Due to the unusually high heats of vaporization of room-temperature ionic liquids (RTILs), volatilization of RTILs through thermal decomposition and vaporization of the decomposition products can be significant. In complex molecules like RTILs, use of chemical intuition to predict reaction pathways can prove unreliable, especially when the internal energy content is high. There may be concerted reactions that are difficult to predict, and once energy stored in the molecule begins to release, the system does not necessarily follow the minimum energy reaction path, i.e., the subsequent behavior is controlled by dynamics. A useful approach to treating such a system is quasi-classical, direct dynamics trajectory simulations, where the motion of the molecule is followed, allowing the molecule to "show us" what the preferred reaction pathways are. The direct dynamics method dispenses with the potential energy surface. Instead, it calculates the energies, force constants, and Hessian "on the fly" using quantum chemistry methods. This method becomes computationally attractive when the dimensionality of the system increases, particularly for RTILs, which typically contain 10 or more heavy atoms. Dynamics simulations allows the partitioning of the energy generated by exothermic reactions into vibrational, rotational, and translational degrees of freedom, thereby increasing the chance of locating new reaction pathways in the system. In addition, by following the variation of the potential energy during the trajectory rather than relying on intuition, we can identify better geometries for TS searching. Results obtained from these direct dynamics simulations are compared to and consistent with the gaseous products detected experimentally via tunable vacuum ultraviolet photoionization mass spectrometry performed at the Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source. The likely reaction mechanisms in the thermal decomposition of RTILs are discussed in this work.
Thermal decomposition mechanisms of ionic liquids by direct dynamics simulations and vacuum ultraviolet photoionization mass spectrometry

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Distribution A: Approved for public release; distribution unlimited.
Outline

• Direct dynamics and RRKM modeling of:
  – 1,5-dinitrobiuret (DNB) pyrolysis.
  – EMIM$^+$dca$^-$, EMMIM$^+$dca$^-$

• IL vapor studies:
  – Photoionization of vaporized ILs.

• IL aerosols + HNO$_3$:
  – Diffusion-limited reactivity: MM

• QM/MM reactive scattering:
  – hyperthermal O($^3$P) off IL surface
What is hypergolicity??!
DOI: 10.1021/jp8038175
Motivation

- Replacement for monomethylhydrazine (MMH) + N₂O₄ (highly volatile and toxic!!)

  - Improved performance.
  - Environmentally "greener".

- Room temperature ionic liquids (RTILs) have:
  - Extremely low vapor pressures, thus low vapor toxicity.
  - High energy density.
  - Low flammability.

- Ignition involves:
  - Pre-ignition chemistry - "chemical spark"
  - Rapid heating: vaporization and thermal decomposition.
  - Combustion.

- How to predict hypergolicity?
Ionic Liquids

- Molten salts with m.p. $\leq 100$ °C.
- Asymmetric ions with diffuse charge distributions.
- $\text{C}^+\text{A}^- : 10^{18}$ possible combinations of cations and anions.
• Dicyanamide-based RTILs first hypergolic ILs discovered with HNO$_3$. 
Gas Phase Decomposition of DNB

Distribution A: Approved for public release; distribution unlimited.
Potential Energy (eV)

= 0.0

= 0.5

= 1.0

= 1.5

= 2.0

DNB

TS_21

O₂NNHCONHCONH + NO₂

TS_31

O₂NNHCONCO + HNNO₂H

twisted DNB

TS_22

TS_32

O₂NNHCONCO + H₂NNO₂

B3LYP/6-31++G(d,p)
## RRKM Results

<table>
<thead>
<tr>
<th>Temp / K</th>
<th>750</th>
<th>1000</th>
<th>1250</th>
<th>1500</th>
<th>1750</th>
<th>2000</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>density of states (1/cm(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DNB</td>
<td>1.95 \times 10^{18}</td>
<td>2.34 \times 10^{22}</td>
<td>5.98 \times 10^{25}</td>
<td>4.94 \times 10^{28}</td>
<td>1.71 \times 10^{31}</td>
<td>2.92 \times 10^{33}</td>
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<tr>
<td>twisted DNB</td>
<td>1.90 \times 10^{18}</td>
<td>2.33 \times 10^{22}</td>
<td>6.04 \times 10^{25}</td>
<td>5.04 \times 10^{28}</td>
<td>1.75 \times 10^{31}</td>
<td>3.02 \times 10^{33}</td>
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</table>

<table>
<thead>
<tr>
<th>unimolecular rates (s(^{-1})) (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
</tr>
<tr>
<td>(0)</td>
</tr>
<tr>
<td>(k_2)</td>
</tr>
<tr>
<td>(k_{31})</td>
</tr>
<tr>
<td>(k_{-31})</td>
</tr>
<tr>
<td>(k_{32})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>branching ratios (%) (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>path 1</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>path 2</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>path 3</td>
</tr>
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<td></td>
</tr>
</tbody>
</table>

\(\cdot\) = loose transition state for path 1

Distribution A: Approved for public release; distribution unlimited.
IL Vaporization

• Strasser, Armstrong, indicate ion pairs by detection of intact cation:\(^1\)
  \[
  \text{Ionic Liquid} + \Delta \rightarrow \text{C}^+\text{A}^- (g)
  \]
  \[
  \text{C}^+\text{A}^- (g) + \text{hv} \rightarrow \text{C}^+\text{A} + \text{e}^- \rightarrow \text{C}^+ + \text{A} + \text{e}^-
  \]

