

Topic 6 NO_x chemistry

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

Synopsis

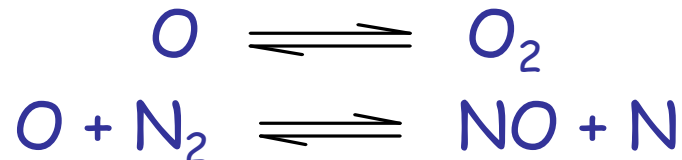
1. Prompt and thermal formation of NO_x (= NO + NO_2) in combustion.
2. Examination of the kinetics of:
 - $\text{CH} + \text{N}_2$ which is involved in prompt NO_x formation
 - $\text{NH}_2 + \text{NO}$, involved in selective non-catalytic reduction of NO_x emissions
 - $\text{HCCO} + \text{NO}$, involved in the reburn method for NO_x emissions reduction.

Mechanisms of NO_x formation

- Prompt Fenimore (13th Int Symp Comb, 1970) observed NO formation in the primary reaction zone in a flame. Attributed to reaction of a hydrocarbon radical with N₂. Suggested



- 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_x (Zeld'ovich mechanism)



Miller and Bowman's mechanism for prompt and fuel N formation of NO (Prog. Energy Combust. 3667 Sci. 15 (1989) 287-338)

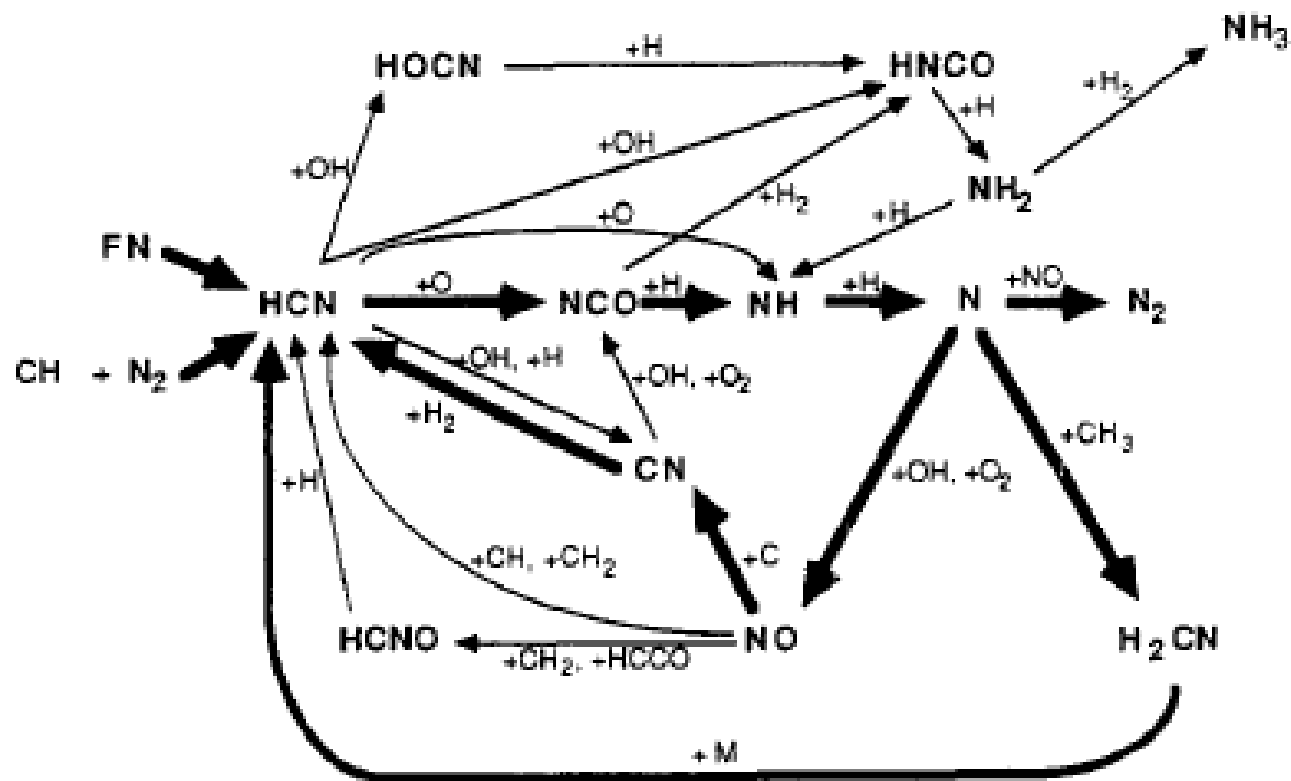
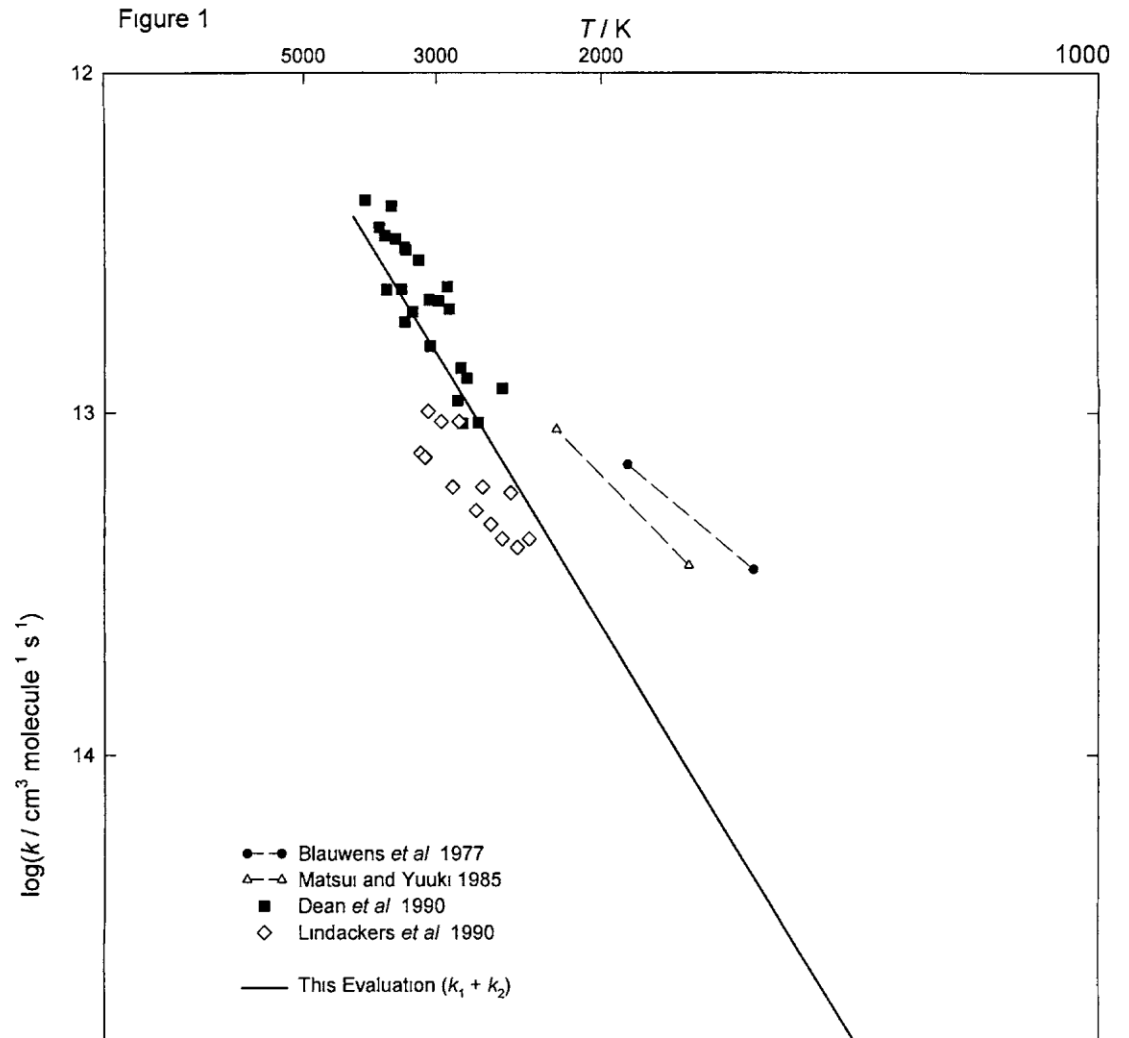
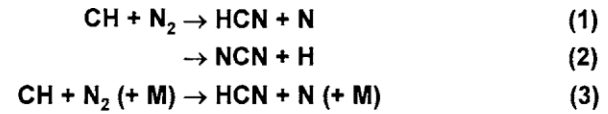


FIG. 11. Reaction path diagram illustrating the major steps in prompt NO formation and conversion of fuel nitrogen (FN) to NO. The bold lines represent the most important reaction paths.

Evaluation of
 $\text{CH} + \text{N}_2$
(Baulch et al.)



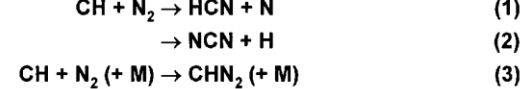
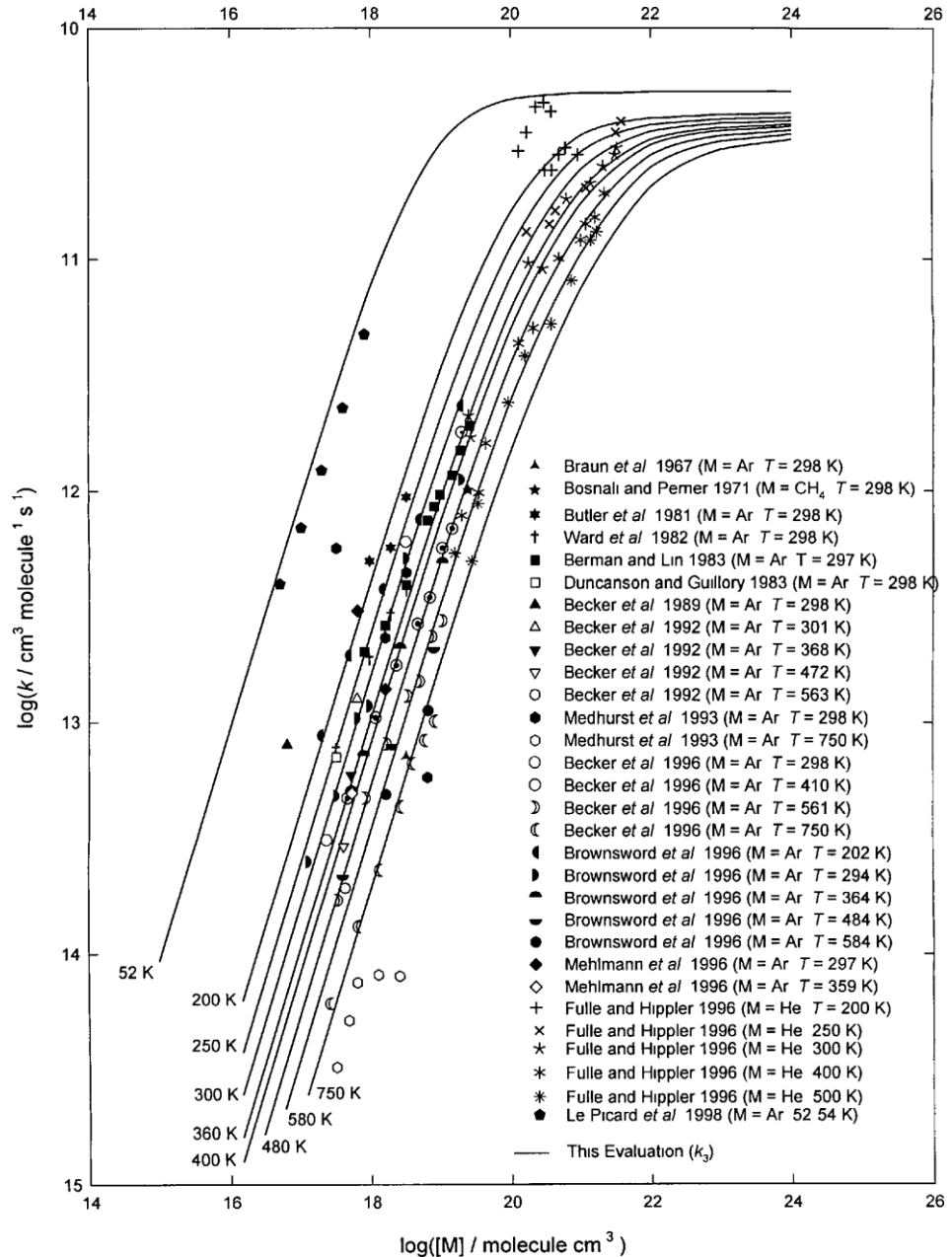


