An examination of 3 key reactions in NOx formation and NOx control in combustion systems
Synopsis

1. Prompt and thermal formation of NO\textsubscript{x} (= NO + NO\textsubscript{2}) in combustion.

2. Examination of the kinetics of:
   - CH + N\textsubscript{2} which is involved in prompt NO\textsubscript{x} formation
   - NH\textsubscript{2} + NO, involved in selective non-catalytic reduction of NO\textsubscript{x} emissions
   - HCCO + NO, involved in the reburn method for NO\textsubscript{x} emissions reduction.
Mechanisms of NO\textsubscript{x} formation

• **Prompt** Fenimore (13\textsuperscript{th} Int Symp Comb, 1970) observed NO formation in the primary reaction zone in a flame. Attributed to reaction of a hydrocarbon radical with N\textsubscript{2}. Suggested
  \[
  \text{CH + N}_2 \rightarrow \text{HCN + N}
  \]

• **Fuel bound N** Reaction of chemically bound N in fossil fuels. Also generates HCN

• Route from HCN to NO discussed by Miller and Bowman (Prog. Energy Combust. Sci. 15 (1989) 287-338)

• **Thermal NO\textsubscript{x} (Zeld’ovich mechanism)**
  \[
  \begin{align*}
  \text{O} & \rightleftharpoons \text{O}_2 \\
  \text{O} + \text{N}_2 & \rightleftharpoons \text{NO} + \text{N}
  \end{align*}
  \]

Fig. 11. Reaction path diagram illustrating the major steps in prompt NO formation and conversion of fuel nitrogen (FN) to NO. The bold lines represent the most important reaction paths.
Evaluation of $CH + N_2$ (Baulch et al.)
Evaluation of \( \text{CH} + \text{N}_2 \) (Baulch et al.) pressure dependence
Moskaleva and Lin
Also includes calcs by Cui et al. J Chem Phys, 1999, 110, 9469

Note:
• Adduct formed at low T and high p not connected to bimolecular reaction products
• Quartet - doublet transition too slow to compete with spin allowed formation of NCN + H

**CH + N₂ - theory**

Major product - NCN + H
Modelling of NO production in natural gas flames

- Using rate coefficient of Moskaleva et al underpredicts rate of prompt NO formation by factor of 6 or more.
- Extrapolation of high T shock tube expts gives better agreement.
What happens to the NCN?

Main routes to NO
• Shock tube study, 1943 - 3543 K, 0.9 - 1.4 atm.
• CH generated from ethane / Ar and acetic acid / Ar
• CH + N$_2$ studied through perturbation expts by adding N$_2$.
• CH detected by laser absorption at 431.1 nm and NCN at 329.13 nm.
• $k : 6.03 \times 10^{12} \exp(-11150/ T/ K) / cm^3 \ mol^{-1} \ s^{-1}$
• Branching ratio for (NCN + H channel) = 1 (2228 - 2905 K) (conservative lower limit = 0.7)
Vasudevan et al. Arrhenius plot
N$_2$ perturbation experiments
ethane / Ar / 3348 K / 1.08 atm

- 0% N$_2$, unperturbed CH
- 10.1% N$_2$, perturbed CH
- 1.75% absorption

CH Mole Fraction [ppm]

Time [µs]
Main contributors to kinetic scheme used to extract $k(\text{CH} + \text{N}_2)$ in ethane expts

