Challenges in NH$_3$ oxidation kinetics

Peter Glarborg
Ammonia oxidation kinetics

- Modeling is important in design and optimization of engines
- Ammonia is a poor fuel
- Ammonia oxidation gives rise to formation of NO\(_x\)
- Global reaction schemes cannot be expected to be of much use due to the complexity of the kinetics
- What do we know and what are the challenges in NH\(_3\) oxidation kinetics?
Reviews on NH$_3$/amine chemistry

• Miller and Bowman, "Mechanism and Modeling of Nitrogen Chemistry in Combustion" (1989)
• Dean and Bozzelli, "Combustion Chemistry of Nitrogen" (2000)
Research on ammonia oxidation kinetics

- Ammonia as energy carrier is a fairly recent interest
- Work on \( \text{NH}_3 \) chemistry has been motivated largely by emission concerns
  - Formation of \( \text{NO}_x \)
  - Control of \( \text{NO}_x \) (SNCR)
Nitrogen chemistry

- Emissions of nitrogen oxides have been a concern since the 1970’s
- Extensive R&D has lead to efficient measures
- **New challenges**
  - Regulations increasingly stringent
  - New fuels and fuel mixtures
    - Natural gas (Thermal NO, prompt NO)
    - Biomass (Fuel-NO, mostly from oxidation of amines)
  - Low-NO\(_x\) burners and Selective Catalytic Reduction of NO (SCR) not applicable for range of fuels and technologies
    - Use primary measures or in-situ NO reduction (e.g., SNCR)
Formation mechanisms for NO

**Fixation of atmospheric N\textsubscript{2}**

\[ O + N\textsubscript{2} \rightarrow NO+N \]  \( (>1800 \text{ K}) \)

\[ CH+N\textsubscript{2} \rightarrow NCN+N \]

\[ O+N\textsubscript{2}+M \rightarrow N\textsubscript{2}O+M \]  \( \text{(High pressure)} \)

**Conversion of fuel nitrogen**

Volatile nitrogen from biomass, waste and low-rank coal is mainly released as NH\textsubscript{3}. 
Reaction path diagram for N-volatile conversion in flames
Pollutant formation – solid and liquid fuels

- Ammonia trace species
- Radical pool controlled by fuel oxidation
- Typically atmospheric pressure
Pollution control: Selective non-catalytic reduction of NO (SNCR)

Dilute concentrations
Presence of NO (NH₂ + NO controls radical pool)
Temperatures of 1100-1400 K
Atmospheric pressure
Chemical kinetic model

  - Thermodynamic data from Active Thermochemical Tables
  - Rate constants and product channels from measurement and/or theory
  - Subsets for C₁-C₂ hydrocarbons, amines, cyanides, and hydrocarbon/nitrogen interactions
  - Predictions tested against experimental data for NH₃ ignition and oxidation, interaction with co-fuels, and Thermal DeNOₓ
  - The mechanism not optimized
Ignition delays for NH$_3$

Shock tube, 1.4 atm.
$\Phi = 0.5, 1.0, 2.0$
$Ar = 99%$

Mathieu and Petersen (2015)
Glarborg, Miller, Ruscic and Klippenstein (2018)
NH$_3$ oxidation in low-pressure flame

Laminar premixed flame:
35 torr
48% NH$_3$, 51% O$_2$; Ar

Bian et al. (1986)
Glarborg, Miller, Ruscic and Klippenstein (2018)
Flow reactor oxidation of CO/NH$_3$ mixture

Quartz flow reactor
NH$_3$ = 250 ppm
CO = 1250 ppm
O$_2$ = 10% in N$_2$
NH₃ oxidation with trace NO

Quartz flow reactor
NH₃ = 500 ppm
NO = 25-100 ppm
O₂ = 40% in N₂

Vilas and Glarborg (2004)
Glarborg, Miller, Ruscic and Klippenstein (2018)
Oxidation of CH$_4$/NH$_3$ in a flow reactor

Quartz flow reactor
CH$_4$ = 2500 ppm
NH$_3$ = 500 ppm
O$_2$ = 0.35/0.5/4.0% in N$_2$

Mendiara and Glarborg (2008)
Glarborg, Miller, Ruscic and Klippenstein (2018)
Low pressure CH$_4$/O$_2$/NH$_3$/Ar flames

Major species

Laminar premixed flame: 4 kPa
$\Phi = 1.0$ (diluted in Ar)
$R = \text{NH}_3/\text{CH}_4$ ratio [0-1]