Figure 2

Evaluation of
 $\text{CH} + \text{N}_2$
 (Baulch et al.)
 pressure
 dependence



Moskaleva and Lin
Proc Comb Inst 2000, 28,
2393 and Chem Phys Letter
2000, 331, 269

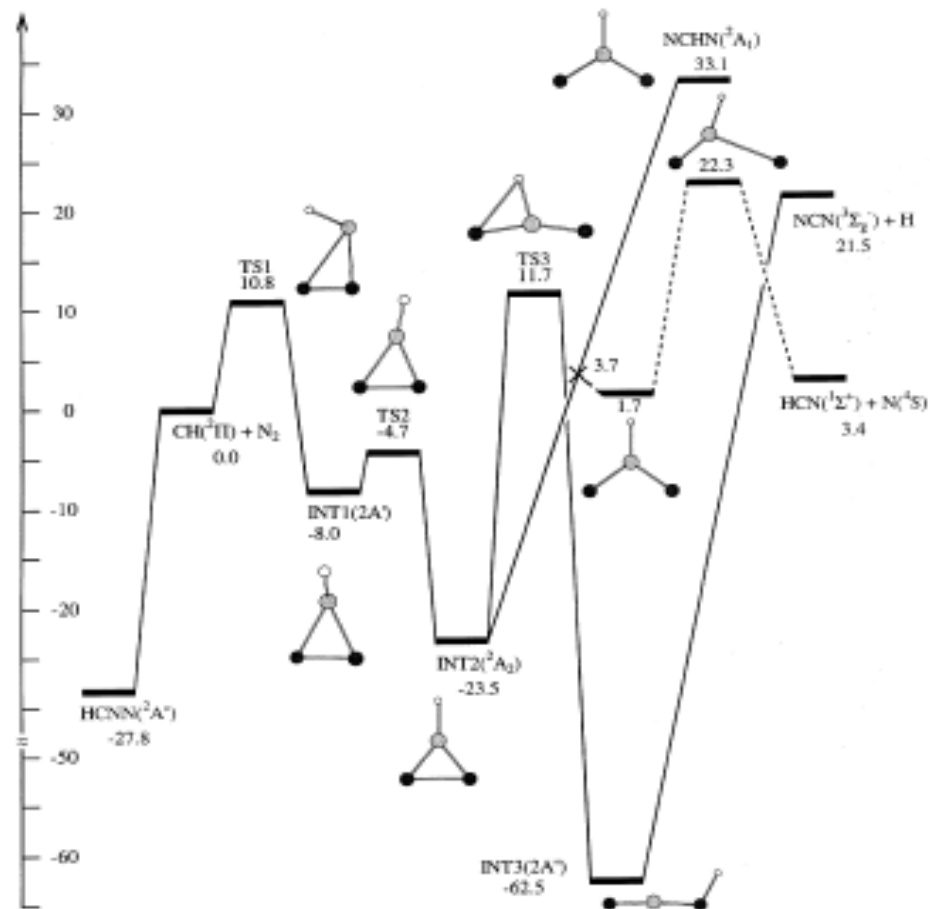
Also includes calcs by
Cui et al. J Chem Phys,
1999, 110, 9469

Note:

- Adduct formed at low T and high p not connected to bimolecular reaction products

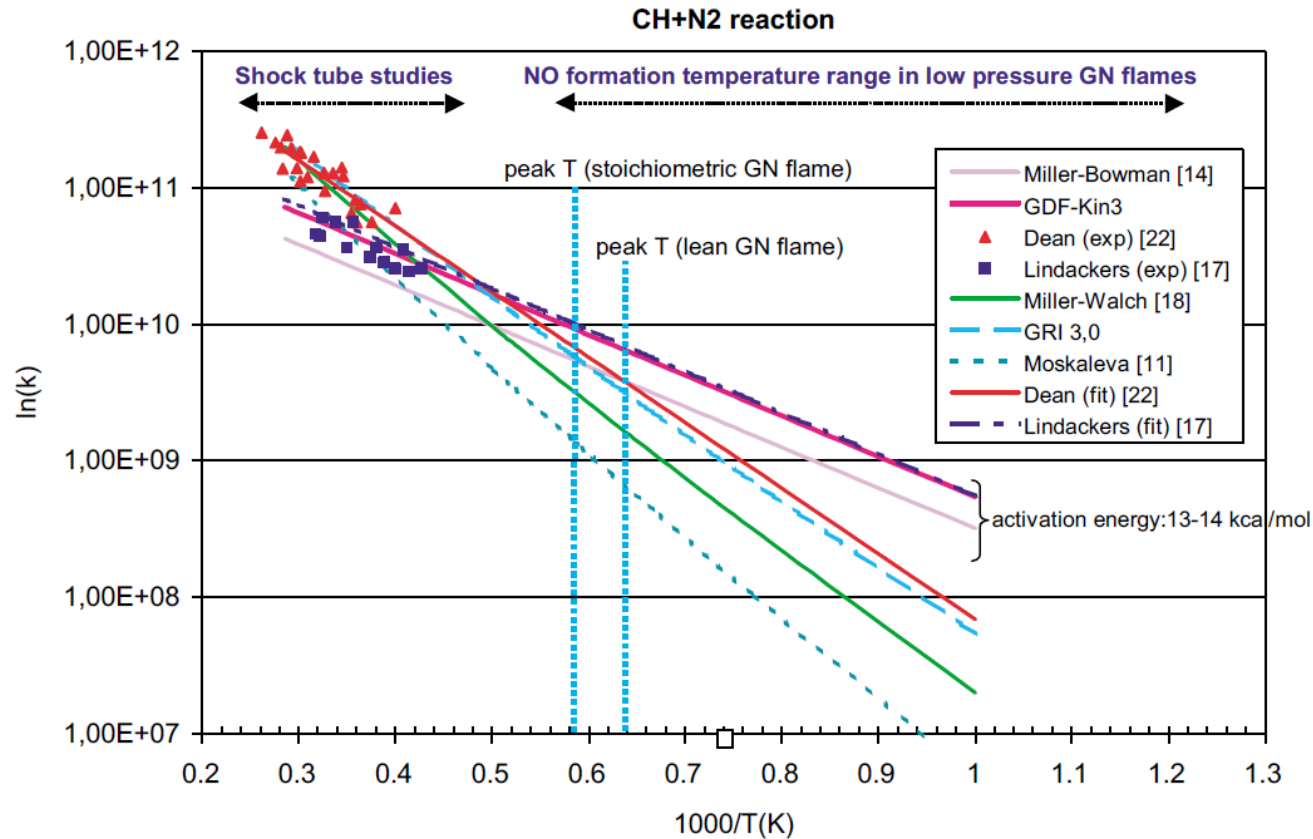
- Quartet - doublet transition too slow to compete with spin allowed formation of NCN + H

CH + N₂ -theory



Major product - NCN + H

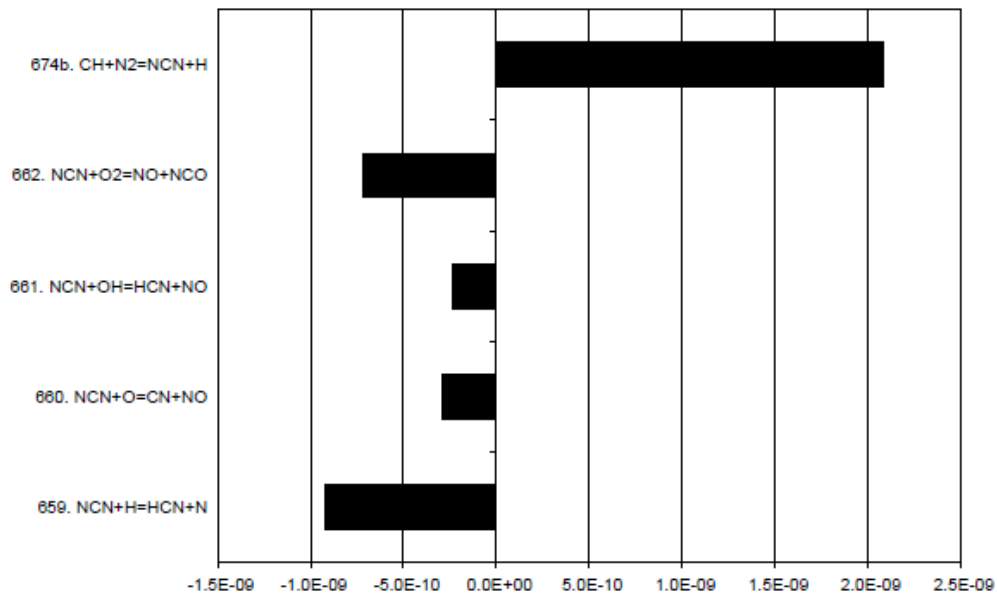
El Bakali et al., Fuel 2006, 85, 896 Modelling of NO production in natural gas flames



- 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.

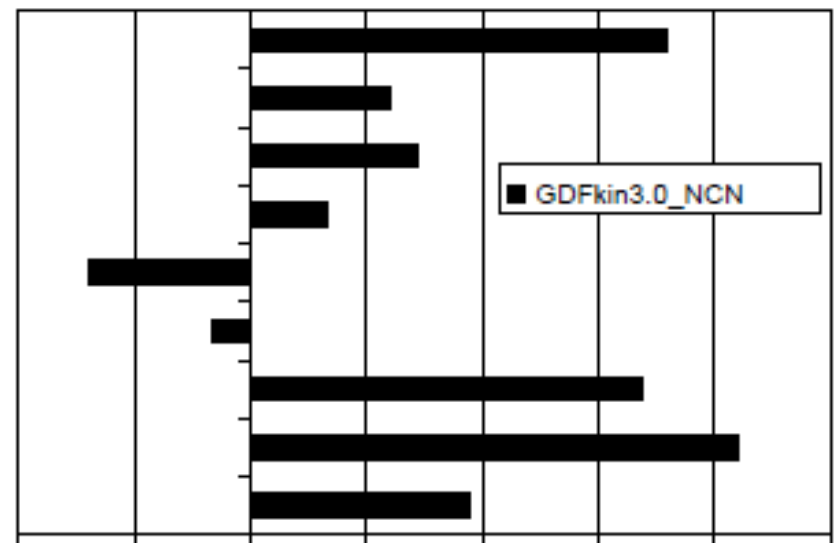
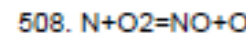
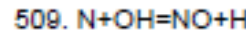
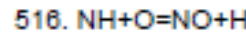
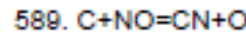
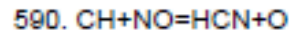
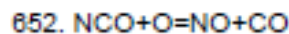
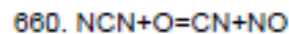
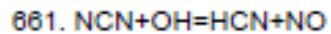
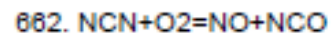
C1 flame ($\phi = 1.0$)

Maximum NCN reaction rate



What happens to the NCN?