### TABLE 1: Rate Parameters for Reactions Important in CH Perturbation Experiments in Ethane/N$_2$/Ar

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate coefficient (cm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CH + N$_2$ $\rightarrow$ products</td>
<td>$6.03 \times 10^{12}$</td>
<td>this work</td>
</tr>
<tr>
<td>(4) H + NCN $\rightarrow$ HCN + N</td>
<td>$1.89 \times 10^{14}$</td>
<td>$12^a$</td>
</tr>
<tr>
<td>(5a) CH$_2$ + M $\rightarrow$ C + H$_2$ + M</td>
<td>$1.15 \times 10^{14}$</td>
<td>$32^b$</td>
</tr>
<tr>
<td>(5b) CH$_2$ + M $\rightarrow$ CH + H + M</td>
<td>$5.60 \times 10^{15}$</td>
<td>$25$</td>
</tr>
<tr>
<td>(6a) CH$_3$ + M $\rightarrow$ CH + H$_2$ + M</td>
<td>$3.09 \times 10^{15}$</td>
<td>$25^b$</td>
</tr>
<tr>
<td>(6b) CH$_3$ + M $\rightarrow$ CH$_2$ + H + M</td>
<td>$2.24 \times 10^{15}$</td>
<td>$25^b$</td>
</tr>
<tr>
<td>(11) CH$_2$ + H $\rightarrow$ CH + H$_2$</td>
<td>$1.1 \times 10^{14}$</td>
<td>$37$</td>
</tr>
<tr>
<td>(13) H + CH $\rightarrow$ C + H$_2$</td>
<td>$1.65 \times 10^{14}$</td>
<td>$38$</td>
</tr>
<tr>
<td>(19) CH + M $\rightarrow$ C + H + M</td>
<td>$1.0 \times 10^{14}$</td>
<td>$32^b$</td>
</tr>
<tr>
<td>(20) C + CH $\rightarrow$ C$_2$ + H</td>
<td>$2.0 \times 10^{14}$</td>
<td>$32$</td>
</tr>
<tr>
<td>(21) C + CH$_2$ $\rightarrow$ 2CH</td>
<td>$1.0 \times 10^{14}$</td>
<td>$32$</td>
</tr>
<tr>
<td>(22) C + CH$_3$ $\rightarrow$ H + C$_2$H$_2$</td>
<td>$5.0 \times 10^{13}$</td>
<td>$38$</td>
</tr>
<tr>
<td>(23) C + CH$_4$ $\rightarrow$ CH + CH$_3$</td>
<td>$5.0 \times 10^{13}$</td>
<td>$32$</td>
</tr>
<tr>
<td>(24) CH + CH$_3$ $\rightarrow$ H + C$_2$H$_3$</td>
<td>$6.0 \times 10^{13}$</td>
<td>$32$</td>
</tr>
</tbody>
</table>
More recent theory: Harding et al: multireference calcs

Harding et al.

Contributions to overall rate constant for $CH + N_2$

Plot of the predicted rate coefficient for $CH + N_2 \rightarrow NCN + H$ via path A when considering different subsets of the transition states along the path.

Plot of the contributions from different pathways to the predicted rate coefficient for $CH + N_2 \rightarrow NCN + H$. 
Plot of the experimental measurements and theoretical predictions for the $CH + N_2 \rightarrow NCN + H$ rate coefficient.
NCN detection in flames

1. LIF, atmospheric pressure, methane/air, nitrous oxide.


- Excitation scans over the region of the main NCN bandhead at 3291.3 Å in the atmospheric pressure CH4/N2O/N2 flame (a) and in the CH4/air flame (b) including simulations

Fig. 8. Calculated mole fractions of NCN, NH, CH$_2$O, OH and CH and calculated temperature for flame A (multiplied by scaling factors). The position of peak CH concentration is defined as $z = 0$ mm, therefore $z$ corresponds to the height above the flame front.
Selective non-catalytic reduction (SNCR)
Thermal De-NO\textsubscript{x}

- Developed by Lyon (EXXON) US Patent 3,900,554 (1975)
- Involves addition of NH\textsubscript{3} which converts NO to N\textsubscript{2}.
- Overall reaction is
  \[ 4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]
- Occurs in T range 1100 - 1400 K
- Window moves to lower T on addition of fuel.
Key elementary reaction is
\[ \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (a) \]
\[ \rightarrow \text{NNH} + \text{OH} \quad (b) \]

The reaction is self-sustaining, i.e. it must not be exclusively terminating. For this to occur, the yield of channel (b) must be at least 0.25, increasing to 0.3 above 1100 K (Miller and Bowman)

Fang et al., Disc Faraday, 2001, 119, 207
Independent of pressure up to several atmospheres
Experimental and modelling studies of rate coefficient and NNH yield

A

Branching in \( \text{NH}_2 + \text{NO} \)

- Diao & Smith 1996
- Miller & Glarborg 1999
- Hahn et al 2001

B

\( \text{NH}_2 + \text{NO} \rightarrow \text{Products} \)

- Miller & Glarborg 1999
- Hahn et al 2001
• Pulsed laser photolysis of NH\textsubscript{3} /NO/He mixtures at 193 nm and total pressures in the range 7-13 mbar. 305 - 1037 K.

