The Centre for Theoretical and Computational Chemistry

Atmospheric Degradation of Amines

ADA

UIO, UMB, UI
IRCELYON, NILU

Fate of $MEA_{(g)}$

$H_2N\text{-}CH_2\text{-}CH_2\text{-}OH$

How much ?

$HN{=}CHCH_2OH$
CH_2OHCH_2NHNO
$CH_2OHCH_2NHNO_2$
$CH_2OHC(O)NHNO_2$

NOT "OK"

NH_2CHO
$NH_2C(O)CH_2OH$

"OK"

NH_2CH_2CHO
NH_2CHO
$NH_2C(O)CHO$
$NH_2C(O)OONO_2$
$NH_2CH_2C(O)OONO_2$
$NH_2C(O)C(O)OONO_2$

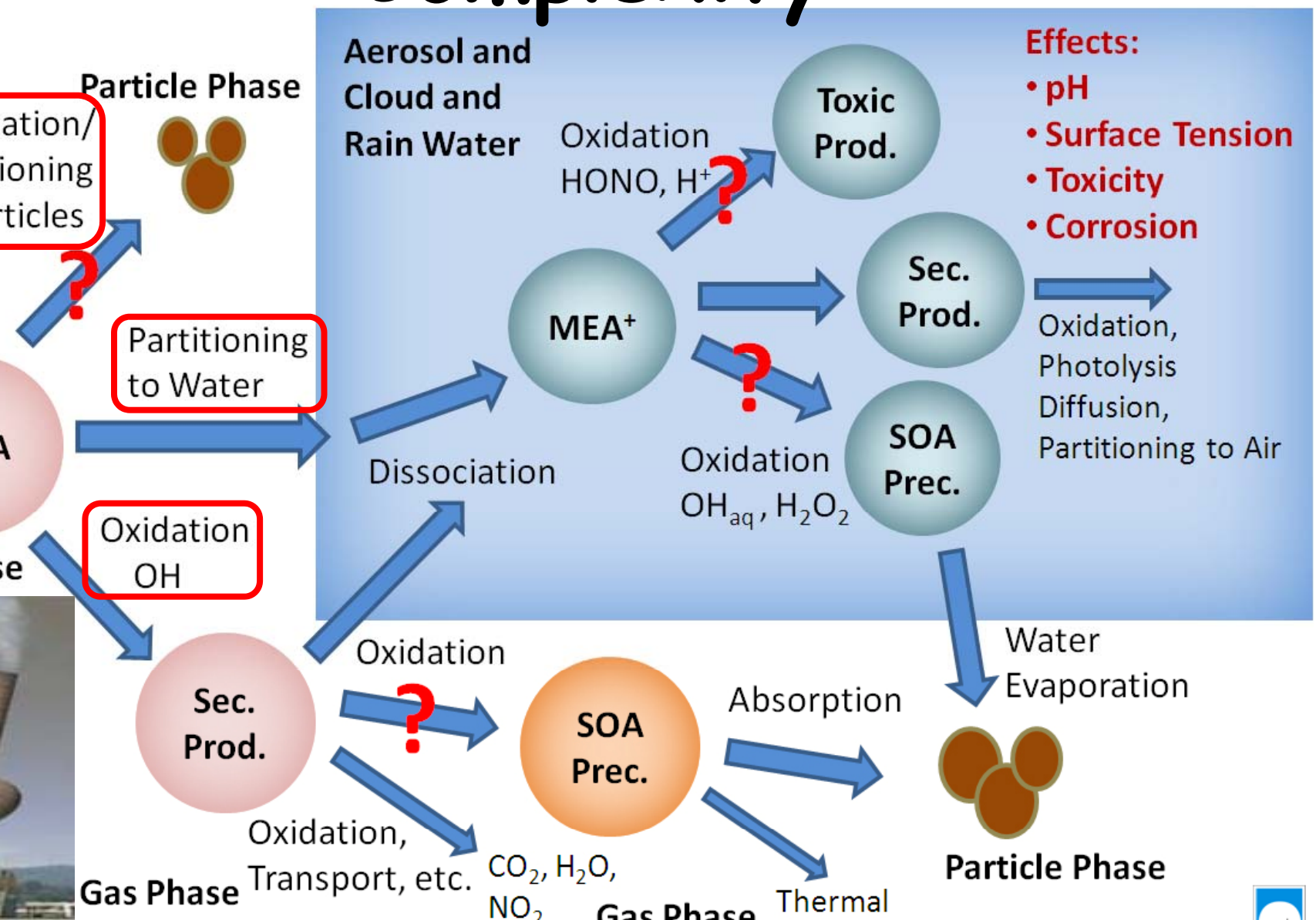
"OK"

Experiments at EUPHORE

nstrumentation:

- FT-IR
- Cryotrap GC-MS
- PTR-TOF-MS (UI)
- Monitors for:
  CO, HCHO, O_3 & NO_x
- Actinometer, Radiometer
- TEOM, SMPS
- AMS (IRCLYON)
- Filters and cartridges (NILU)

Complexity


Particle Phase
ation/
ioning
rticles
Partitioning
to Water
Oxidation
OH
se
Gas Phase
Aerosol and
Cloud and
Rain Water
Oxidation
HONO, H+
Toxic
Prod.
Effects:
• pH
• Surface Tension
• Toxicity
• Corrosion
MEA+
Sec.
Prod.
Oxidation,
Photolysis
Diffusion,
Partitioning to Air
Dissociation
Oxidation
OHaq , H2O2
SOA
Prec.
Sec.
Prod.
Oxidation
SOA
Prec.
Absorption
Water
Evaporation
Oxidation,
Transport, etc.
CO2, H2O,
NO2
Gas Phase
Thermal
Particle Phase

Aerosol formation

Photo-oxidation of MEA with NOx present results in high concentrations of stable particles.

Experiments with 100-700 ppbV MEA resulted in up to 10^4 particles/cm^3 and the total aerosol mass increased up to 230 $\mu g/m^3$.

