The Reactions of Flame Soot with Nitrogen Oxides (NO_2, NO_3, N_2O_5, HONO, HNO_3): a brief Overview

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ÉCOLE POLYTECHNIQUE
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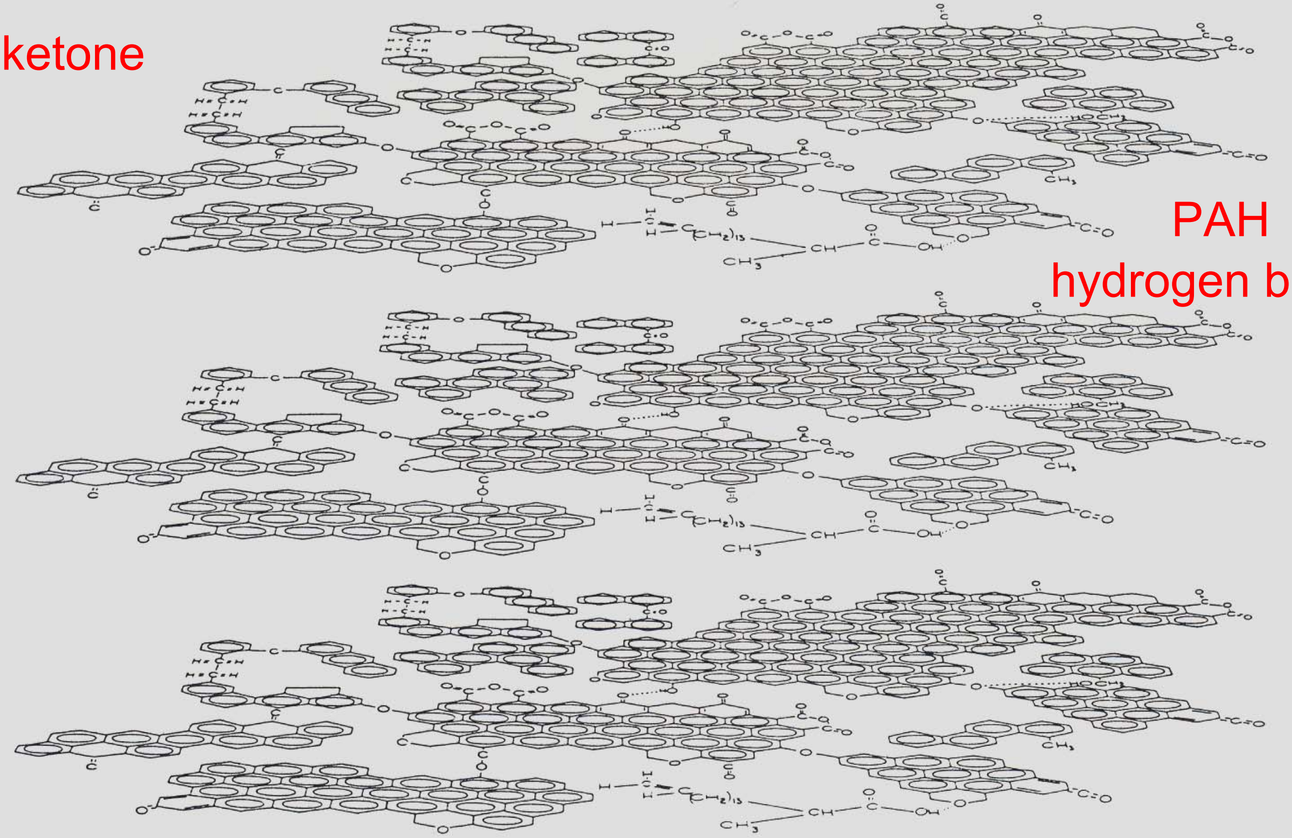
SOOT

- Definition: Soot is a product of incomplete flame combustion of hydrocarbon fuels at a given value of fuel/oxygen ratio λ (stoichiometric c. at $\lambda = 1.0$)

  Stoichiometric Combustion: $C_nH_{2n+2} + (1.5n + 0.5)\ O_2 \rightarrow nCO_2 + (n + 1)H_2O$
- Soot = EC (=BC) + Organic Phase (OC)
- Ubiquitous occurrence (on a global level)
- 10-50% of all tropospheric particulate matter is carbonaceous
- Worldwide anthropogenic emissions: 12-24 Tg/yr (Penner, 1998): N.B. Uncertainty!
- Long range transport observed (Arctic Haze)

Chemical Model of Soot Structure (Sergides et al., 1987)



aldehyde, ketone

ether linkage

acid anhydride

quinone

lactone

ketene

PAH

hydrogen bonding

FIG. 24. A proposed model of the three-dimensional *n*-hexane soot.

SOOT (cont.)

- The only atmospheric aerosol with a sizable optical absorption in the UV/VIS range
- Remarkable influence on climate (positive radiative forcing), public health (inhalation of nanoparticles) and tropospheric chemistry (reducing properties)
  - **Decrease** in albedo (SSA) owing to absorption of radiation (short- and longwave radiation)
  - **Increase** in cloud albedo owing to activation of CCN and decrease in precipitation (Twomey)

JJA Surface Temperatures (Hansen, 2002)

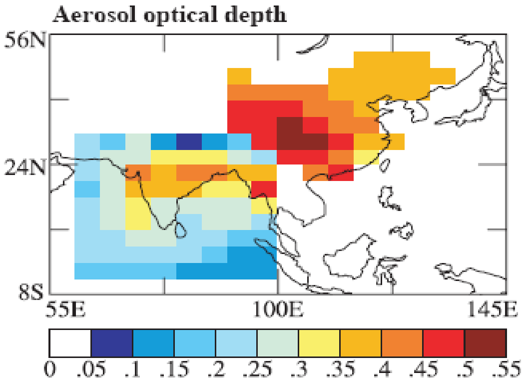
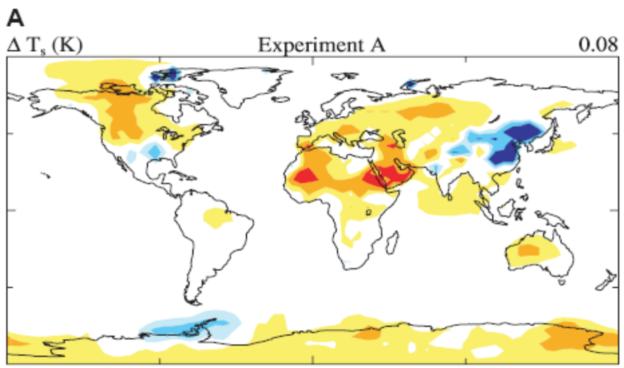


Fig. 1. Incremental aerosol optical depth $\Delta\tau_{aer}$ (0.55 μm), which is used to drive the climate change simulations. Latitude and longitude are denoted.

