Formation of highly oxidized multifunctional compounds in alkane autoxidation: relevance to atmospheric and combustion chemistry

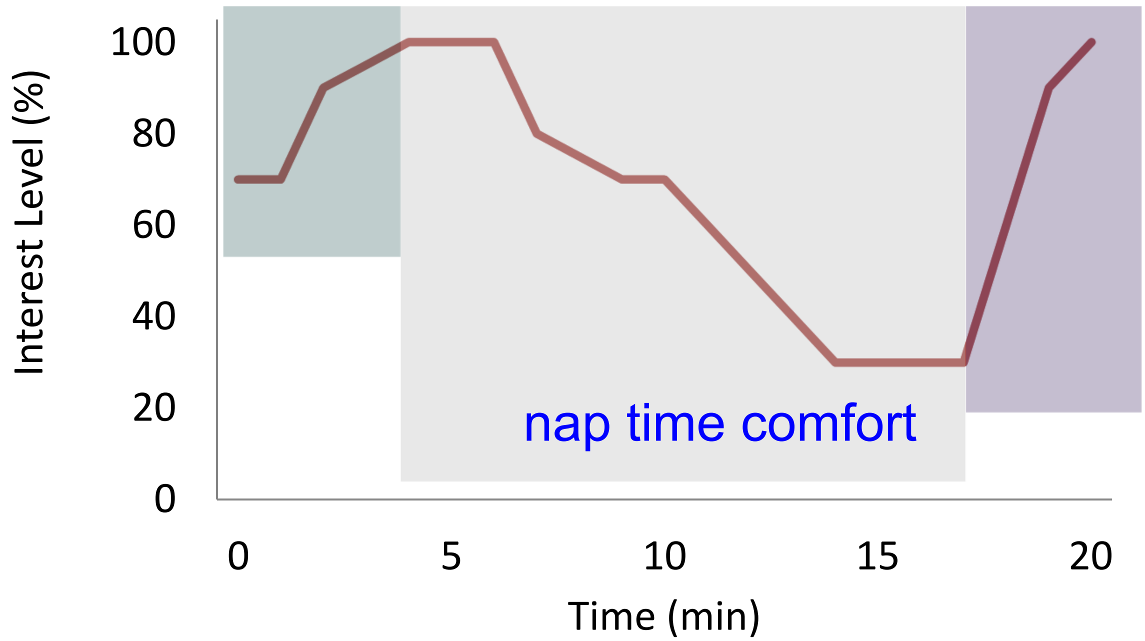
Mani Sarathy[1], Zhandong Wang[1], Matti P Rissanen[2], Mikael Ehn[2]

1 Clean Combustion Research Center, KAUST
2 University of Helskinki (INAR)

Presentation Outline/Timeline

- Introduction
- Auto-oxidation
  - Background
  - Combustion
  - Atmosphere
- Questions

Simulated Attention Span
P=1 atm, T=298 K, τ=1800 s



سكاكا
Sakaka
رفحاء
Rafha
الكويت
Kuwait
شيراز
Shiraz
Eilat
محمية الطبيق
تبوك
Tabuk
حفر الباطن
Hafar Al Batin
شرم الشيخ
Sharm
El-Sheikh
حائل
Hail
الغردقة
Hurghada
الجبيل
Al Jubail
Persian Gulf
بندر عباس
Bandar Abbas
سوهاج
Sohag
بريدة
Buraydah
الزلفي
Az Zulfi
كيش
Kish
البحرين
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Ar Rass
رأس الخيمة
Ras Al-Khaimah
دبي
Dubai
مرسى علم
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المدينة المنورة
Medina
الدوادمي
Al Duwadimi
الرياض
Riyadh
أسوان
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ينبع
Yanbu
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عفيف
Afif
الإمارات
العربية
المتحدة
United Arab
Emirates
العين
Al Ain
السعودية
Saudi Arabia
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عمان
Oman
الباحة
Al Bahah
بيشة
Bishah
Red Sea
بورتسودان
Port Sudan
خميس مشيط
Khamis
Mushait
أبها
Abha
الدامر
Ad-Damar
شرورة
Sharorah
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KAUST Quick Facts