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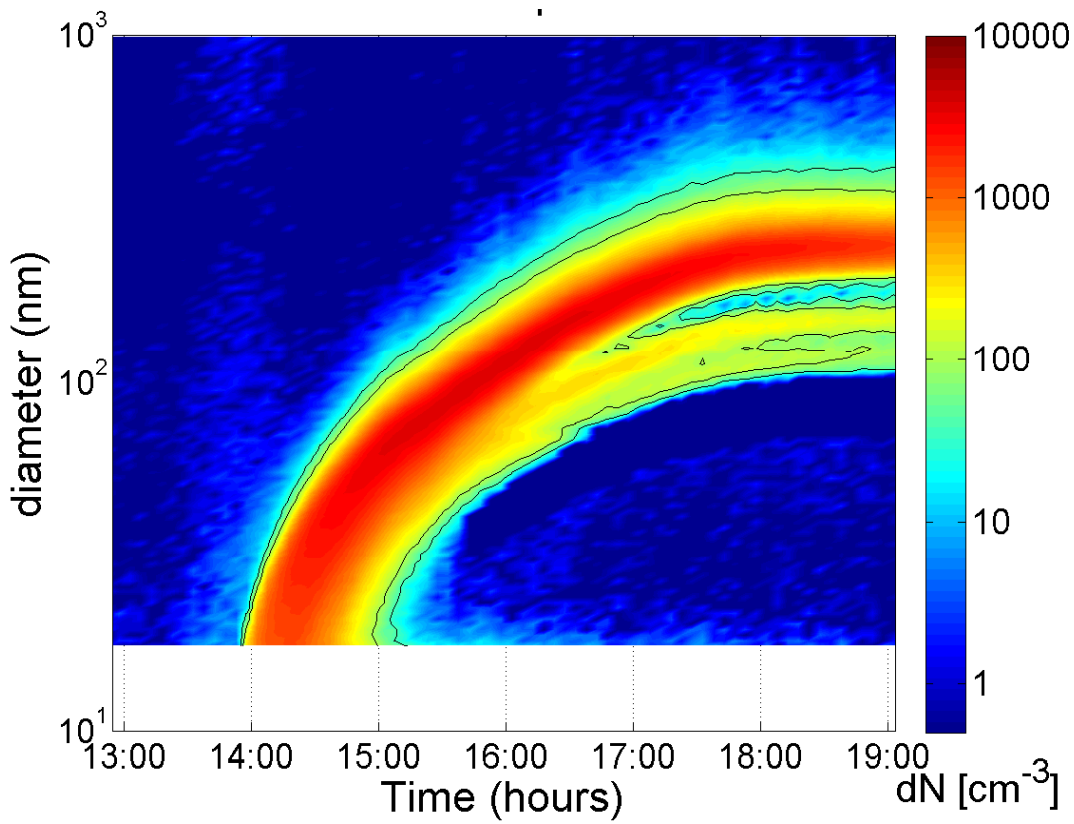
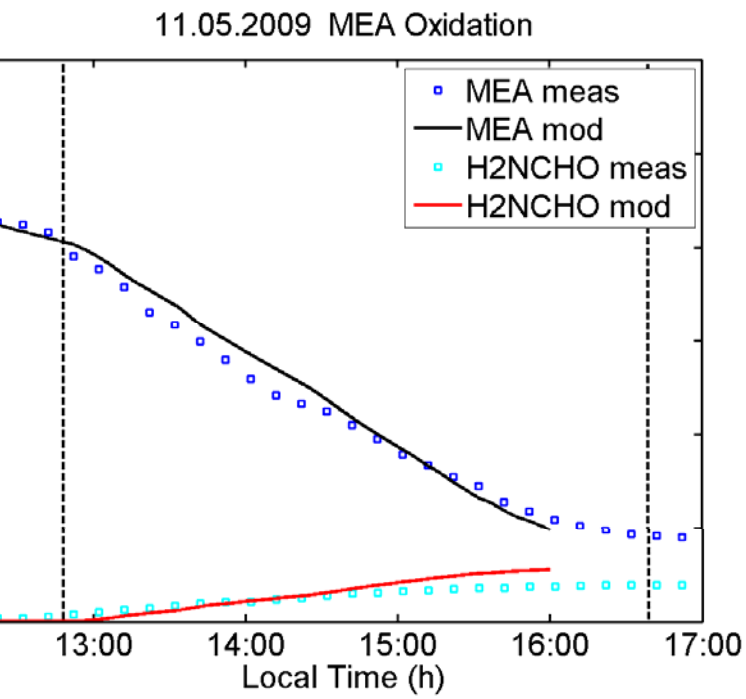
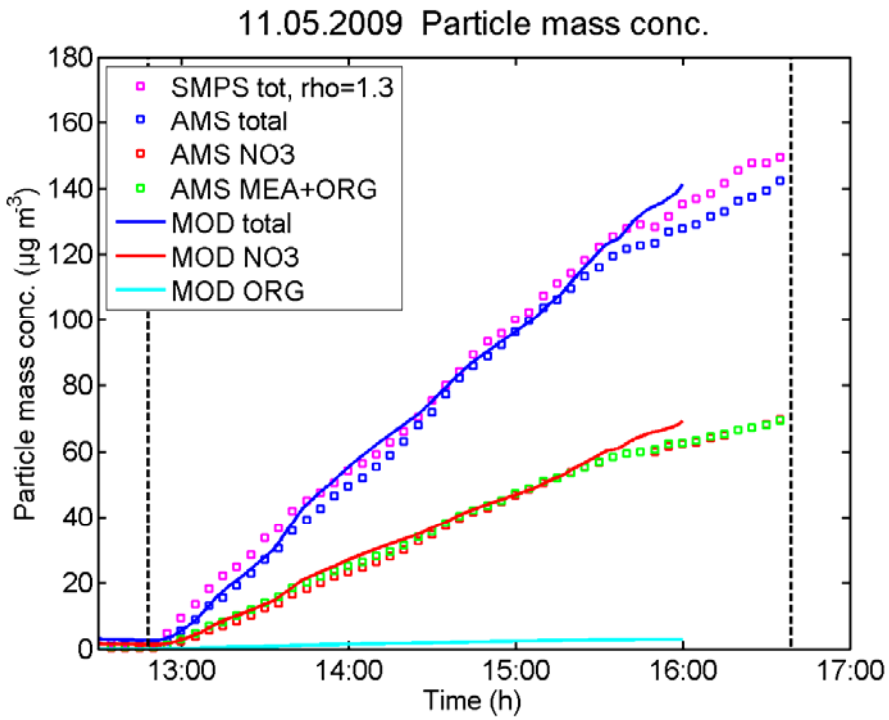
article growth - "banana-curve"



equential aerosol size distributions in the MEA photo-oxidation experiment on 4.05.2009 (high-NO/low-NO_2 experiment). Time is given as local time. A particle urst is observed one hour after the chamber canopy was opened at 12:56. Lower ze cut-off of the SMPS instrument is at 17.5 nm diameter.