Maximum NO reaction rate



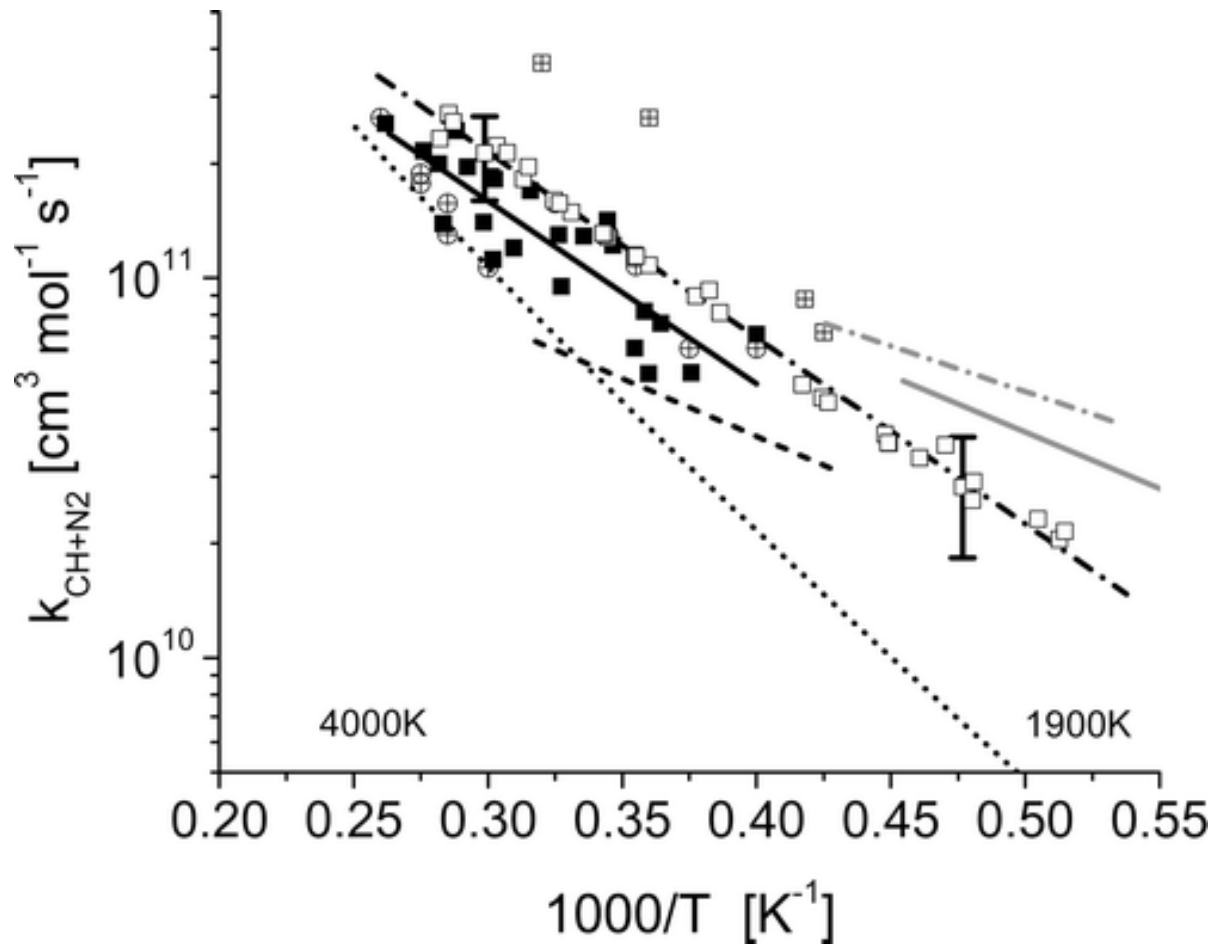
Main routes to NO

-4.E-10 -2.E-10 0.E+00 2.E-10 4.E-10 6.E-10 8.E-10 1.E-09

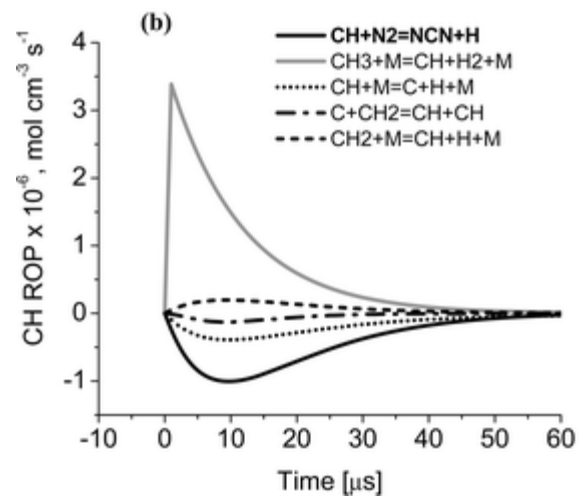
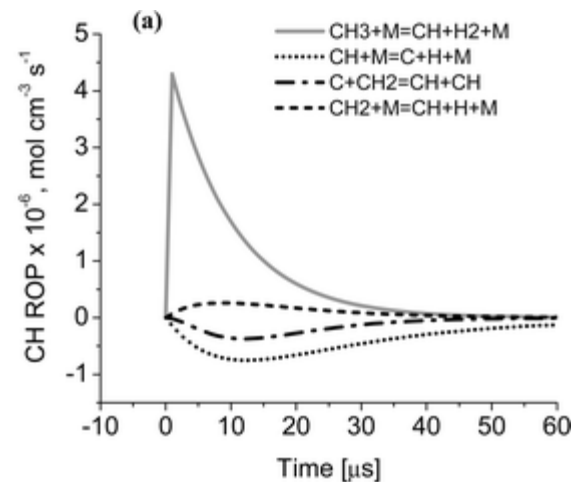
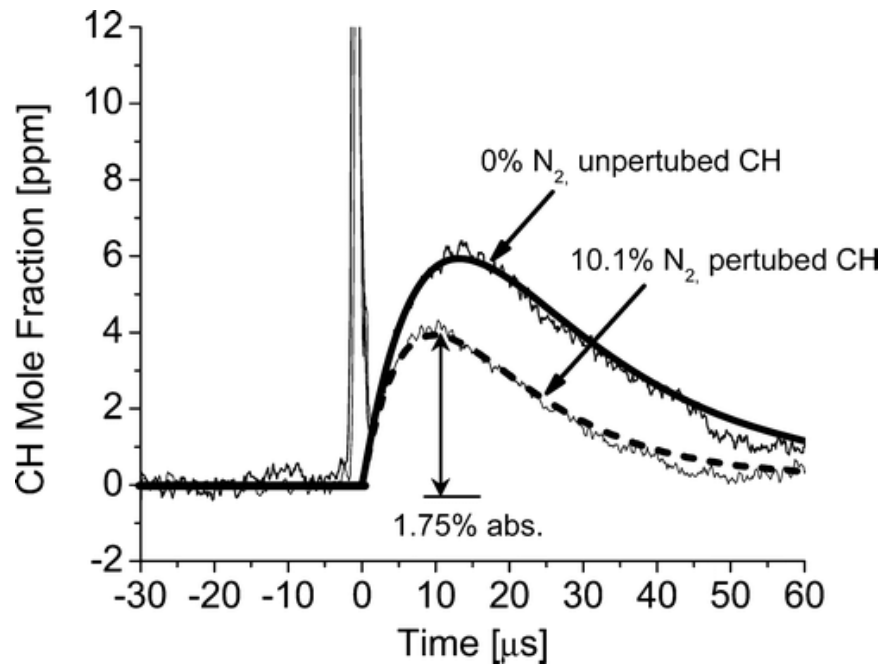
Vasudevan et al.
J. Phys. Chem. A 2007, 111, 11818-11830

- Shock tube study, 1943 - 3543 K, 0.9 - 1.4 atm.
- CH generated from ethane / Ar and acetic acid / Ar
- CH + N₂ studied through perturbation expts by adding N₂.
- CH detected by laser absorption at 431.1 nm and NCN at 329.13 nm.
- k : $6.03 \times 10^{12} \exp(-11150/T/K) / \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
- Branching ratio for (NCN + H channel) = 1 (2228 - 2905 K) (conservative lower limit = 0.7)

Vasudevan et al. Arrhenius plot



N₂ perturbation experiments ethane / Ar/3348 K/1.08 atm

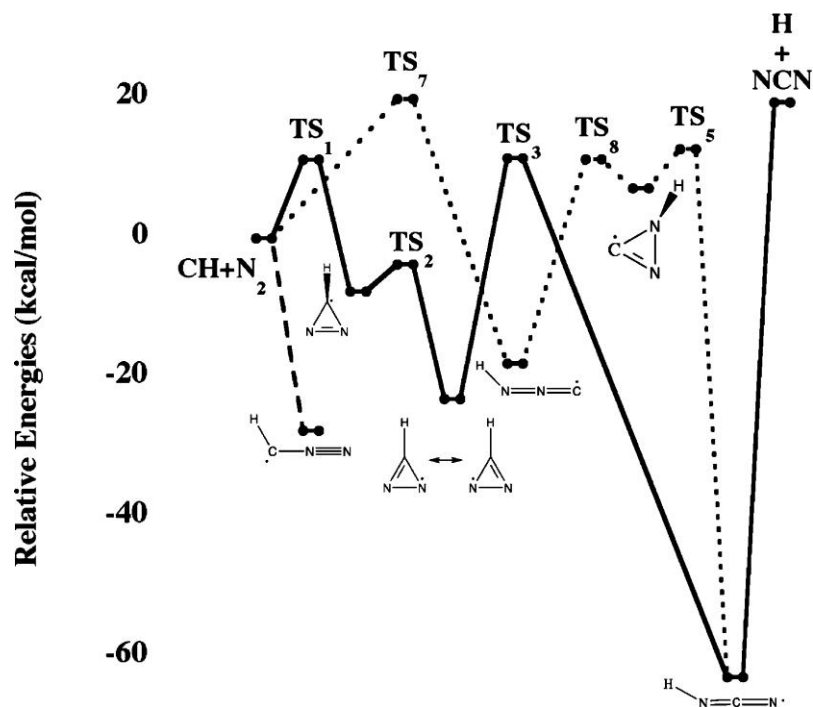


Main contributors to kinetic scheme used to extract $k(\text{CH} + \text{N}_2)$ in ethane expts

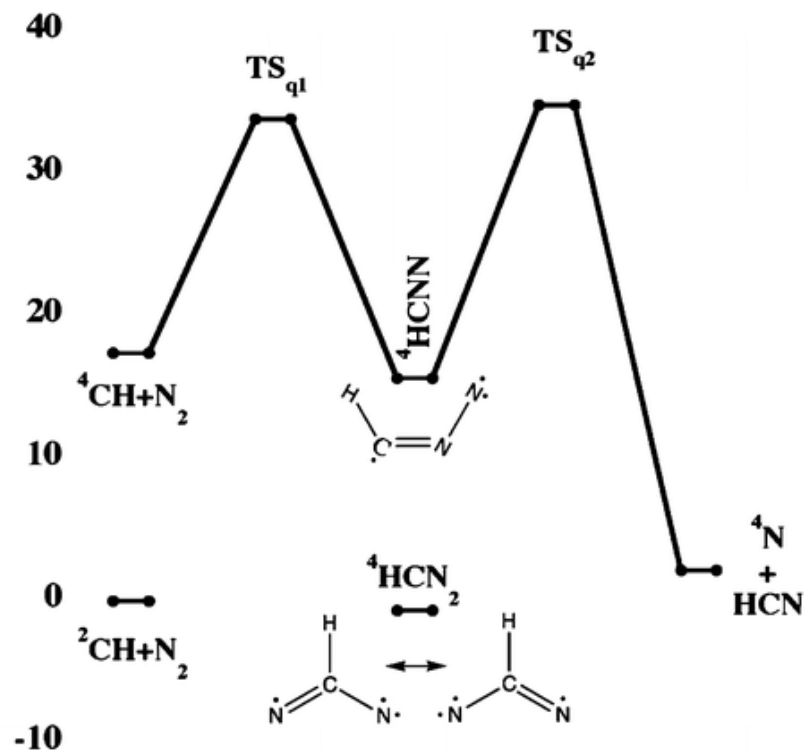
TABLE 1: Rate Parameters for Reactions Important in CH Perturbation Experiments in Ethane/N₂/Ar

reaction	rate coefficient (cm ³ mol ⁻¹ s ⁻¹)			ref
	<i>A</i>	<i>n</i>	<i>E</i> (kcal/mol)	
(1) CH + N ₂ → products	6.03 × 10 ¹²	0	22.1	this work
(4) H + NCN → HCN + N	1.89 × 10 ¹⁴	0	8.4	12 ^a
(5a) CH ₂ + M → C + H ₂ + M	1.15 × 10 ¹⁴	0	55.8	32 ^b
(5b) CH ₂ + M → CH + H + M	5.60 × 10 ¹⁵	0	89.6	25
(6a) CH ₃ + M → CH + H ₂ + M	3.09 × 10 ¹⁵	0	80.9	25 ^b
(6b) CH ₃ + M → CH ₂ + H + M	2.24 × 10 ¹⁵	0	82.7	25 ^b
(11) CH ₂ + H → CH + H ₂	1.1 × 10 ¹⁴	0	0.0	37
(13) H + CH → C + H ₂	1.65 × 10 ¹⁴	0	0.0	38
(19) CH + M → C + H + M	1.0 × 10 ¹⁴	0	64.0	32 ^b
(20) C + CH → C ₂ + H	2.0 × 10 ¹⁴	0	0.0	32
(21) C + CH ₂ → 2CH	1.0 × 10 ¹⁴	0	0.0	32
(22) C + CH ₃ → H + C ₂ H ₂	5.0 × 10 ¹³	0	0.0	38
(23) C + CH ₄ → CH + CH ₃	5.0 × 10 ¹³	0	0.0	32
(24) CH + CH ₃ → H + C ₂ H ₃	6.0 × 10 ¹³	0	0.0	32

