Study of the Nighttime Atmospheric Reactivity of Furan Compounds with NO_3 Radical in the Atmospheric Simulation Chamber "CHARME"

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Introduction and Objectives

- Biomass burning is the burning of dead or living vegetation which is a significant source of non-methane organic compounds (NMOCs) which will react with oxidants producing secondary organic aerosols (SOA) and ozone. However, biomass burning is an important alternative energy source *(Warneke et al., 2011; Bruns et al., 2017)*
- Recent studies have shown that furan compounds are an important family of NMOCs in biomass burning plumes released from cellulose and hemicellulose pyrolysis (Stockwell et al.,2015).
- The few studies on nighttime oxidation of furan compounds with NO_3 show that these processes are significant sinks for furan compounds *(Kind et al.,1996; Berndt et al.,1997; Cabañas et al., 2004)*
- **The objective of this research is to improve our understanding of furan compound reactivity with NO_3 radical: 1-Determination of the rate coefficient as function of temperature**
  2-Products characterization & quantification in gaseous and particulate phases (SOA formation)

Experimental Set up

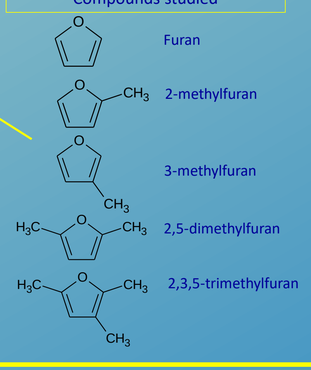
CHARME is an atmospheric simulation tool to reproduce atmospheric processes under controlled environmental conditions

Charme Characteristics
9.2 m³ , stainless steel, cylindrical
Room temperature (293 ± 2) K
Vacuum compatible
Mixing system (4 fans)
Variable RH (1-100%) Pressure (0.05-1100 mbar)

Analytical Instruments coupled to CHARME

Instrument	Species
PTR-TOF-MS, IONICON 1000	VOCs
GC-MS (Inficon Hapsite ER)	VOCs & SVOCs
LC/MS (ESI-LC-QToF-MS/MS - Agilent LC 1100 - MS 6540)	VOCs-SVOCs Particles
SMPS (DMA "TSI 3081",CPC "TSI 3775")	Particles

Compounds studied



Reactions leading to N_2O_5 production in the system:

$NO + ½ O_2 \rightarrow NO_2$
$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_3 + NO_2 \rightarrow N_2O_5$

NO_3 Introduction into chamber
$N_2O_5 \rightarrow NO_3 + NO_2$

N_2O_5 VOC

Synthesis of N_2O_5 : Precursor of NO_3

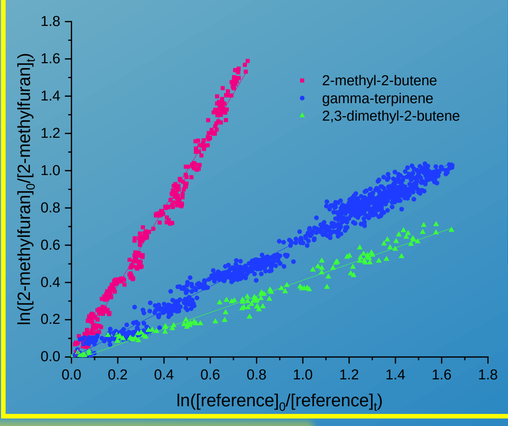
Results

Gas Phase Rate Coefficients

Experimental Procedure

- 2 or 3 references used for each tested compound
- 3 experiments were done per each reference (achieving repeatability)
- Concentrations of furan compound and reference ranged between 200 ppbv and 1200 ppbv (to assess no concentration effect)
- VOC concentrations monitored every 10 s using PTR-TOF-MS
- N2O5 added in concentration between 1 ppmv and 5 ppmv gradually

$$ln\frac{[Furan\ compound]_0}{[Furan\ compound]_t} = \frac{k_{furan}}{k_{reference}} \times ln\frac{[Reference\ compound]_0}{[Reference\ compound]_t}$$

