In-situ monitoring of atmospheric degradation product studies of aromatic hydrocarbons with CAPI- and APLI-MS

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Introduction

Overview:

General procedure for photochemical degradation experiments:

1) The compound of interest and the photo labile precursor for the formation of OH radicals are inserted into a UV/VIS transparent chamber and backfilled with synthetic air.
2) Initiation of the experiment by the exposure to visible/near-UV light.
3) Investigation of reactant degradation and product formation.

Challenge:

Formation of diverse degradation products in mixing ratios down to the sub-ppbV as well as in the ppmV range (NO_x, HNO_x) requires the application of sophisticated analytical methods and tools. Care has to be taken regarding the impact of superimposed ion chemistry when analyzing unknown compositions with API MS.

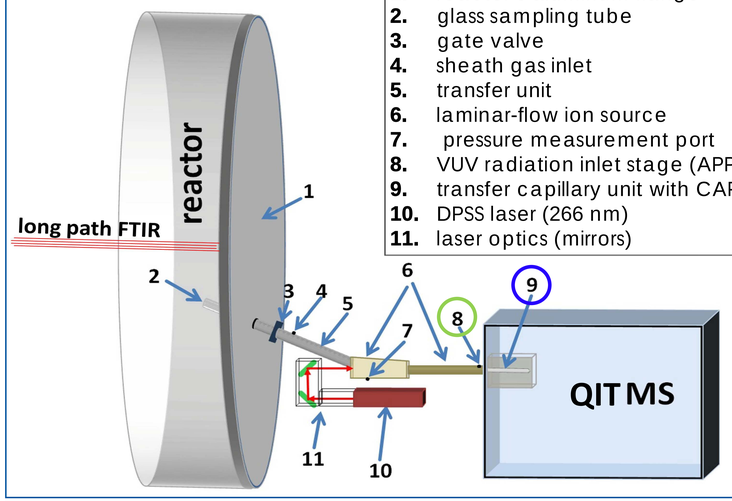
Approach:

Multidimensional analytical setup with Atmospheric Pressure Laser Ionization(APLI)/Capillary Photo Ionization(CAPI) MS and Fourier Transform Infrared (FTIR) spectrometry. Mechanistic conclusions are derived from all the available analytical information.

Methods

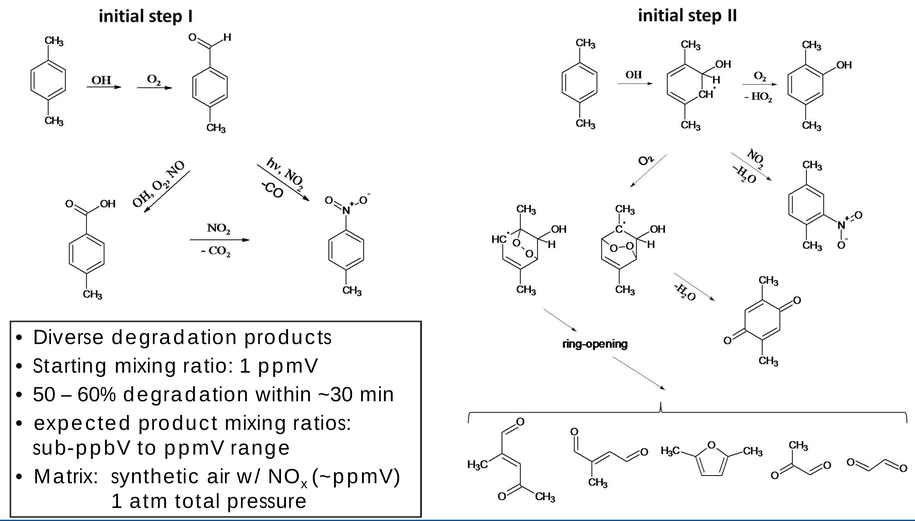
MS	Bruker esquire6000 quadrupole ion trap equipped with a home-built laminar flow ion sources (LFIS) for gas phase sample introduction.
Ionization sources	Home-built argon spark discharge lamps and DPSS Laser 266 nm (FQSS 266-50, CryLas, Berlin, Germany)
FT-IR	Long path FT-IR with 484.7 m path length (Nexus, Thermo Nicolet Corp., Madison, WI, USA)
Degradation experiments	Large Volume photoreactor (1080 L) for gas phase degradation studies of atmospherically relevant compounds with OH radicals
Chemicals	P-xylene, MeONO, NO

Experimental Setup



1. reactor's aluminum flange
2. glass sampling tube
3. gate valve
4. sheath gas inlet
5. transfer unit
6. laminar-flow ion source
7. pressure measurement port
8. VUV radiation inlet stage (APPI)
9. transfer capillary unit with CAPI
10. DPSS laser (266 nm)
11. laser optics (mirrors)

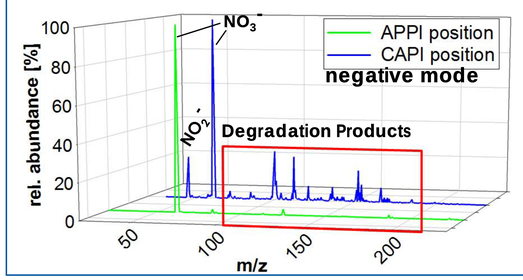
p-xylene Degradation Pathways (excerpt)