• Kelkar and Maginn: ion pairs more energetically favorable than clusters of ion pairs and non-neutral clusters.\(^2\)

---

ALS: Chemical Dynamics Beamline

IL vapor source reflectron MS

aerosol reflectron MS

7.4-15.0 eV photons, 0.025 eV resolution
Experimental

IL effusive source:

- Steel plate with 1mm orifice
- Aluminum block
- Sample in glass test tube
- Cartridge heater
- Thermocouple
EMIM dcyn
200 °C, 9.0 eV
T(decomposition)=240 °C

110 = ion pair - 67
150 = ion pair – 27 (HCN)

intact cation
# EMIM⁺dca⁻ MD results

<table>
<thead>
<tr>
<th>MD reaction</th>
<th># of trajectories</th>
<th>branching ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 H+ xfer to dca (term)</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>C2H5 dissoc</td>
<td>11</td>
<td>17</td>
</tr>
<tr>
<td>NCN + CN</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>dca dissoc</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>NR</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>dca abstract H from CH3 --&gt; Hdca (term)</td>
<td>3</td>
<td>5</td>
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<tr>
<td>C2 H+ &lt;-&gt; dca (central)</td>
<td>2</td>
<td>3</td>
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<tr>
<td>CH3 dissoc</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Et: CH3CH2⁻ + dca --&gt; CH2CH2 + Hdca (term)</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>H2 elim from -CH3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>NCN-CN elongation</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>-C2H5 + dca &lt;-&gt; -C2H4 + Hdca</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C2H5 abstraction by dca (term)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C2H5 and dca dissoc</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C4H xfer to N3 and elim HC4C5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CH3 abstraction by dca (central)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CH3 abstraction by dca (term)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Et: H2 + dca --&gt; HCN + HNCN</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>total=</strong></td>
<td><strong>63</strong></td>
<td></td>
</tr>
</tbody>
</table>
PCM Model for ILs

- Truhlar: SMD-GIL (generic ionic liquid)*
  - benchmark to experimental $\Delta G_{\text{solv}}$ for ILs.

Mass 150
=(111-1) + 40

+ HCN
addition-elimination mechanism

R=Et, Bu
EMMIM dcyn
200 °C, 9.0 eV
T(decomposition)=320 °C

no HCN detected!
Total Energy along IRC

Intrinsic Reaction Coordinate
$h\nu = 7.5 \text{ eV}$

$160 \, ^\circ\text{C}$
photoionization efficiency of ion pair


IP = 6.6 ± 0.5 eV

IP (M06/6-31+G(d,p)) = 7.3 ± 0.2 eV
Aerosol reactivity

• RTILs very low vapor:
  – Aerosols are liquid droplets suspended in gas phase.
Monitoring isolated ion pairs

- Use it to study reaction kinetics of ‘hypergolic ionic liquid reaction with an oxidizer’

Hypergolic Ionic liquid aerosol  Hypergolic Ionic liquid aerosol ‘reacted’

+ hv

Reaction dynamics and kinetics

Ionic liquid aerosol generation

Hypermolic Ionic liquid aerosol

- size distribution

- Tunable light source
Experimental setup

Aerosol source (Ionic liquid)

N₂

IL (aq)

Nitric acid

Bubbler

Flow Tube
(Reaction: IL+HNO₃)

N₂

Na₂CO₃ pellets

Nitric acid denuder

Orifice

Aerodynamic lens

Detection

SMPS

TOF-AMS

Copper block

Nitric acidAbs. cell

+ hv

Aerosol inlet
Identification of reaction products

- photoionization efficiency curve measured

![Graph showing photoionization efficiency curves for different compounds.](image)
Reaction with heavy HNO₃

Ionic liquid only

CO₂ and N₂O

Cyanoamide

H¹⁵NO₃

Mass (amu/α)

Ion yield (counts)
aerosol kinetics data

\[
\begin{align*}
\text{CO}_2 & \quad \text{44 amu at 13.5 eV} \\
^{15}\text{NNO} & \quad \text{45 amu at 14.3 eV}
\end{align*}
\]
MD simulations of IL/oxidizer interphases: liquid-liquid

in liquid/liquid systems, mixing is rapid!
For the liquid-liquid interphase intermixing occurs fast (few ns time scale for investigated dimensions).
MD simulations of IL/oxidizer interphases: liquid-gas
At the liquid-gas interphase, HNO₃ quickly adsorbs to the surface and then slowly diffuses to the bulk.

There is a certain concentration of HNO₃ at the surface that the system would like to maintain to reduce the surface tension.
Conclusions

• Molecular dynamics can greatly improve our understanding of reactivity of ionic liquids:
  – ID thermal decomposition mechanisms
  – surface tension/diffusion limited processes
• Tunable VUV-PI-TOFMS a powerful experimental tool:
  – Direct detection of ion pairs upon vaporization
  – ID products my mass and ionization potential
  – Aerosols make ionic liquids more accessible by MS
• Design a better green rocket fuel with ionic liquids !!!
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  – Lt. Anna Sheppard
Questions?!
O + EMIM$^+\text{NO}_3^-$
$\text{O} + \text{EMIM}^+\text{NO}_3^-$