• Branching ratios were determined from mass spectrometric detection of NH\textsubscript{2}, H\textsubscript{2}O, and CO\textsubscript{2}. The OH yield was determined by reaction with CO and measurement of the CO\textsubscript{2} produced.
• Found that \( \alpha \) increases sharply above \(~1000\, \text{K}\)
Reanalysis, Park and Lin 1999

• J. Park and M. C. Lin, J. Phys. Chem. A 103, 8906 1999 (and refs therein)
• Pulsed laser photolysis of NH$_3$ /NO mixtures at 193 nm. NH$_2$ monitored by cavity ring down laser absorption between 536 and 539 nm. The NO reactant and H$_2$O product were monitored by mass spectrometry. Rate constants were derived from kinetic modelling of the NO and H$_2$O profiles
• Problems attributed to incorrect values for OH + NH$_3$, one of the key reactions in their kinetic scheme. Re-determined via reverse, combined with equilibrium constant.
Open circles – remodelled results from 1997 paper

Figure 1. Arrhenius plot of the rate constant for the NH$_2$ + H$_2$O reaction: solid curve (ref 28); dashed line (ref 32); dotted line (ref 33); dash–dotted curve (ref 34); dash–dot-dotted curve (ref 40); ref 27 (●); ref 35 (▲); ref 36 (▽); ref 37 (□); ref 38 (×); ref 39 (♦). (Inset) Arrhenius plot of the OH + NH$_3$ → NH$_2$ + H$_2$O reaction: solid line (ref 27); dashed curve (ref 30); dotted line (extrapolation of ref 27).

- 1826-2159 K 1.10 to 1.21 bar.
- Measurement of \( \text{NH}_2 \) by frequency modulation absorption behind reflected shock waves in monomethylamine (\( \text{CH}_3\text{NH}_2 \)/\( \text{NH}_3 \)/\( \text{NO} \)/Ar mixtures at pressures in the range 1.1-1.2 bar. The branching ratio was determined by kinetic modeling with a detailed, 125-reaction, mechanism with the branching ratio as a fitting parameter.

### TABLE 1: Selected Reactions Used in the Reaction Mechanism

<table>
<thead>
<tr>
<th>reaction</th>
<th>Arrhenius parameters ( k(T) = A T^n \exp(-E_a/RT) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A ) (cm(^3)mol(^{-1})s(^{-1}))</td>
</tr>
<tr>
<td>R2 ( \text{CH}_3\text{NH}_2 + M \rightarrow \text{CH}_3 + \text{NH}_2 + \text{M} )</td>
<td>8.17E16</td>
</tr>
<tr>
<td>R3 ( \text{NNH} \rightarrow \text{N}_2 + \text{H} )</td>
<td>6.70E07</td>
</tr>
<tr>
<td>R4 ( \text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O} )</td>
<td>2.00E13</td>
</tr>
<tr>
<td>R5 ( \text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2 )</td>
<td>6.40E05</td>
</tr>
<tr>
<td>R6 ( \text{NH}_2 + \text{H} \rightarrow \text{NH} + \text{H}_2 )</td>
<td>1.58E14</td>
</tr>
<tr>
<td>R7 ( \text{NH}_2 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{NH} )</td>
<td>1.70E13</td>
</tr>
</tbody>
</table>
Two dimensional contour plot of the NNH-OH interaction potential. The heavy solid contours correspond to zero (NNH-OH) and positive energy. The lighter solid contours correspond to negative energies. The contour increment for positive contours is 5 kcal mol$^{-1}$. For negative contours, the increment is 1 kcal mol$^{-1}$. 
One dimensional, CAS + 1 + 2/cc-pvdz, potentials for the planar dissociation of HNNOH. The internal degrees of freedom of the NNH and OH fragments are fixed. Solid symbols refer to the ground state, open symbols to the lowest excited state. The solid curves are for the most favorable covalent (cis, trans) orientation. The dashed curve is for the most favorable hydrogen bonding orientation (NOH angle = 0° and the NNO angle = 40°).
Comparison of theoretical predictions for $\alpha(T)$ with experiment. The solid, the dashed, and the dotted lines denote the Fang theoretical predictions. The solid line represents the reference case with the $\text{N}_2\text{H} + \text{OH}$ reaction endothermicity reduced to 1.2 kcal mol$^{-1}$. For the dashed line the endothermicity is reduced to 0.8 kcal mol$^{-1}$ and the ts3/4 barrier height is reduced by 2 kcal mol$^{-1}$. For the dotted line the endothermicity is reduced to 0.3 kcal mol$^{-1}$ and the ts3/4 barrier height is reduced by 4 kcal mol$^{-1}$. 