Simulation of the particle growth with the sectional aerosol model MAFOR



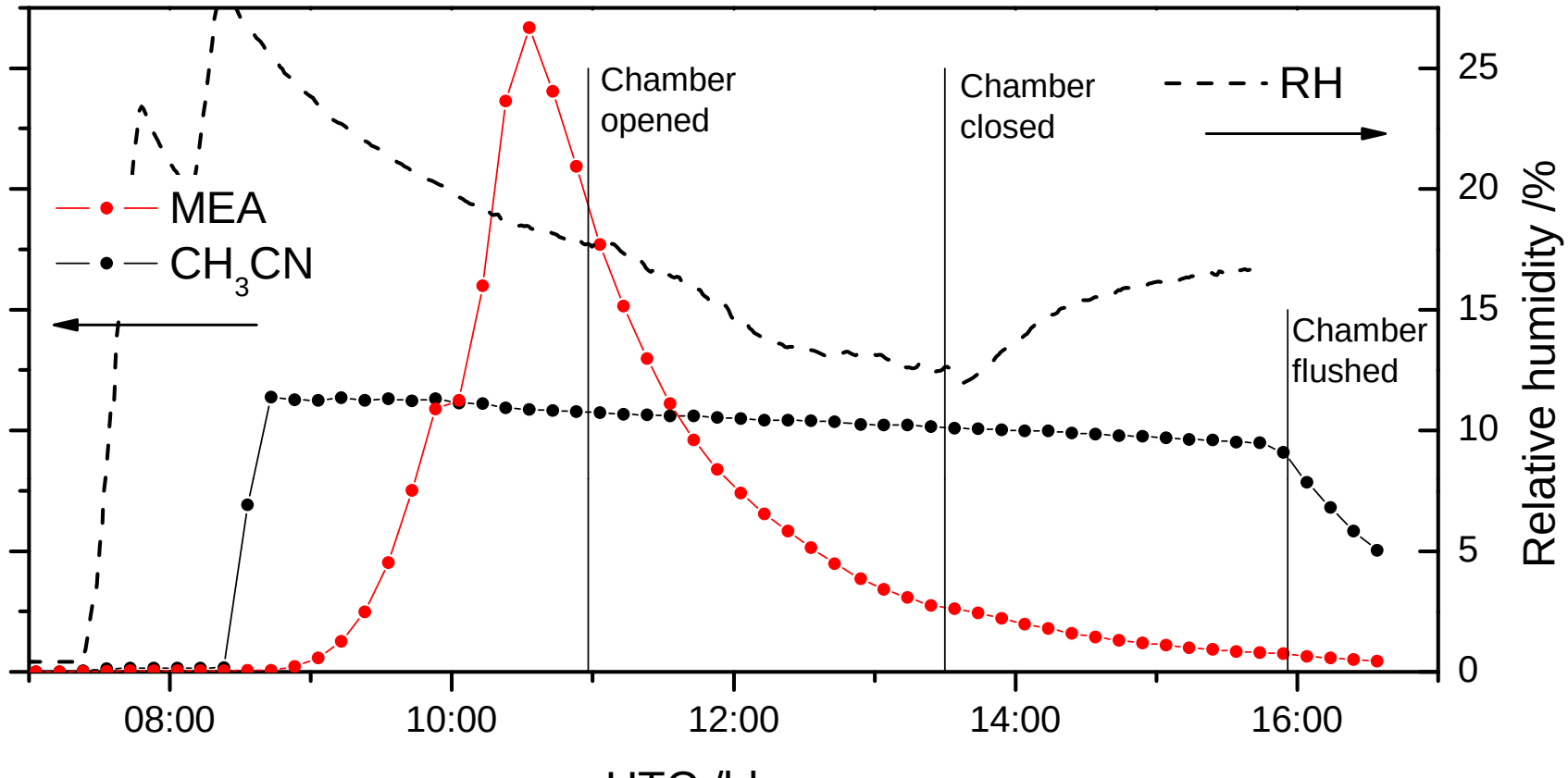


MEA degradation and production of formamide in the gas phase (11.05.2009); modeled vs. measured.

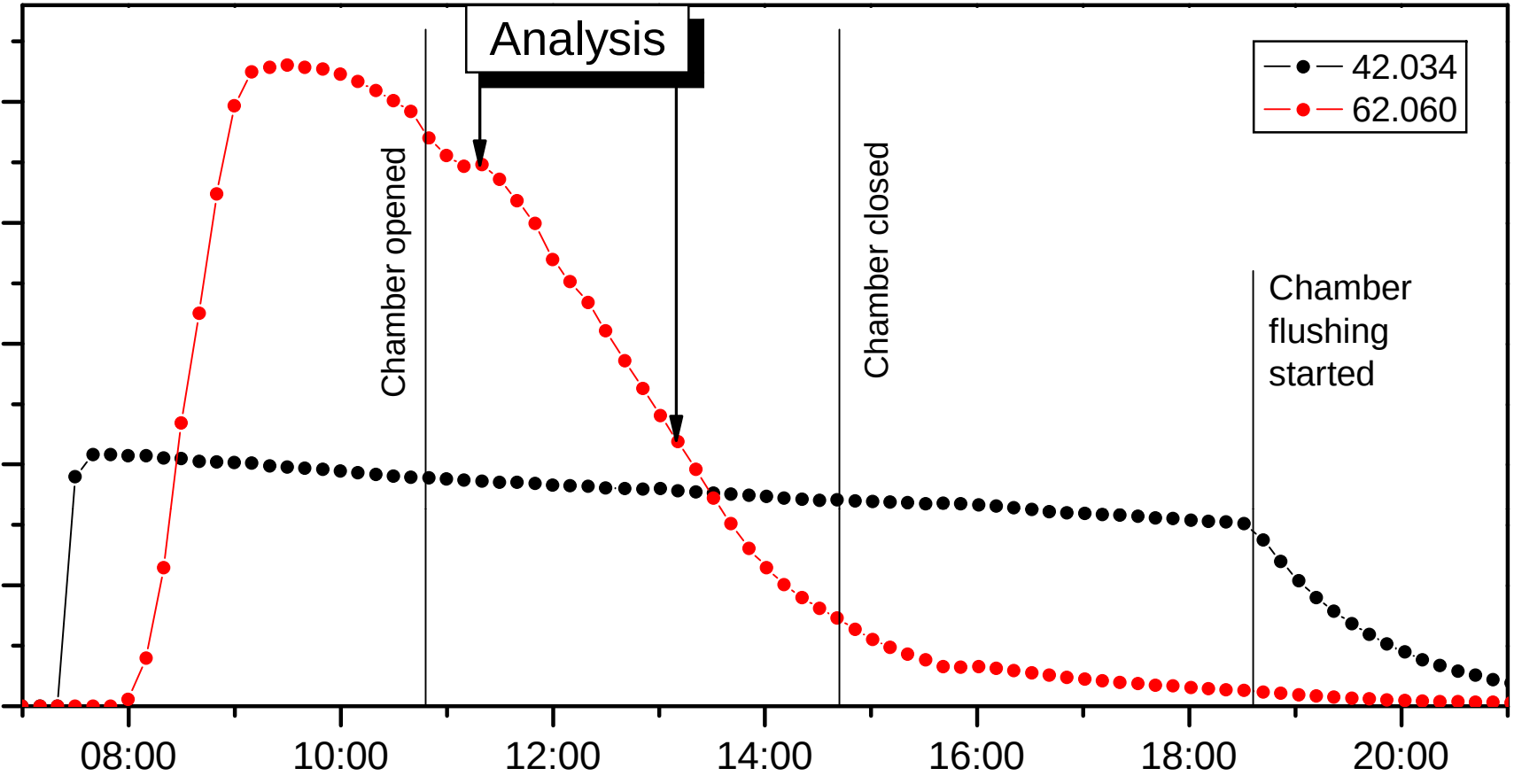
Total aerosol mass (11.05.2009). Measured by SMPS and AMS vs. modeled.
Red squares: measured NO_3 mass conc.

