Synthesis, Characterization and Combustion of Triazolium Based Salts

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outline

- synthesized triazolium salts
- definition of Ionic Liquids
- history and development of Ionic Liquids
- results and potential applications
- summary and conclusions
synthesized triazolium salts

- protic and aprotic triazolium salts

protonated

- AHTN
- AHTP

methylated

- AMTN
- AMTP

liquid at room temperature

AMTN: first mentioned in literature 2002 by Greg W. Drake

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definition Ionic Liquids (ILs)

- consisting entirely of cations and anions
- without molecular solvent
- mp: < 100 °C (definition)

attributed properties:
- electric conductivity
- thermal stability
- very low vapor pressure
- good solvent abilities
- high heat capacity
history

first Ionic Liquids (IL):
- 1888 ethanolammonium nitrate \( \text{mp: 52-55 °C} \) S. Gabriel
- 1914 ethylammonium nitrate \( \text{mp: 13-14 °C} \) P. Walden

since 1996 exponential growth of scientific publications about ILs
aspects favoring ILs

- organic cation with low structural symmetry
  (e.g. asymmetric imidazolium cation)
- weak intermolecular interactions
- anion with diffuse negative charge

Symmetric cation

Ionic solid, e.g. NaCl

Asymmetric cation

Ionic Liquid
commercial ILs

all relevant properties are determined by anion AND cation

$10^{18}$ possible ILs

3000 described in literature

300 commercial available
results and potential applications

4-amino-1-methyl-1,2,4-triazolium perchlorate (AMTP)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact sensitivity [Nm]</td>
<td>7.5</td>
</tr>
<tr>
<td>Friction sensitivity [N]</td>
<td>64</td>
</tr>
<tr>
<td>Melting point [°C]</td>
<td>+84</td>
</tr>
<tr>
<td>Decomposition temperature [°C]</td>
<td>+259</td>
</tr>
</tbody>
</table>

component in melt cast formulations
results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium perchlorate (AMTP)

**comparison to TNT**

<table>
<thead>
<tr>
<th></th>
<th>TNT</th>
<th>AMTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>melting point [°C]</td>
<td>80</td>
<td>84</td>
</tr>
<tr>
<td>decomposition temperature $^\text{[a]}$ [°C]</td>
<td>253</td>
<td>290</td>
</tr>
<tr>
<td>oxygen balance [%]</td>
<td>-74</td>
<td>-44</td>
</tr>
<tr>
<td>heat of explosion $^\text{[b]}$ [J/g]</td>
<td>3766</td>
<td>4096</td>
</tr>
<tr>
<td>shock velocity $^\text{[c]}$ [m/s]</td>
<td>6886</td>
<td>7287</td>
</tr>
</tbody>
</table>

$^\text{[a]}$ DSC onset; heating rate 5 K/min. $^\text{[b]}$ calculated with ICT Code water liquid. $^\text{[c]}$ calculated with CHEETAH 2.0.
EILs – Energetic Ionic Liquids

- requirements for EILs:
  - liquid between -40 °C and +150 °C
  - energetic
  - long-term stable
  - insensitive
## results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)

<table>
<thead>
<tr>
<th>Property</th>
<th>AMTN</th>
</tr>
</thead>
<tbody>
<tr>
<td>impact sensitivity</td>
<td>[Nm] 15</td>
</tr>
<tr>
<td>friction sensitivity</td>
<td>[N] 144</td>
</tr>
<tr>
<td>glass transition temperature</td>
<td>[°C] -55</td>
</tr>
<tr>
<td>decomposition temperature</td>
<td>[°C] +259</td>
</tr>
</tbody>
</table>

*Wide operating temperature range*
results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)
- gelatinization of nitrocellulose (N = 12.6%)

- microscopic picture of gelatinized NC
- film of NC / AMTN (1:4)
- transparency of film
results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)
- combustion in atmospheric air
results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)

combustion under nitrogen

- no combustion at lower pressures
Results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)

Combustion under nitrogen

Graph showing burning rate vs. pressure for different compositions:
- AMTN / AMTP
- AMTN / 4-AT
- AMTN

Chemical structures:
- AMTP
- AMTN

94/6 wt% deflagration of pure AMTP.
results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)

**combustion under nitrogen**

[Diagram showing burning rate vs. pressure for AMTN, AMTP, AMTN/4-AT, and AMTN samples.]

- Fuel mixture: 66/34 wt%
results and potential applications

4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)

combustion under nitrogen

linear regression rate

regression image

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results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)
- comparison to conventional liquid energetic materials

<table>
<thead>
<tr>
<th></th>
<th>melting point</th>
<th>boiling point</th>
<th>density [g/cm³]</th>
<th>vapor pressure [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitromethane</td>
<td>-28 [°C]</td>
<td>101 [°C]</td>
<td>1.14</td>
<td>4.8</td>
</tr>
<tr>
<td>isopropyl nitrate</td>
<td>-82 [°C]</td>
<td>100 [°C]</td>
<td>1.03</td>
<td>3.5</td>
</tr>
<tr>
<td>AMTN</td>
<td>-55 [°C]</td>
<td>$T_{\text{dec}} &gt; 200$</td>
<td>1.44</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

[a] glass transition temperature
results and potential applications

- 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN)
- Comparison to conventional liquid energetic materials

potential high density powerful propellant
outlook

- performance
- thermal stability
- mechanical sensitivity
- freezing point
- oxygen balance
- enthalpy of formation

wide variety of anion and cation combination possibilities

tailoring possible

task specific EILs
summary and conclusion

EILs – Energetic Ionic Liquids

- relative new research area
- improved physical properties in comparison to conventional energetic materials
- increased performance possible
- very low toxicity of the vapor phase
acknowledgment

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