Tian, Li, Zhang, Glarborg and Qi (2009)
Low pressure CH$_4$/O$_2$/NH$_3$/Ar flames

Minor species

Laminar premixed flame: 4 kPa
Φ = 1.0 (dilued in Ar)
R = NH$_3$/CH$_4$ ratio = 1.0
SNCR with NH₃ as agent (Thermal DeNOₓ)

Quartz flow reactor
NH₃ = 830 ppm
NO = 500 ppm
H₂O = 0-10%
O₂ = 4% in N₂

Duo (1990)
Glarborg, Miller, Ruscic and Klippenstein (2018)
SNCR: effect of combustibles

Addition of $H_2$

Addition of CO

Hardy and Lyon (1986)
Alzueta et al. (1997)
Glarborg, Miller, Ruscic and Klippenstein (2018)
Ammonia oxidation kinetics

All well?

Oh yes!

• Detailed mechanisms available
  • NH$_3$ ignition and oxidation
  • CH$_4$/NH$_3$ oxidation
  • Thermal DeNO$_x$
• Comprehensive
• Generally good agreement with experiment
Ammonia oxidation kinetics

All well?

Oh - wait...
Ammonia oxidation kinetics

Issues?

- Experimental data range limited
- Experimental artifacts
- Kinetic issues
Experimental techniques

- Shock tube
- Rapid Compression Machine
- Premixed flame
- Flow reactor
- Batch reactor
- Jet-stirred reactor
Experiments - concerns

- Batch reactor
  - Surface reactions, conditioning, temperature
- Flow reactor
  - Surface reactions, conditioning, temperature
- Jet-stirred reactor
  - Mixing, probe system (surface reactions?)
- Shock tube
  - Temperature and pressure
- Rapid Compression Machine (RCM)
  - Temperature and pressure
- Laminar, premixed flames
  - Interaction with burner surface, stabilization, probe effects

NH$_3$ surface sensitive
NH₃ oxidation in a laminar flow quartz reactor

900 ppm NH₃, 4% O₂, trace H₂O
1 atm., 1279 K

- Surface dependent:
  - Induction time
- Surface independent (low S/V):
  - dNH₃/dt
  - dNO/dt
  - NOᵢ

Dean and Lyon (1982)
Selective non-catalytic reduction of NO in a laminar flow quartz reactor

Flow reactor:
450 ppm NH₃, 225 ppm NO, 1.2% O₂

SNCR:
initiation unimportant => independent of surface
(Lyon and Benn, 1979)

Lyon and Hardy (1986)
Surface effects for SNCR in a laminar flow quartz reactor

Quartz flow reactor
NH$_3$ 1000 ppm
O$_2$ 40%
NO 50 ppm

Effect of iron carbonyls?

Vilas and Glarborg (2004)
Need for additional experiments

- Experimental techniques
  - Shock tube, RCM (ignition delays)
  - Laminar premixed flame (flame speed)
  - Flow reactors (PFR, JSR) (species profiles)
- Investigate
  - Ignition, oxidation, pollutants
  - Expand T, P, conc. range
  - Effect of co-fuels
NH₃ oxidation pathways

NH₂+O₂ slow:
High temperature: NH₂+O/H
Medium temperature: NH₂+NO
Kinetic issues

- Ignition and oxidation rate
- Interaction with co-fuels
- Thermal DeNO\(_x\)
- Formation of NO and other pollutants
NH₃ oxidation in a flow reactor

NH₃ ~ 1000 ppm
O₂ varying; N₂

Neither ignition delay, oxidation rate or NO captured

Abian et al. (2019 – ECM)
NH₃ oxidation in a flow reactor
- effect of CO

Wargadalam et al. (2000)
Hulgaard and Dam-Johansen (1993)
Glarborg (2019)
SNCR with NH$_3$ as agent (Thermal DeNO$_x$)

Duo (1990)
Rota et al. (2001)
Glarborg, Miller, Ruscic and Klippenstein (2018)
Thermal DeNO\textsubscript{x} reaction pathways
Sensitivity analysis for NO in SNCR
**Thermal DeNO\(_x\): radical generation**

**Chain branching**

\[
\begin{align*}
     \text{NH}_2+\text{NO} & \rightarrow \text{NNH}+\text{OH} \\
     \text{NNH} & \rightarrow \text{N}_2+\text{H} \\
     \text{H}+\text{O}_2 & \rightarrow \text{O}+\text{OH} \\
     \text{O}+\text{H}_2\text{O} & \rightarrow \text{OH}+\text{OH}
\end{align*}
\]