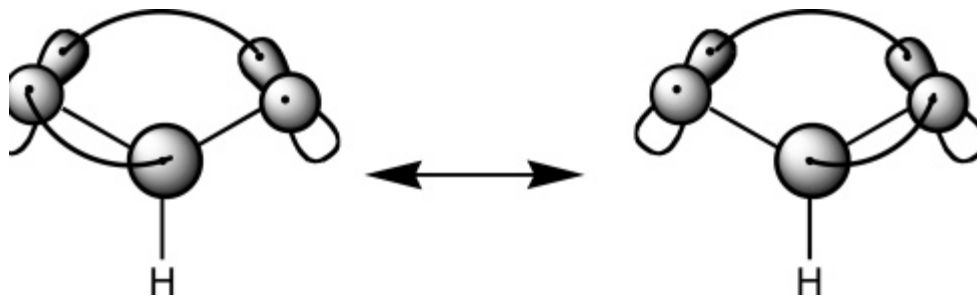
More recent theory: Harding et al: multireference calcs (J. Phys. Chem. A 2008, 112, 522-532)



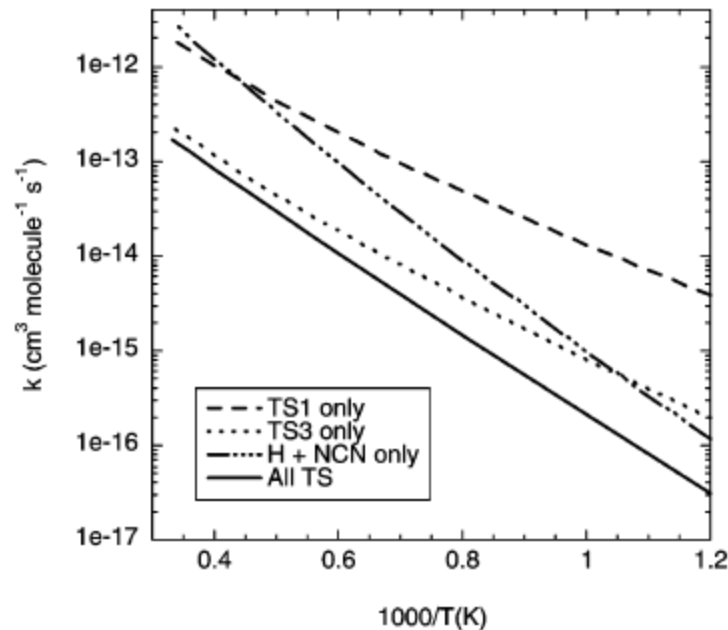
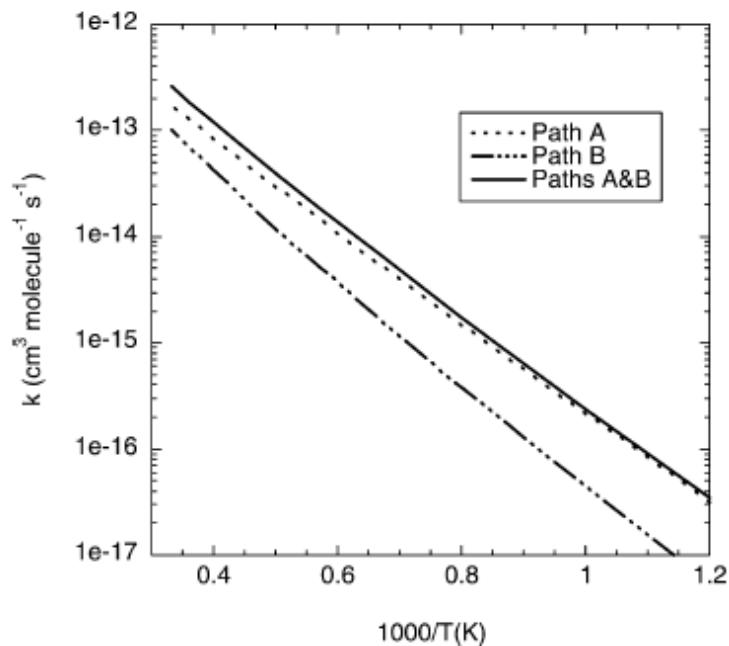
Doublet surface



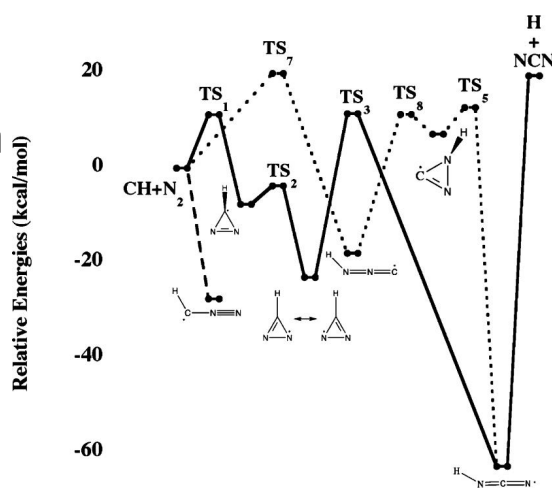
Quartet surface



Harding et al. Contributions to overall rate constant for CH + N₂

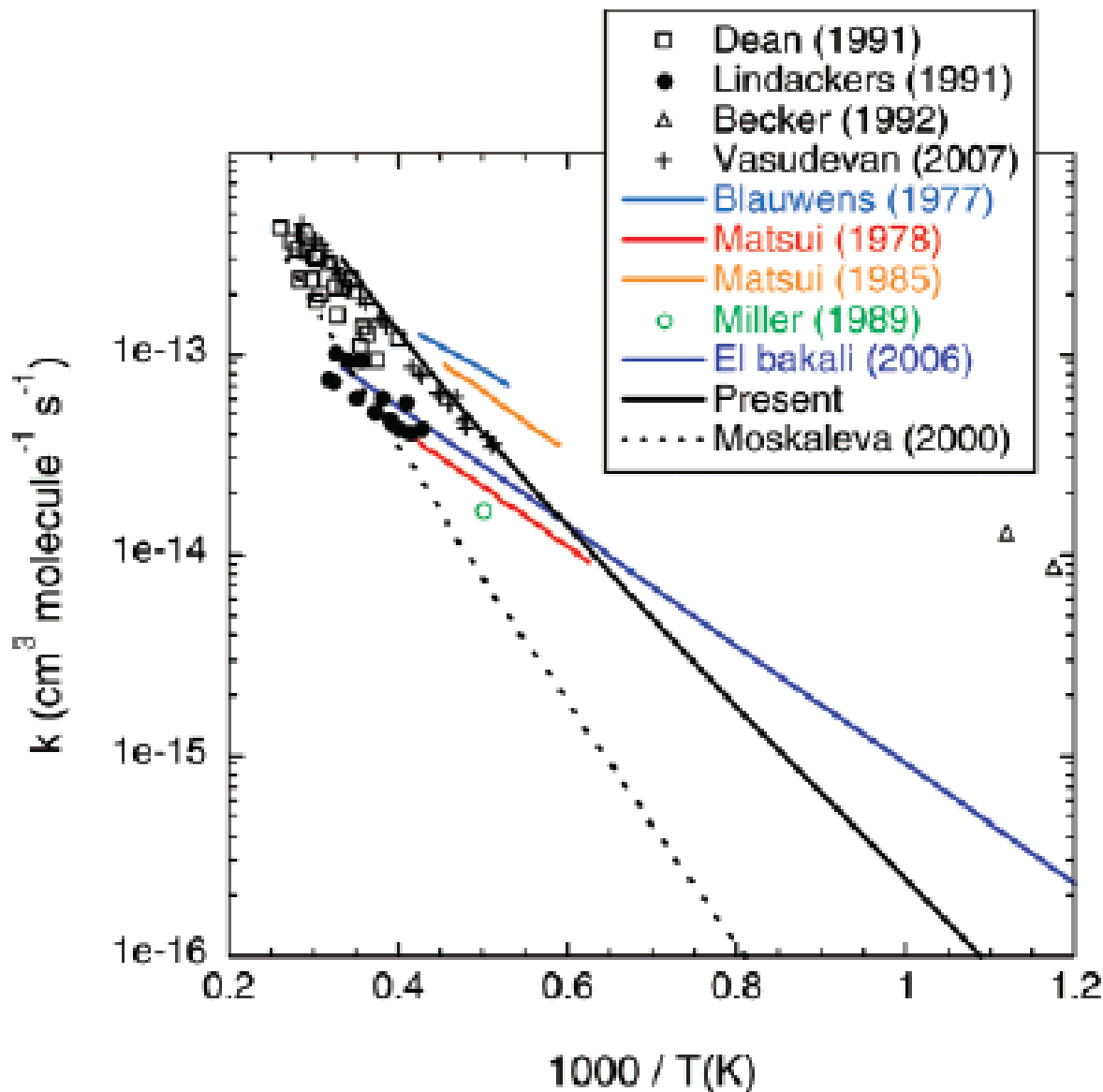


Plot of the predicted rate coefficient for $\text{CH} + \text{N}_2 \rightarrow \text{NCN} + \text{H}$ via path A when considering different subsets of the transition states along the path.



Plot of the contributions from different pathways to the predicted rate coefficient for $\text{CH} + \text{N}_2 \rightarrow \text{NCN} + \text{H}$.

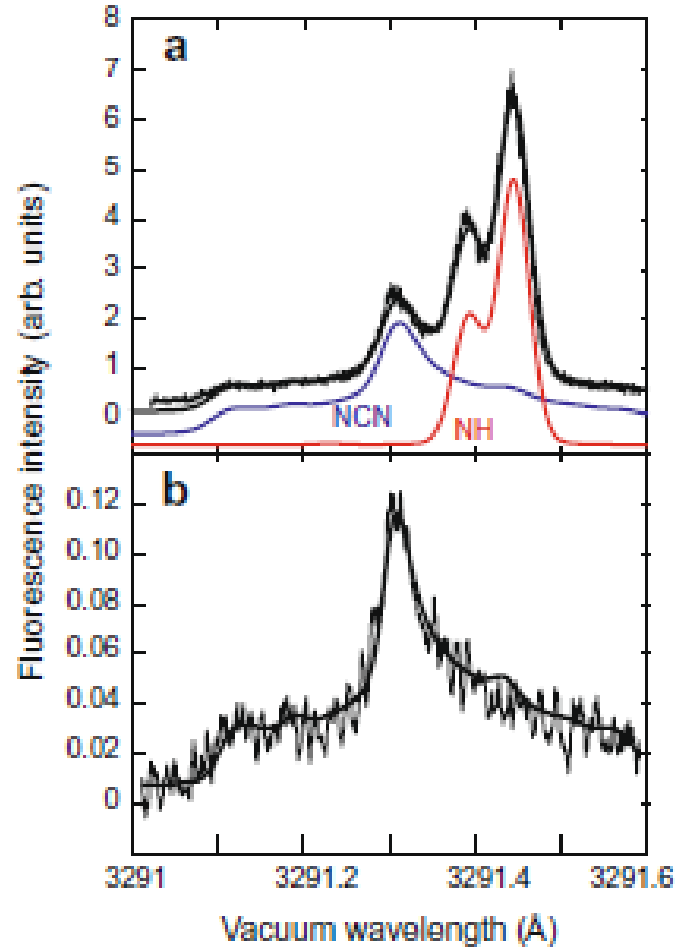
Plot of the experimental measurements and theoretical predictions for the $\text{CH} + \text{N}_2 \rightarrow \text{NCN} + \text{H}$ rate coefficient