940
Students

150
Faculty

400
Postdocs

310
Research Scientists /Staff

6700
Community members

2200
Workforce

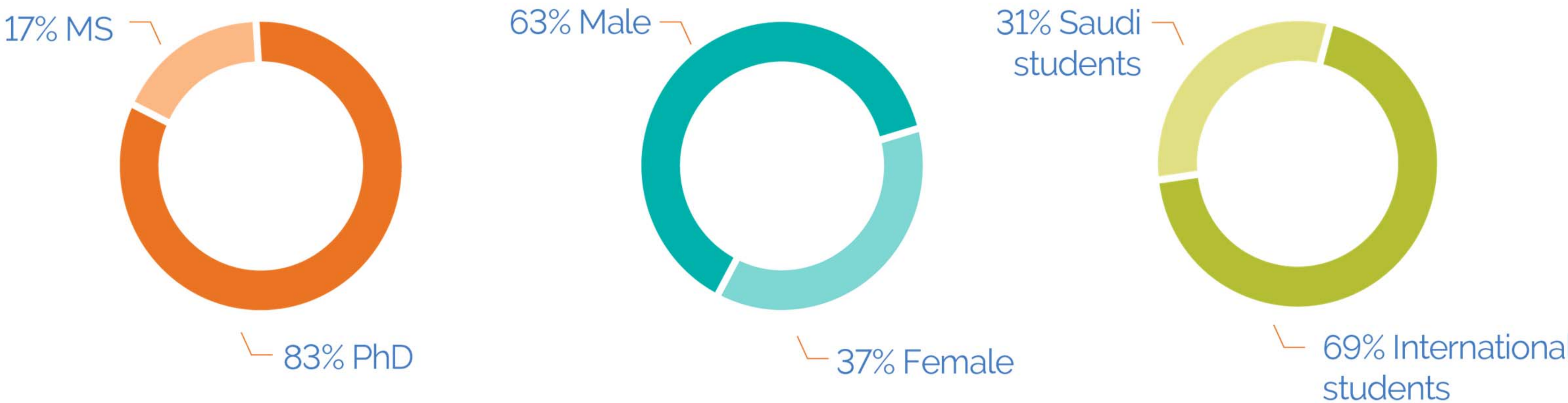
1460
School children

100
Community

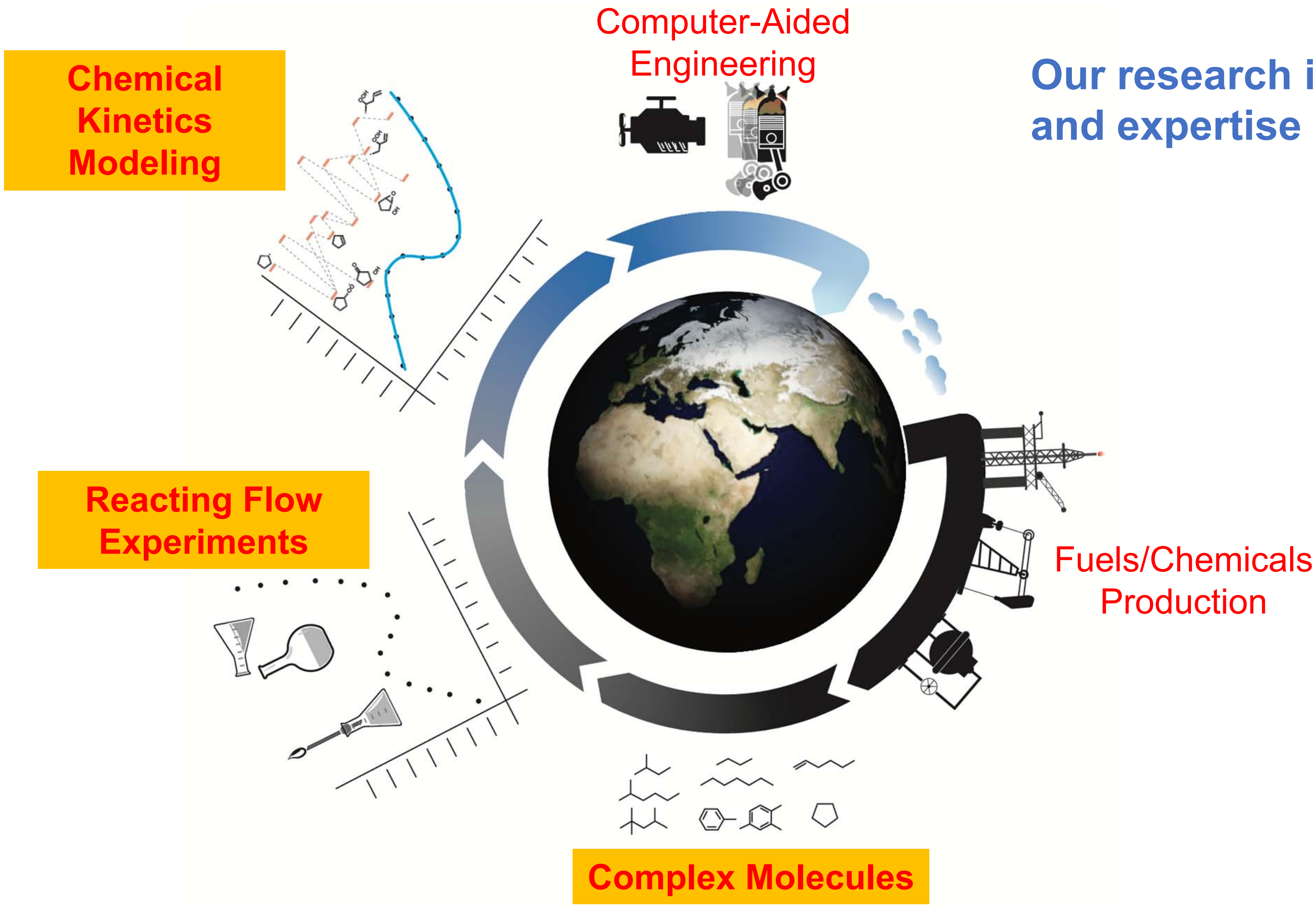
80
Workforce

Nationalities

KAUST Current Student Body

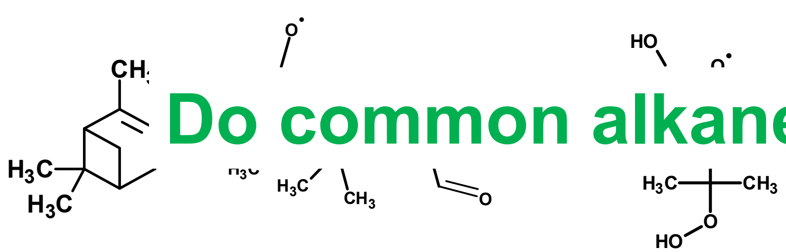


Our research interests and expertise

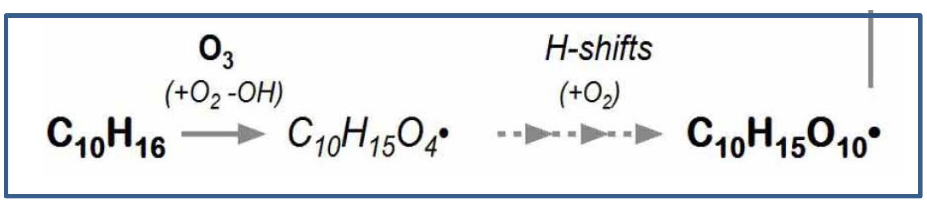


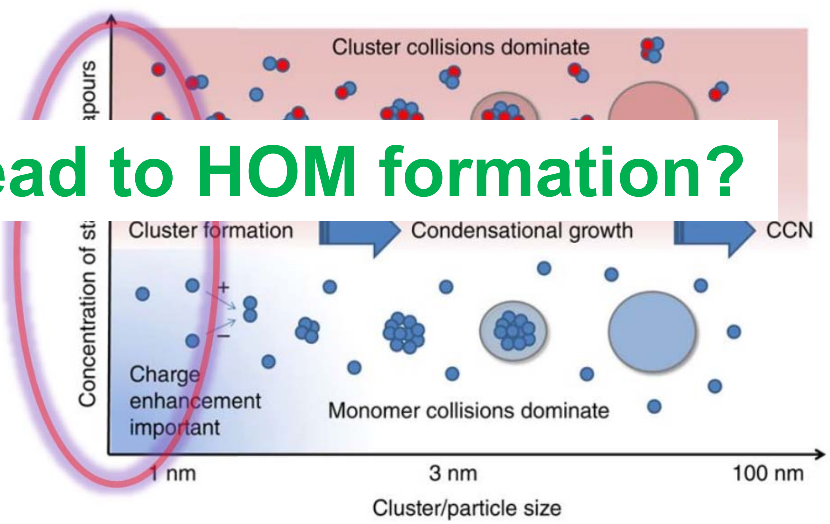
Auto-oxidation is important in atmospheric and combustion systems

- **Gas-phase autoxidation** is a pseudo-unimolecular fast lane to molecular growth and reduction in vapor pressure
- Results in **low volatile HOM** (=*highly oxidized multifunctional compounds*)
- Condensable **low volatile vapors form SOA** (=*secondary organic aerosol*)
- **HOMs lead to auto-ignition** in combustion engines



Do common alkanes also lead to HOM formation?





From: Lehtipalo, K. et al. Nature Comm. 2016

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للعلوم والتقنية
King Abdullah University of Science and Technology
Clean Combustion Research Center

Zhandong Wang, Sarathy

BERKELEY LAB

Popolan-Vaida, Leone

cnrs advancing the frontiers

Dagaut

Sandia National Laboratories

Hansen, Taatjes

Universität Bielefeld

Kohse-Höinghaus

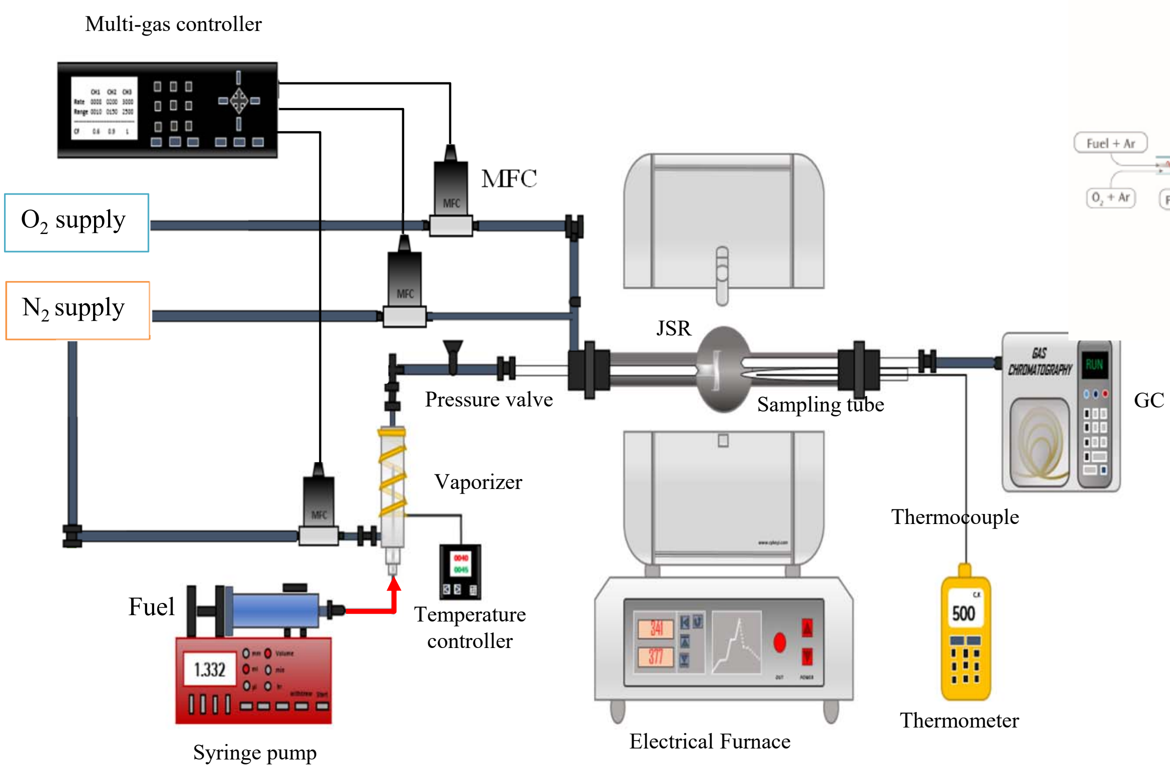
PTB
Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin

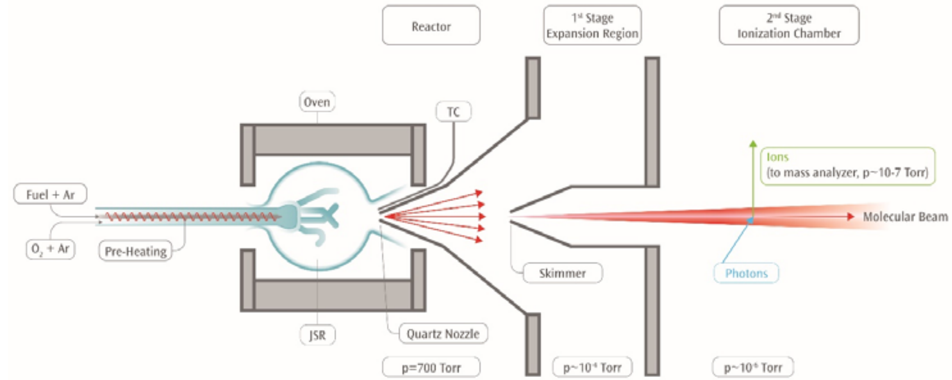
Moshammer

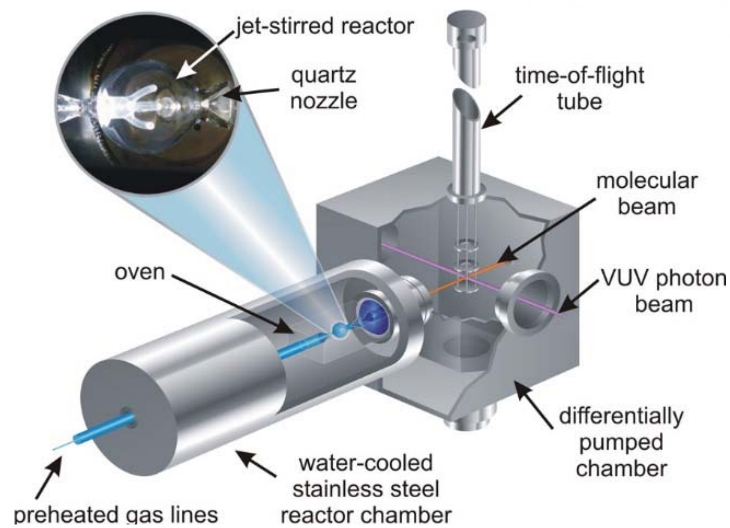
COMBUSTION

High fidelity experiments to explore auto-oxidation chemistry

- Jet-Stirred Reactor-Synchrotron Radiation Photoionization Mass Spectrometry

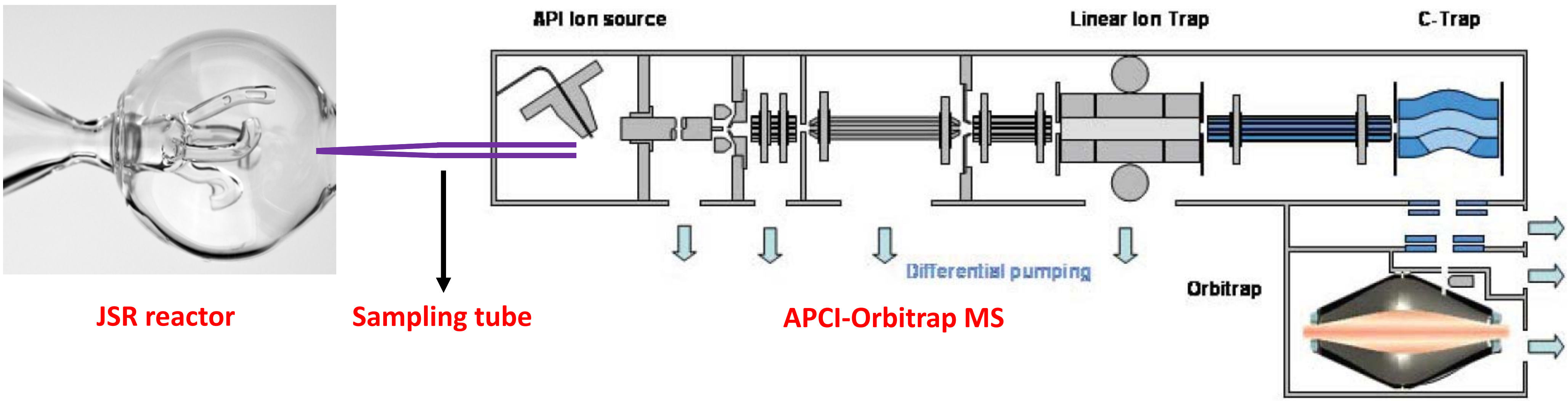






High fidelity experiments to explore auto-oxidation chemistry

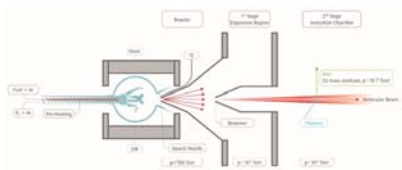
- JSR-APCI-Orbitrap mass spectrometer analysis, KAUST
  - ✓ Atmospheric pressure chemical ionization (APCI), soft ionization, mono-charged ions, proton transfer (M+1)
  - ✓ High mass resolution: 100000 to 200000 and Ultra-high detection limit: 1 ppt