MEA phase transfer

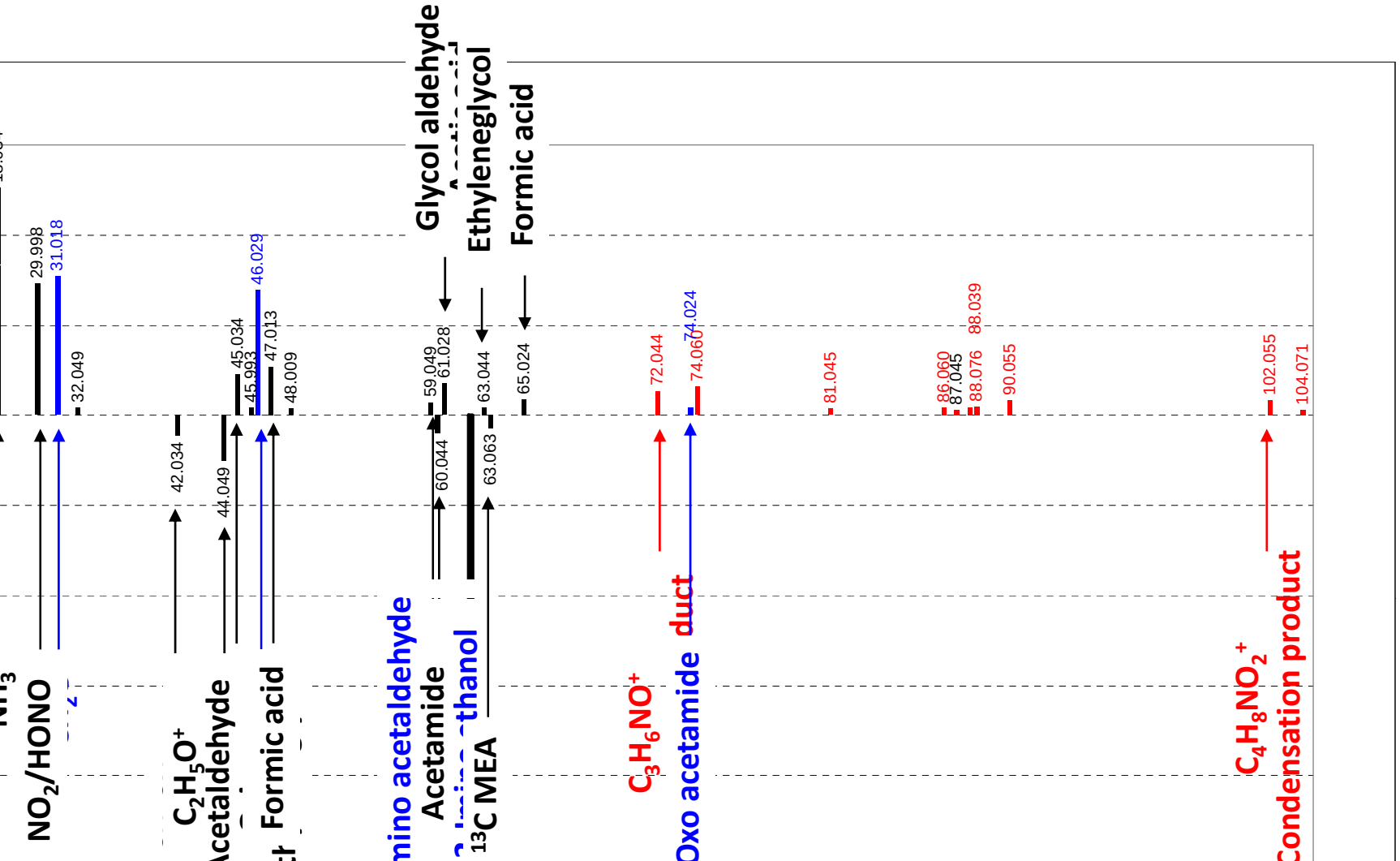
MEA is primarily lost to the wetted walls and not to the wet particles



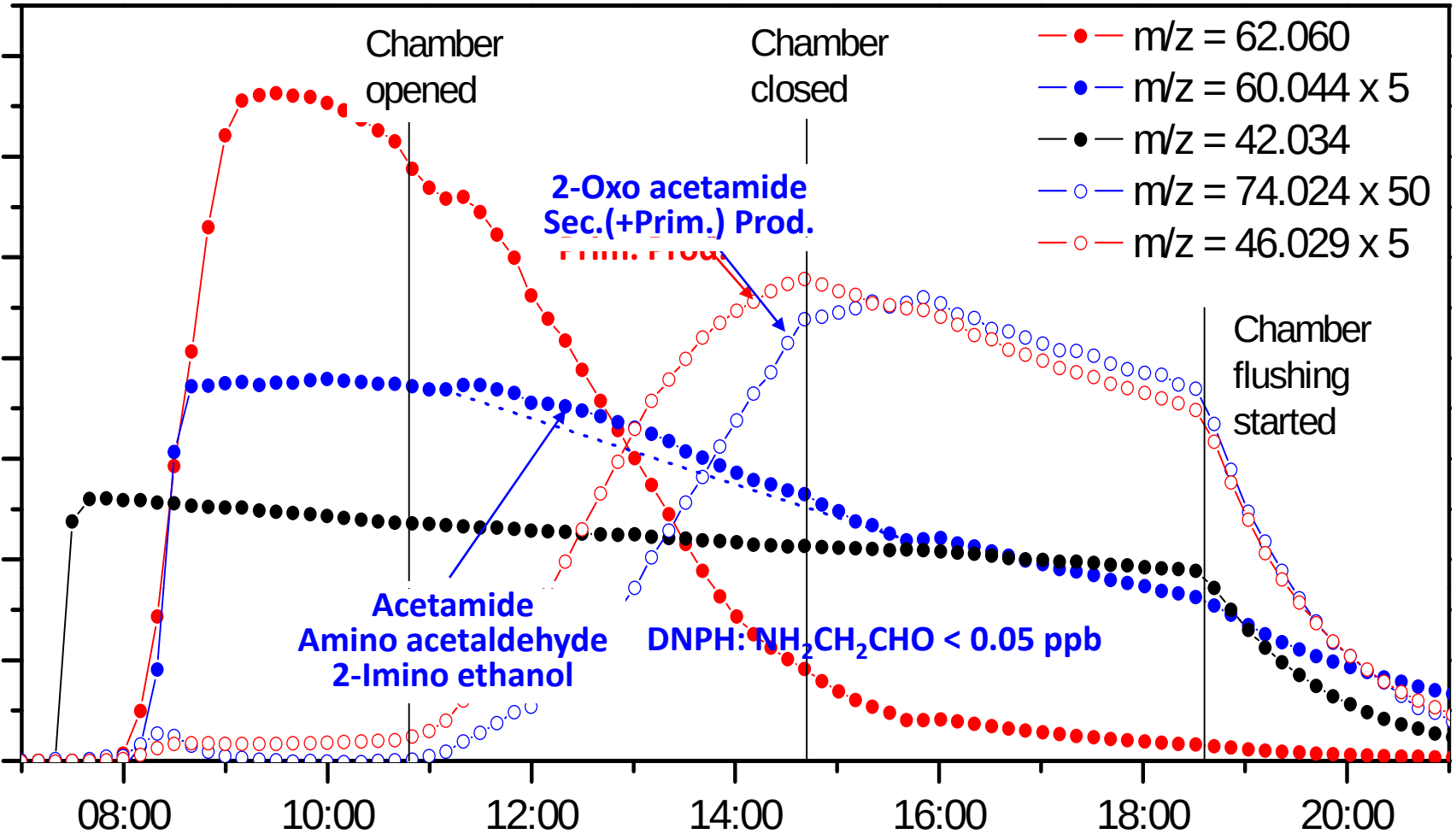
Gas phase chemistry
PTR-TOF-MS data series



