

Towards a Better Understanding of the Complex Oxidation Processes Occurring in Cool Flames.

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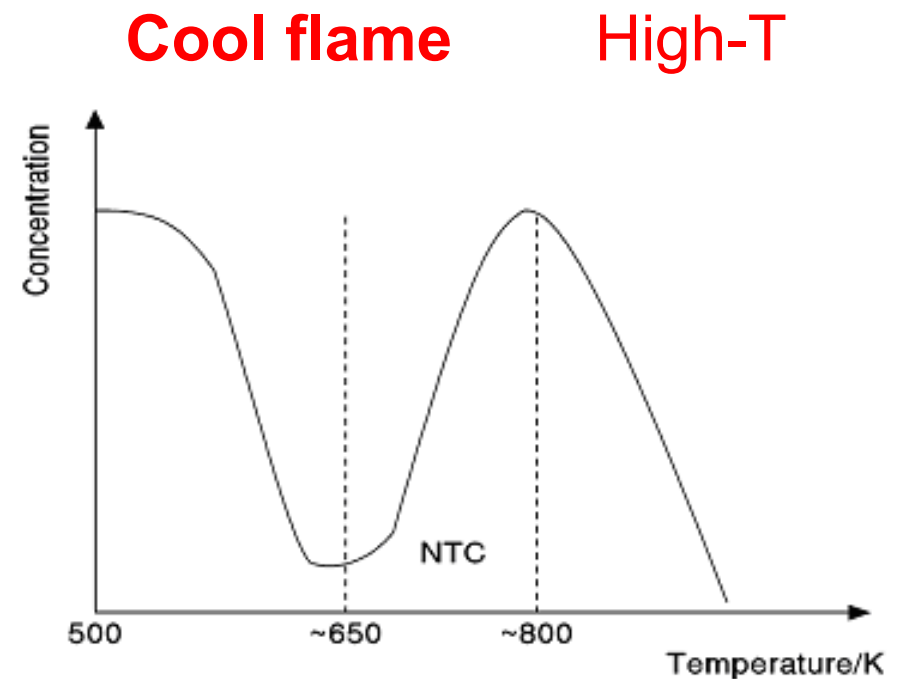
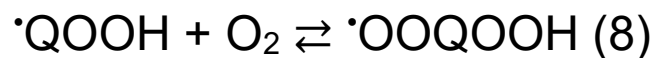
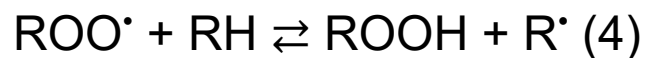
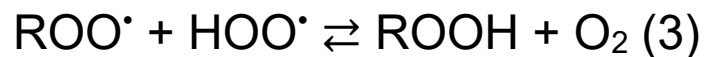
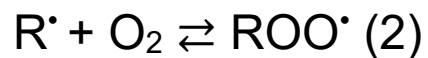
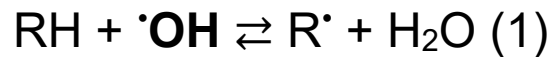