NCN detection in flames

1. LIF, atmospheric pressure, methane/air, nitrous oxide.
Sun et al *Combustion and Flame* 157 (2010) 834-836

- 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



2. Cavity ring down, low pressure, methane/air, nitrous oxide. Klien-Douwel et al. Combustion and Flame 158 (2011) 2090-2104

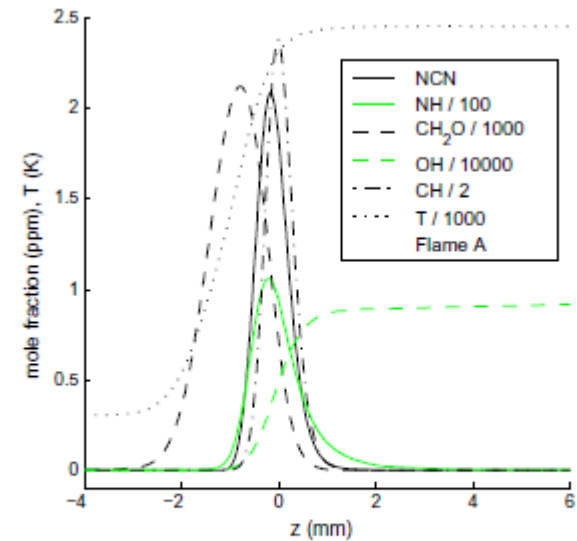
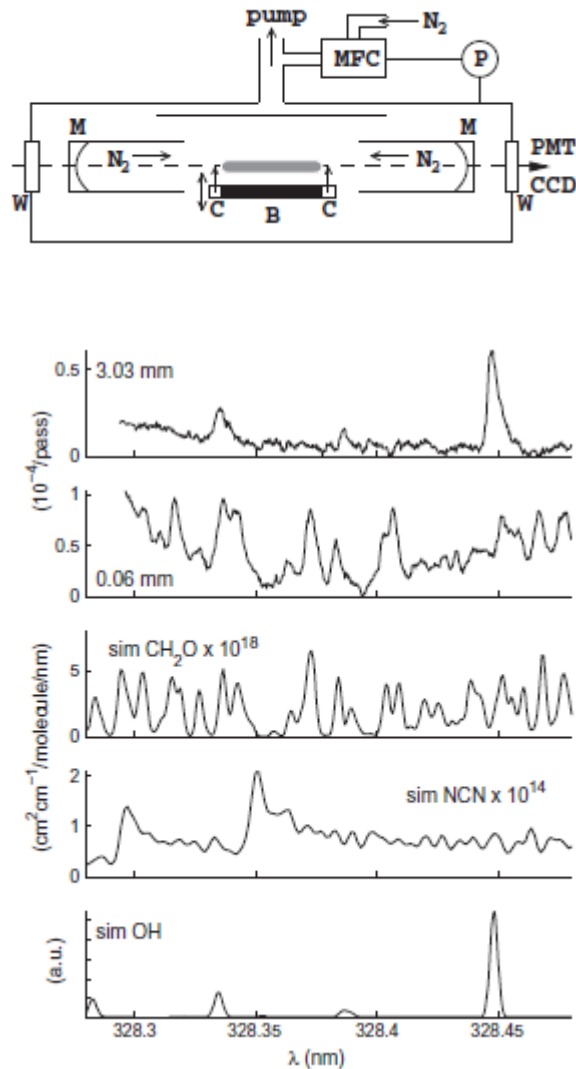


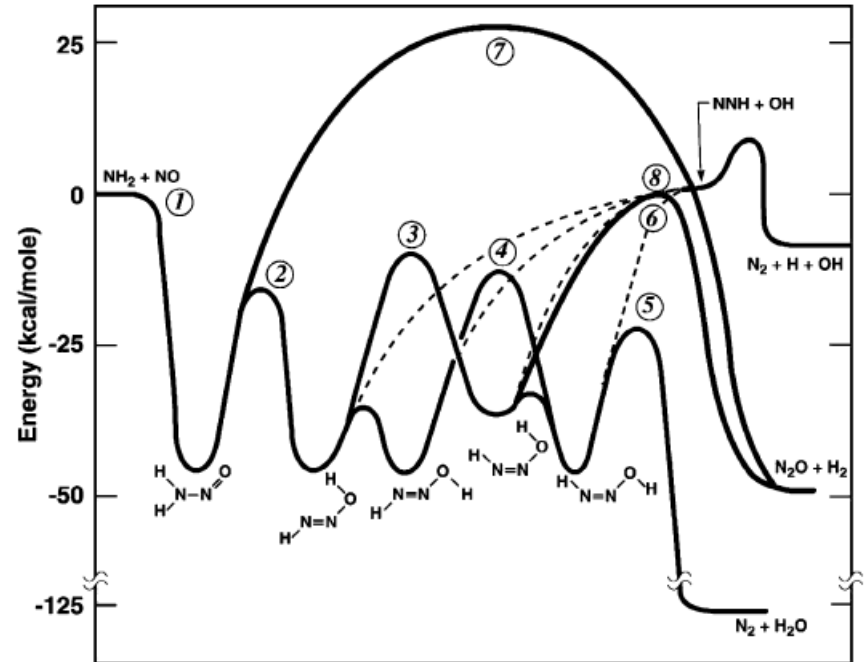
Fig. 8. Calculated mole fractions of NCN, NH, CH₂O, OH and CH and calculated temperature for flame A (multiplied by scaling factors). The position of peak CH concentration is defined as $z = 0$ mm, therefore z corresponds to the height above the flame front.

Selective non-catalytic reduction (SNCR) Thermal De-NO_x

- Developed by Lyon (EXXON) US Patent 3,900,554 (1975)
- Involves addition of NH₃ which converts NO to N₂.
- 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.

NH₂ + NO

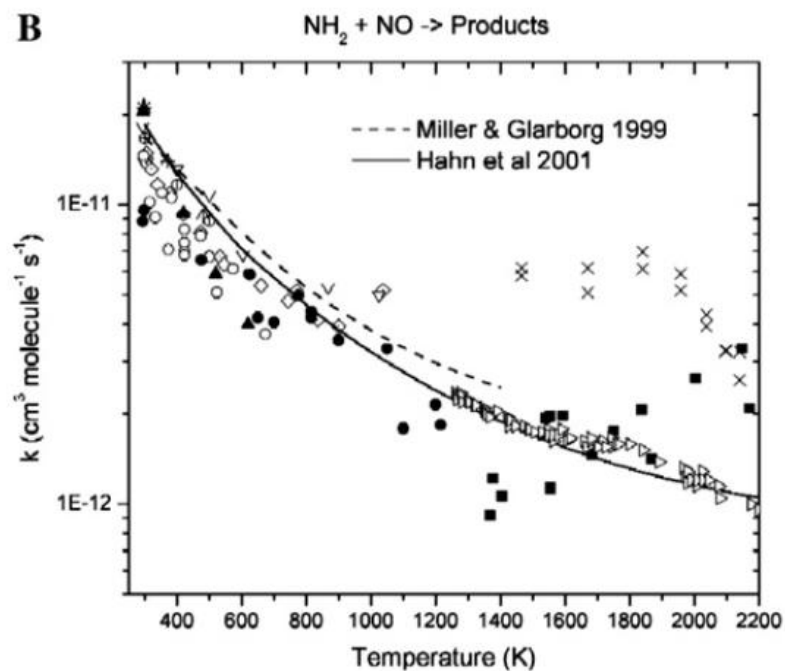
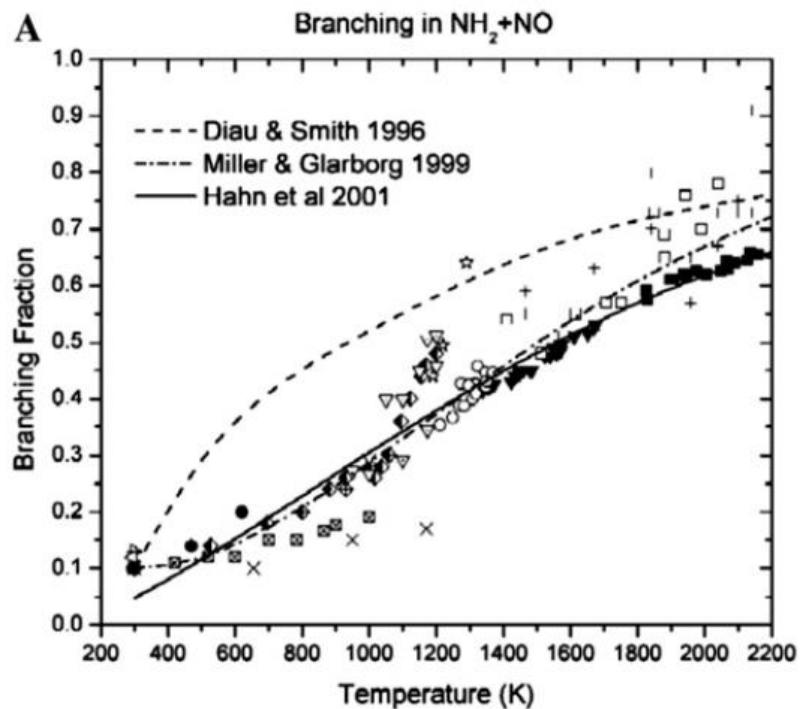
- Key elementary reaction is
 $\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$ (a)
 $\rightarrow \text{NNH} + \text{OH}$ (b)
- The reaction is self sustaining, i.e. it must not be exclusively terminating. For this to occur, the yield of channel (b) must be at least 0.25, increasing to 0.3 above 1100 K (Miller and Bowman)



Fang et al., Disc Faraday, 2001,
119, 207

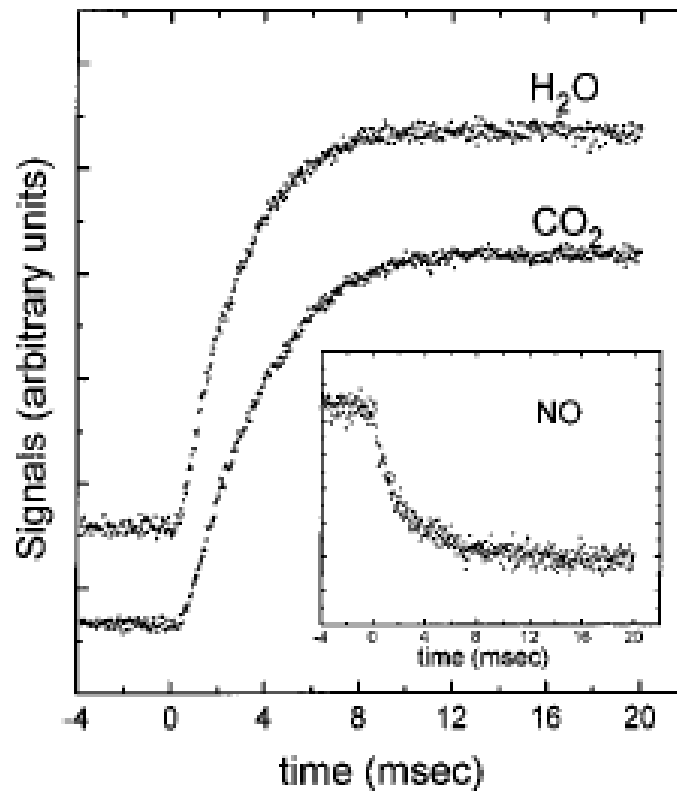
Independent of pressure up to
several atmospheres