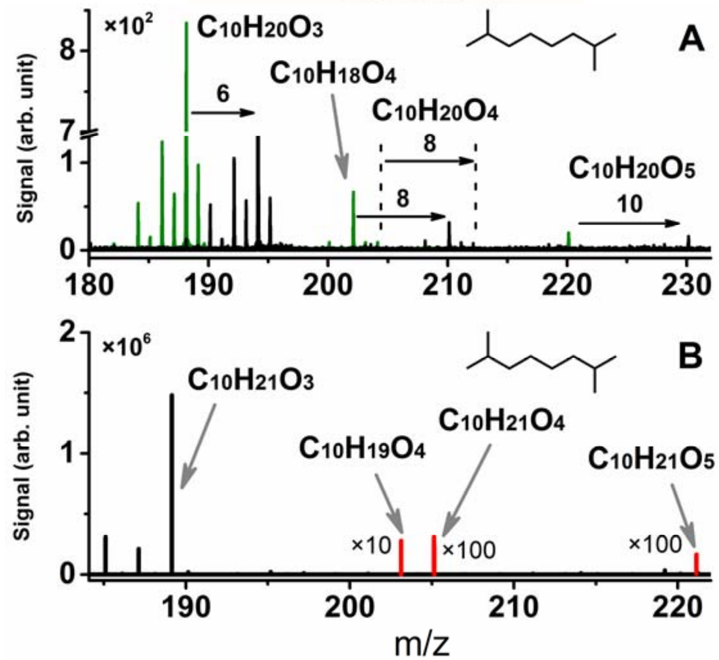


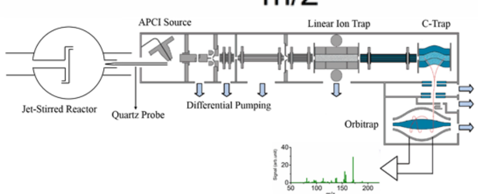
Wang et al., Combust Flame, 2017

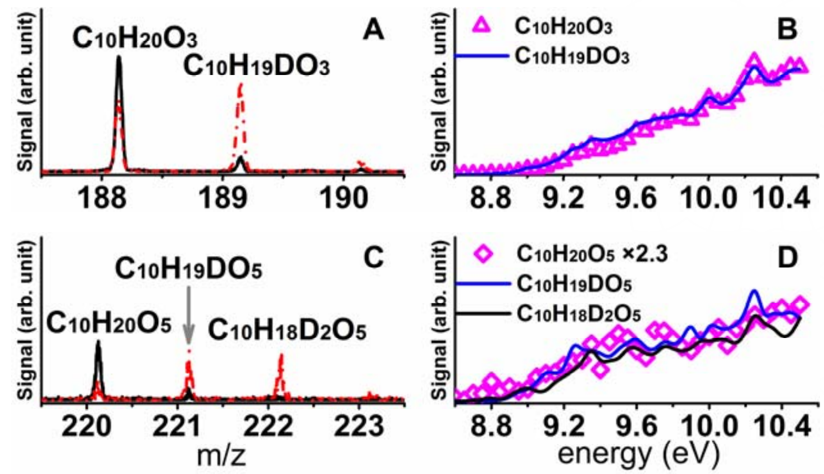
Auto-oxidation intermediates under combustion conditions

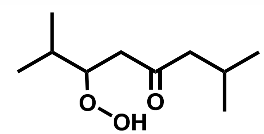
T= 520 K
P= 1 atm
τ= 2 s



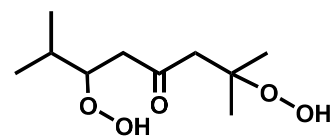








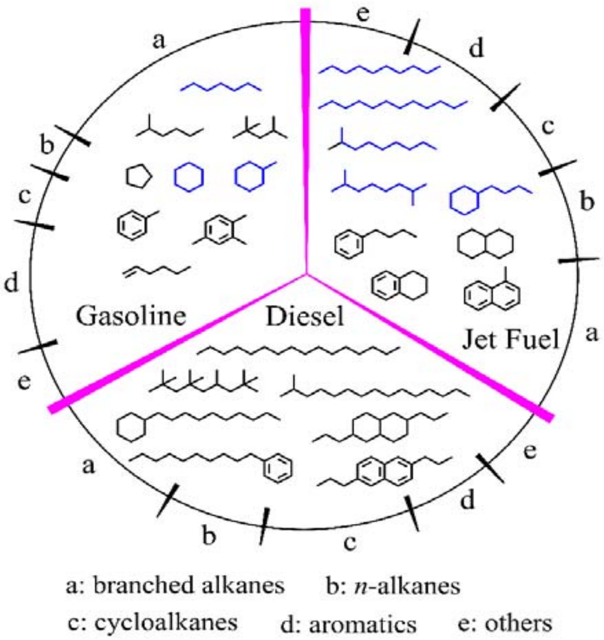
O_3 species has one –OOH



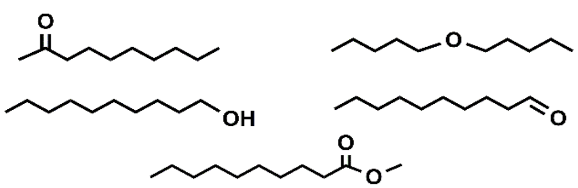
O_5 species has two –OOHs

Wang et al. PNAS (2017), 114, 13102

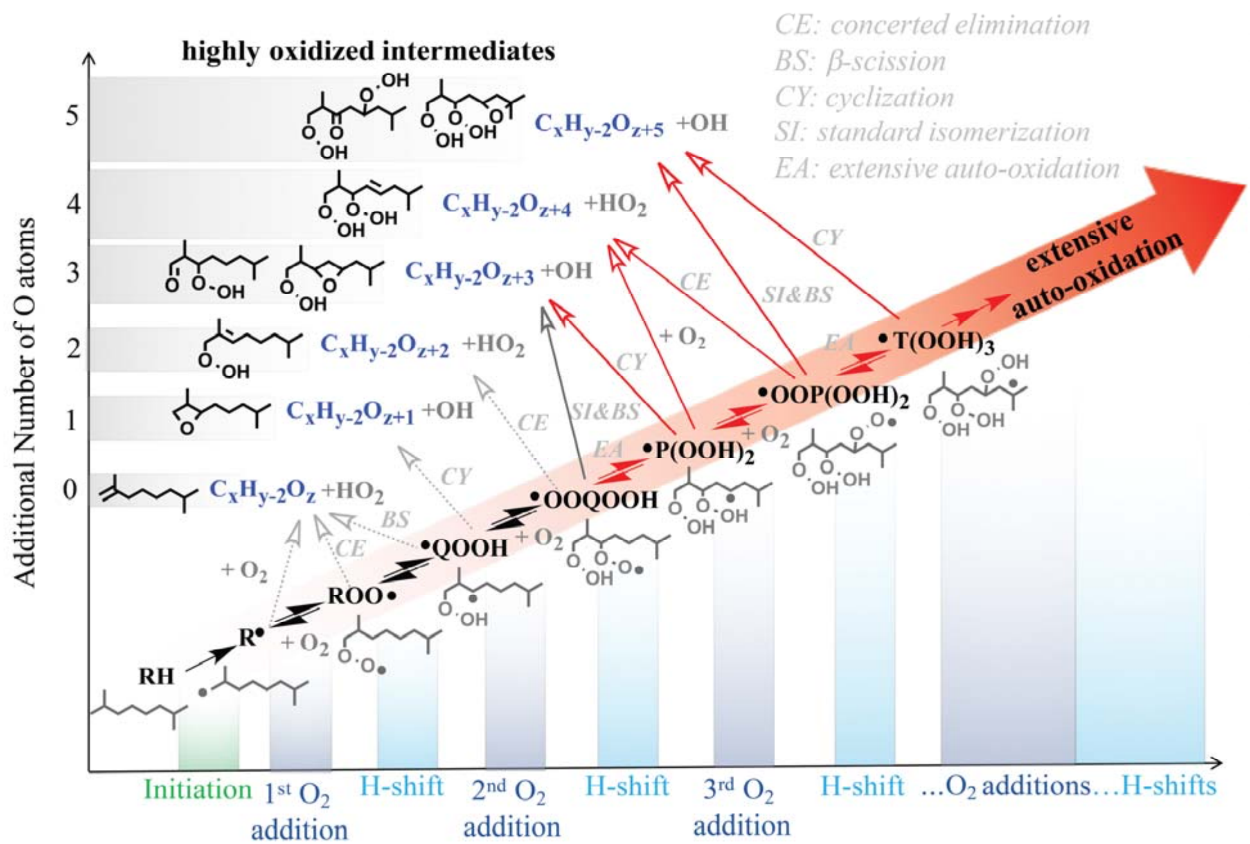
Multiple O_2 addition auto-oxidation scheme