→

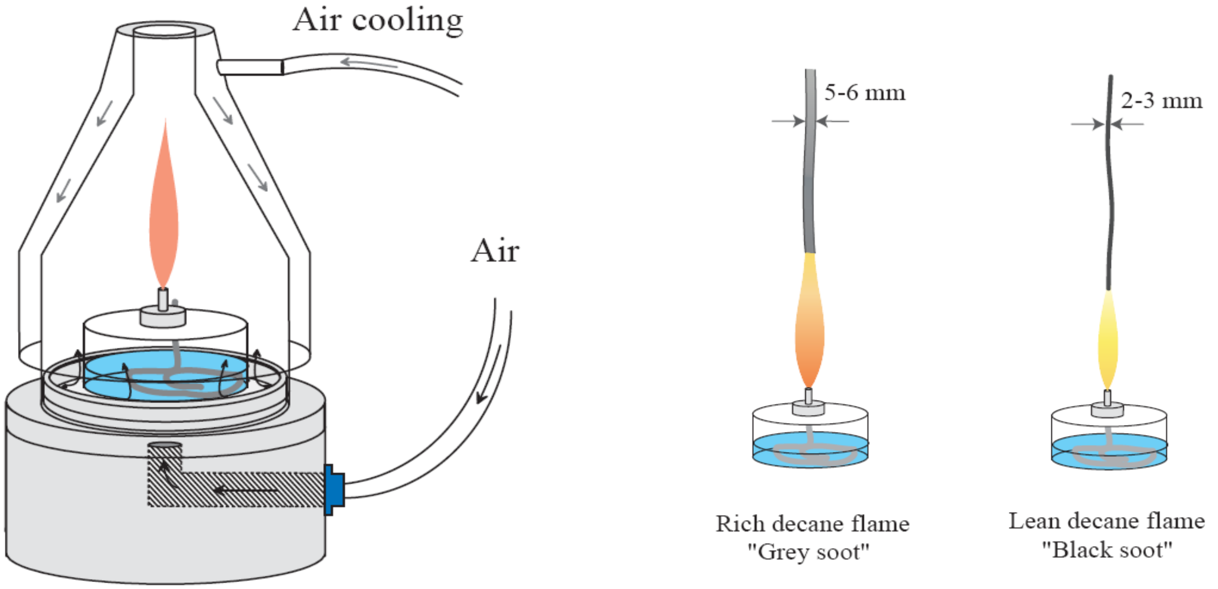
Fig. 2. (A) Simulated JJA surface air temperature change (ΔT_S) for experiments A and B. The significance of these changes is shown in fig. S2. (B) Observed JJA ΔT_S between 1951 and 2000, based on the linear trend. Global mean changes are in the upper right corner.



SSA = 0.85

No GH Gases!

Custom-designed Co-Flow Device for reproducible generation of decane ($C_{10}H_{22}$) soot: Diffusion Flame



Flame type	Flame height [mm]	Flame colour	Soot deposition [mg min^{-1}]	Air flow [l min^{-1}]	Fuel duct (pore ⌀) [μm]	Soot type
Decane						
rich	~ 60	orange–red	2.0±0.5	1.2–1.4	17–40	”grey”
lean	~ 55	yellow–white	0.8±0.4	1.3–1.5	11–16	”black”

Control of Soot Production is mandatory in view of its Effects on Kinetics

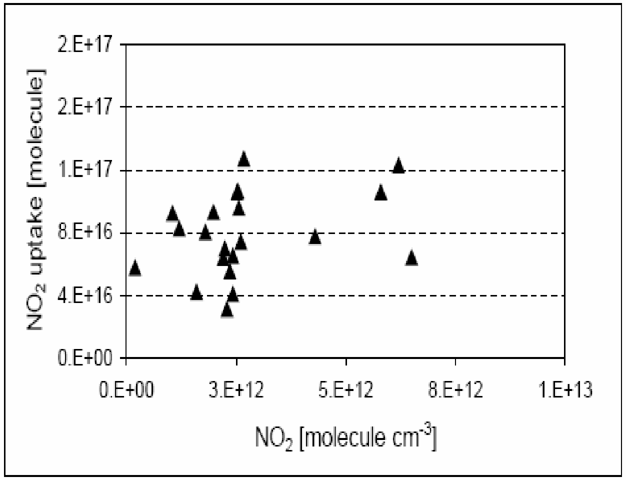


Figure 6.1.1: Uptake of NO_2 on decane soot as a function of the NO_2 concentrat samples were produced using a simple oil lamp; 4 mm diameter escape orifice, i over 100 seconds, mean sample weight was 17.3 mg.

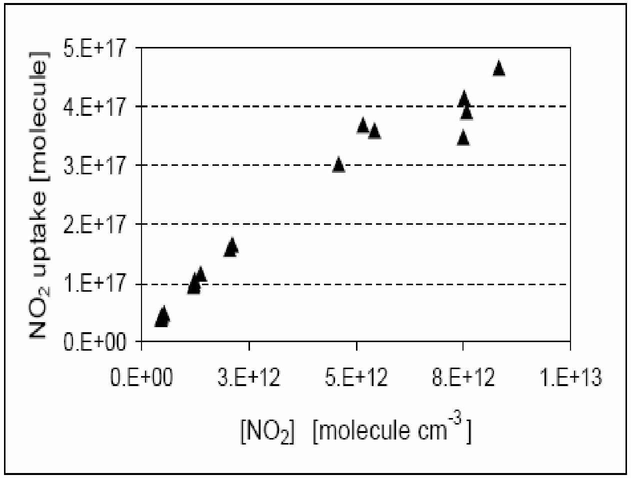


Figure 6.1.2: Uptake of NO_2 on decane soot as a function of the NO_2 steady state concentration. Soot samples were produced using the new co-flow device; 4 mm diameter escape orifice, integrated over 100 seconds, mean sample weight was 16.4 mg.