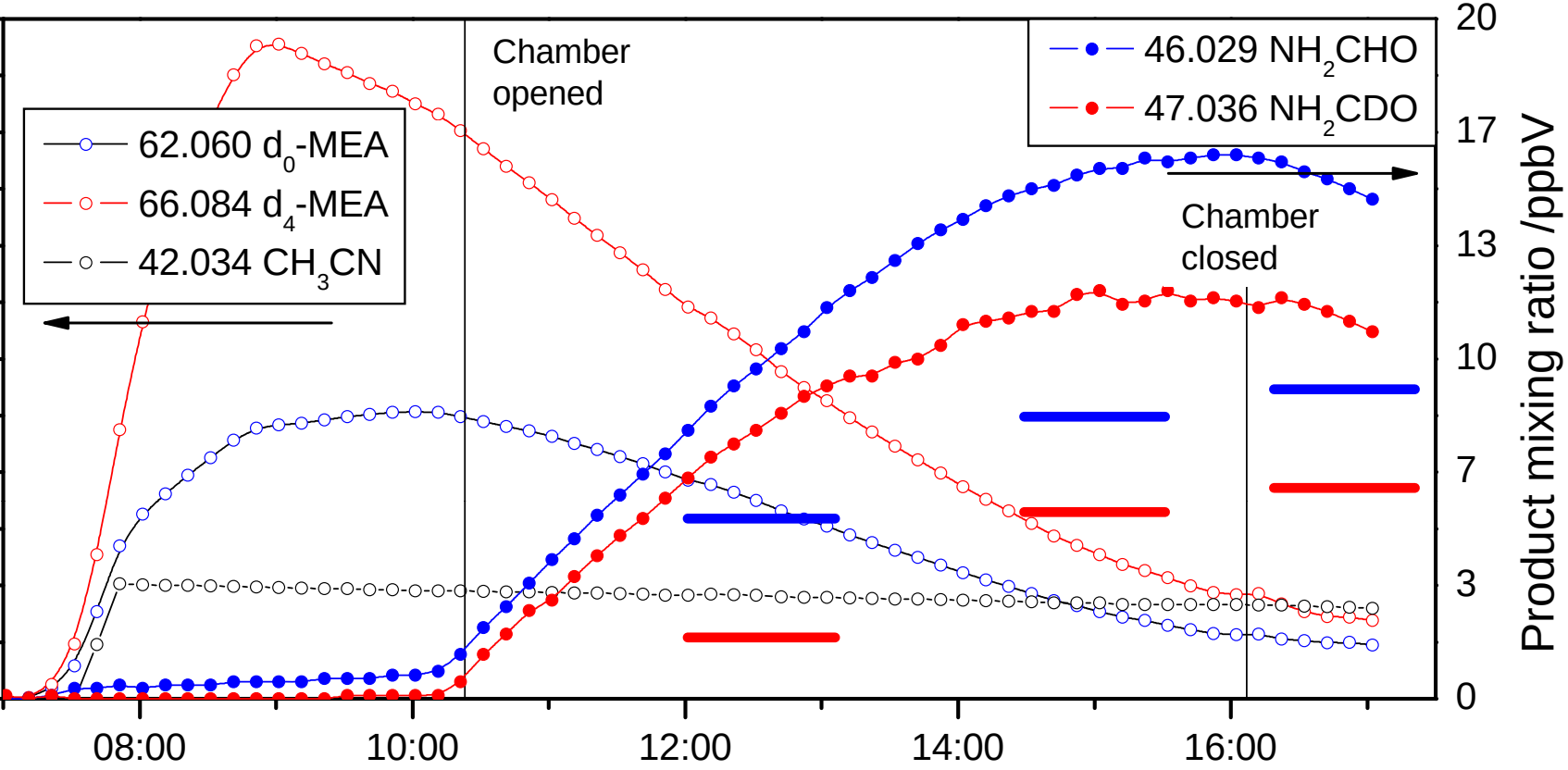
PTR-TOF-MS $\Delta_{\text{Ion Signals}}$