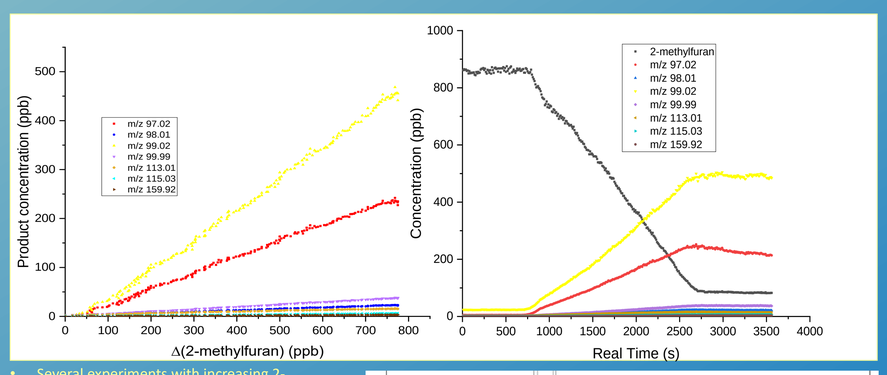


Compound	k × 10⁻¹¹ (cm³.molecule⁻¹. s⁻¹) (this study)	k × 10⁻¹¹ (cm³.molecule⁻¹. s⁻¹) (literature)	NO_3 Life time (min) * (this study)	OH Life time (min) (Kind et al., Chem. Phys. Lett., 1996)
Furan	0.15 ± 0.01	0.14 ± 0.02 (Atkinson et al., Environ. Sel. Techno., 1985) 0.13 ± 0.02 (Cabañas et al., J. Phys. Chem. , 2004) 0.10 ± 0.06 (Kind et al., Chem. Phys. Lett., 1996)	43.8	252
2-methylfuran	1.9 ± 0.1	2.57 ± 0.17 (Kind et al., Chem. Phys. Lett., 1996)	3.5	168
3-methylfuran	1.5 ± 0.1	2.86 ± 0.06 (Kind et al., Chem. Phys. Lett., 1996) 1.31 ± 0.46 (Alvarado *et al.*, Int. J. Chem. Kinet., 1996) 1.26 ± 0.18 (Tapia *et al.*, Atmos. Chem. Phys., 2011)	4.4	114
2,5-dimethylfuran	5.8 ± 0.3	5.78 ± 0.34 (Kind et al., Chem. Phys. Lett., 1996)	1.1	78
2,3,5-trimethylfuran	16.6 ± 1.1	-	0.4	-

- Rate coefficients determined for five furan compounds
- For methylated furan compounds, the rate coefficient increases by a factor of 3 with each additional methyl group.
- The lifetime of furan compounds studied due to reaction with NO_3 is in the order of minutes, and thus their nighttime degradation is a significant sink for this class of compounds.