Unstable flickering flame

Stabilized (controlled) flame

CAST or Co-Flow Device

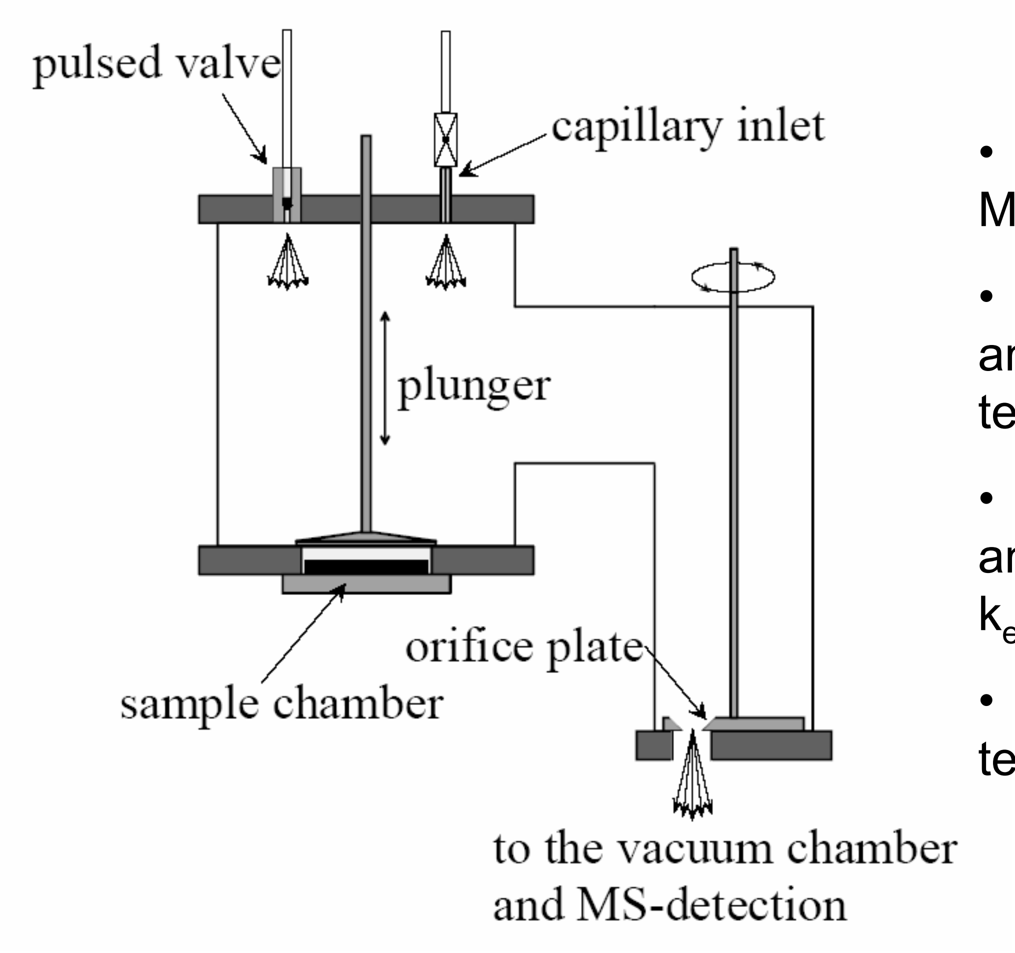
Elemental analysis for several types of soot

Anticorrelation of H- and O-content of soot depending on λ - ratio

Author	Soot (λ)	Elemental analysis			
		C(% wt)	H(% wt)	N(% wt)	O(% wt)
Salgado, 2002	hexane (λ=0.82)	94.73 ± 0.15	1.50 ± 0.01	~0	3.78 ± 0.16
CAST Burner	hexane (λ=0.16)	93.01 ± 0.31	0.77 ± 0.03	0.26 ± 0.02	5.99 ± 0.36
Matter Engineering	hexane (λ=0.09)	92.03 ± 0.34	0.44 ± 0.07	0.23 ± 0.02	7.27 ± 0.42
Stadler, 2000	gray decane soot (rich flame)	97.27 ± 0.05	0.83 ± 0.04	0.20 ± 0.18	1.65 ± 0.19
	black decane soot (lean flame)	96.39 ± 0.22	0.19 ± 0.01	0.27 ± 0.09	3.22 ± 0.25
Akhter, 1985	n-hexane	87-92.5	1.2-1.6	___	6-11

λ = fuel /O_2 on a per C basis

Knudsen Flow Reactor: Kinetics, Branching Ratios and Reaction Products using MBMS



- Gas Phase is monitored: Molecular Beam-modulated MS
- Multispecies capabilities: MS and laser-based *in situ* detection techniques
- Relative Rate Technique put on an absolute Basis using measured k_{esc} (rate constants for effusion)
- Measurement of gas “uptake” in terms of uptake probabilities (γ)

NO_2 Reaction Mechanism for Amorphous Carbon

DEGUSSA Materials (Tabor 1994)

- Net reaction: NO_2 + {C} ➔ NO + {C•O}
- $\gamma = 5 \times 10^{-2}$
- Evolution of CO, CO_2 upon heat treatment of soot (incandescent lamp).

NO_2 + {SS} ← → {SS•NO_2}p
Reversible adsorption

NO_2 + {SS} ← → {L}
Reversible adsorption to a non-reactive species

{SS•NO_2}p ➔ {NO_2•I} + {SS}
Conversion into an intermediate I (deeper layer)

{NO_2•I} ➔ {NO_2•R}
Transfer to reservoir R

{NO_2•I} ➔ NO + {C•O}
Decomposition to NO and a surface oxygen complex {C•O}.