- Diverse degradation products
- Starting mixing ratio: 1 ppmV
- 50 – 60% degradation within ~30 min
- expected product mixing ratios: sub-ppbV to ppmV range
- Matrix: synthetic air w/ NO_x (~ppmV) 1 atm total pressure

Challenge for MS Investigations @ 1 atm: Ion Transformation Processes

Same sample composition, two different ionization positions



Degradation in the presence of NO_x:

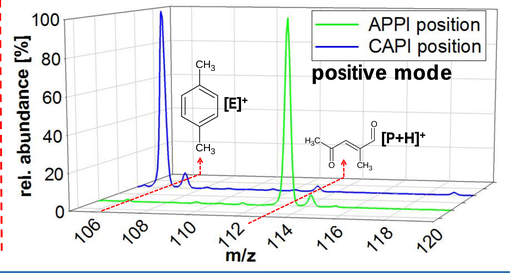
$NO + OH + M \longrightarrow HNO_2 + M$

$NO_2 + OH + M \longrightarrow HNO_3 + M$

APPI position: High gas phase acidity of HNO_3 leads to complete loss of MS information due to generation of a *thermodynamically controlled ion distribution.*

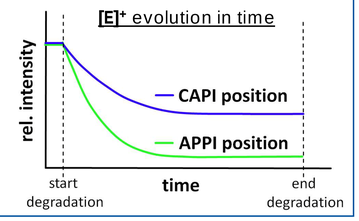
CAPI position: Preservation of MS information due to generation of a *kinetically controlled ion distribution.*

One degradation sample, two different ionization positions

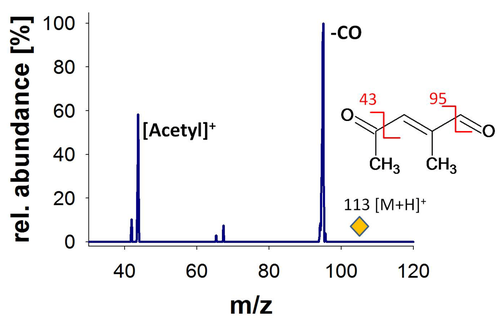


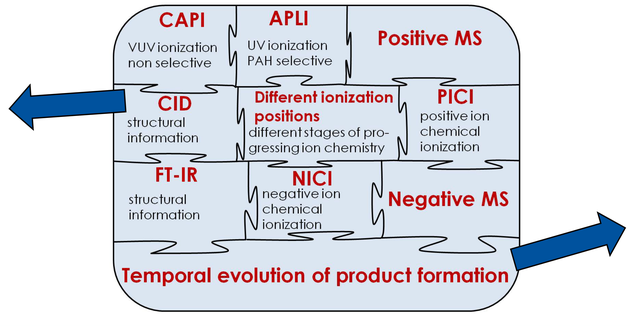
Proton donor characteristics of ionized p-xylene:

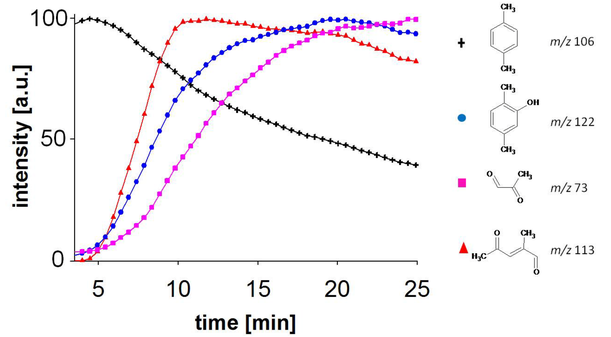
$[E]^+ + P \longrightarrow E\text{-}H + [P+H]^+$



Pool of Available Analytical Information







Conclusions

- **A multidimensional analytical setup was establshed for *in-situ* monitoring of degradation studies in particular aromatic hydrocarbons**

→ **APLI** selective and sensitive for ring retaining products

→ **CAPI** non-selective and sensitive

→ **PICI** information on gas phase basicity

→ **NICI** e.g., nitro-group containing compounds are amenable; information on electron affinity or gas phase acidity

→ **Different ionization positions** comparison of differently progressed ion chemistry yields information on chemical reactivity of species; preservation of MS information

→ **Temporal evolution of product formation** time resolution below 1s, with limits of detection in the lower ppbV range for CAPI and pptV range for APLI; positive and negative mode

→ **CID** structural information

→ **FT-IR** structural information; partial quantification, but low sensitivity

- **Several degradation studies were successfully performed**

Literature

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3) Kersten, H. *Development of an Atmospheric Pressure Ionization source for in situ monitoring of degradation products of atmospherically relevant volatile organic compounds*, Dissertation, Bergische Universität Wuppertal, Wuppertal, **2011**; urn:nbn:de:hbz:468-20110418-092806-6

4) Kersten, H.; Derpmann V.; Barnes, I.; Brockmann, K. J.; Benter, T.; O´Brien, R. *A novel APPI-MS setup for in situ degradation product studies of atmospherically relevant compounds: Capillary Atmospheric Pressure Photo Ionization (CAPI)*, to be published **2011**.

Acknowledgement

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