Tunneling of hydrogen transfer reactions on and in interstellar ices

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Accurate rate constants are needed as input for astrochemical models.
Quantum tunneling

Minimum energy path is not a good approximation to the tunneling path for thin barriers

Figure courtesy Meisner & Kästner ACIE (2016)
Rate constants including tunneling!

Instanton theory

Typical approach

**Benchmark DFT to CCSD(T)-F12**
- Gas-phase reaction
- Interaction energies (dimers)

**Energy profile (gas phase)**
- Intrinsic reaction coordinate
- Encounter complex

**Surface molecules**
- Small clusters as test case
- QM/MM

**Rate calculations**
- Classical
- Eckart approximation
- Instanton theory
Surface approximations

- High concentration
- Activation energy
- Implicit surface model
- Restricted rotation
- Energy dissipation

\[ \text{rot. } RS = Q_{\text{rot. } TS} \]
\[ \sigma = 1 \]
Surface chemistry mechanisms

Bimolecular
A adsorbed
+ gas-phase B

Unimolecular
both A and B adsorbed
+ diffusion
Competition with diffusion

\[ R_{LH} = P_{react} \cdot R_{diff} \]

\[ = \frac{k_{react}}{k_{react} + k_{diff,A} + k_{diff,B}} \cdot \frac{k_{diff,A} + k_{diff,B}}{N_{sites}} \cdot n_A \cdot n_B \]
Tunneled reactions: rate constants

**Studied reactions:**

- \( \text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_3 \)
- \( \text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 \)
- \( \text{HCOOH} + \text{H} \rightarrow \text{HOCO} + \text{H}_2 \)
- \( \text{HCOOH} + \text{NH}_2 \rightarrow \text{HOCO} + \text{NH}_3 \)
- \( \text{HCOOH} + \text{OH} \rightarrow \text{HOCO} + \text{H}_2\text{O} \)
- \( \text{CH}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3 \)
- \( \text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH} \)
- \( \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \)
- \( \text{H} + \text{H}_2\text{S} \rightarrow \text{HS} + \text{H}_2 \)

**Within the framework of:**

- Cometary chemical inventory
- ‘Complex’ organic molecule precursors
- Water formation
- Sulfur chemistry

H + H$_2$O$_2$  Gas vs. Clusters (I)

DFT: MPW1B95 / MG3S

Lamberts et al. (2016)
$H + H_2O_2$  

Gas vs. Clusters (II)

$E_{\text{act.}} \approx 2910 - 3200 \text{ K}$

Lamberts et al. (2016)
H + H$_2$O$_2$  Clusters vs. Surface (I)

Lamberts et al. (2017)

DFT: MPW1B95 / MG3S
FF: TIP3P
Clusters vs. Surface (II)

\[ k_{\text{reac}} = 10^{12} e^{-2a/h\sqrt{2\mu E_{\text{act}}}} \]

\( E_{\text{act}} \approx 2740 - 3065 \text{ K} \)

Lamberts et al. (2017)
H + H₂O₂

Surface vs. Bulk (I)

DFT: MPW1B95 / MG3S
FF: TIP3P

Lamberts et al. (2017)
$H + H_2O_2 \quad \text{Surface vs. Bulk (II)}$

$E_{\text{act.}} \approx 2500 - 2840 \text{ K}$

Lamberts et al. (2017)
H$_2$ + OH  Surface (I)

DFT: BHLYP / def2-SVPD
FF: TIP3P

Meisner et al. (2017)
H₂ + OH Surface (II)

$E_{\text{act.}} \approx 2700 – 2900 \text{ vs. } 2935 \text{ K}$

Meisner et al. (2017)
H + H$_2$S Gas phase vs. Clusters (I)

DFT: MPWB1K / def2-TZVP

Lamberts et al. (2017) in prep.
Diffusion and binding energies?

\[ R_{LH} = P_{react} \cdot R_{diff} \]

\[ = \frac{k_{react}}{k_{react} + k_{diff,A} + k_{diff,B}} \cdot \frac{k_{diff,A} + k_{diff,B}}{N_{sites}} \cdot n_A \cdot n_B \]

Combination of activation and binding energy determines if a reaction is limited by diffusion: what about binding energy distributions?

