Investigating Methylamine Oxidation with Multiplexed Photoionization Mass Spectrometry: Insight into the Reactivity of C-centered and N-centered Radicals

Sommer L. Johansen¹, Arkke Eskola², Kendrew Au¹, Judit Zádor¹, Leonid Sheps¹

1. Gas Phase Chemical Physics, Combustion Research Facility, Sandia National Laboratories, Livermore, CA
2. Laboratory of Physical Chemistry, Department of Chemistry, University of Helsinki, Helsinki, Finland
Amines in the Atmosphere

Amines are released in combustion of biomass and industrial processes:

- Biofuels
- Agriculture
- Wildfires
- Carbon capture agents
Amines in the Atmosphere

Amines are released in combustion of biomass and industrial processes:

- Biofuels
- Agriculture
- Wildfires
- Carbon capture agents

Amines in the Atmosphere

\[
\begin{align*}
\text{HN} & \quad \text{NH}_2 \\
\text{HN} & \quad \text{NH}_2 \\
\hline
\end{align*}
\]


Image credit: https://www.usatoday.com/
Methylamine Oxidation

- Methylamine is a common degradation product of amines used for carbon capture
- Byproduct of NH₃/methane combustion
- Limited work on oxidation pathways


Methylamine Oxidation

- Methylamine is a common degradation product of amines used for carbon capture.
- Byproduct of NH₃/methane combustion.
- Limited work on oxidation pathways.

Methylamine Oxidation

\[
\begin{align*}
\text{CH}_2\text{NH}_2 + \text{O}_2 & \quad \text{and} \quad \text{CH}_3\text{CHNH}_2 + \text{O}_2 \quad \text{Reaction Kinetics: Photoionization Mass Spectrometry Experiments and Master Equation Calculations} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C}\text{NH}_2 + \text{O}_2 & \quad \text{and} \quad \text{H}_3\text{C}\text{CHNH}_2 + \text{O}_2 \\
\text{H}_3\text{C}\text{NH}_2 + \text{OH} & \quad \text{H}_3\text{C}\text{NH}_2 - \text{H}_2\text{O} \\
\text{H}_2\text{C}\text{NH}_2 + \text{O}_2 & \quad \text{H}_2\text{C}\text{NH}_2 - \text{HO}_2 \\
\text{H}_2\text{C}\text{NH} & \quad \text{???} \\
\end{align*}
\]
Methodology: Multiplexed VUV Photoionization Mass Spectrometer

4 Torr
300 K

< 10^{-4} Torr

~10^{-6} Torr

photolysis laser

pulsed mass spec

< 10^{-5} Torr

gas flow
Methodology: Multiplexed VUV Photoionization Mass Spectrometer

Methodology:

- Multiplexed VUV Photoionization Mass Spectrometer
- Photolysis laser
- Gas flow
- Pulsed mass spec
- Products

Diagram:

- ~10^-6 Torr
- < 10^-5 Torr
- 4 Torr 300 K
- < 10^-4 Torr

Chemical Reaction:

\[
\text{HO}_2 + h^\nu \rightarrow 2 \text{OH}^* \\
\text{RH} + \text{OH}^* \rightarrow \text{R}^* + \text{H}_2\text{O} \\
\text{R}^* + \text{O}_2 \rightarrow \text{products}
\]
Methodology: Multiplexed VUV Photoionization Mass Spectrometer

Tunable monochromatic VUV radiation at the Advanced Light Source (Chemical Dynamics Beamline)

\[ \text{HO} - \text{OH} + h^\nu \rightarrow 2 \text{OH}^- \]

\[ \text{RH} + \text{OH}^- \rightarrow \text{R}^- + \text{H}_2\text{O} \]

\[ \text{R}^- + \text{O}_2 \rightarrow \text{products} \]
Methodology: Multiplexed VUV Photoionization Mass Spectrometer

