RESOLVED RATE MEASUREMENTS

Marsha Lester

In Situ Generation of Reactive Intermediates
- QOOH – Alkylhydroperoxy Radicals
- Criegee Intermediates

Supersonic Expansion to Cool Reactants

IR Pump – UV Probe Action Spectroscopy
- \( k(E, J\sim0) \) for a range of Energies

Exquisite Tests of RRKM Theory

Boltzmann Averaging gives Canonical Rates
HIGH ACCURACY RATE PREDICTIONS

Rovibrational Properties
- CCSD(T)/TZ
- CCSD(T)-F12/DZ-F12

Energies
- CCSD(T)/CBS
- CCSDT(Q)/DZ
- Core-Valence
- Relativistic
- DBOC
- Anharmonic

Benchmarked vs 150 Species from Active Thermochemical Tables


Tunneling: 2nd Order Expansion of Action

Diagonal Cubic and Quartic; Semidiagonal Cubic

\[ \alpha^{(3)} = \frac{\pi}{8} \left[ \frac{5}{3} \frac{\overline{V}_{0,0,0}^{(3)} - \sum_{i=1}^{3} \overline{V}_{0,0,i}^{(3)} 8 \omega_b^2 + 3 \omega_i^2}{\omega_b \omega_i 4 \omega_b^2 + \omega_i^2} \right] \]

\[ \alpha^{(4)} = -\frac{\pi}{8} \frac{\overline{V}_{0,0,0,0}^{(4)}}{\omega_b} \]

HIGH ACCURACY ENERGIES FOR LARGE MOLECULES

- Connectivity Based Hierarchy – CBH-n; n=0, 1, 2, …
- Automated “Isodesmic” Reactions
- Higher Levels are more similar, but references are larger
  - CBH-ANL; Laddering of ANL values for references

Elliott, Keceli, Ghosh, Somers, Curran, SJK

https://tcg.cse.anl.gov/papr/codes/automech

https://github.com/Auto-Mech

- Modular
- Reusable
- Extensible
- Maintainable
- Scalable
- Usability
- Robust
MULTIDIMENSIONAL ROTORS

Methyl-Ethyl Criegee Intermediate
Barber, Hansen, Georgievskii, SJK, Lester
JCP, 152, 094301 (2020)

Multidimensional Rotors

Test of Rotors in RRKM Theory
1,6 H TRANSFER IN AN UNSATURATED CRIEGEE

Hansen, Qian, Sojdak, Kozlowski, Esposito, Francisco, SJK, Lester
JACS, 144, 5945 (2022)
**MVKOO UNIMOLECULAR DISSOCIATION**

Barber, Pandit, Green, Trongsiriwat, Walsh, SJK, Lester, JACS, 140, 10866 (2018)

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**Diagram:**

- **OH LIF Intensity:**
  - Total intensity over IR excitation energy range.
  - Syn and Anti peaks highlighted.

- **Trans and cis Isomers:**
  - Molecular structures for trans and cis isomers are shown.
  - Energies (in cm⁻¹) are listed: 0.00, 1.76, 2.57, 3.05.

- **Chemical Reactions:**
  - **Molecular Structure 7:**
    - Reaction: vinyl 1.4 H-atom transfer.
    - Energy: ~10³ s⁻¹.
  - **Molecular Structure 8:**
    - Reaction: barrierless.
    - Energy: 18.8 kJ mol⁻¹.

  - **Molecular Structure 9:**
    - Reaction: vinyl 1.5 H-atom transfer.
    - Energy: >40.0 kJ mol⁻¹.

  - **Molecular Structure 10:**
    - Reaction: Loss of hydroxide (OH⁻).

- **Thermodynamic Data:**
  - Anti-cis step:
    - ΔG°: -2.5 kcal mol⁻¹
    - 1,2 H transfer:
      - ΔG°: -18.1 kcal mol⁻¹
  - Keto-enol tautomerization:
    - ΔG°: -37.4 kcal mol⁻¹

- **Graph:**
  - *x* axis: IR excitation energy (cm⁻¹).
  - *y* axis: OH radical (vertical) and lifetime (horizontal).
  - Reaction rates (in 10⁵ s⁻¹).
  - Lifetimes (in ns).

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**Chemical Structures:**

- **Molecular Structures:**
  - 7, 8, 9, 10, 11, 12, 13, 14, 15.
ROAMING RADICAL REACTIONS
Ketones are formed in dissociation of (CH$_3$)$_2$COO


Roaming is the Answer


What about in MVKOO?

Barber, Pandit, Green, Trongsiriwat, Walsh, SJK, Lester, JACS, 140, 10866 (2018)
ROAMING IN H$_2$CO DISSN

NON-STATISTICAL?