Correlation between NO_2 and HONO for reaction of NO_2 on gray (rich flame) decane soot (Stadler 2000)

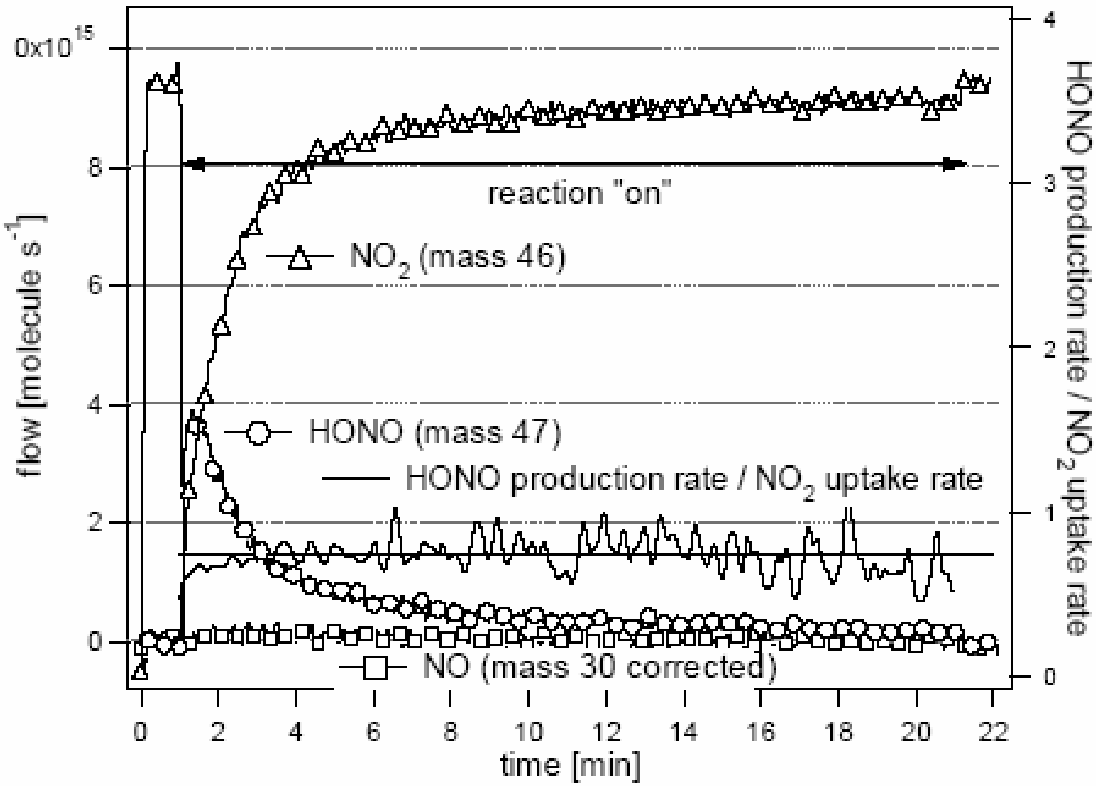


Figure 6.2.1: Uptake experiment of NO_2 on 'grey' decane soot; sample mass = 16.3 mg, 4 mm diameter escape orifice, NO_2 concentration = 8.3×10^{12} molecule cm^{-3}.

Suggested Reaction Mechanism for HONO Formation on rich Flame Soot

- $NO + NO_2 + M \rightarrow N_2O_3 + M$

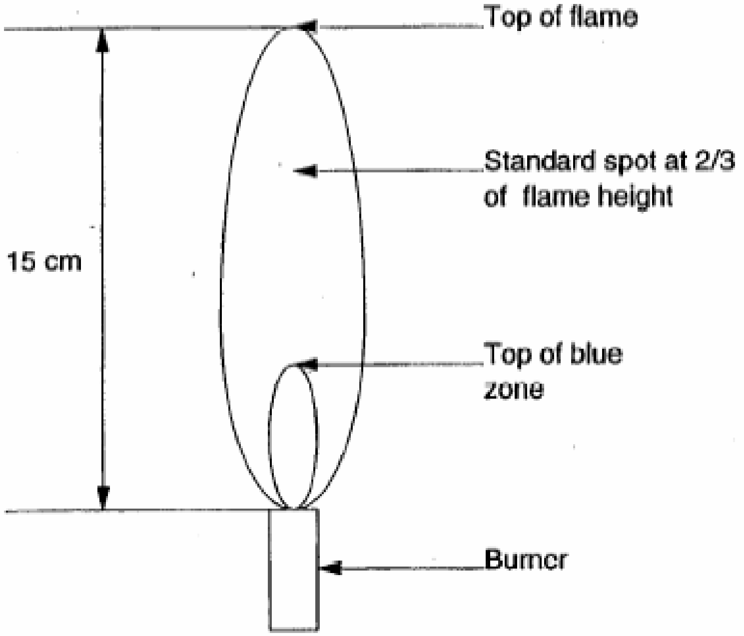
  gas phase reaction
- $N_2O_3 + H_2O \rightarrow 2HONO$

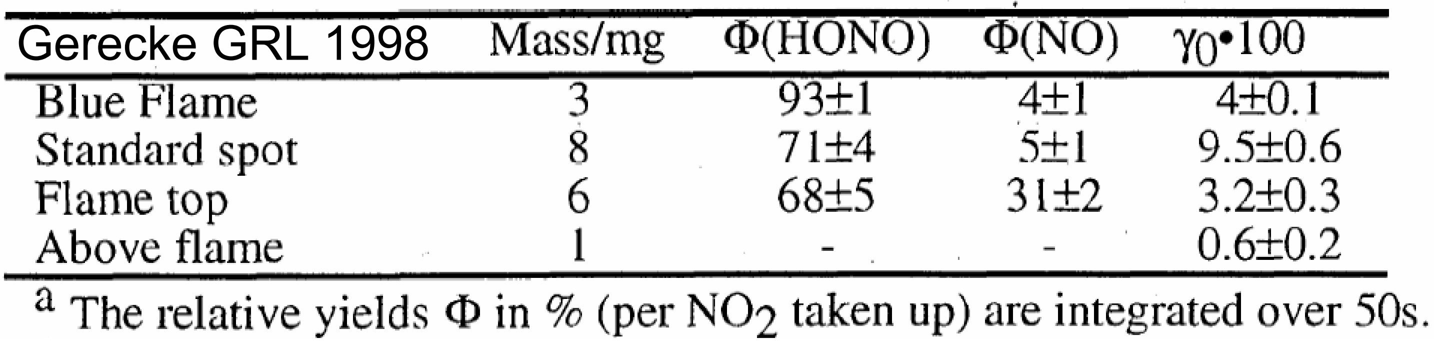
  heterogeneous reaction
- $2NO_2 + H_2O \rightarrow HONO + HNO_3$