Experimental and modelling studies of rate coefficient and NNH yield

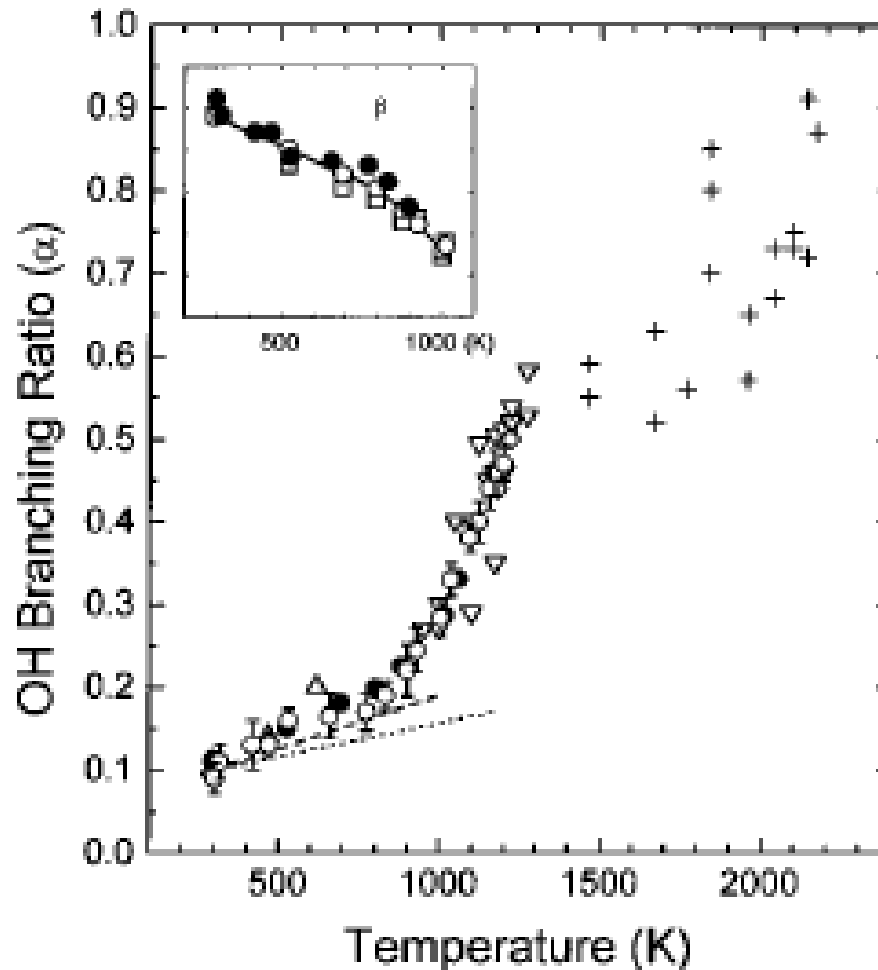


Park and Lin, *J. Phys. Chem. A* 1997, 101, 5-13

- Pulsed laser photolysis of NH_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_2 , H_2O , and CO_2 . The OH yield was determined by reaction with CO and measurement of the CO_2 produced.



Park and Lin contd



- Found that α increases sharply above ~ 1000 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_2O product were monitored by mass spectrometry. Rate constants were derived from kinetic modelling of the NO and H_2O profiles
- Problems attributed to incorrect values for $\text{OH} + \text{NH}_3$, one of the key reactions in their kinetic scheme. Re-determined via reverse, combined with equilibrium constant.

Park and Lin, 1999, contd

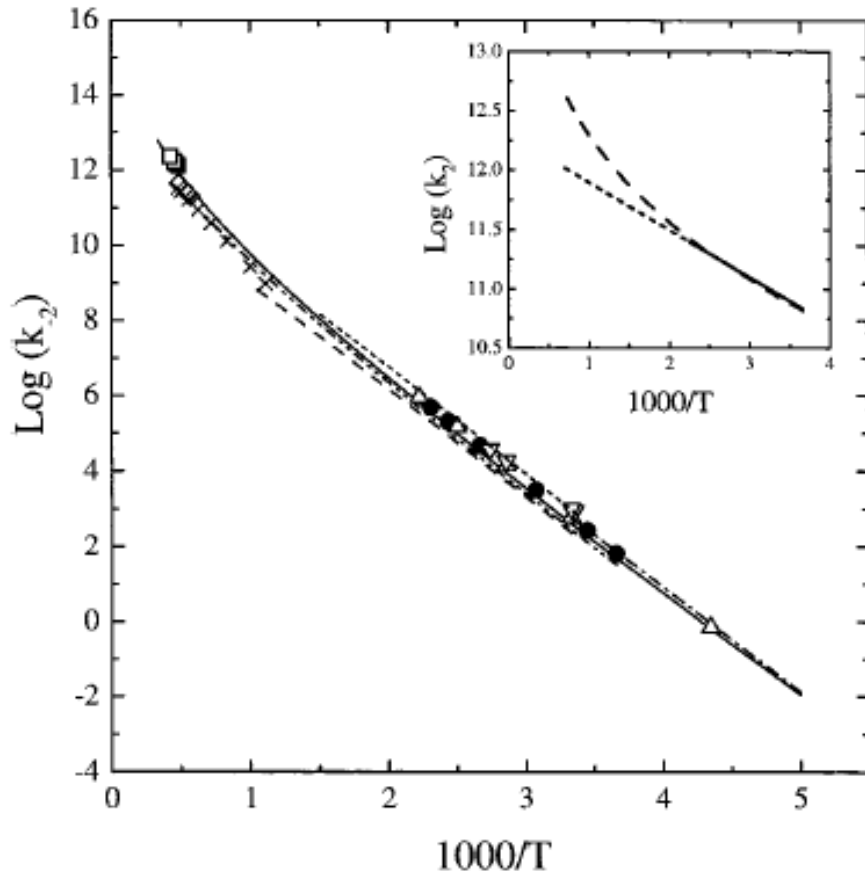
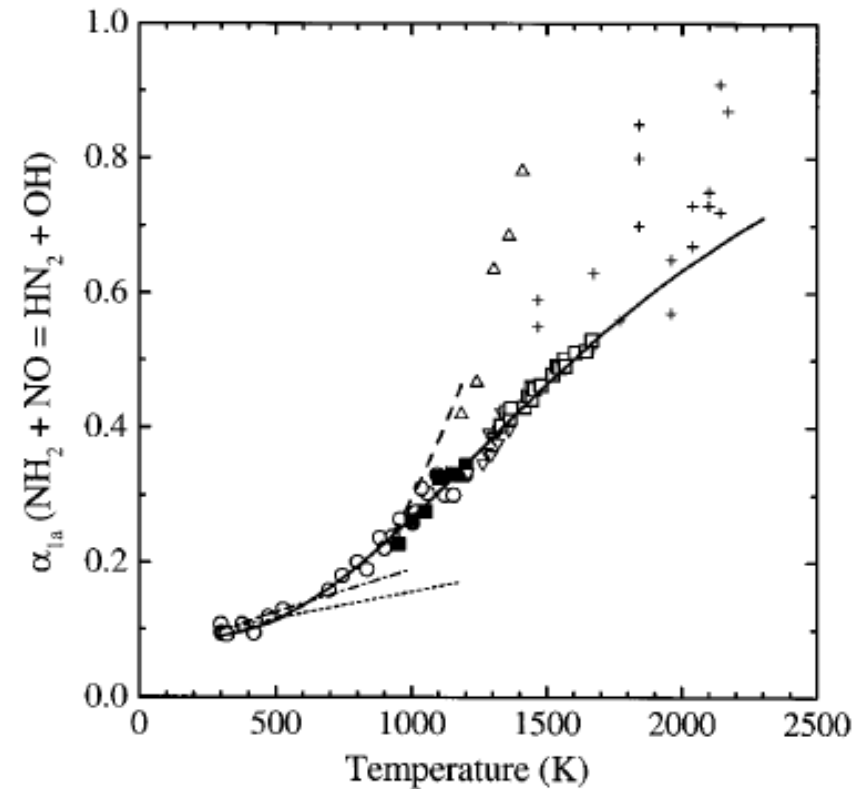


Figure 1. Arrhenius plot of the rate constant for the $\text{NH}_2 + \text{H}_2\text{O}$ reaction: solid curve (ref 28); dashed line (ref 32); dotted line (ref 33); dash-dotted curve (ref 34); dash-dot-dotted curve (ref 40); ref 27 (●); ref 35 (Δ); ref 36 (∇); ref 37 (\square); ref 38 (\times); ref 39 (\blacklozenge). (Inset) Arrhenius plot of the $\text{OH} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H}_2\text{O}$ reaction: solid line (ref 27); dashed curve (ref 30); dotted line (extrapolation of ref 27).



Open circles – remodelled results from 1997 paper

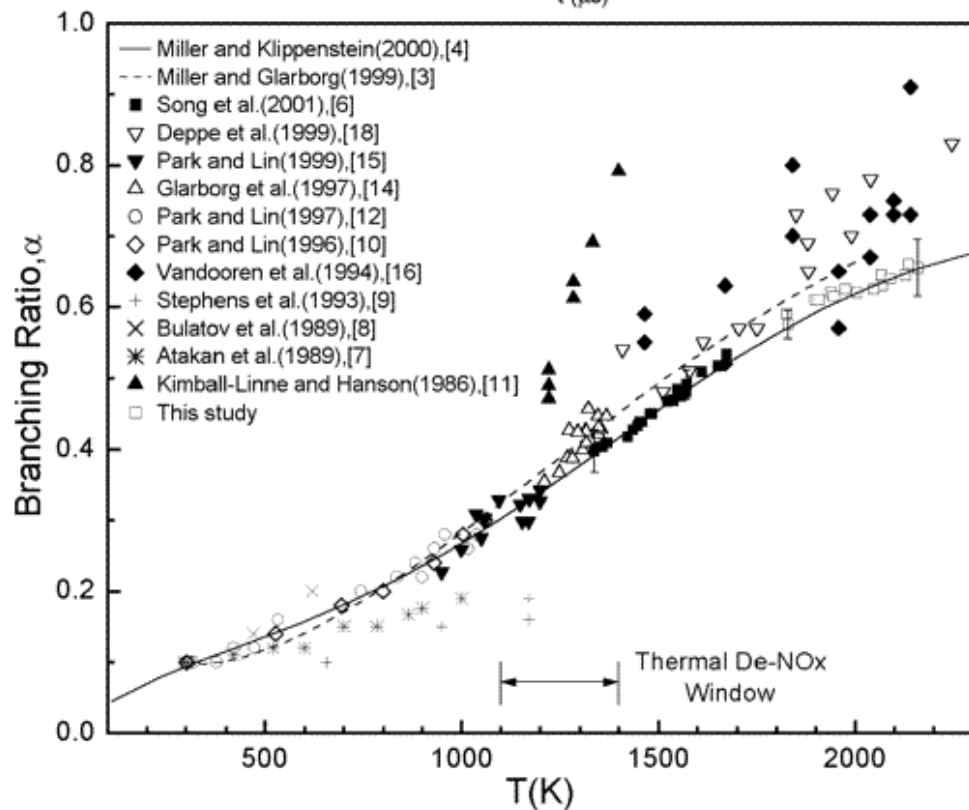
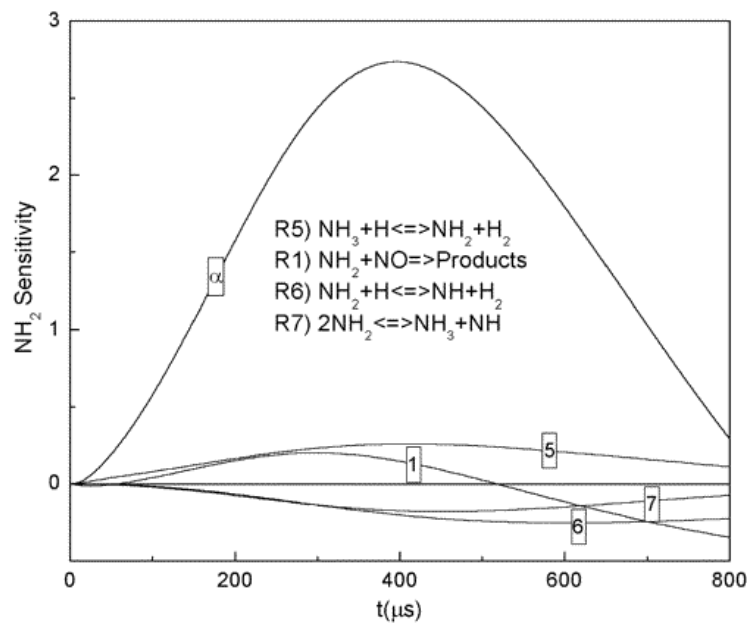
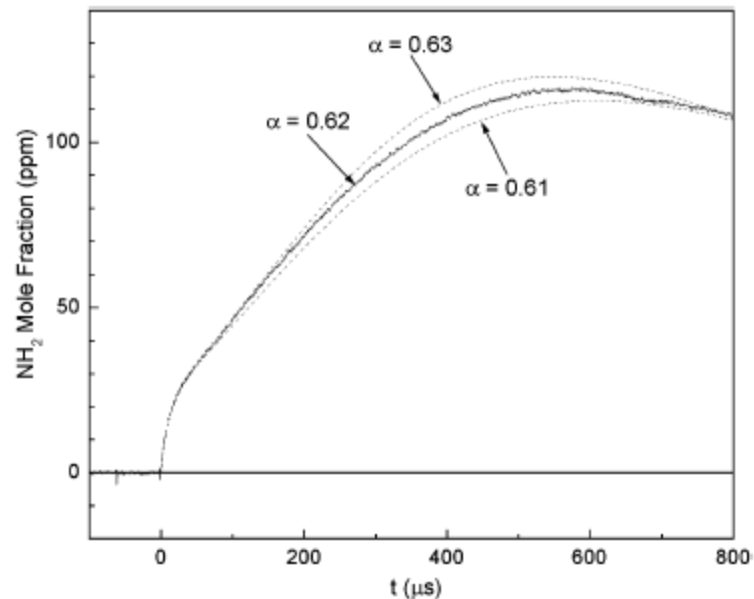
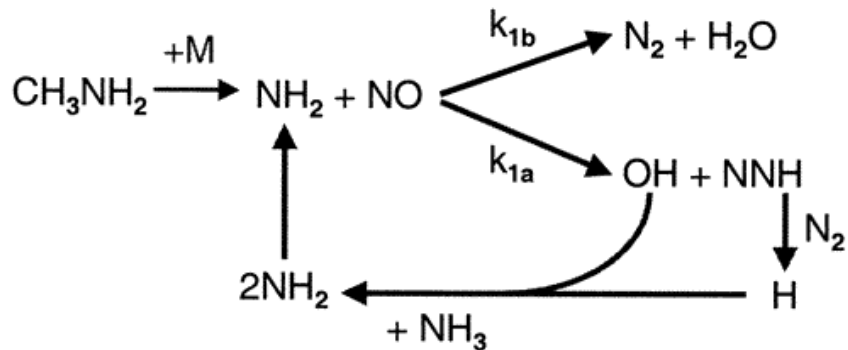
Song et al., , Proc. Comb. Inst., 2000, 28, 2403. J. Phys. Chem. A 2002, 106, 9233-9235; Shock tube study of NH₂ + NO