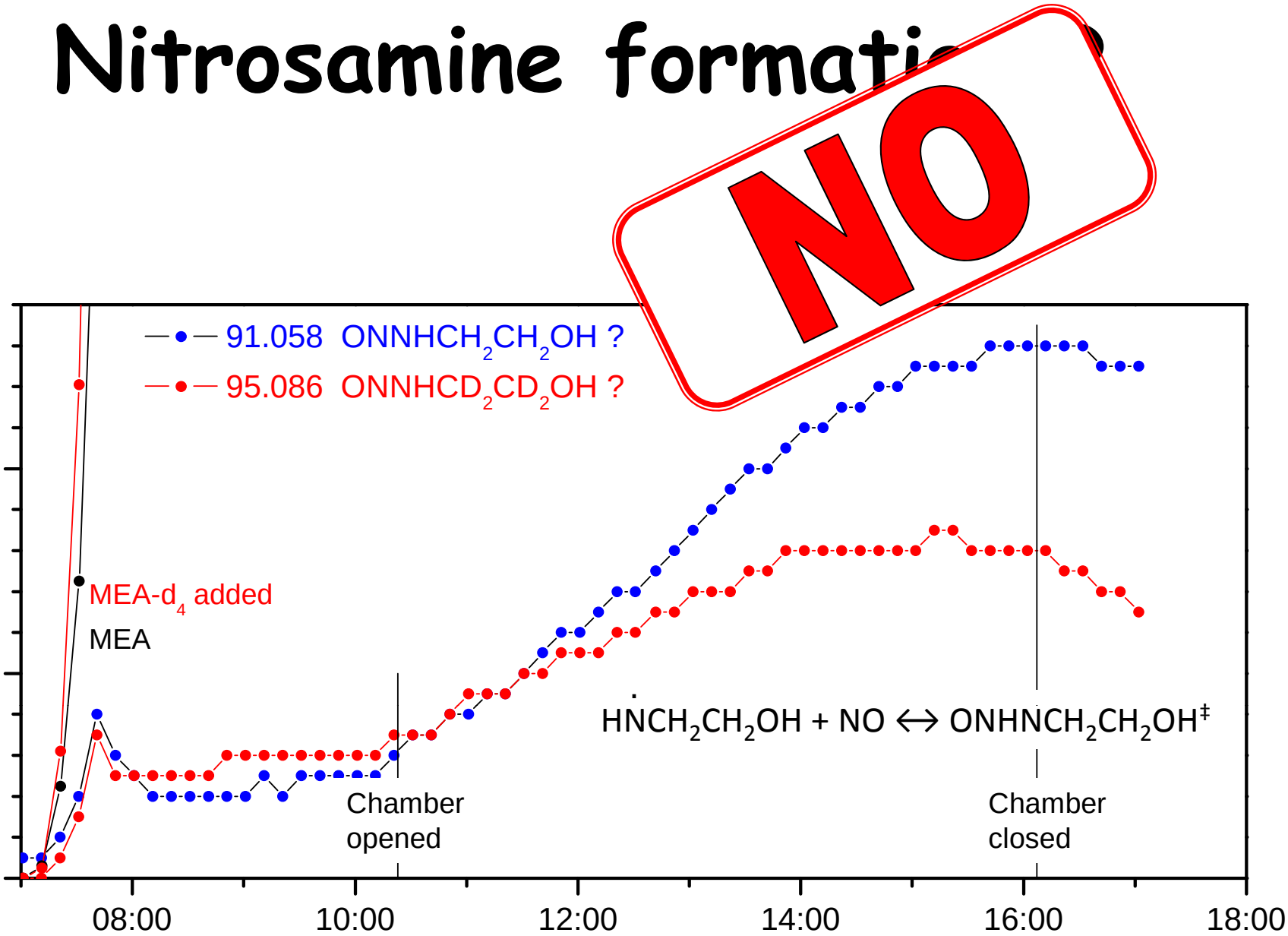
MEA → Products



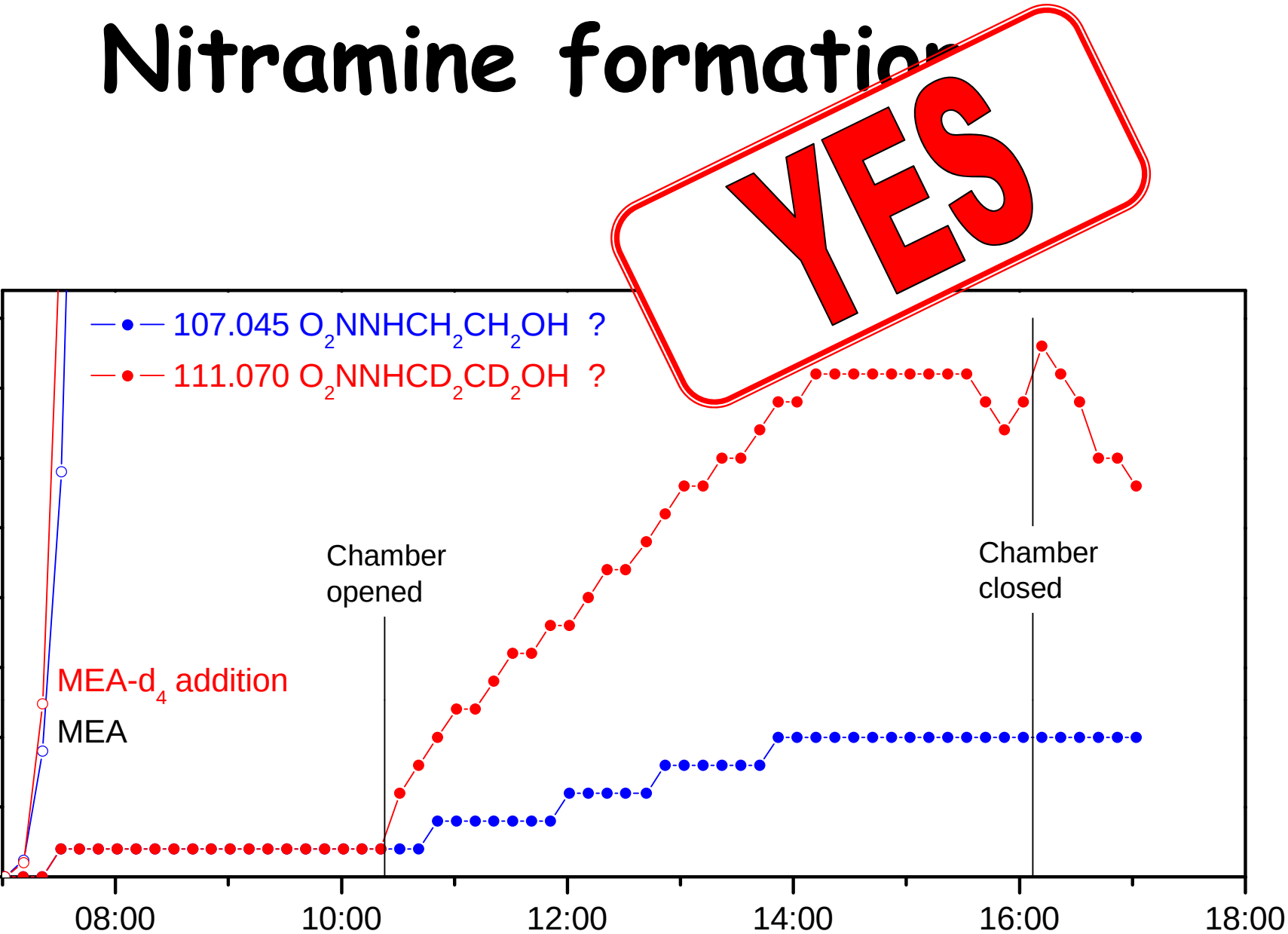
Isotope experiments & Kinetic isotope effects