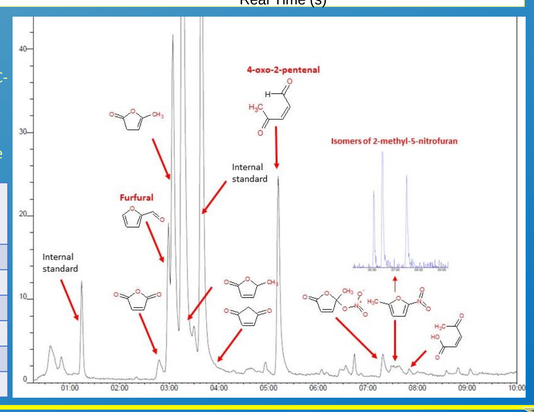
2-Methylfuran Oxidation

Gaseous Phase Oxidation Products

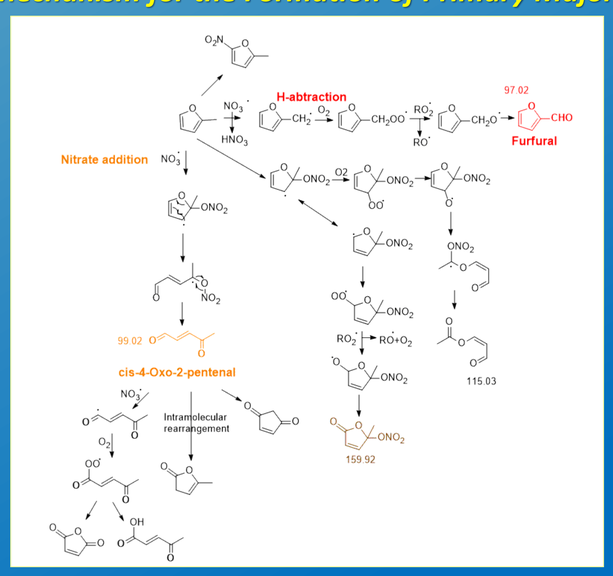


- Several experiments with increasing 2-methylfuran concentrations were done and concentrations followed on PTR-MS-TOF
- Samples of reaction mixture were analysed by GC-MS at different time intervals
- Two major primary gaseous compounds were identified: Furfural (H-abstraction) and cis-4-oxo-2-pentanal (NO_3 addition), the two products have slow reaction with NO_3

Experiment	[2-methylfuran] (ppbv)	Yield m/z 97.01 Furfural	Yield m/z 99.01 Cis-4-oxo-2-pentanal
1	315	0.31	0.51
2	660	0.34	0.67
3	860	0.32	0.56
4	1250	0.34	0.65
5	1500	0.32	0.69
Average yield		0.32 ± 0.02	0.62 ± 0.07

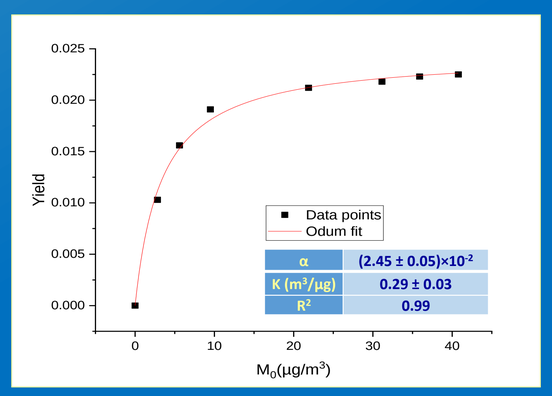


Mechanism for the Formation of Primary Major Products



- Both nitrate addition to C-2 and hydrogen abstraction from methyl group occur, but addition is more favored over abstraction (higher yield of cis-4-oxo-2-pentanal over furfural)
- Secondary products identified by GC-MS (like 2(3H)-Furanone,5-methyl-and cyclopentene-1,3-dione) can also be explained by intramolecular rearrangement or NO_3 oxidation of cis-4-oxo-2-pentenal.

SOA Formation Yield



α	(2.45 ± 0.05)×10⁻²
K (m³/µg)	0.29 ± 0.03
R²	0.99

- Seeds of ammonium sulfate of constant initial particle number ~1.6×10^4 particles.cm^{-3} were injected to enhance formation of SOAs
- A total of 9 experiments were carried out to measure yield of SOA formation at increasing concentration of 2-methylfuran