  Too slow
- $NO_2 + \{C\text{-}H\}_{red} \rightarrow HONO + \{C\text{-}\}_{ox}$
- $NO_2 + H_2O \rightarrow HONO + OH$

☐ ΔH_r^0 = 40 kcal/mol (est.)

Yields of HONO and NO are position dependent and complementary (anticorrelated) in ethylene flame





Gerecke GRL 1998	Mass/mg	Φ(HONO)	Φ(NO)	$\gamma_0 \cdot 100$
Blue Flame	3	93±1	4±1	4±0.1
Standard spot	8	71±4	5±1	9.5±0.6
Flame top	6	68±5	31±2	3.2±0.3
Above flame	1	-	-	0.6±0.2

[a] The relative yields Φ in % (per NO_2 taken up) are integrated over 50s.

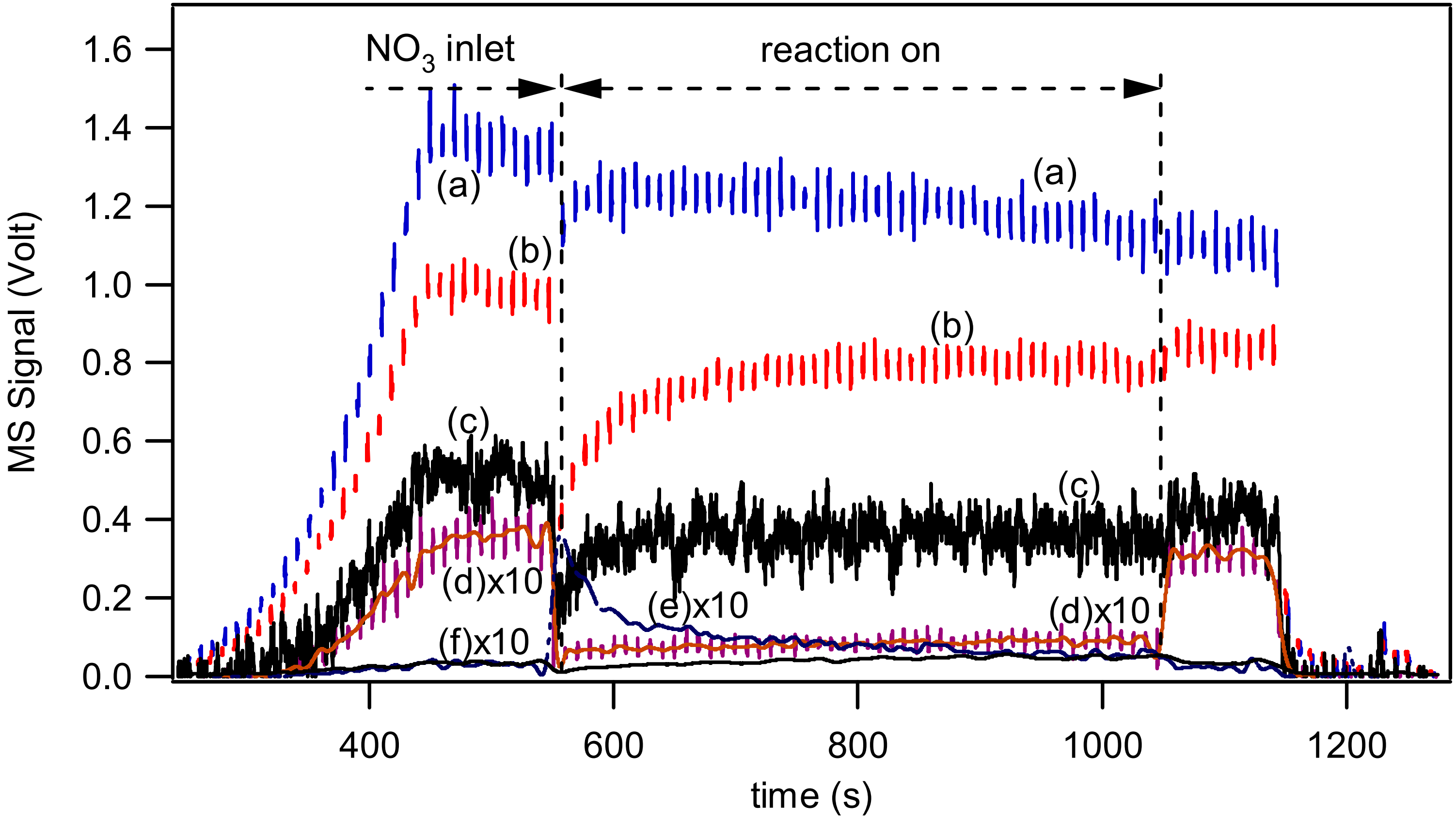
CONCLUSIONS: NO_2 - Soot

- Reaction products depend on type of soot unlike kinetics (γ).
- Reaction occurs with reducing surface functional groups on substrate, NOT CATALYTIC decomposition.
- X-tremes: 100% NO on amorphous carbon FW2 (channel black)