Tunable monochromatic VUV radiation at the Advanced Light Source (Chemical Dynamics Beamline)

- Photolysis laser
- Gas flow
- VUV ionization
- Pulsed mass spec
- 

\[
\text{HO} + \text{OH} \rightarrow_h \text{2 OH}^· \\
\text{RH} + \text{OH}^· \rightarrow \text{R}^· + \text{H}_2\text{O} \\
\text{R}^· + \text{O}_2 \rightarrow \text{products}
\]
Methodology: PIMS results

![Diagram showing normalized intensity vs m/z with intermediates and products reactants labeled.]
Methodology: KinBot

Automated reaction kinetics workflow tool for elementary gas-phase reactions.

- Searches for reaction paths starting from a parent compound, continuing over multiple wells
- Characterizes stationary points
- Assembles the chemical master equation
- Includes uncertainty quantification
- Open source

https://github.com/zadorlab/KinBot/
Methodology: KinBot

Automated reaction kinetics workflow tool for elementary gas-phase reactions.

- Searches for reaction paths starting from a parent compound, continuing over multiple wells
- Characterizes stationary points
- Assembles the chemical master equation
- Includes uncertainty quantification
- Open source

Great at finding new reaction pathways!

https://github.com/zadorlab/KinBot/

Methylamine Oxidation: $\text{CH}_2\text{NH}_2 + \text{O}_2$

Methylamine Oxidation: \( \text{CH}_2\text{NH}_2 + \text{O}_2 \)

Too short-lived to see

\( \text{H}_2\text{C} \text{---NH}_2 \quad \text{D}_2\text{C} \text{---NH}_2 \)

Methylamine Oxidation: \( \text{CH}_2\text{NH}_2 + \text{O}_2 \)

Methylamine Oxidation: $\text{CH}_2\text{NH}_2 + \text{O}_2$

Methylamine Oxidation: $\text{CH}_3\text{NH}$

\[
\text{HC} \quad \text{NH}^* + h\nu \\
\Downarrow \\
\text{HC} \quad \text{NH}^* + \text{H}_2
\]

Methylamine Oxidation: CH$_3$NH

$$\text{H}_3\text{C}-\text{NH}^* + h^\nu$$

$$28 \left[ \text{HC}-\text{NH} \right]^+ + \text{H}_2$$

Methylamine Oxidation: CH₃NH

What reactions are occurring?

Methylamine Oxidation: \( \text{CH}_3\text{NH} \)

What reactions are occurring? \( \text{O}_2? \)

Methylamine Oxidation: CH$_3$NH + O$_2$

**Figure 1** Potential energy surface for the CH$_3$NH + O$_2$ reaction. Energies are 0 K enthalpies in kcal mol$^{-1}$, at the G3X-K level of theory.

$3.6 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
Methylamine Oxidation: $\text{CH}_3\text{NH} + \text{O}_2$

CCSD(T)-F12a/cc-pVDZ-F12//ωB97X-D/6-311++G**
Methylamine Oxidation

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{NH}_2 \\
+ \text{OH} & \quad - \text{H}_2\text{O} \\
74\% & \quad 26\% \\
\cdot\text{H}_2\text{C} & \quad \text{NH}_2 \\
+ \text{O}_2 & \quad - \text{HO}_2 \\
\text{H}_2\text{C} & \quad \text{NH} \\
?? & \\
\text{H}_3\text{C} & \quad \text{NH} \\
\text{O}_2? & \\
\end{align*}
\]
Methylamine Oxidation

Methylamine Oxidation: CH$_3$NH + ?

What masses increase by 3 m/z in the d3-methylamine results?

H$_3$C—NH$_2$  D$_3$C—NH$_2$

31  34

Methylamine Oxidation: $\text{CH}_3\text{NH} + ?$

What masses increase by 3 m/z in the d3-methylamine results?