$$Y_{SOA} = M_0(\mu g/m^3) / \Delta HC\ (\mu g/m^3)$$

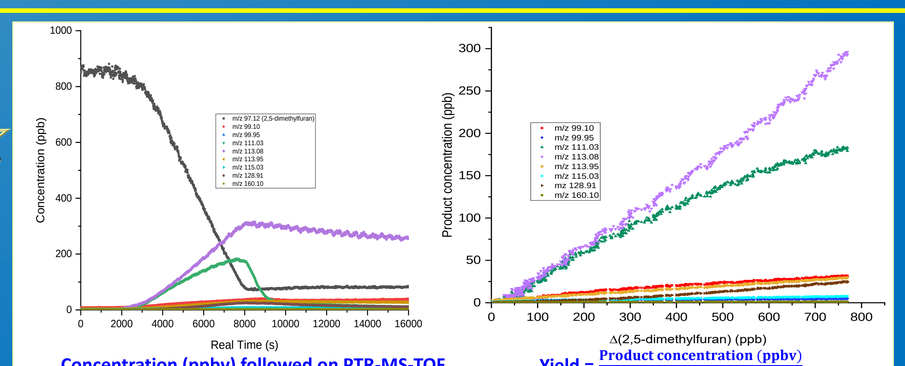
Aerosol mass concentration (M_0) → SMPS (µg/m³)
Reacted concentration of VOCs→ PTR-TOF-MS (µg/m³)

- Yield of SOA formation was fitted with mass concentration of SOA according to ODUM fit (Odum et al., 1996) using a one-product model

$$\text{Odum Fit}: Y_{SOA} = M_0 \sum \frac{\alpha K}{1+K.M_0}$$

α: mass-based stoichiometric coefficient of the oxidation product
K: gas-particle partitioning constant (m³ /µg)

2,5-Dimethylfuran Oxidation

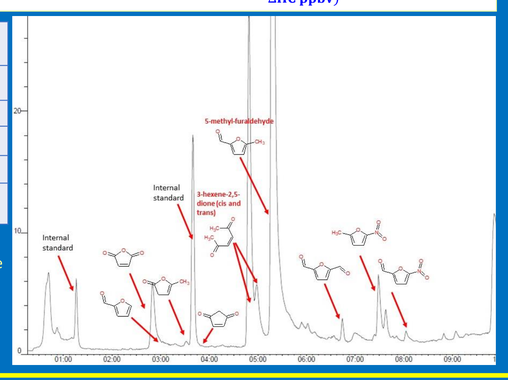


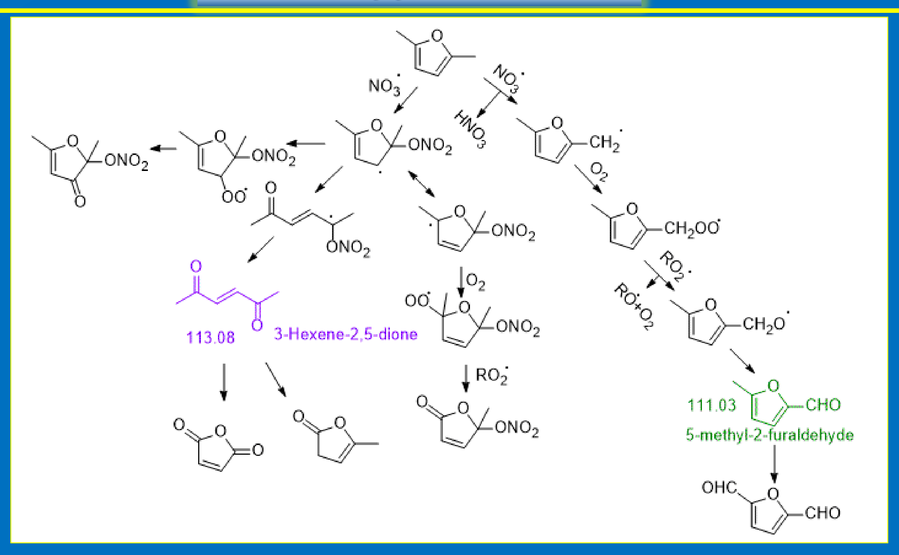
Concentration (ppbv) followed on PTR-MS-TOF