Fang et al.
Reburn - fuel staged burners

- NO formed in primary combustion zone.

- Fuel injected downstream to create secondary ‘reburn’ zone where NO is reduced to N2.

- Air added downstream to complete combustion, with careful T control to minimize thermal NO formation.

- \( \text{HCCO} + \text{NO} \rightarrow \text{HCNO} + \text{CO} \)
  \( \rightarrow \text{HCN} + \text{CO}_2 \)

identified as key reaction
**Evaluation**

- Limited measurements. Good agreement at room T. Temp dependence by Boullart et al.
- \( k = 1.0 \times 10^{-10} \exp(-350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over the range 300-2000 K
- \( \Delta \log k = \pm 0.2 \) at 300 K, rising to \( \pm 0.4 \) at 2000 K

Reaction path diagram for reburn under flow reactor conditions (Miller)
Product studies:

\[ \text{HCCO} + \text{NO} \rightarrow \text{HCNO} + \text{CO} \quad (a) \quad \beta = \frac{k_b}{k_a+k_b} \]

\[ \rightarrow \text{HCN} + \text{CO}_2 \quad (b) \]

- Boullart et al., J. Phys. Chem. 1994, 98, 8036-8043
- C2H2/O/NO systems at a pressure of 2 Torr (He bath gas) using discharge flow-molecular beam mass spectrometry techniques
- \( k \) measured relative to \( O + \text{HCCO} \) by observing effect of added NO on steady state [HCCO].
- Product distribution determined at 700 K by measuring CO (77±9%) and CO2 (23 ± 9%), \( \beta = 0.23 \)
Product studies:

\[ \text{HCCO} + \text{NO} \rightarrow \text{HCNO} + \text{CO} \quad (a) \quad \beta = \frac{k_b}{(k_a+k_b)} \]

\[ \rightarrow \text{HCN} + \text{CO}_2 \quad (b) \]

- U. Eickhoff and F. Temps, Phys. Chem. Chem. Phys. 1, 243 (1999). 312 nm photolysis of \( \text{NO}_2/\text{C}_2\text{H}_2/\text{NO}/\text{Ar} \) mixtures at a total pressure of 570 mbar. Products were detected using FTIR spectroscopy. \( \beta = 0.28 \) (298 K)

- K.T. Rim and J.F. Hershberger, J. Phys. Chem. A 104, 293 (2000) excimer laser photolysis (193 nm) of \( \text{CH}_2\text{CO}/\text{NO}/\text{M} \) mixtures at total pressures of approximately 8 mbar. \( \text{CO} \) and \( \text{CO}_2 \) detection by infrared laser absorption ( \( \beta = 0.14 \) (298 K))
Vereecken et al. - Theory

Fig. 3. Temperature dependent CO$_2$ yield, $\alpha(T) = k_{1a}/k_1$, for the HCCO + NO reaction.