Eight hydrocarbons



Five oxygenates

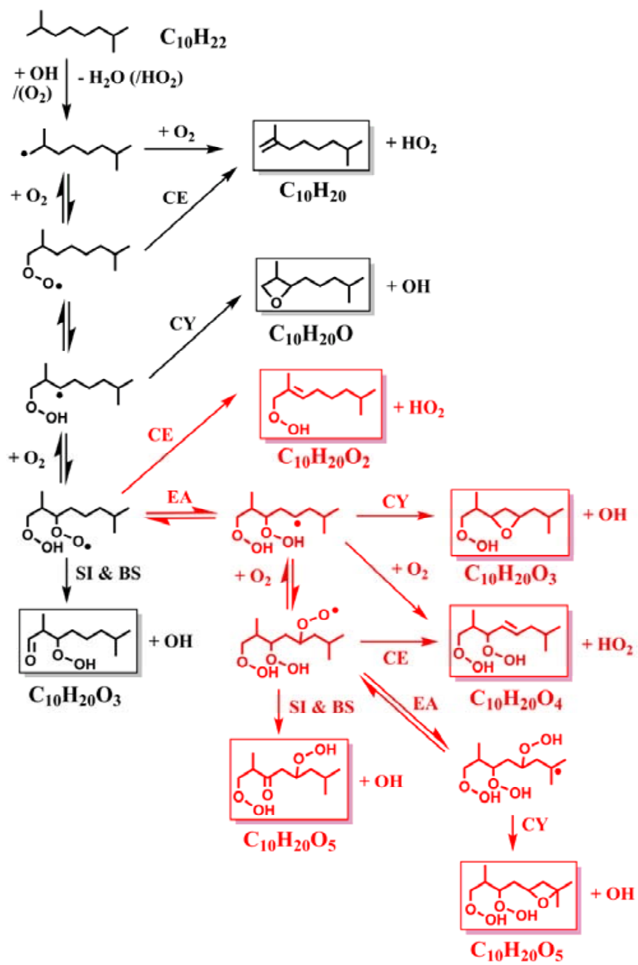


Organic compounds autoxidation scheme

Wang et al. PNAS (2017), 114, 13102

3^{rd} O_2 addition auto-oxidation scheme

OOQOOH



2,7-dimethyloctane autoxidation

OOQOOH radicals

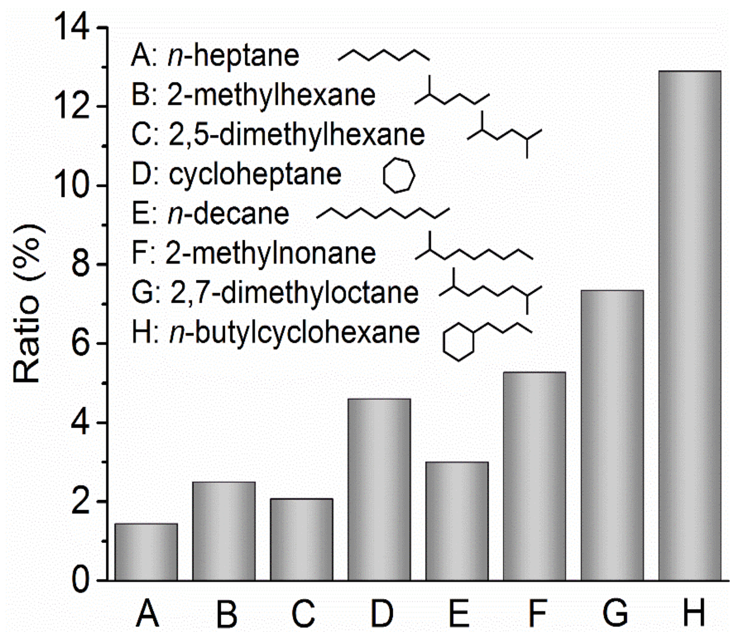
2^{nd} O_2 addition: intramolecular H-atom abstraction of the C-H alpha to the -OOH group

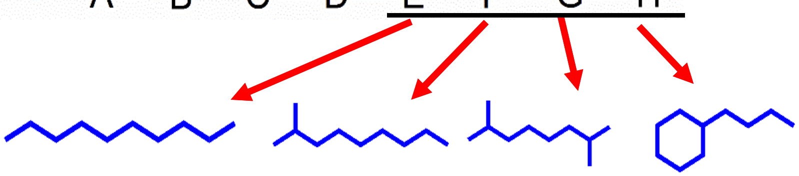
3^{rd} O_2 addition: intramolecular H-atom abstraction of the C-H not alpha to the -OOH group

Wang et al. PNAS (2017), 114, 13102

Auto-oxidation is structure dependent

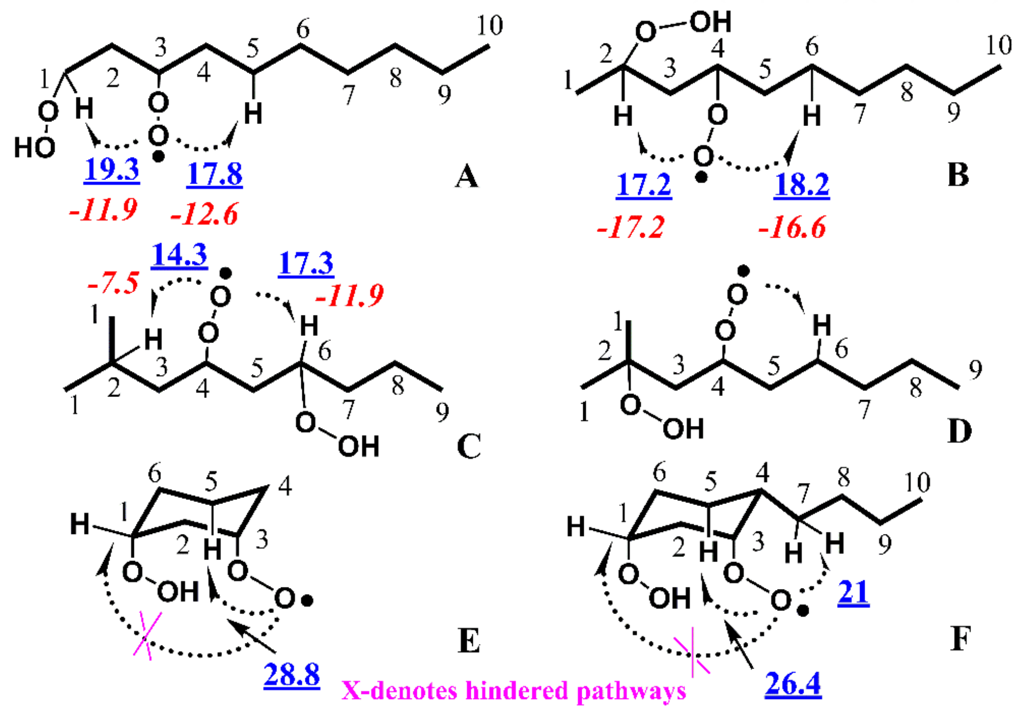
3rd O_2 addition autoxidation tendency





Relative ratios of $C_xH_{y-2}O_5$ to $C_xH_{y-2}O_3$ in eight hydrocarbon autoxidation reactions

α,γ-OOQOOH intramolecular H-abstraction

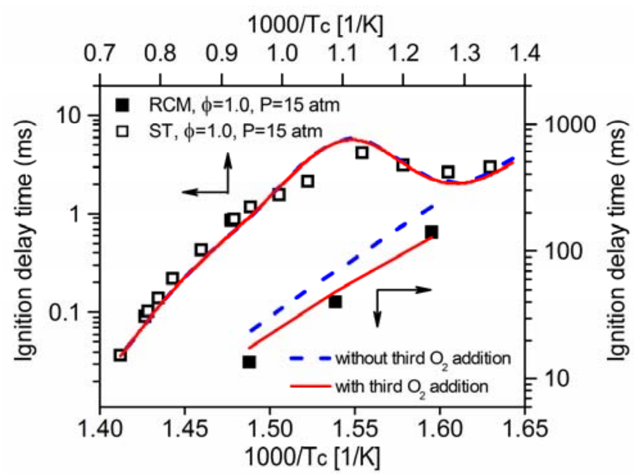


Blue underlined numbers denote activation energy, unit is kcal/mol; red italicized numbers denote entropy change, unit is cal/mol/K.

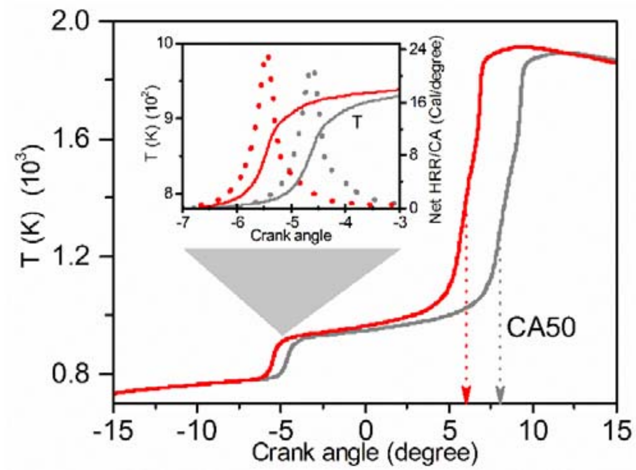
Wang et al. PNAS (2017), 114, 13102

Multiple O_2 additions promote ignition

- Effect of 3rd O_2 addition reaction scheme on ignition



ST (top-left axes) and RCM (bottom-right axes) auto-ignition delay times for stoichiometric *n*-hexane/air mixtures at 15 atm



Crank angle dependent temperature profiles and net heat release rate (HRR) per crank angle for *n*-hexane/air mixtures in an HCCI engine

- Third O_2 addition promotes the ignition of *n*-hexane at RCM conditions
- Engine ignition is advance when third O_2 addition is considered
- Production of HOM increases advances OH radical production.