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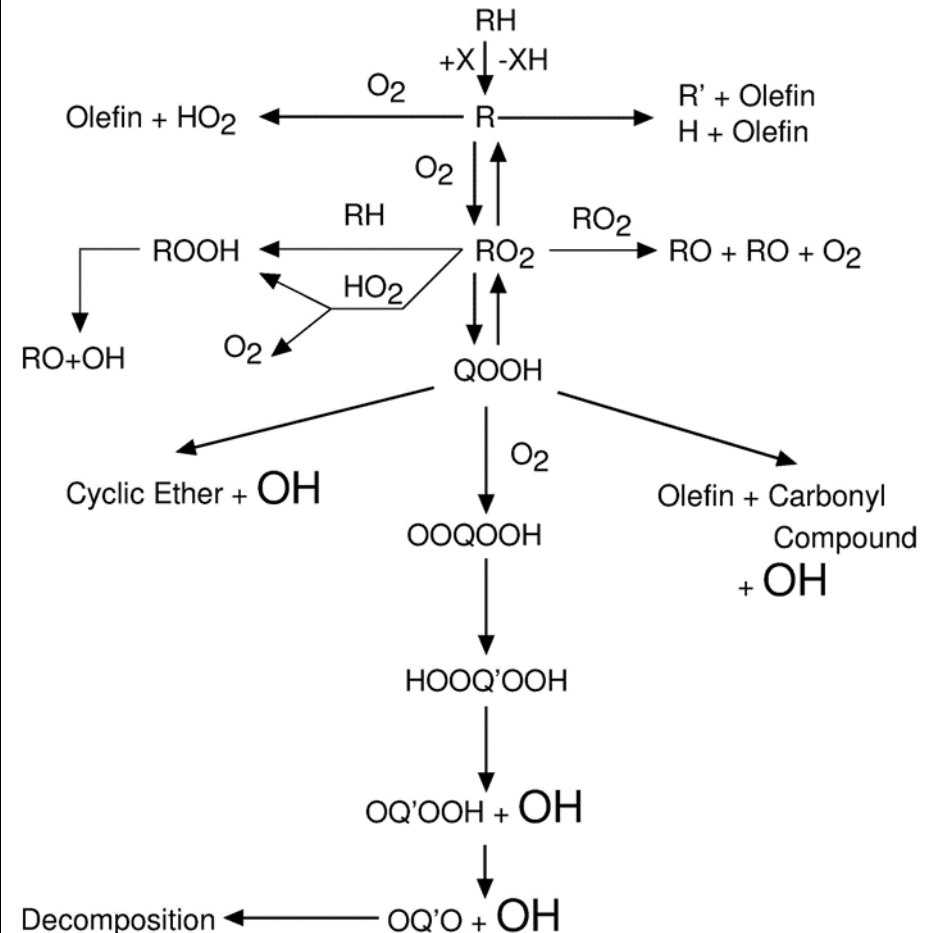
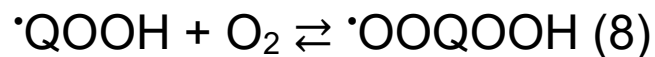
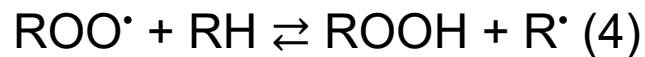
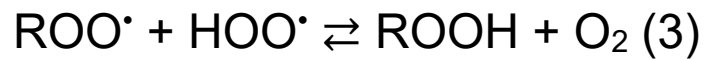
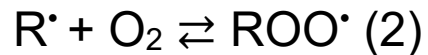
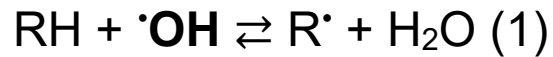
1 Introduction

In combustion we consider that autoxidation of hydrocarbons (RH) produces oxygenated products such as ketohydroperoxides (**KHPs**) which lead to chain branching via decomposition:

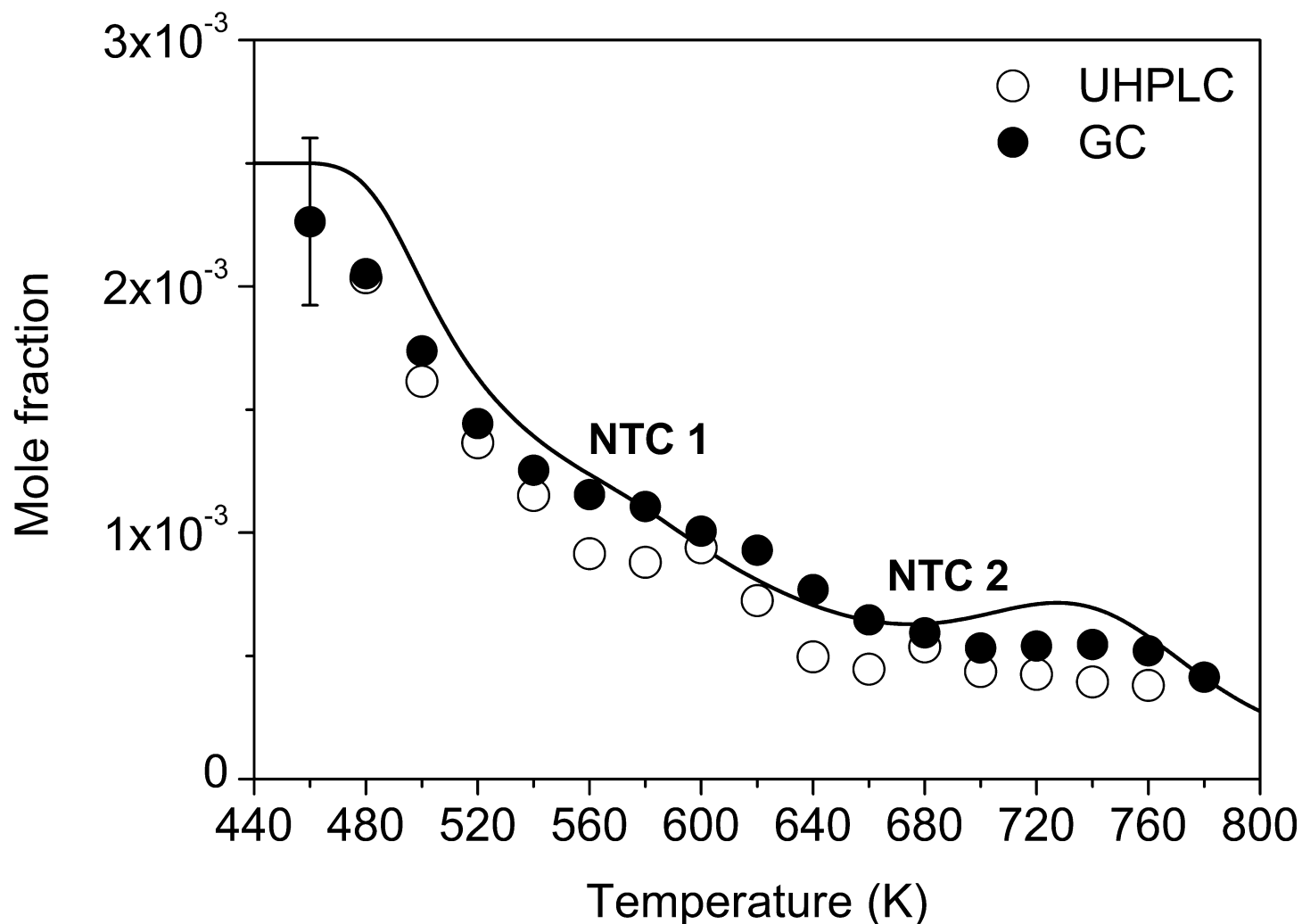


Fuel concentration vs. temperature

Introduction



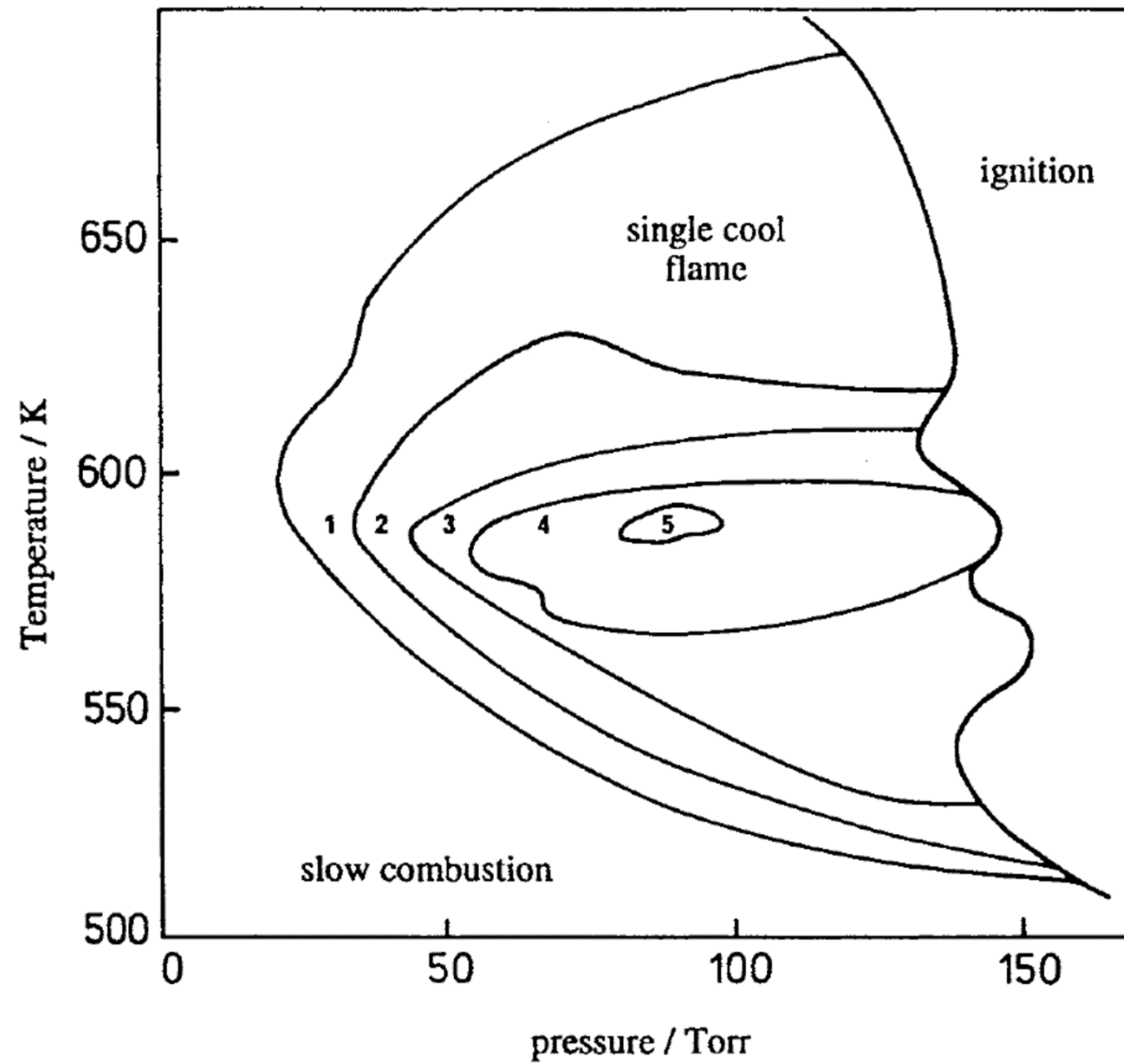
Introduction



DBE mole fraction profile during its low temperature (460-780 K) and high pressure (10 atm) oxidation in a JSR (2500 ppm of DBE, $\phi = 2$ and residence time of 1s). The line corresponds to modeling results, symbols to GC and UHPLC experimental results (UHPLC-positive APCI-HRMS, $C_8H_{19}O^+$, m/z 131.1430).

Source: Belhadj et al., *Molecules* 26, 7174 (2021).