- 1826-2159 K 1.10 to 1.21 bar.
- Measurement of NH₂ by frequency modulation absorption behind reflected shock waves in monomethylamine (CH₃NH₂)/NH₃/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.

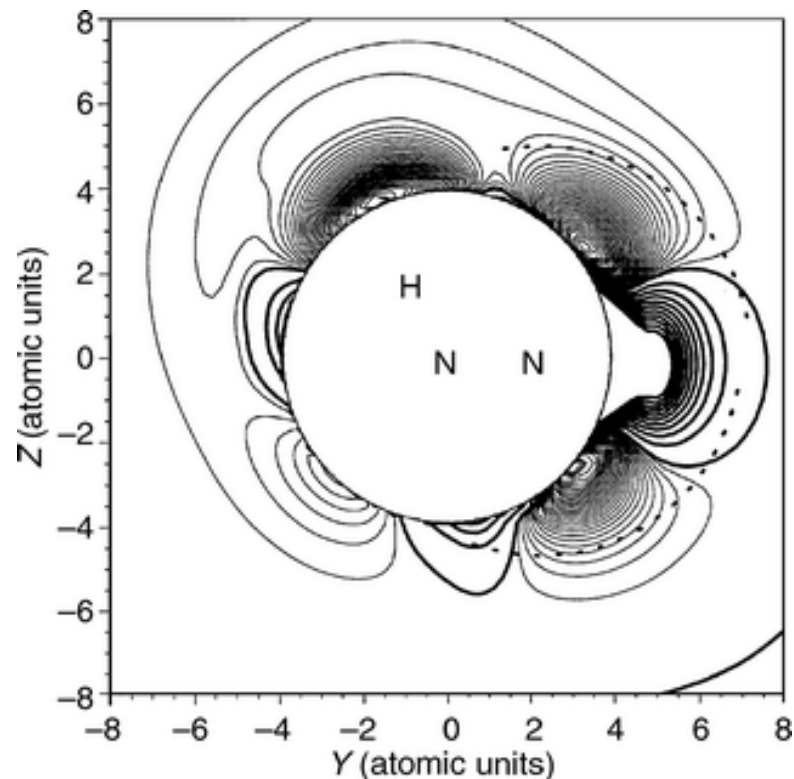
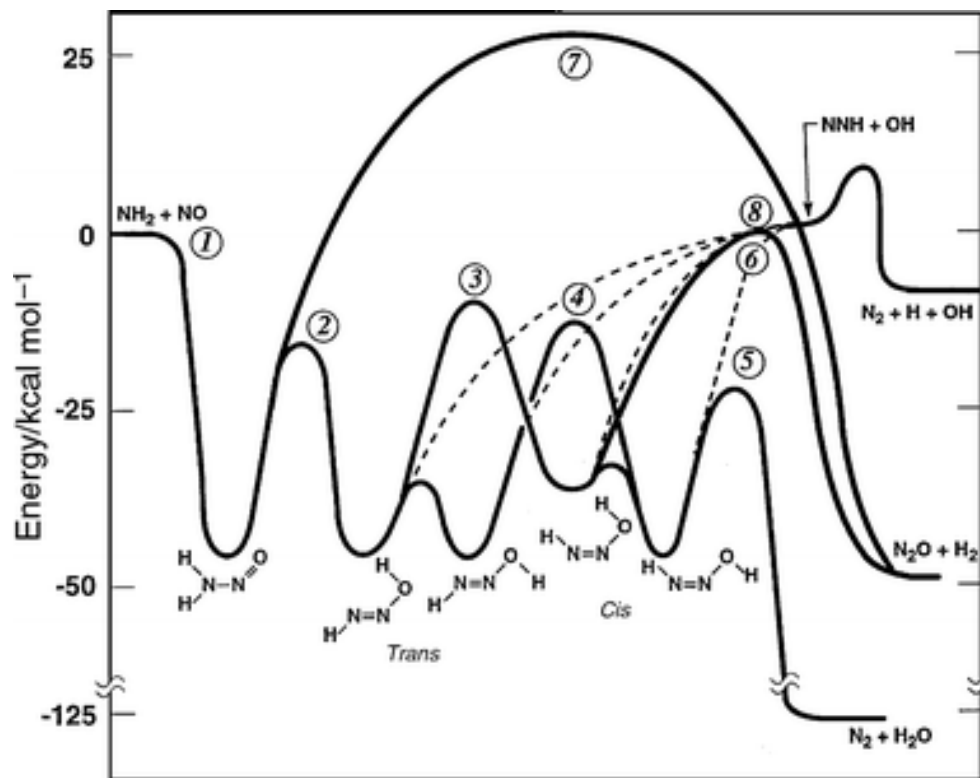
TABLE 1: Selected Reactions Used in the Reaction Mechanism

reaction	Arrhenius parameters $k(T) = AT^n \exp(-E_a/RT)$			ref
	A (cm ³ mol ⁻¹ s ⁻¹)	n	E_a (J mol ⁻¹)	
R2 CH ₃ NH ₂ + M → CH ₃ + NH ₂ + M	8.17E16	0.0	255337	20
R3 NNH → N ₂ + H	6.70E07	0.0	0	3
R4 NH ₃ + OH → NH ₂ + H ₂ O	2.00E13	2.04	2368	21
R5 NH ₃ + H → NH ₂ + H ₂	6.40E05	2.39	42555	21
R6 NH ₂ + H → NH + H ₂	1.58E14	0.0	29267	5
R7 NH ₂ + NH ₂ → NH ₃ + NH	1.70E13	0.0	27899	5

Song et al. contd



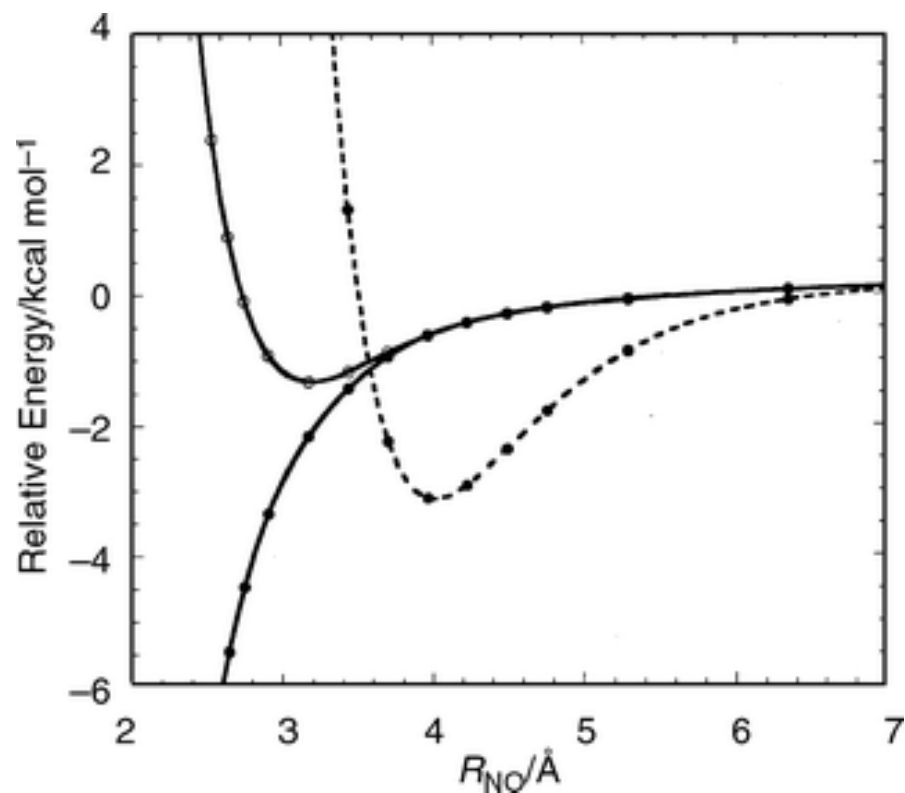
Fang et al. Faraday Disc



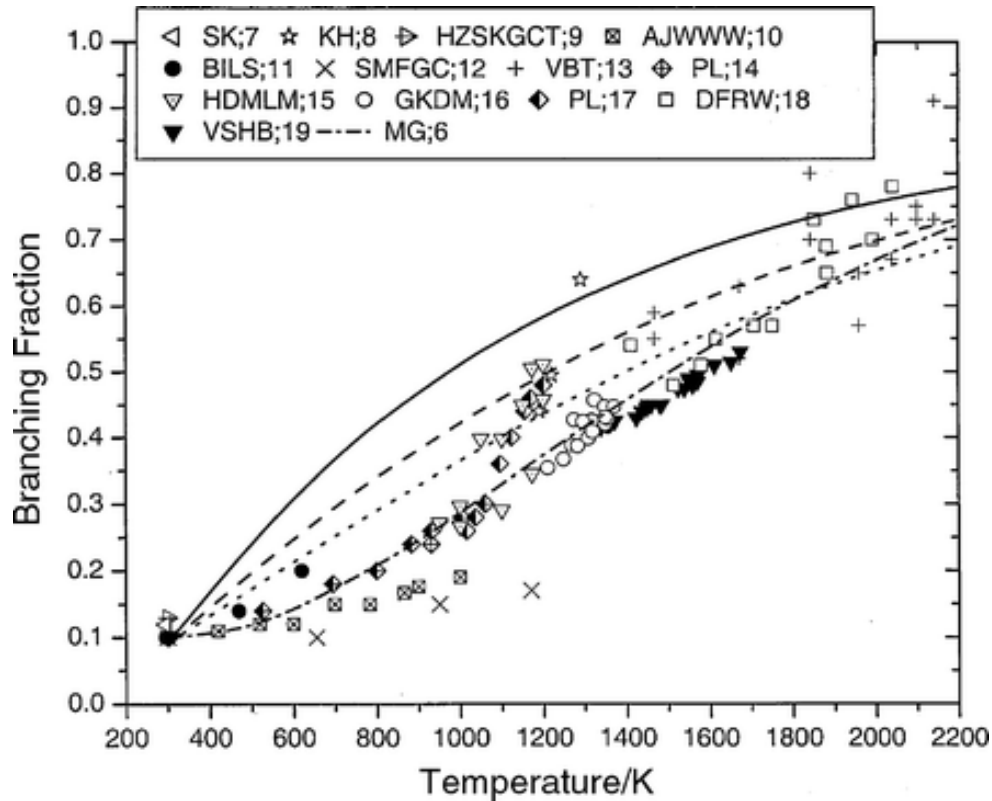
Two dimensional contour plot of the NNH-OH interaction potential. The heavy solid contours correspond to zero (NNH-OH) and positive energy. The lighter solid contours correspond to negative energies. The contour increment for positive contours is 5 kcal mol⁻¹. For negative contours, the increment is 1 kcal mol⁻¹.