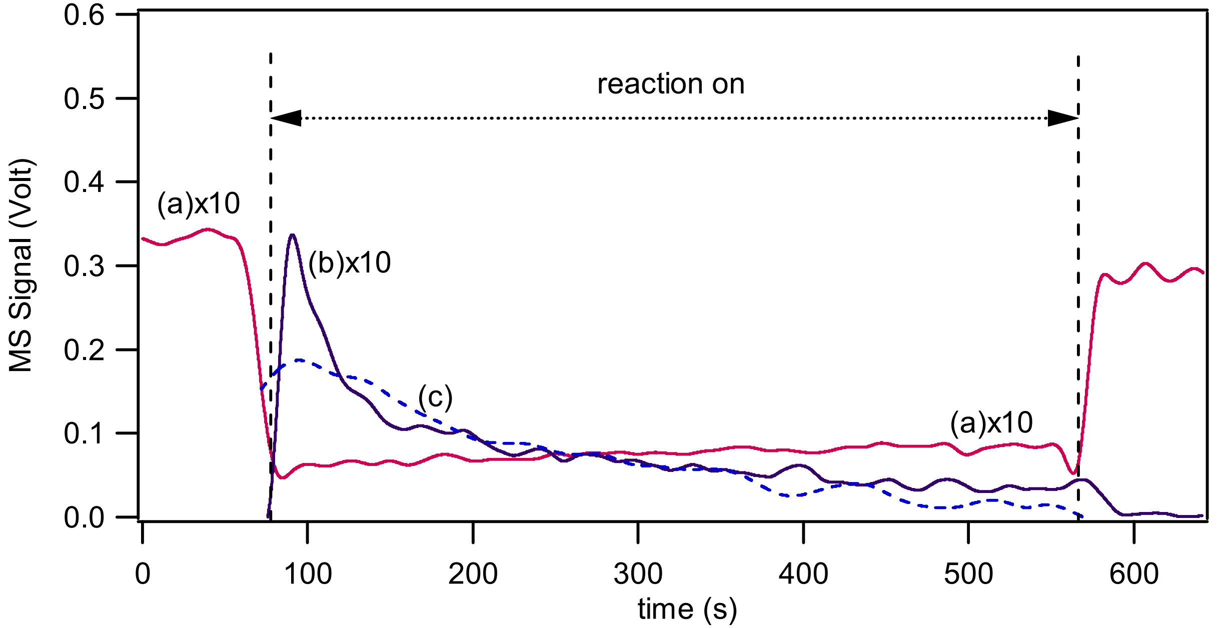
  100% HONO on hexane, decane soot from rich flame
- Both carbon-matrix as well as semivolatile organic fraction of soot partake in heterogeneous chemical reaction.
- HONO decomposes on (black) soot from lean combustion to yield NO as a final product: $2HONO \rightarrow NO + NO_2 + H_2O$.
- Complex surface reaction mechanism: inhibition and competition.

NO_3 / gray (rich flame) decane soot
$N_2O_5 \rightarrow NO_3 + NO_2$

Kinetics and Reaction Products have been investigated in Knudsen flow reactor under molecular flow conditions using in situ REMPI detection of NO, NO_2

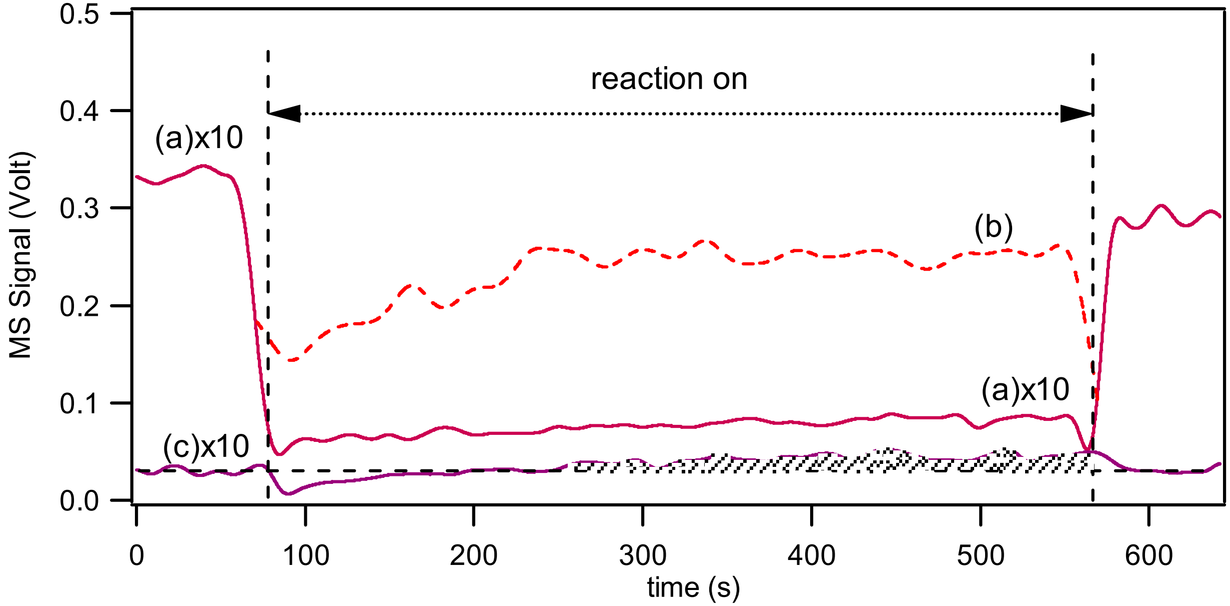


(a) m/e 30, (b) m/e 46, (c) raw REMPI signal for NO_2 detection at $\lambda = 511$ nm scaled to a MS signal at m/e 46, (d) m/e 62, (e) m/e 47, (f) m/e 63



(cont.)