**Chain termination**

\[
\begin{align*}
     \text{NH}_2+\text{NO} & \rightarrow \text{N}_2+\text{H}_2\text{O} \\
     \text{NNH}+\text{O}_2 & \rightarrow \text{N}_2+\text{HO}_2 \\
     \text{H}+\text{O}_2+\text{M} & \rightarrow \text{HO}_2+\text{M} \\
     \text{H}+\text{O}_2+\text{H}_2\text{O} & \rightarrow \text{HO}_2+\text{H}_2\text{O}
\end{align*}
\]

*Unrestrained chain branching not supported experimentally*
The NNH lifetime issue

NNH lifetime necessary to avoid unrestrained chain branching (through $N_2 + H$)

- Miller and Bowman (1989): $\tau_{NNH} = 10^{-4}$ s ($NNH + NO$)
- Glarborg et al. (1994): $\tau_{NNH} = 10^{-6}$ s ($NNH + O_2$)
- Miller and Glarborg (1996): $\tau_{NNH} = 10^{-7}$ s
- Miller and Glarborg (1999): $\tau_{NNH} = 1.5 \times 10^{-8}$ s
- Klippenstein et al. (2011): $\tau_{NNH} = 10^{-9}$ s (best theory)
  - NNH largely dissociates
  - Chain branching restrained by the $NH_2+NO$ branching fraction
    - $NH_2 + NO \rightarrow N_2 + H_2O$
    - $NH_2 + NO \rightarrow NNH + OH$
The $\text{NH}_2 + \text{NO}$ reaction

\[ \text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH} \quad (1a) \]
\[ \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (1b) \]

Overall rate constant

Branching fraction $k_{1a}/k_{tot}$

Glarborg, Miller, Ruscic and Klippenstein (2018)
Thermal DeNO$_x$: the effect of H$_2$O

Short NNH lifetime

$\Rightarrow$

Stronger predicted impact of H$_2$O

H + O$_2$ + H$_2$O $\rightarrow$ HO$_2$ + H$_2$O
Thermal DeNO$_x$

NH$_3$: 1000 ppm
NO: 500 ppm
O$_2$: 1-50%

Kasuya et al. (1995)
Glarborg et al. (2018)
The \( \text{NH}_2 + \text{NO}_2 \) reaction

\[
\begin{align*}
\text{NH}_2 + \text{NO}_2 & \rightarrow \text{H}_2\text{NO} + \text{NO} \quad (2a) \\
\text{NH}_2 + \text{NO}_2 & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad (2b)
\end{align*}
\]

Overall rate constant

Branching fraction \( k_{1a}/k_{\text{tot}} \)

Klippenstein et al. (2013)
Glarborg, Miller, Ruscic and Klippenstein (2018)
The NO$_2$ recycle

\[
\begin{align*}
\text{NNH}+\text{O}_2 & \rightarrow \text{N}_2+\text{HO}_2 \\
\text{H}+\text{O}_2+\text{M} & \rightarrow \text{HO}_2+\text{M} \\
\text{NO}+\text{HO}_2 & \rightarrow \text{NO}_2+\text{OH} \\
\text{NH}_2+\text{NO}_2 & \rightarrow \text{H}_2\text{NO}+\text{NO} \\
\text{H}_2\text{NO}+\text{O}_2 & \rightarrow \text{HNO}+\text{HO}_2 \\
\text{HNO}+\text{O}_2 & \rightarrow \text{NO}+\text{HO}_2
\end{align*}
\]

\{\text{uncertain}\}

How strong is the NO$_2$ pump?
NH$_3$ ignition delays at high pressure and high temperature

Mathieu and Petersen (2015)
Impact of N$_2$-amine chemistry on ignition delays

Mathieu and Petersen (2015): Leave out N$_2$-amine subset to predict IDT for NH$_3$.

\[
\text{NH}_2 + \text{NH}_2 = \text{N}_2\text{H}_4 (k_\infty)
\]
Co-combustion issues: NH$_3$+hydrocarbon fuel

- Ignition delay
- Flame speed
- Pollutants
  - Hydrocarbon amines
  - Cyanides
  - Isocyanides
  - Nitrous oxide
C₂ amine oxidation in premixed flames
Challenges in NH$_3$ oxidation kinetics

- Experimental artifacts
  - Surface effects
- Experimental data range (shock tube, RCM, flow reactors)
  - Expand T, P, conc. range
  - Effect of co-fuel
- Kinetic issues
  - Ignition and oxidation rate
  - Co-combustion
  - Formation of NO and other pollutants
  - Thermal DeNO$_x$
- Establish fundamental and engineering models