Atmospheric Degradation of Amines ADA

UIO, UMB, UI IRCELYON, NILU
Fate of MEA\(_{(g)}\)

**How much?**

- \(\text{HN=CHCH}_2\text{OH}\)
- \(\text{CH}_2\text{OHCH}_2\text{NHNO}\)
- \(\text{CH}_2\text{OHCH}_2\text{NHNO}_2\)
- \(\text{CH}_2\text{OHC(O)NHNO}_2\)

- \(\text{NH}_2\text{CHO}\)
- \(\text{NH}_2\text{C(O)CH}_2\text{OH}\)

- \(\text{NH}_2\text{CH}_2\text{CHO}\)
- \(\text{NH}_2\text{C(O)CHO}\)
- \(\text{NH}_2\text{C(O)OONO}_2\)
- \(\text{NH}_2\text{CH}_2\text{C(O)OONO}_2\)
- \(\text{NH}_2\text{C(O)C(O)OONO}_2\)

**NOT “OK”**

**“OK”**
Experiments at EUPHORE

Instrumentation:

- FT-IR
- Cryotrap GC-MS
- PTR-TOF-MS (UI)
- Monitors for: CO, HCHO, O₃ & NOₓ
- Actinometer, Radiometer
- TEOM, SMPS
- AMS (IRCLYON)
- Filters and cartridges (NILU)
Aerosol formation

Photo-oxidation of MEA with NOx present results in high concentrations of stable particles.

Experiments with 100-700 ppbV MEA resulted in up to $10^4$ particles/cm$^3$ and the total aerosol mass increased up to 230 µg/m$^3$.

The observed chamber aerosol mainly consisted of secondary organic salt particles and to a less extent of non-salt organics. The particles resemble ethanolammonium nitrate, but there are clearly other compounds present.
Particle growth - "banana-curve"

Sequential aerosol size distributions in the MEA photo-oxidation experiment on 4.05.2009 (high-NO/low-NO₂ experiment). Time is given as local time. A particle burst is observed one hour after the chamber canopy was opened at 12:56. Lower size cut-off of the SMPS instrument is at 17.5 nm diameter.
Simulation of the particle growth with the sectional aerosol model MAFOR

MEA degradation and production of formamide in the gas phase (11.05.2009); modeled vs. measured.

Total aerosol mass (11.05.2009). Measured by SMPS and AMS vs. modeled.
Red squares: measured NO$_3$ mass conc.
MEA phase transfer

MEA is primarily lost to the wetted walls and not to the wet particles.
Gas phase chemistry
PTR-TOF-MS data series

Analysis

Chamber opened

Chamber closed

Chamber flushing started

08:00 10:00 12:00 14:00 16:00 18:00 20:00
**MEA → Products**

- Chamber opened
- Chamber closed
- 2-Oxo acetamide Sec. (+Prim.) Prod.
- Acetamide
- Amino acetaldehyde
- 2-Imino ethanol
- DNPH: \( \text{NH}_2\text{CH}_2\text{CHO} < 0.05 \text{ ppb} \)

**Mass/Charge Values:**
- \( m/z = 62.060 \)
- \( m/z = 60.044 \times 5 \)
- \( m/z = 42.034 \)
- \( m/z = 74.024 \times 50 \)
- \( m/z = 46.029 \times 5 \)
Isotope experiments & Kinetic isotope effects

![Graph showing isotope experiments and kinetic isotope effects](image_url)
Nitrosamine formation

MEA-d\textsubscript{4} added

MEA

\[ \text{HNCH}_2\text{CH}_2\text{OH} + \text{NO} \leftrightarrow \text{ONHNCH}_2\text{CH}_2\text{OH}^\dagger \]

08:00 10:00 12:00 14:00 16:00 18:00

Chamber opened

Chamber closed

- \text{91.058 ONNHCH}_2\text{CH}_2\text{OH} ?
- \text{95.086 ONNHCD}_2\text{CD}_2\text{OH} ?
Nitramine formation

- 107.045 \( \text{O}_2 \text{NNHCH}_2\text{CH}_2\text{OH} \) ?
- 111.070 \( \text{O}_2 \text{NNHCD}_2\text{CD}_2\text{OH} \) ?

Graph showing:
- MEA-d\(_4\) addition
- MEA
- Chamber opened
- Chamber closed

Time points:
- 08:00
- 10:00
- 12:00
- 14:00
- 16:00
- 18:00
\[ \Delta_r H = -35 \text{ kJ mol}^{-1} \]

Fast unimolecular reaction
Fate of MEA\(_{(g)}\)

\[
\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-OH}
\]

- How much?
- CHCH\(_2\)OH
- NH\(_2\)CHO
- NH\(_2\)CH\(_2\)CHO
- NH\(_2\)CHO
- NH\(_2\)C(O)CHO

Not "OK" "OK" "OK"
## Branching Ratios from 4 Exp.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$\frac{k_1 + k_2}{k_{tot}}$</th>
<th>$\frac{k_3}{k_{tot}}$</th>
<th>$\frac{k_4}{k_{tot}}$</th>
<th>Nitramine</th>
</tr>
</thead>
<tbody>
<tr>
<td>industrial area</td>
<td>0.08</td>
<td>0.80</td>
<td>0.12</td>
<td>1.3 %</td>
</tr>
<tr>
<td>on point, high NOx</td>
<td>0.05</td>
<td>0.87</td>
<td>0.08</td>
<td>1.5 %</td>
</tr>
<tr>
<td>on point, high NOx</td>
<td>0.06</td>
<td>0.83</td>
<td>0.07</td>
<td>0.6 %</td>
</tr>
<tr>
<td>rural area</td>
<td>0.12</td>
<td>0.83</td>
<td>0.05</td>
<td>0.3 %</td>
</tr>
<tr>
<td>average</td>
<td>$0.08 \pm 0.03$</td>
<td>$0.84 \pm 0.03$</td>
<td>$0.08 \pm 0.03$</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

Based on the results from on-line and in situ instrumentation it is found that more than 80 % of the reaction between MEA and OH radicals takes place at –CH₂–, while less than 10 % occurs at -NH₂, and less than 10 % at –CH₂OH.

The major products (>80 %) in the photo-oxidation are formamide (NH₂CHO) and formaldehyde (CH₂O), of which the latter has a short atmospheric lifetime. Minor products (<10 %) are the short-lived amino acetaldehyde (NH₂CH₂CHO) and the longer lived 2-oxo acetamide (NH₂C(O)CHO).

The nitrosamine, ONNHCH₂CH₂OH, was NOT detected in any of the experiments.

The nitramine, O₂NNHCH₂CH₂OH, was confirmed as product in the experiments. The yield depends upon the mixing ratio of NOx. For rural regions with NOx levels of 0.2-10 ppbV, less that 3 % of emitted MEA will end up as the nitramine.
http://ada.nilu.no

Atmospheric Degradation of Amines (ADA)

Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA)

CLIMIT project no. 193438

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