Fang et al

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°).



Fang et al.

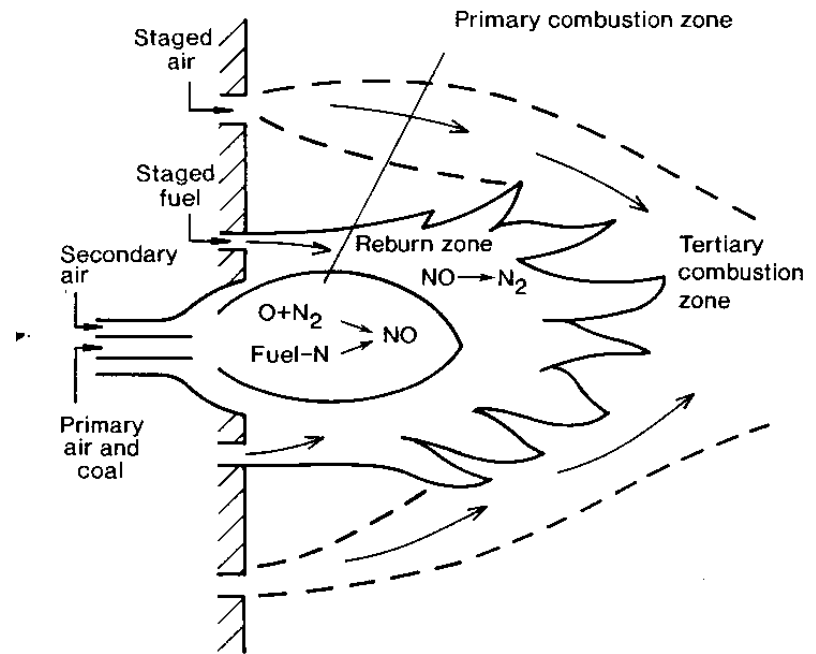


- Comparison of theoretical predictions for $\alpha(T)$ with experiment. The solid, the dashed, and the dotted lines denote the Fang theoretical predictions. The solid line represents the reference case with the $N_2H + OH$ reaction endothermicity reduced to $1.2 \text{ kcal mol}^{-1}$. For the dashed line the endothermicity is reduced to $0.8 \text{ kcal mol}^{-1}$ and the $ts_{3/4}$ barrier height is reduced by 2 kcal mol^{-1} . For the dotted line the endothermicity is reduced to $0.3 \text{ kcal mol}^{-1}$ and the $ts_{3/4}$ barrier height is reduced by 4 kcal mol^{-1} .

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



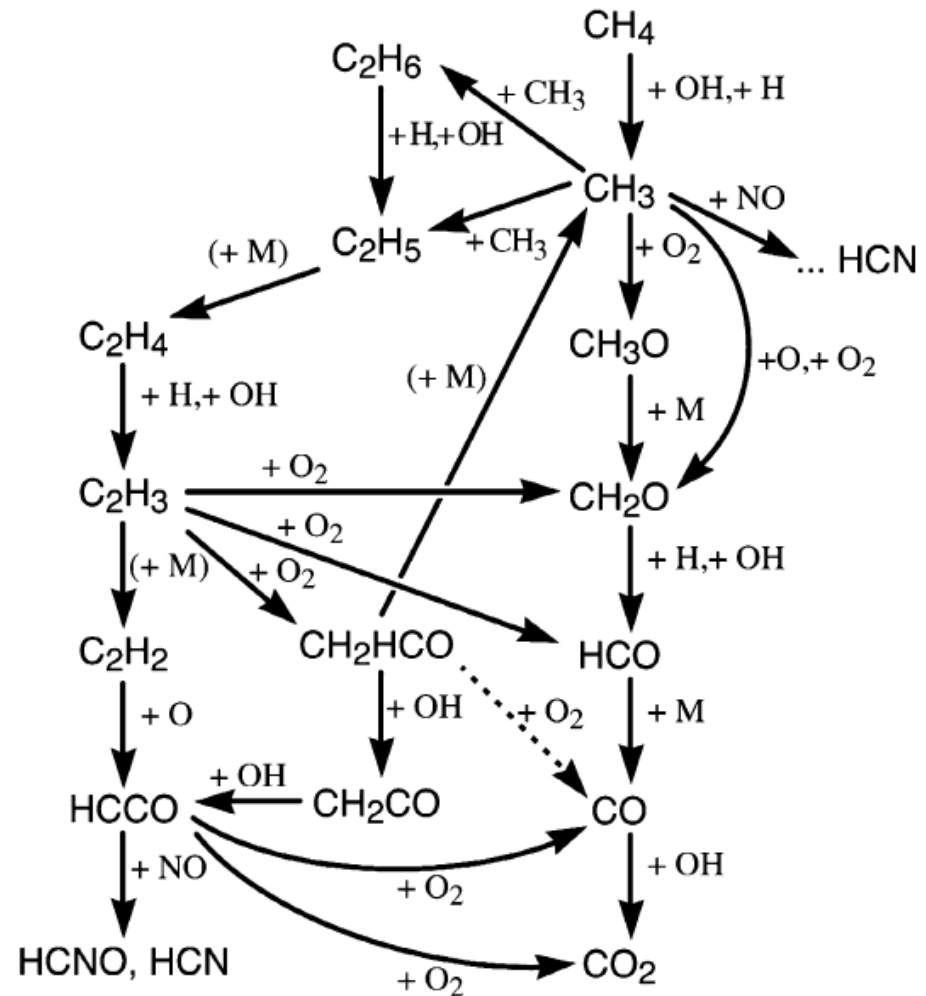
Fuel - Staged Burner

HCCO + NO

Rate coefficient evaluation

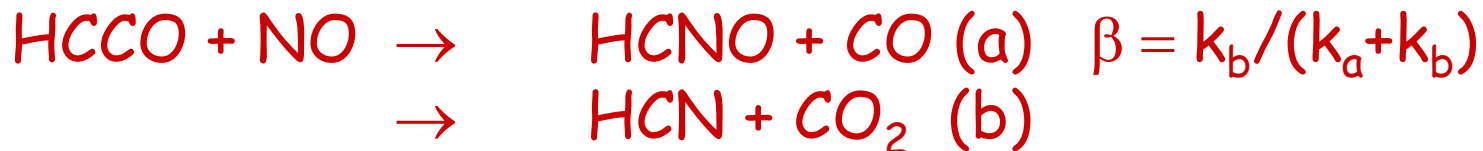
Evaluation

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



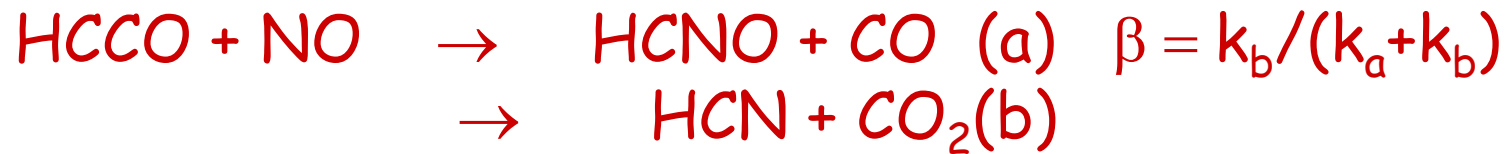
Reaction path diagram for reburn under flow reactor conditions (Miller)

Product studies:



- 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 + 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:



- 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. CO and CO_2 detection by infrared laser absorption ($\beta = 0.14$ (298 K))

Vereecken et al. - Theory Chem Phys Letters, 2001, 344, 400

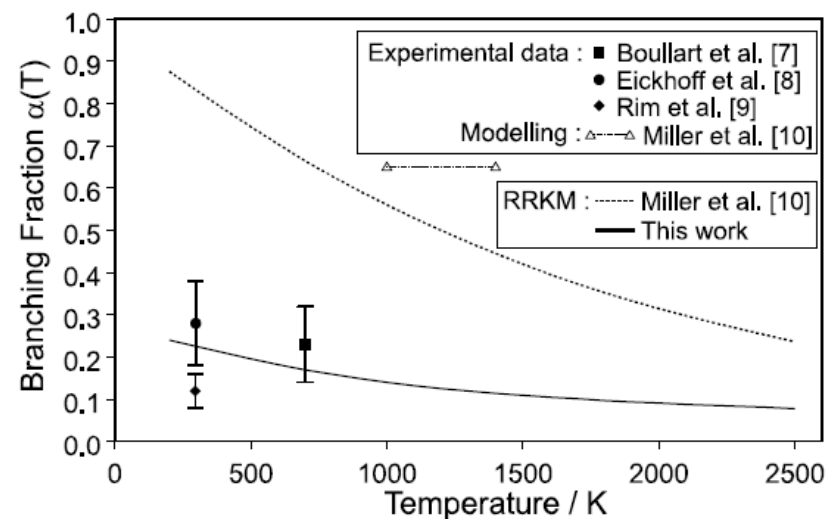
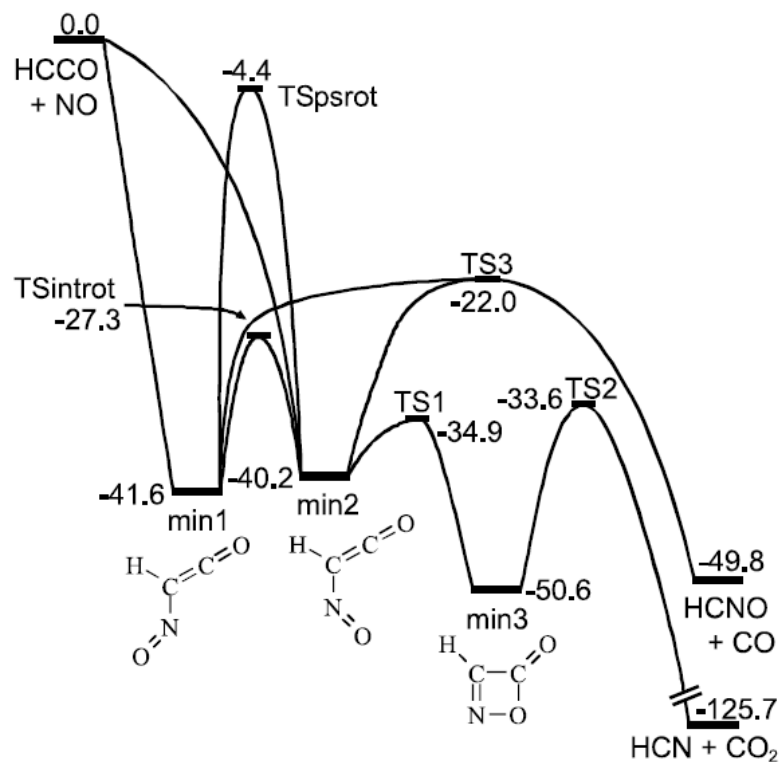


Fig. 3. Temperature dependent CO₂ yield, $\alpha(T) = k_{1a}/k_1$, for the HCCO + NO reaction.