Theoretical Gas Phase Chemical Kinetics

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Training in theoretical chemical kinetics

1. CEFRC – Summer School
   Ab Initio Theoretical Chemical Kinetics

2. Peng Zhang (Ed Law graduate student; now a CEFRC Fellow)
   Monomethylhydrazine decomposition

3. Franklin Goldsmith (Bill Green graduate student)
   Allyl + HO2

4. Mike Burke (Fred Dryer & Yiguang Ju graduate student)
   H2/O2 Combustion
Monomethyl hydrazine decomposition

- Monomethylhydrazine (MMH)
  - Diamine-based rocket fuel
  - Commonly used as bipropellant and monopropellant
  - Exothermically decomposes upon contact with either a hot surface or an oxidizer

- Thermal decomposition of MMH
  - Fuel stability and storability
  - Necessary components of mechanism of MMH oxidation
  - Have not been sufficiently studied

- Dominant reactions of MMH decomposition: NN and CN bond fission
  
  \[
  \text{MMH} \rightarrow \text{NH}_2 + \text{CH}_3\text{NH} \\
  \text{MMH} \rightarrow \text{CH}_3 + \text{NHNH}_2
  \]

- Barrierless radical-radical recombination reactions
  
  \[
  \text{NH}_2 + \text{CH}_3\text{NH} \rightarrow \text{MMH} \\
  \text{CH}_3 + \text{NHNH}_2 \rightarrow \text{MMH}
  \]
Potential Energy Surface

- On-the-fly Calculation of Interaction Potential
  - aug-cc-pVTZ: accurate but too computationally demanding → cc-pVDZ and aug-cc-pVDZ were used
  - Reacting fragments have fixed internal geometries

- Orientation-Independent Corrections
  - One-dimensional basis set correction
  - One-dimensional correction for geometric relaxation

\[
V = V_{\text{CASPT2/ADZ}}(R, \Omega; \text{rigid}) \\
+ \left[ V_{\text{CASPT2/ADZ}}(R, \Omega^*; \text{rigid}) - V_{\text{CASPT2/ADZ}}(R, \Omega^*; \text{rigid}) \right]
\]

basis set correction from CASPT2/aug-cc-pVTZ

\[
+ \left[ V_{\text{CASPT2/ADZ}}(R, \Omega; \text{relaxed}) - V_{\text{CASPT2/ADZ}}(R, \Omega; \text{rigid}) \right]
\]
correction for relaxing of the internal structure
Potential Energy Surface

Potential curves

\[ V_{\text{NH}_2+\text{CH}_3\text{NH}} \left( R_{\text{N-N}} = \infty \right) = 0 \]

Relative Energy (kcal/mol)

- \( \text{NH}_2+\text{CH}_3\text{NH} \)
- \( \text{CH}_3+\text{NHNH}_2 \) front side
- \( \text{CH}_3+\text{NHNH}_2 \) back side

\[ R_{\text{N-N}} \text{ or } R_{\text{C-N}} \,(\text{au}) \]

Equivalent sides

Front side

Back side
VRC-TST Capture Rates

$k_{1} = 8.34 \times 10^{-10} T^{-0.429} \exp(20.1/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$

$k_{2} = 3.99 \times 10^{-12} T^{-0.085} \exp(404.2/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$
MMH Dissociation: Theory-Experiment Comparison

- Kerr et al (1963): the first-order rate coefficient for the homogeneous dissociation of NN bond of MMH.
  - Very good agreement with the present theory

- Golden et al (1972): very low pressure reactor → complicated by gas-wall interactions
  - Not appropriate for a direct comparison with the theory

- Eberstein et al (1965): total thermal decomposition rate of MMH
  - Modeled by a mechanism containing 43 species and 160 reactions (Sun and Law 1007)
  - Sensitivity analysis identified two qualitatively important reaction channels:
    \[
    \text{CH}_3\text{NNH}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{NNH}_2 + \text{CH}_4 \\
    \text{CH}_3\text{NNH}_2 \rightarrow \text{CH}_3\text{NNH} + \text{H}
    \]
  - Disagreement with the theory might be due to the absence of the two reaction channels:
Allyl + HO2
Allyloxy Decomposition
Allyloxy Decomposition