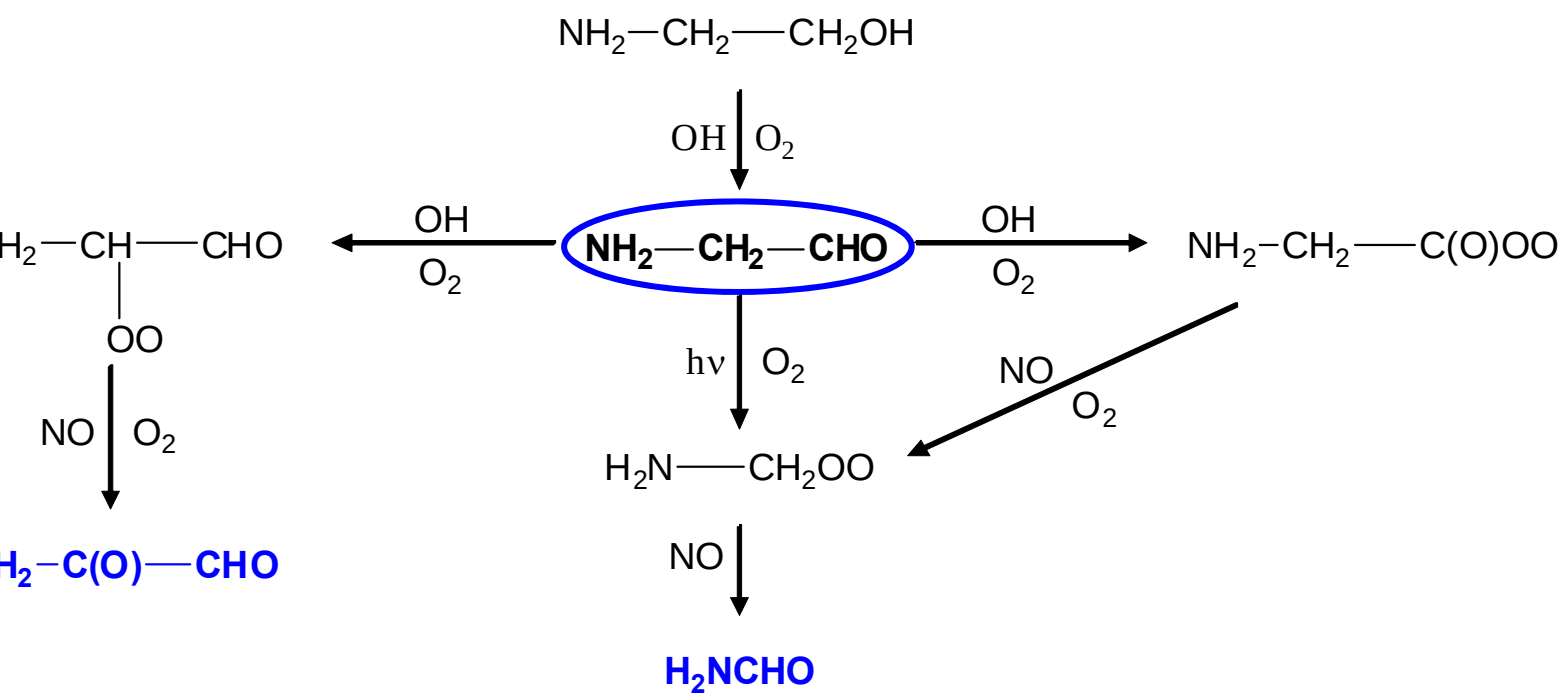
Nitrosamine formation



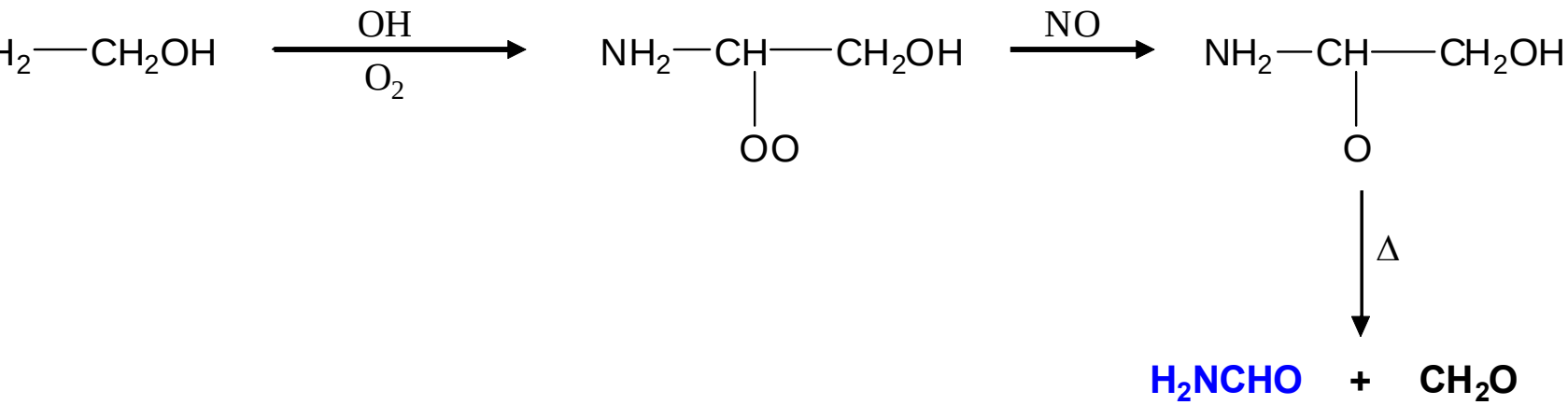
Nitramine formation



NH_2-CH_2-CH_2OH



NH_2-CH_2-CH_2OH

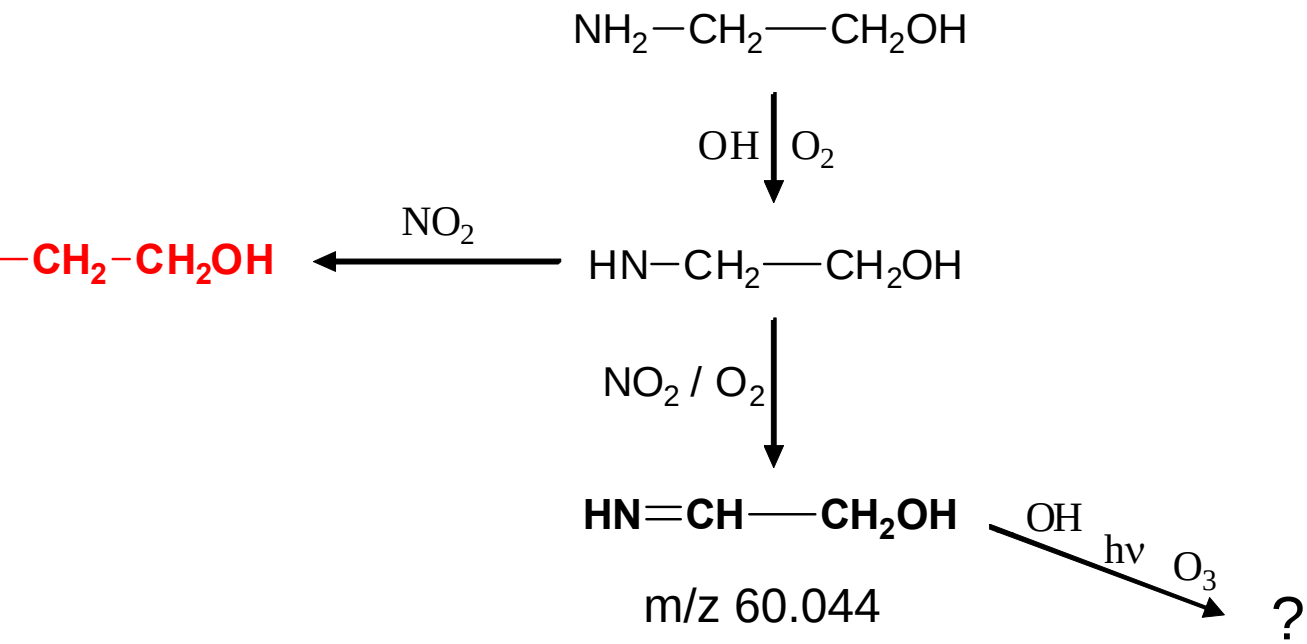


$\Delta_r H$ = -35 kJ mol^{-1}

↓

Fast unimolecular reaction

NH_2-CH_2-CH_2OH



Fate of $MEA_{(g)}$

$H_2N\text{-}CH_2\text{-}CH_2\text{-}OH$

ow much ?

$CHCH_2OH$

$OHCH_2NHNO_2$

w much do we
t of this one?

NH_2CHO

NH_2CH_2CHO
NH_2CHO
$NH_2C(O)CHO$

NOT "OK"

"OK"

"OK"

Branching Ratios from 4 Exp.

	$NH_2CH_2CH_2OH$	$NH_2CH_2CH_2OH$	$NH_2CH_2CH_2OH$	Nitramine
onditions	$(k_1 + k_2) / k_{tot}$	k_3 / k_{tot}	k_4 / k_{tot}	
' industrial area	0.08	0.80	0.12	1.3 %
on point, high NOx	0.05	0.87	0.08	1.5 %
on point, high NOx	0.06	0.83	0.07	0.6 %
rural area	0.12	0.83	0.05	0.3 %
ge	0.08 ± 0.03	0.84 ± 0.03	0.08 ± 0.03	

Conclusions