Wang and Sarathy, Combust Flame (2016)

جامعة الملك عبدالله
للعلوم والتقنية
King Abdullah University of
Science and Technology
Clean Combustion
Research Center

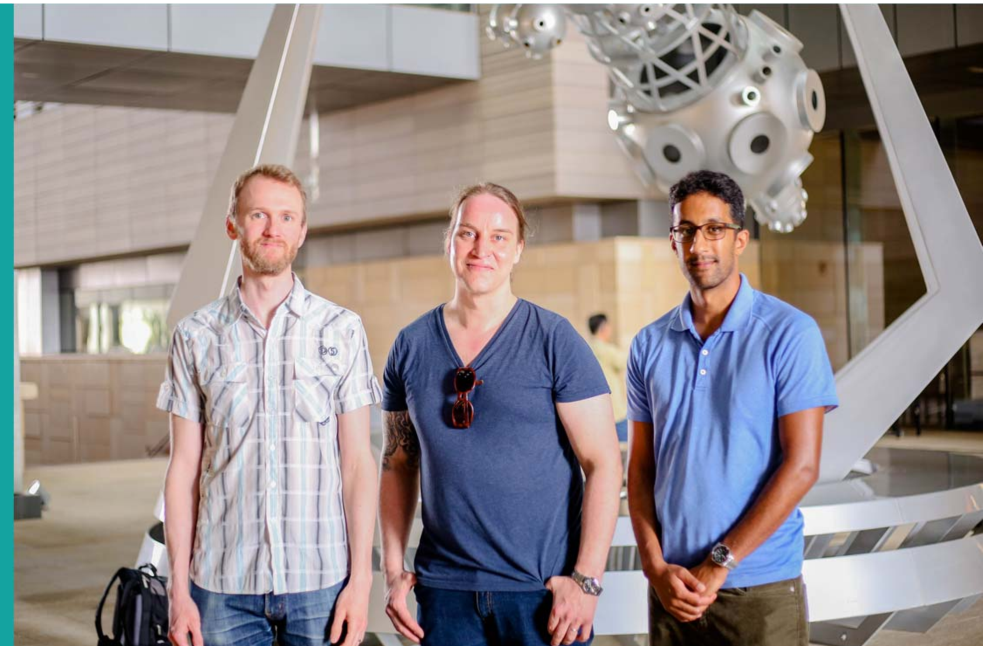
Monge-Palacios
Sarathy

UNIVERSITY OF HELSINKI

Rissanen, Ehn

中国科学技术大学
1958
University of Science and Technology of China

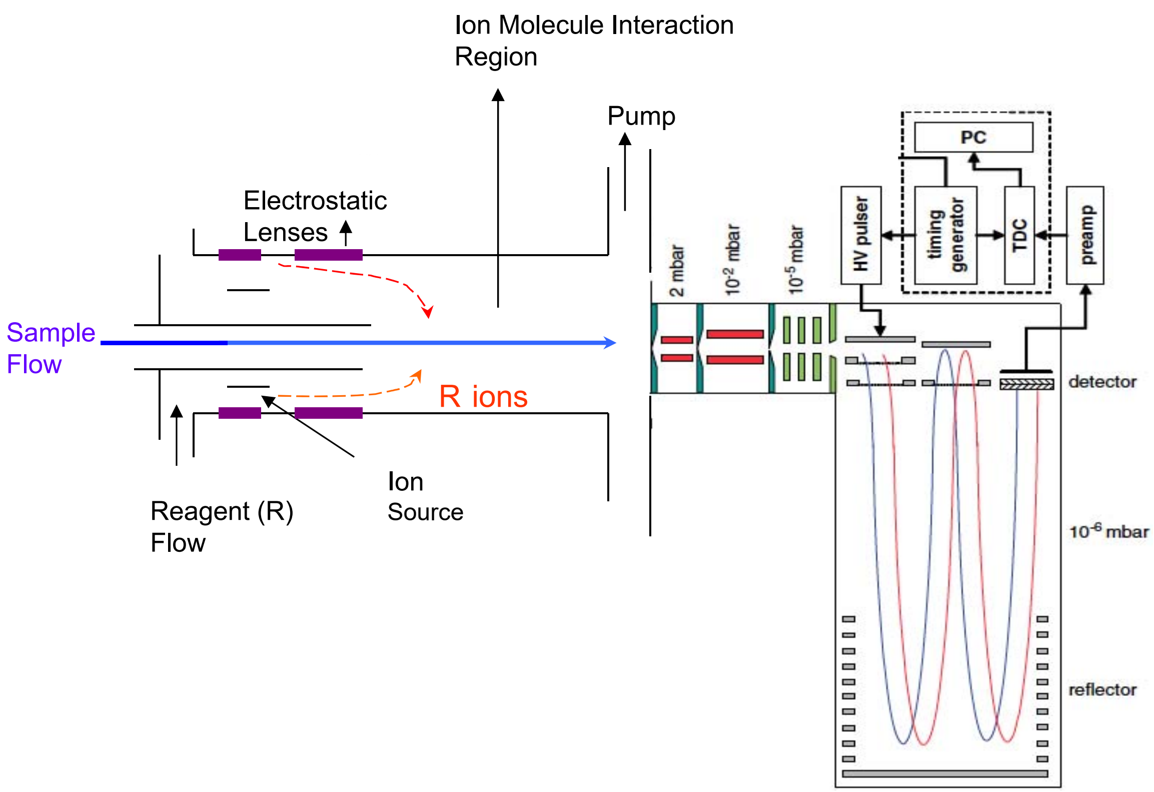
Zhandong Wang

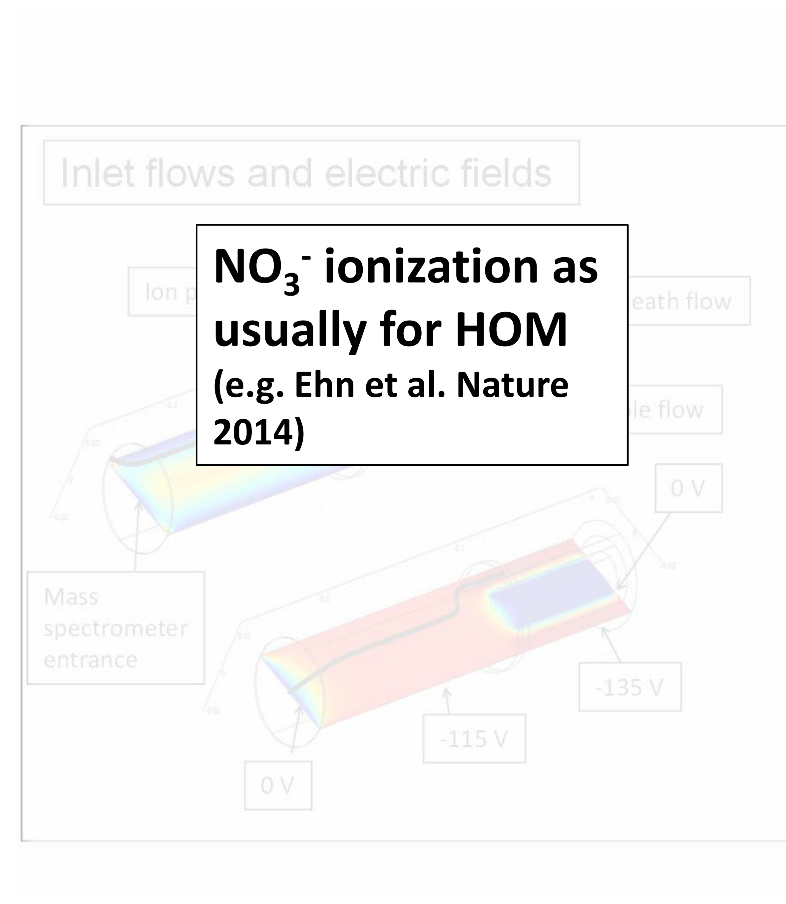


ATMOSPHERE

High fidelity experiments to explore auto-oxidation chemistry

CI-APi-ToF – *Chemical Ionization Atmospheric Pressure interface Time-of-Flight Mass Spectrometer*