Steady State for 1, 2

$\frac{k_{P2}}{k_{P1}} = \frac{N_{2,P2}}{N_{2,P1} \left(1 + \frac{N_{1,P1}}{N_{12}}\right) + N_{1,P1} \left(1 + \frac{N_{2,P2}}{N_{12}}\right)}$

Roaming TS:
Portion of Planes
Separating
1 From 2

Roaming Flux:
$N_{12}$

Rigid Body Trajectories

SJK, Georgievskii, Harding JPCA, 115, 14370 (2011)
ROAMING IN METHYL ETHYL CRIEGEE

Liu, Zou, Vansco, Elliott, Sojdak, Markus, Almeida, Au, Sheps, Osborn, Percival, Taatjes, SJK, Caravan, Lester

CASPT2(4e,4o)/TZ

Energy (kcal mol⁻¹)

1H2B
RC-1b
RC-1a
TS-1c
TS-1b
TS-1a

H₂C⁻CH₂⁻CH₂⁻OH

θ_{O,C₂O'} (degrees)

R_{C₁O'} (Å)
MULTI-CHANNEL ROAMING

Liu, Zou, Vansco, Elliott, Sojdak, Markus, Almeida, Au, Sheps, Osborn, Percival, Taatjes, SJK, Caravan, Lester

SYN

- MVK + H₂O
- 3H2B
- TS-2d

- H transfer
- C-O elongation
- TS-2c
- -5.4 kcal mol⁻¹

- RC-2b
- -5.7 kcal mol⁻¹
- reorientation
- roaming

- RC-2a
- -5.5 kcal mol⁻¹
- reorientation

- TS-2b
- -4.7 kcal mol⁻¹
- roaming
- C-O elongation

- TS-2a
- -3.4 kcal mol⁻¹
- roaming
- O-O elongation

θ_{OC₂O'} (degrees)

R_{C₃O'} (Å)

Energy (kcal mol⁻¹)

-18 ≤ -20
ROAMING IN METHYL ETHYL CRIEGEE

Timescale matches calculated time for isomerization to vinylhydroperoxide.

Liu, Zou, Vansco, Elliott, Sojdak, Markus, Almeida, Au, Sheps, Osborn, Percival, Taatjes, SJK, Caravan, Lester
OLIGOMERIZATION
OF CRIEGEE INTERMEDIATES
CRIEgee KINETICS

Rebecca Caravan Poster

Formic Acid + Methyl Vinyl Ketone Oxide

Caravan, Vansco, Au, Khan, Li, Winiberg, Zuraski, Lin, Chao, Trongsiriwat, Walsh, SJK, Taatjes, Lester

PNAS, 117, 9733-9740 (2020)
How do highly oxygenated molecules form in the atmosphere?

FA + CH₂OO + CH₂OO + CH₂OO + ...

Amazon Field Measurements

Caravan, Bannan, Winiberg, Khan, Rousso, Jasper, Worrall, Bacak, Artaxo, Brito, Priestley, Allan, Coe, Ju, Osborn, Hansen, SJK, Shallcross, Taatjes, Percival
CRIEGEE KINETICS

How do highly oxygenated molecules form in the atmosphere?

FA + CH$_2$OO + CH$_2$OO + CH$_2$OO + ...

Caravan, Bannan, Winiberg, Khan, Rousso, Jasper, Worrall, Bacak, Artaxo, Brito, Priestley, Allan, Coe, Ju, Osborn, Hansen, SJK, Shallcross, Taatjes, Percival
Formic Acid (FA) + CH$_2$OO + CH$_2$OO + …

All Submerged Barriers

Other Criegees

FA + MVKOO + MVKOO + …

FA + MACROO + MACROO + …

Rate $\sim [FA]([CH_2OO]^n + [MVKOO]^n + [MACROO]^n + \ldots)$

Other Initiators

H$_2$O$_2$, CH$_3$OOH, …, Acetic Acid, …

Rate $\sim \{[FA] + [Acetic Acid] + \ldots + H_2O_2 + CH_3OOH + \ldots\}[CH_2OO]^n + [MVKOO]^n + [MACROO]^n + \ldots\}$

Cross Linkings

FA + (MVKOO)$_j$ + (MACROO)$_k$ + (CH2OO)$_l$; $j + k + l = n$

Rate $\sim \{[FA] + [Acetic Acid] + H_2O_2 + CH_3OOH + \ldots\}[CH_2OO] + [MVKOO] + [MACROO] + \ldots\]^n$
ARE OLIGOMERIZATION BARRIERS SUBMERGED?

MVKOO
- Anti decomposes too fast
- Syn-cis and syn-trans should rapidly equilibrate
- Focus on Syn-trans

SJK, Caravan, work in progress
ARE OLIGOMERIZATION BARRIERS SUBMERGED?

MACROO

- Syn-cis decomposes too fast
- Anti-cis and anti-trans should rapidly equilibrate
- Focus on Anti-trans

SJK, Caravan, work in progress
SUMMARY
CONCLUSION

- Sound Understanding of Criegee Intermediate Kinetics
- A Priori Predictions and Measurements are in Good Agreement for a Wide Range of CIs and Conditions
- Roaming Radical Reactions Should be Accounted For in Dissociation of CIs
- Oligomerization Seems Possible – Quantitative Modeling Required
  Accounting for all Manner of Initiators and CIs

FUNDING

DOE-BES Gas Phase Chemical Physics
(Wade Sisk)
- Core Program - Chemical Dynamics in the Gas Phase

ACKNOWLEDGEMENTS

Lester, Caravan
Elliott, Vansco, Liu
+ many others