Yield = $\frac{\text{Product concentration (ppbv)}}{\Delta HC\ ppbv)}$

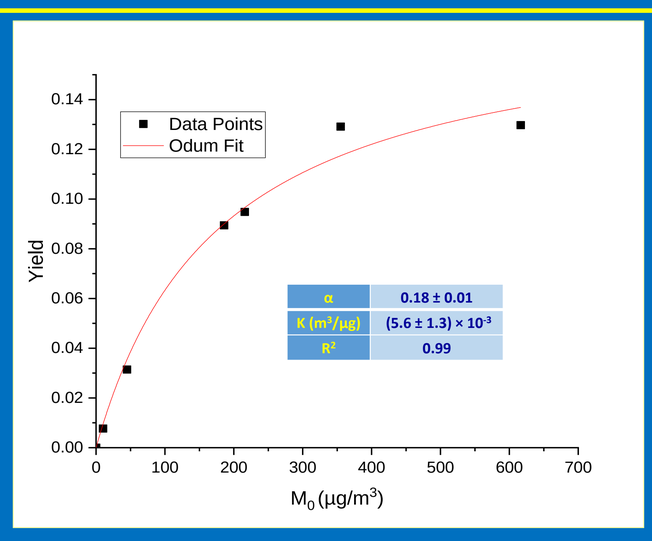
Experiment number	[2,5-dimethylfuran] (ppbv)	Yield m/z 111.06 5-methyl-2-furaldehyde	Yield m/z 113.08 3-hexane-2,5-dione
1	416	0.36	0.38
2	859	0.32	0.37
3	1300	0.35	0.39
4	1100	0.39	0.44
Average yield		0.36 ± 0.03	0.39 ± 0.03

The following chromatogram resembles the sample of the reaction mixture analysed by GC-MS at the end of the reaction



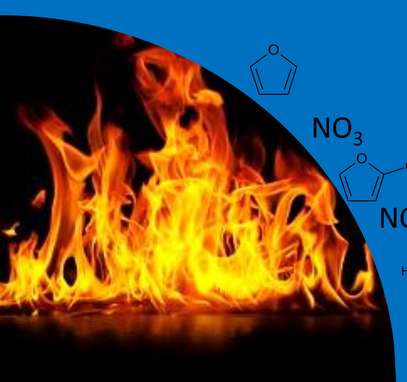


- Both nitrate addition to C-2/C-5 and hydrogen abstraction from methyl groups are favored in nearly equal percentages
- Two major primary products formed: 5-methyl-2-furaldehyde (H-abstraction) and 3-hexane-2,5-dione (NO_3 addition)
- One of the products formed (5-methyl-2-furaldehyde) undergoes fast reaction with NO_3 leading to its depletion and formation of secondary products.



α	0.18 ± 0.01
K (m³/µg)	(5.6 ± 1.3) × 10⁻³
R²	0.99

- A total of 6 experiments were carried out to measure yields of SOA formation yields at increasing concentration of 2,5-dimethylfuran.
- No seed needed.
- Higher yields of SOAs were formed from 2,5-dimethylfuran reaction with nitrate radical compared to those of 2-methylfuran.



Conclusion

- **Reaction with NO_3 is the dominant removal pathway of furan compounds during the night in the atmosphere (Lifetime = 0.4-44 min).**
- **The position of the methyl group on furan ring doesn't have an important effect on the rate coefficient of the reaction.**
- **Addition of a methyl group on furan ring plays an important role increasing the rate coefficient with the increase of methyl groups number.**
- **Both addition of nitrate radical to furan ring and hydrogen abstraction from methyl-group can occur for the reaction of methylated-furans with NO_3 radical**
- **These reactions produce SOAs thus affecting climate and human health. The increase of the methyl group number on furan ring enhances the yield of aerosol formation.**

Perspectives

- **Gaseous oxidation products will be characterized using LC-MS and GC-MS to enhance mechanism understanding.**
- **SOA chemical composition characterization.**
- **Kinetic and gaseous phase studies will be done as function of temperature using THALAMOS chamber in IMT Nord Europe.**

References

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