$\text{H}_3\text{C} ---- \text{NH}_2$  $\text{D}_3\text{C} ---- \text{NH}_2$

31  →  34
45  →  48
47  →  50
Methylamine Oxidation: CH$_3$NH + ?


Methylamine Oxidation: $\text{CH}_3\text{NH} + \text{HO}_2$
Methylamine Oxidation: \( \text{CH}_3\text{NH} + \text{HO}_2 \)
Methylamine Oxidation: \( \text{CH}_3\text{NH} + \text{HO}_2 \)
Methyamine Oxidation

\[
\begin{align*}
\text{H}_3\text{C} - &\text{NH}_2 + \text{OH} \\
&\rightarrow 74\% \\
\text{H}_2\text{C} - &\text{NH}_2 + \text{HO}_2 \\
&\rightarrow 26\%
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} - &\text{NH}^* + \text{O}_2 \\
&\rightarrow \text{H}_2\text{C} - \text{NH} \\
&\rightarrow \text{H}_3\text{C} - \text{NH}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} - &\text{N}^* - \text{H}_2\text{O} \\
&\rightarrow \text{H}_3\text{C} - \text{O} \\
&\rightarrow \text{H}_3\text{C} - \text{OH} \\
&\rightarrow \text{H}_3\text{C} - \text{O}_{2}^*
\end{align*}
\]
Methylamine Oxidation

\[
\begin{align*}
\text{H}_3\text{C}-\text{NH}_2 & \quad + \text{OH} \quad - \text{H}_2\text{O} \\
\text{H}_3\text{C}-\text{NH} & \quad + \text{O}_2 \quad - \text{HO}_2 \\
\text{H}_2\text{C}-\text{NH} & \quad - \text{H}_2\text{O} \quad - \text{OH}
\end{align*}
\]
Methylamine Oxidation

\[
\begin{align*}
\text{H}_3\text{C} & \text{NH}_2 + \text{O}_2 \rightarrow \text{H}_3\text{C} \text{NH} \cdot \\text{HO}_2 \rightarrow \text{H}_3\text{C} \text{NH} + \text{HO}_2 \\
\text{H}_3\text{C} & \text{NH} \rightarrow \text{H}_3\text{C} \text{NH}_2 + \text{OH} \rightarrow \text{H}_3\text{C} \text{NH}_2 + \text{HO}_2 \rightarrow \text{H}_3\text{C} \text{N} \text{O} \\
\end{align*}
\]
Methylamine Oxidation

Signals normalized to height of CH3NH for comparison
Methylamine Oxidation

\[
\begin{align*}
\text{H}_3\text{C}-&\text{NH}_2 \\
+ &\text{OH} \\
- &\text{H}_2\text{O} \\
\text{H}_2\text{C}-&\text{NH}_2 \\
+ &\text{O}_2 \\
- &\text{HO}_2 \\
- &\text{H}_2\text{O} \\
\text{H}_2\text{C}-&\text{NH} \\
+ &\text{HO}_2 \\
- &\text{OH} \\
\text{H}_3\text{C}-&\text{NH} \\
\Delta E = -58 \text{ kcal/mol} \ast \\
\end{align*}
\]

\ast \omega_{\text{B97X-D/6-311++G**}}
Conclusions

- Can detect CH$_3$NH
- Unlikely to see products of CH$_3$NH + O$_2$
- CH$_3$NH undergoes rapid reactions, potentially with HO$_2$ and OH
Current/Future Work

- Building comprehensive chemical kinetics model (Cantera)
- Theory to explore additional reactions of CH$_3$NH
  - Looking for graduate student intern!
- Atmospheric pressure experiments
Acknowledgements

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

This research used resources of the Advanced Light Source, a U.S. DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

Jill Hruby Fellowship

Lenny Sheps

Judit Zádor

Kendrew Au

Arkke Eskola
Methyamine Oxidation: $\text{CH}_3\text{NH} + \text{O}_2$