Overview

- Having now examined mechanisms for fuel oxidation (H₂, CO and HC), the goal here is to revisit mechanisms for NOₓ production:
  1. thermal mechanism (extended Zeldovich) for high T, lean conditions
  2. N₂O mechanism for low T, lean conditions
  3. NNH mechanism for high T, stoich/rich, H₂
  4. Fenimore/prompt mechanism for hydrocarbon fuel-conversion zones
  5. NO₂ mechanism for NO→NO₂ conversion in low T regions
**NOx Formation**

- NO\textsubscript{x} (NO, NO\textsubscript{2}, NO\textsubscript{3}) important pollutant
  - NO\textsubscript{2} leads to acid rain/photochemical smog/O\textsubscript{3}
  - combustion NO converted to NO\textsubscript{2} in atmosphere
  - can also directly impact human health
- Observation: original Zeldovich mechanism does not accurately predict NO production in
  - wet air
  - low T combustion with long residence times
  - stoichiometric and rich H\textsubscript{2}-air flames
  - low residence time or rich hydrocarbon flames
- Need more advanced NO mechanisms

**Thermal NO Mechanism**

- Already described basic Zeldovich mechanism
  - add reaction for “wet” systems (H species) \(\Delta H_R\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H_R)</th>
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<tbody>
<tr>
<td>Extended Zeldovich Mechanism</td>
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<tr>
<td>(N_2 + O \leftrightarrow NO + N) ({NO.1})</td>
<td>+75.1 kcal/mol</td>
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<tr>
<td>(O_2 + N \leftrightarrow NO + O) ({NO.2})</td>
<td>-32.1 kcal/mol</td>
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<tr>
<td>(OH + N \leftrightarrow NO + H) ({NO.3})</td>
<td>-48.7 kcal/mol</td>
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</tbody>
</table>
- Thermal NO Formation
  - still rate limited by \(\{NO.1f\}\)
  - dominates at high T (\(\geq 1800\)K), lean environments
  - long \(\tau_{res}\) usually required (postflame gases)
  - superequilibrium \([O]\), \([OH]\) increases NO prod. rate
Intermediate $N_2O$ Mechanism

- $N_2$ first converted to $N_2O$ then $NO$  
  $N_2 + O( + M ) \leftrightarrow N_2O( + M ) \{ NO.4 \}$  
  $\Delta H_R = -40 \text{ kcal/mol}$
- $N_2O + H \leftrightarrow NO + NH \{ NO.5 \}$  
  $\Delta H_R = +35 \text{ kcal/mol}$
- $N_2O + O \leftrightarrow NO + NO \{ NO.6 \}$  
  $\Delta H_R = -36 \text{ kcal/mol}$

**NO Formation**
- $\{ NO.4 \}$ has Lindemann-like $p$ dependence ($k_0 \rightarrow k_{\infty}$)
- medium to high activation energies
  - $E_a(\text{kcal/mol})$: 18$\{ NO.4 \}; 35\{ NO.5 \}; 23\{ NO.6 \}$
- important in low $T$, fuel lean ( $\phi \leq 0.8$ ) systems (+ high $p$)
- $NH$ from $\{ NO.5 \}$ can also lead to $NO$
  - $NH + O \rightarrow NO + H \{ NO.10 \}$
  - $NH + O_2 \rightarrow NO + OH \{ NO.11 \}$

$N_2O$ destruction via $N_2 + O \leftrightarrow N_2 + OH \{ NO.7 \}$

**NNH Mechanism**

- Thermal + nitrous mechanisms “ok” for $H_2$-air, BUT
- NO also produced via NNH intermediate  
  $N_2 + H( + M ) \leftrightarrow NNH( + M ) \{ NO.12 \}$  
  $\Delta H_R = +6.5 \text{ kcal/mol}$
  $NNH + O \leftrightarrow NO + NH \{ NO.13 \}$  
  $\Delta H_R = -11.3 \text{ kcal/mol}$
- $\{ NO.13 \}$ has same products as $\{ NO.5 \}$
- and $NH$ can also lead to $NO$ via $\{ NO.10 \}$ and $\{ NO.11 \}$
- Where is $NNH$ mechanism (path) important?
  - for $T \geq 2200 \text{ K}$, important for stoichiometric and rich, low residence time systems, $H_2$-air flames
  - for $T \geq 1900 \text{ K}$, most impact (relative to thermal $NO_x$ ) near stoichiometric (and at lower $T$)
Fenimore/Prompt Mechanism

- In thermal, $N_2O$, and $NNH$ mechanisms, $NO$ produced via conversion from attack on $N_2/O_2$ via radicals containing only $N$, $O$, $H$ nuclei
- Sufficient for wet air and hydrogen combustion
- $NO$ can also be produced in hydrocarbon combustion via $C$ species
  - prompt NOx – Fenimore observed $NO$ formed earlier in HC combustion than possible from thermal mechanism
- General reaction scheme
  - $CH_x$ (e.g., $CH$, $CH_2$ and $CH_3$) radicals react with molecular nitrogen to form $HCN$ (hydrogen cyanide)
  - conversion to NO through various intermediates

Fenimore Scheme

- Early version of the mechanism
- Rate limiting step
  \[
  CH + N_2 \leftrightarrow HCN + N \quad \text{conversion of $N_2$}
  \]
- Conversion to NO
  \[
  HCN + O \leftrightarrow NCO + H \\
  NCO + H \leftrightarrow NH + CO \\
  NH + H \leftrightarrow N + H_2 \\
  N + OH \leftrightarrow NO + H
  \]
- conversion to NO via radical/radical reactions
- Limited accuracy (e.g., $\phi<1.2$)
**General Prompt Mechanism**

- Many reactions for range of rich mixtures/fuels
  - graphical representation (ref. Bowman, 24th Combustion Symposium)

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CH_x (x=1,2,3) \[\rightarrow\] H, OH \[\rightarrow\] HCN \[\rightarrow\] NHCN \[\rightarrow\] OCN \[\rightarrow\] NCHN \[\rightarrow\] NH \[\rightarrow\] NO \[\rightarrow\] N\_2 \[\rightarrow\] \text{also in thermal mech.}
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**NO\textsubscript{2} Mechanism**

- Noted that NO converted to NO\textsubscript{2} in atmosphere
  - combustion systems also convert NO to NO\textsubscript{2}
    - sometimes be significant fraction of total combustor NOX emissions \([NO]+[NO_2]\)

\[
NO + HO_2 \leftrightarrow NO_2 + OH \quad \{NO_2.1\} \quad \text{HO}_2 \text{ formed @ low T}
\]

\[
NO_2 + H \leftrightarrow NO + OH \quad \{NO_2.2\}
\]

\[
NO_2 + O \leftrightarrow NO + O_2 \quad \{NO_2.3\}
\]

- No NO\textsubscript{2} from hot regions
- NO\textsubscript{2} in combustion systems often comes from NO formed in hotter regions mixing into low T regions
Example: Premixed Laminar Flame

- NO₂, prompt important in reaction zone; thermal in downstream
- \( \phi = 0.85 \)
- \( \text{NO}_2 + \text{H} \rightarrow \text{N} + \text{H}_2 \) => Prompt mech.
- \( \text{N}_2 + \text{O} \) => Thermal Mech.

\( \text{CH}_4/\text{air} \)
1 atm
300K/80°F inlet

\( \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \)

Primary source of N?