(a) m/e 62,
(b) m/e 47
(HONO),
(c) NO



(a) m/e 62,
(b) N_2O_5
(m/e 46), (c)
m/e 63

Reaction Mechanism for NO_3 + decane soot

Source (N_2O_5 thermal dec.) → NO_3 (25%) + NO_2 (75%)

$NO_3 + \{C\} \rightarrow NO + \{C \bullet O_2\}$ (12-17%)

Most of the lost NO_3 remains adsorbed on soot

$NO_2 + \{NO_3\} \rightarrow N_2O_5$ (20-24%) ($+ H_2O \rightarrow 2HNO_3$)

Rich (gray) Flame Soot:

$NO_2 + \{C\text{-}H\}_{red} \Rightarrow HONO + \{C\text{-}\}_{ox}$ (≈ 100%)

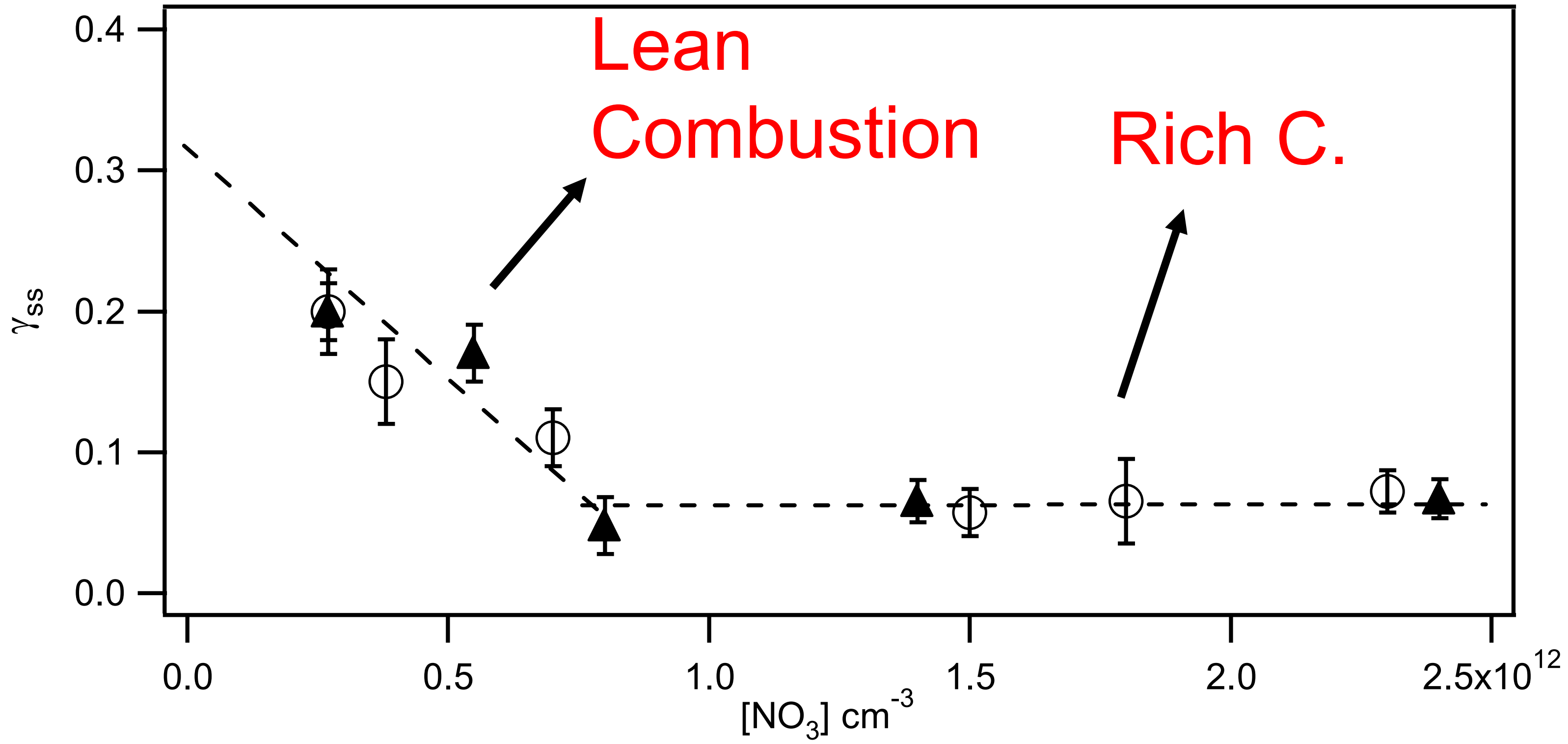
Lean (black) Flame Soot:

$\{2HONO\} \rightarrow \{H_2O\} + NO + NO_2$ (5%) (A lot of NO_2 remains adsorbed!)

RED: genuine NO_3 reaction

BLUE: complication as a consequence of the presence of NO_2.

Steady State Uptake Coefficient for NO_3 on decane soot: extrapolation to ambient concentrations enabled by known rate law



Uptake coefficient γ_{ss} of NO_3 as a function of $[NO_3]$ (orifice diameter = 8 mm): NO_3 on black (full triangles) and gray soot (open circles).

CONCLUSIONS: NO_3 - Soot

- Most of lost NO_3 remains adsorbed on soot
- Yield of NO is 12 (gray) -17 % (black) soot
- Adsorbed NO_3 leads to N_2O_5 formation in the gas phase with excess NO_2
- Small yield of HNO_3
- Large γ @ $[NO_3] \rightarrow 0$ (ambient conditions: hundred ppt at night)
- Renoxification mechanism: $NO_y \rightarrow NO_x$
- Soot substrate is partaking in the reaction

Reaction Mechanism: N_2O_5 + Decane Soot

- $N_2O_5 + \{C\} \rightarrow NO + NO_2 + \{C{\bullet}O_2\}$ Redox reaction
- $N_2O_5 + \{H_2O\} \rightarrow 2\,HNO_3$ heterogeneous Hydrolysis reaction – surprisingly SLOW!