NO_3^- ionization as usually for HOM (e.g. Ehn et al. Nature 2014)

Experiments under atmospheric conditions

(1) VOC+TME+O3

TME + O_3 → OH + other products

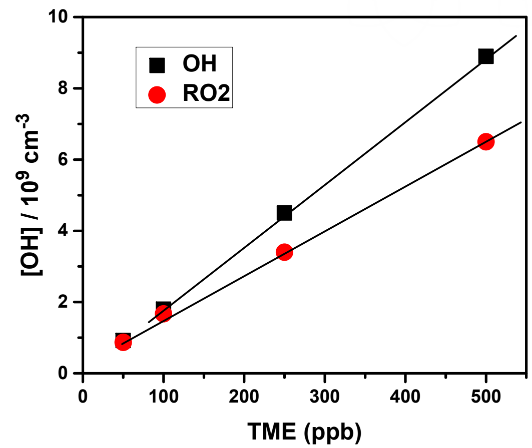
- Ozone around 100 ppb
- TME varied 50, 100, 250, 500 ppb

1 m Quartz 2.4 cm i.d. Reactor, High [VOC] ≈ 10 ppm, Residence time ~3s, Room *T* and *p*

Simple simulation for [RO_2]:

1. TME + O_3 → OH + TME_RO_2
2. VOC + OH → RO_2
3. TME + OH → TME_2_RO_2

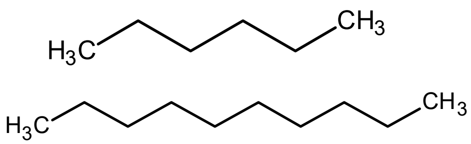
[OH] and [RO_2] at 3 seconds for butylcyclo-hexane:



Alkane autoxidation Model compounds

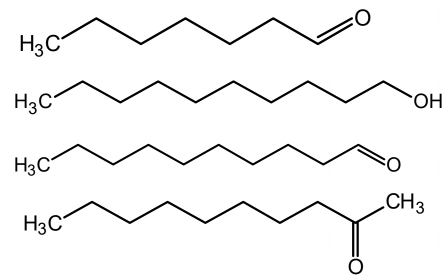
Straight chain C, H

- *n-hexane*
- *n-dodecane*



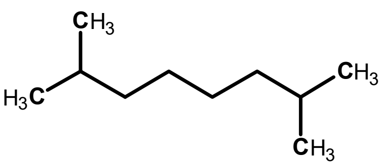
Straight chain C, H, O

- Heptanal
- Decanal, Decanol, 2-decanone



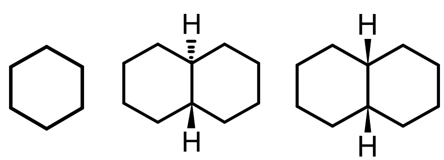
Branched

- 2,7-dimethyl octane



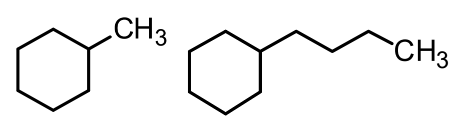
Cyclic

- Cyclohexane
- Decalin



Branched and cyclic

- Methyl cyclohexene, butyl cyclohexene



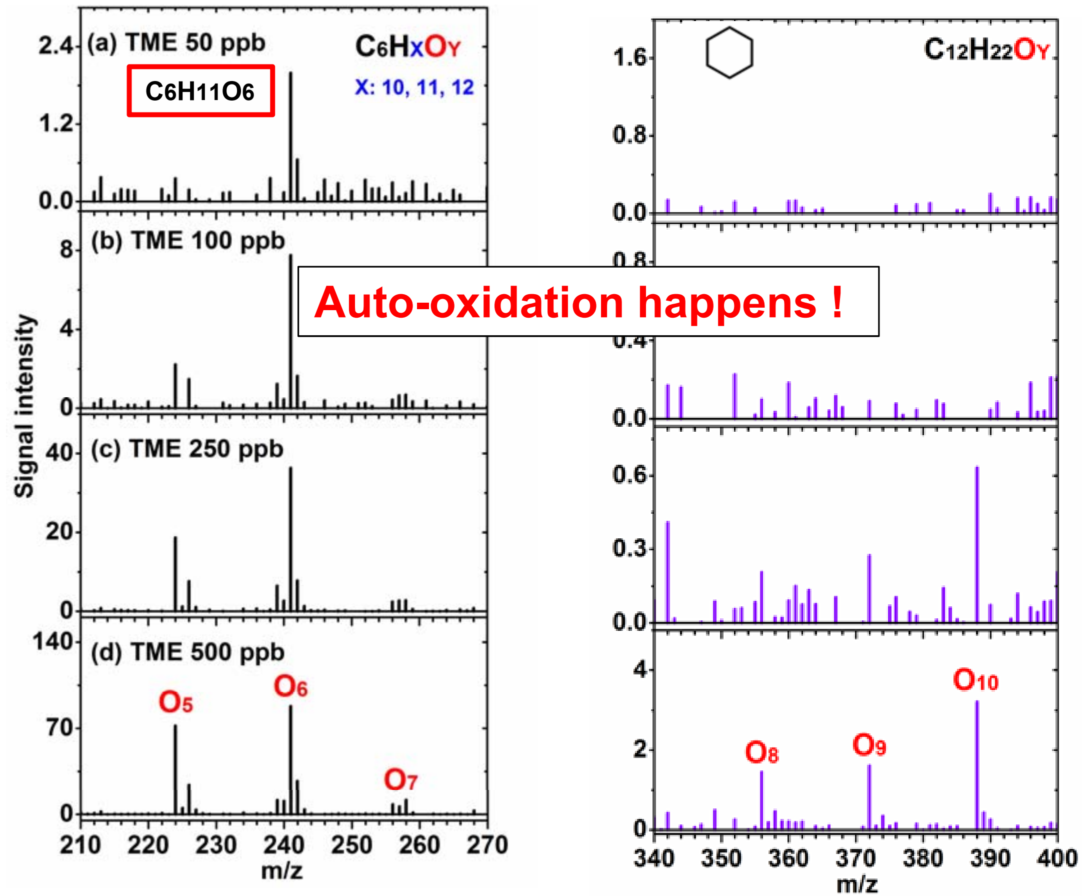
Cyclohexane (C_6H_{12})+TME+O_3

Monomers

$C_6H_{10}O_5$
$C_6H_{12}O_5$

$C_6H_{10}O_6$
$C_6H_{11}O_6$
$C_6H_{12}O_6$

$C_6H_{10}O_7$
$C_6H_{11}O_7$
$C_6H_{12}O_7$



Dimers

$C_{12}H_{22}O_8$

$C_{12}H_{22}O_9$

$C_{12}H_{22}O_{10}$

The dominant RO_2 radical: $C_6H_{11}O_6$

cycloalkane vs aldehyde

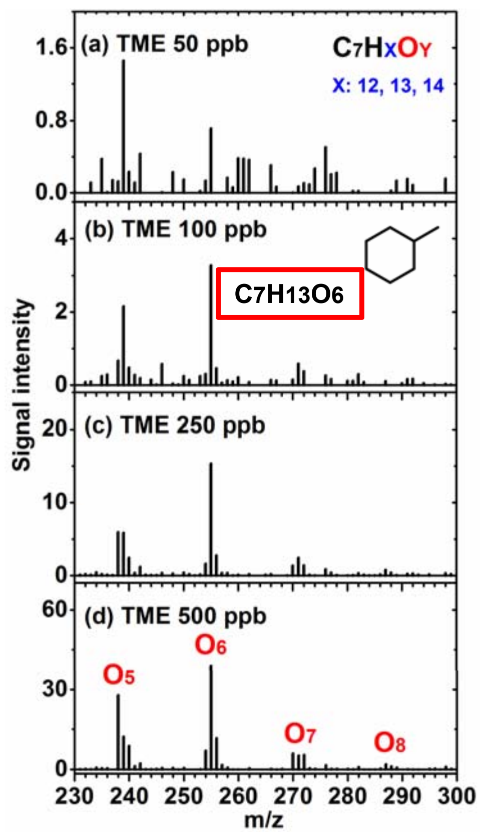
Monomers

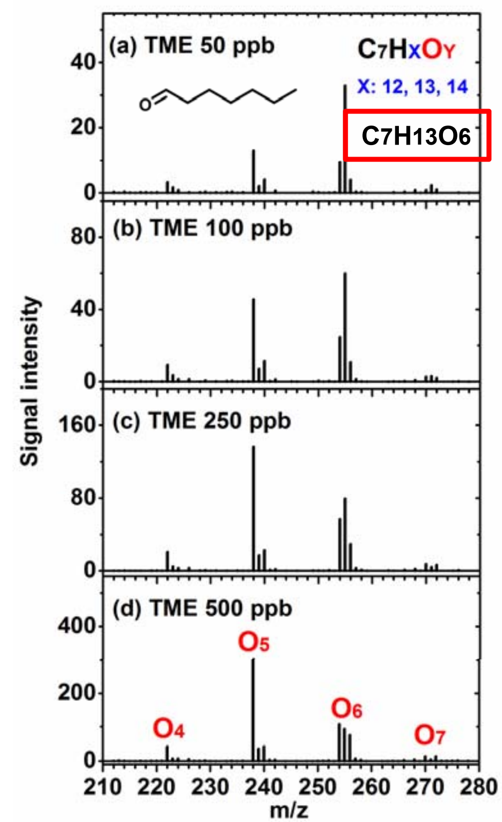
$C_7H_{12}O_5$
$C_7H_{14}O_5$

$C_7H_{12}O_6$
$C_7H_{13}O_6$
$C_7H_{14}O_6$

$C_7H_{12}O_7$
$C_7H_{13}O_7$
$C_7H_{14}O_7$

$C_7H_{12}O_8$
$C_7H_{13}O_8$
$C_7H_{14}O_8$





Monomers

$C_7H_{12}O_4$

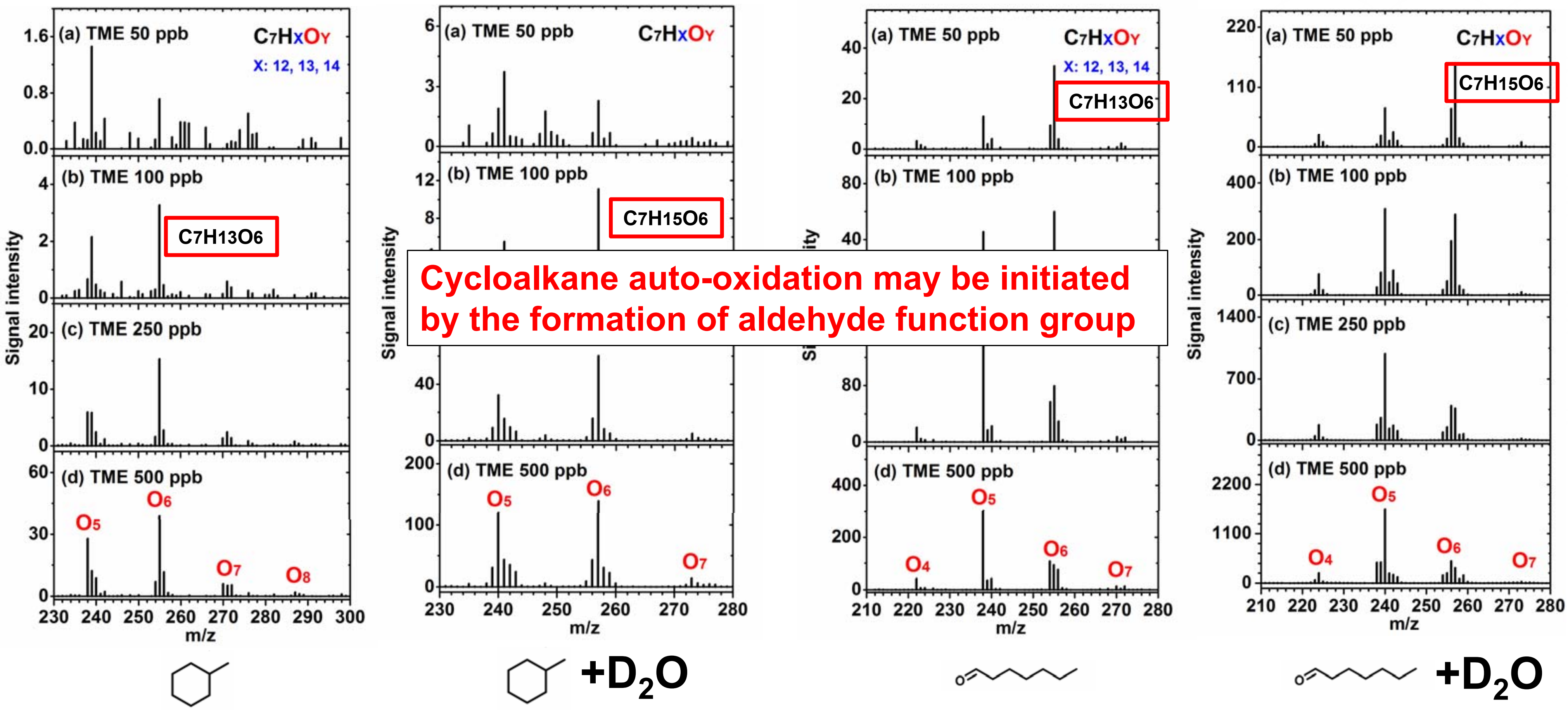
$C_7H_{12}O_5$
$C_7H_{14}O_5$

$C_7H_{12}O_6$
$C_7H_{13}O_6$
$C_7H_{14}O_6$

$C_7H_{12}O_7$
$C_7H_{13}O_7$
$C_7H_{14}O_7$

Both the dominant RO_2 radical: $C_7H_{13}O_6$

cycloalkane vs aldehyde +D_2O



In both cases $C_7H_{13}O_6$ radcials has two acid H atoms

Cyclohexane oxidation → going for that prompt RO_6 radical!

Can you escape this carbonyl forming reaction?

*RO intermediate needed to break the ring, right?
**Leads to odd oxygen RO_2 (i.e., RO_3)
→ So then we need two times RO_2 + RO_2 to get to RO_6
(...also RO_2 + HO_2)

Can H-scrambling avoid decomposition?
(e.g. Knap, H. C. et al

Does this need to decompose?

RO_6

Need to esca potential termination reactions!

Summary

- Auto-oxidation under combustion and atmospheric conditions shares many similarities
- Experimental and theoretical techniques/skills from both fields complement each other
- Alkanes auto-oxidation leads to HOM formation in both environments, albeit the underlying chemistry is different.
- RO2+RO2 : atmosphere, RO2=QOOH : combustion


谢谢
ขอบคุณ
Thank you
Danke
நன்றி
감사합니다
Obrigado
شكرا
Merci
Grazie
ありがとう
takk
شكريا
धन्यवाद
Dank u
Спасибо
ευχαριστώ
Efharistó
Gracias
Děkuju
hvala
Dziękuję
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terima kasih
متشكرم
Kiitos
mani.sarathy@kaust.edu.sa
http://cpc.kaust.edu.sa