Song et al. (2016, 2017), Senevirathne et al. (2017), Ásgeirsson et al. (2017)
Lessons learned

- Water ice: may impact on barrier height and width, may decrease the barrier
- Hydrogen bonds: restricted orientations determine binding energy
- Binding energies: a large spread
- Rectangular barrier: often underestimates rate constants, often results in error in the KIE
- Rate constants available for roughly a dozen reactions!
Thank you!

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BWForCluster Justus

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Lessons learned

• Water ice:
  - may impact on barrier height and width
  - may decrease the barrier

• Hydrogen bonds:
  - restricted orientations
  - determine binding energy

• Binding energies:
  - a large spread

• Rectangular barrier:
  - often underestimates rate constants
  - often results in error in the KIE

• Rate constants available for roughly a dozen reactions!
In a nutshell

Imaginary F theory: $k \propto \text{Im}(F) = \frac{\text{Im}(Q)}{\text{Re}(Q)}$

Transition state theory: $k \propto \frac{Q_{TS}}{Q_{RS}}$

$Q_{TS} = tr\left[e^{-\beta H}\right] = \oint Dx\ e^{-\frac{1}{\hbar}S_E[x]} \rightarrow \text{path integral formulation}$

$x$ that minimizes $S_E[x]$ is ‘the instanton’, discretized: $P$ segments in $3N$ dimensions

This ring-polymer with $k=k(T)$ can be seen as wrapped around the barrier

Deviations from the most-likely tunneling path: harmonic approximation

Hydrogenation of $\text{H}_2\text{O}_2$

- Experiments show a kinetic isotope effect
  - $\text{H}_2\text{O}_2 + \text{H}$ vs. $\text{H}_2\text{O}_2 + \text{D}$
  - $\text{D}_2\text{O}_2 + \text{H}$ vs. $\text{D}_2\text{O}_2 + \text{D}$

- In models
  - Rectangular barrier approximation
  - Eckart barrier approximation

$P_{\text{react}} \propto e^{-2a/\hbar\sqrt{2\mu E_{\text{act}}}}$

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Taquet et al. (2013), Oba et al. (2014)
Surface formation of water

Radical-radical reactions:
barrierless

Radical-neutral reactions:
tunneling!

$H + H_2O_2 \rightarrow H_2O + OH : E_{act.} \approx 26 \text{ kJ/mol}$

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction 1 ( H + H_2O_2 \rightarrow H_2O + OH )</th>
<th>Reaction 2 ( H + H_2O_2 \rightarrow HO_2 + H_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>CCSD(T)-F12 / VTZ-F12</td>
<td>25.5</td>
<td>39.4</td>
</tr>
<tr>
<td>ic-MRCCSD(T) / cc-pVQZ</td>
<td>24.9</td>
<td>38.3</td>
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<tr>
<td>Ellingson et al. (2007)</td>
<td>27.2</td>
<td>41.4</td>
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<tr>
<td>MPW1B95 / MG3S</td>
<td>26.5</td>
<td>23.7</td>
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<tr>
<td>M05-2X / MG3S</td>
<td>45.9</td>
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<td>PWB6K / MG3S</td>
<td>35.9</td>
<td>35.4</td>
</tr>
<tr>
<td>B3LYP / MG3S</td>
<td>11.2</td>
<td>8.1</td>
</tr>
<tr>
<td>B3LYP / def2-TZVPD</td>
<td>10.8</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Energies in kJ/mol and Kelvin, without ZPE corrections, no dispersion correction.
## Kinetic Isotope Effect

All KIE’s calculated at 50 K

<table>
<thead>
<tr>
<th>System</th>
<th>Instanton theory</th>
<th>Eckart Barrier</th>
<th>Rectangular Barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eley-Rideal / bimolecular</td>
<td>197</td>
<td>27</td>
<td>6945</td>
</tr>
<tr>
<td>Langmuir-Hinshelwood / unimolecular</td>
<td>229</td>
<td>60</td>
<td>7033</td>
</tr>
</tbody>
</table>

Experimental KIE = 30 at 15 K, but ... includes diffusion!