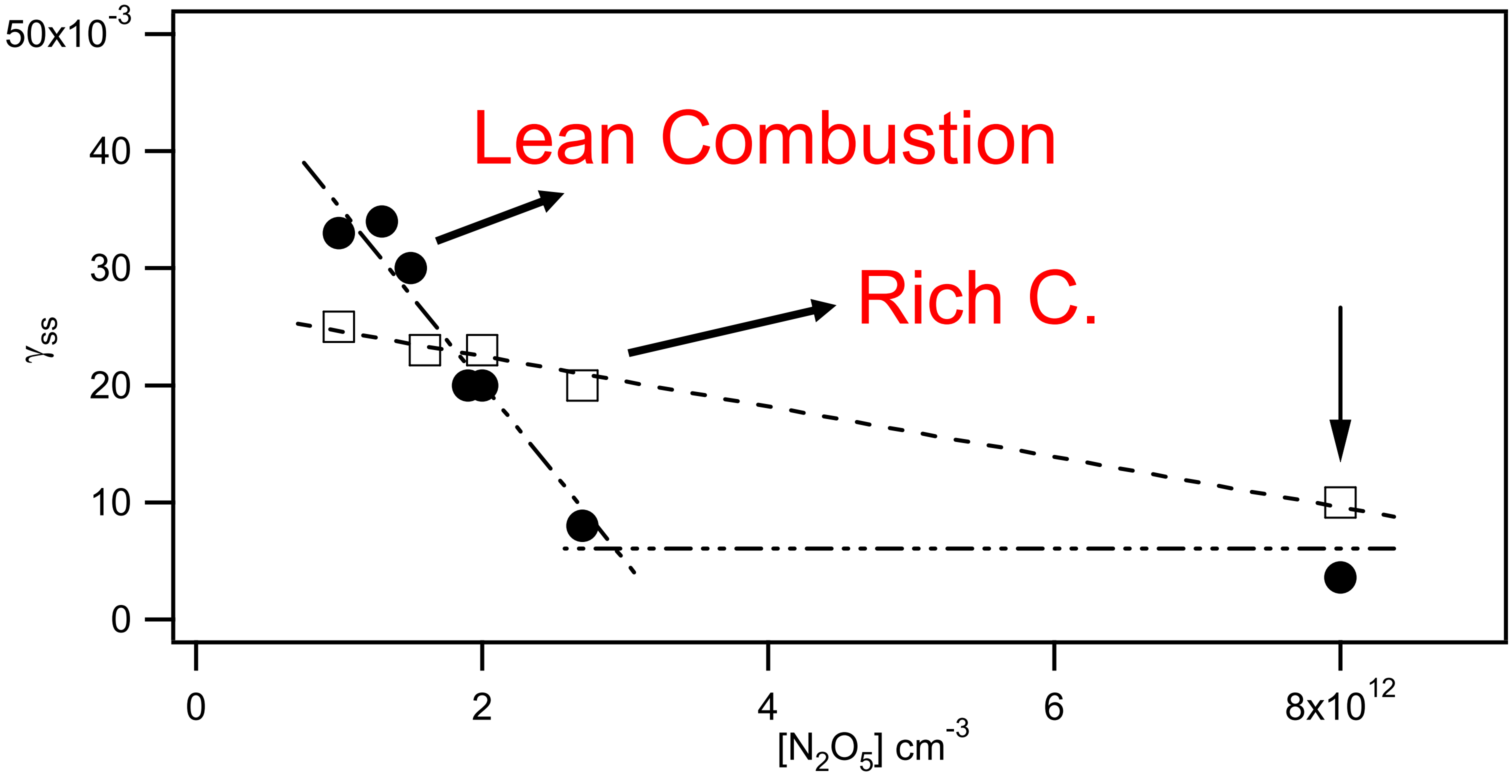
Mechanism:

$$N_2O_{5(ads)} + \{C\} \rightarrow N_2O_{3(ads)} + \{C{\bullet}O_2\}$$

$$N_2O_{3(ads)} + \rightarrow NO + NO_2$$

equimolar amounts of NO and NO_2 approaching 100% at low concentration.

Steady State Uptake Coefficient for N_2O_5 on Decane Soot: Importance of Rate Law !!!



Uptake coefficient γ_{ss} of N_2O_5 as a function of [N_2O_5]: N_2O_5 on black (circles) and gray soot (open squares). For all measurements we used the 8 mm orifice diameter except for the point marked by the arrow where a 4 mm orifice diameter has been used.

CONCLUSIONS: N_2O_5 - Soot

- Hydrolysis (HNO_3) and Redox (NO) reaction are concurrent and depend on the type of soot. Redox reaction occurs until exhaustion of redox reactive sites.
- Reaction products are equimolar NO + NO_2. Relative yields depend on type of carbon substrate. No NO_3 observed in the gas phase.
- Renoxification Mechanism, soot substrate is reacting
- Large γ value (roughly 10 times lower than for NO_3)

Reaction Mechanism for HNO_3 + Soot

$2HNO_3 \rightarrow \{N_2O_5\}$	Hypothesis
$\{N_2O_5\} \rightarrow \{NO_2\} + \{NO_3\}$	Surface decomposition
$HNO_3 \rightarrow \{C\text{-}H\}_{red} \rightarrow \{HONO\} + \{C{\bullet}O_2\}_{ox}$	Reduction of HNO_3 on rich flame (gray) soot (NO_2!!)
$\{HONO\} \rightarrow HONO$	gray soot (rich combustion)
$2\{HONO\} \rightarrow \{H_2O\} + \{N_2O_3\} \rightarrow NO + \{NO_2\}$	black soot (lean combustion)

In addition:

$NO + \{HNO_3\} \rightarrow HONO + \{NO_2\}$	gray soot (rich or stoichiometric flame): Supports adsorbed HNO_3
$HNO_3 + \{HONO\} \rightarrow 2\{NO_2\} + \{H_2O\}$	High surface coverage: Supports adsorbed HONO
$\{NO_2\} + \{C\text{-}H\}_{red} \rightarrow NO + \{C\}_{ox}$	secondary reaction of NO_2

CONCLUSIONS: HNO_3 - Soot

- Reaction products depend on type of soot
- X-tremes: amorphous carbon FW2 (channel black), lean flame soot (decane): NO, small amounts of NO_2.

  hexane, decane soot from rich flame: HONO exclusively.
- Evidence for adsorbed HNO_3, HONO. N_2O_5??
- Renoxification – atmospheric significance: ratio $[NO_y]$ / $[NO_x]$ or $[HNO_3]$ / $[NO_x]$ is overpredicted by photochemical transport (CRT) models. Models "need" more NO_x.