Based on the results from on-line and *in situ* instrumentation it is found that more than 80 % of the reaction between MEA and OH radicals takes place at $–CH_2–$, while less than 10 % occurs at $-NH_2$, and less than 10 % at $–CH_2OH$.

The major products (>80 %) in the photo-oxidation are formamide (NH_2CHO) and formaldehyde (CH_2O), of which the latter has a short atmospheric lifetime. Minor products (<10 %) are the short-lived amino acetaldehyde (NH_2CH_2CHO) and the longer lived 2-oxo acetamide ($NH_2C(O)CHO$).

The nitrosamine, **$ONNHCH_2CH_2OH$**, was NOT detected in any of the experiments

The nitramine, **$O_2NNHCH_2CH_2OH$**, was confirmed as product in the experiments. The yield depends upon the mixing ratio of NOx. For rural regions with NOx levels of 0.2-10 ppbV, less that 3 ‰ of emitted MEA will end up as the nitramine.

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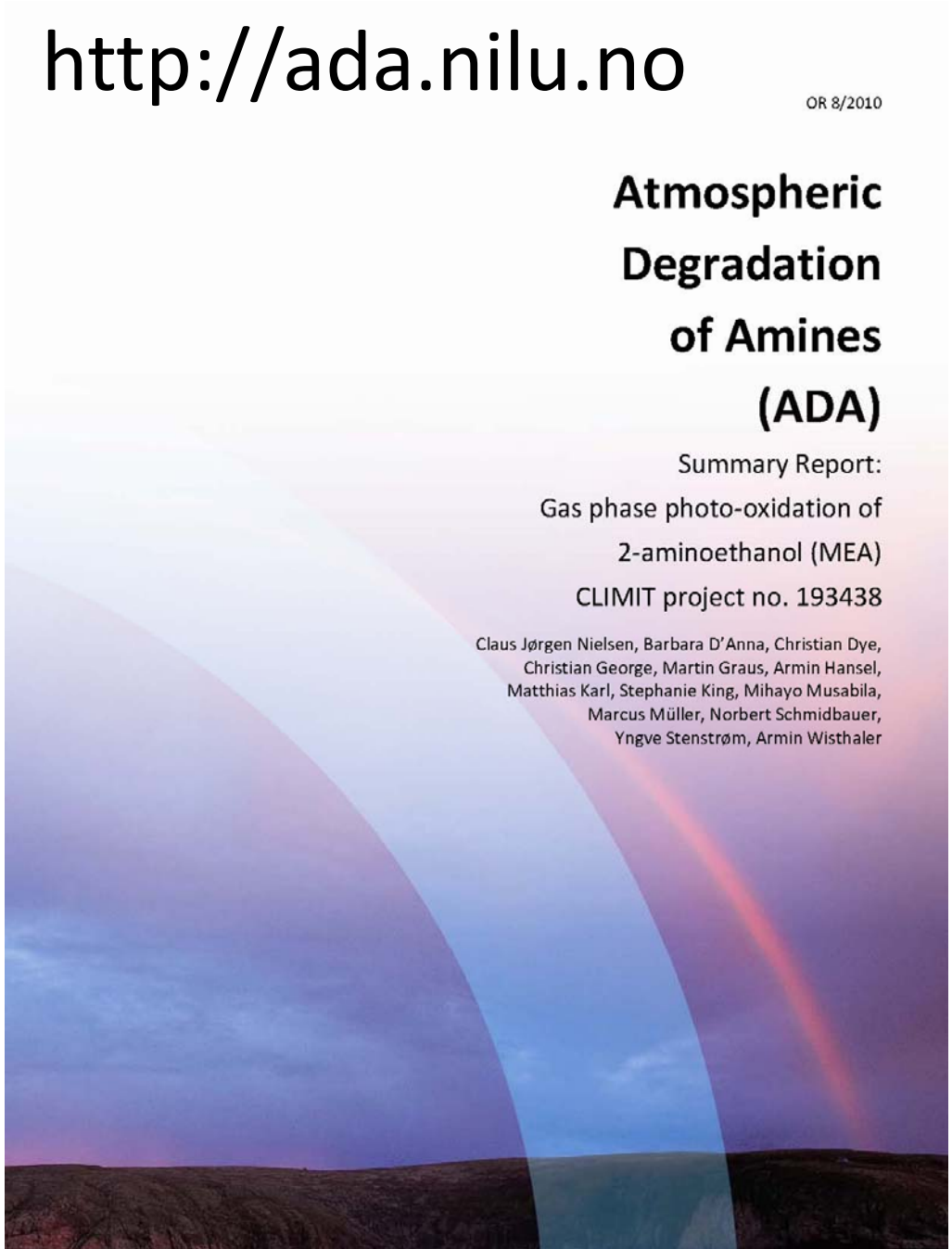
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