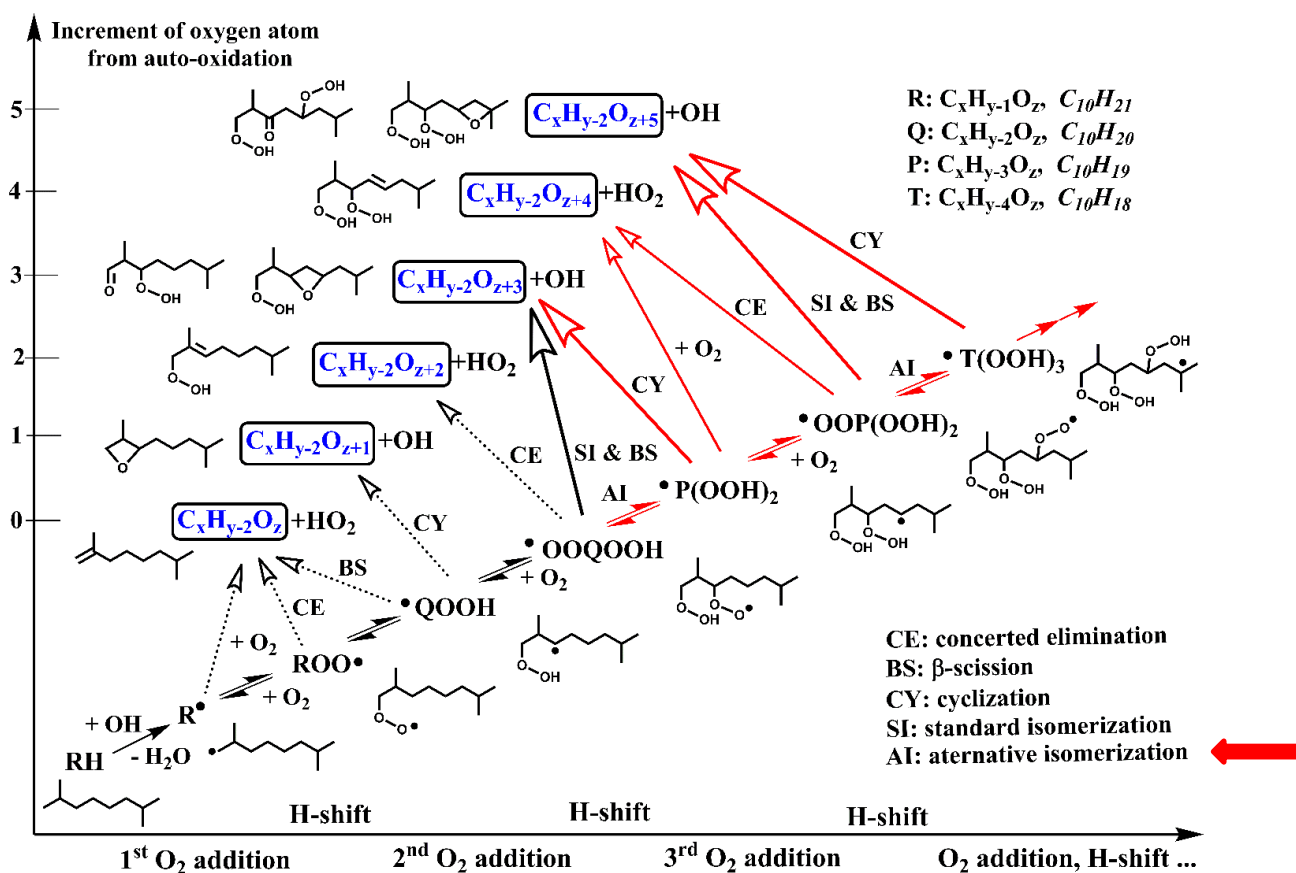
Introduction



n-Pentane oxidation (R.W. Walker and C. Morley, 1997)

Introduction

Besides, the production of highly oxidized organic products in cool flames of alkanes, cycloalkanes, alcohols, aldehydes, ethers, and esters has been reported (Wang et al., *Combust. Flame* **187** (2018) 199-216; Wang et al., *PNAS* **114** (2017) 13102-13107; Belhadj et al., *Combust. Flame* **222** (2020) 133-144).



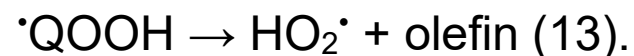
Source: Wang et al., *PNAS* **114** (2017) 13102-13107

Introduction

This alternative oxidation pathway proceeds via an H-shift in the $\cdot\text{OOQOOH}$ intermediate involving a H-C group (**Alternative Isomerization**) other than the H-C(OOH)- group responsible for the formation of KHPs.

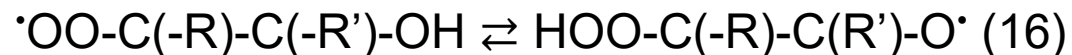
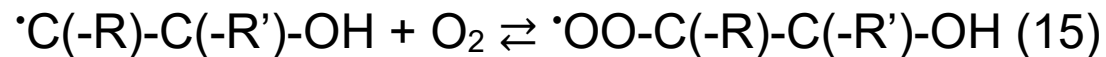
It opens **new oxidation pathways**, e.g., a 3rd O_2 addition to $\text{HOOP}\cdot\text{OOH}$ yielding $\cdot\text{OOP}(\text{OOH})_2$. This sequence of H-shift and O_2 addition can repeat, yielding **highly oxidized products**.

Besides, $\cdot\text{QOOH}$ can decompose to yield radicals and stable products:



Introduction

In the case of **unsaturated reactants**, the **Waddington** mechanism, which involves **OH** addition to the C=C double bond followed by O₂ addition and H-shift from the -OH group to the —OO[•] peroxy group, followed by decomposition, can occur:



Through this mechanism, the **OH** radical initially consumed is finally regenerated in Reaction (17).

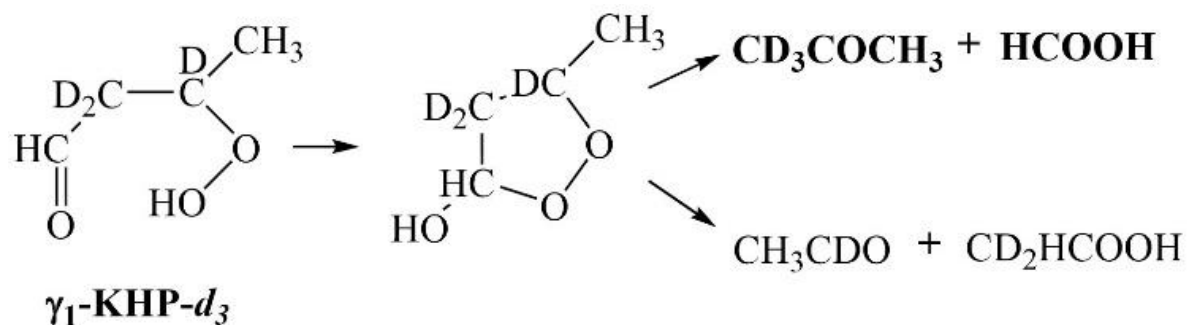
Introduction

Also, as demonstrated initially in the liquid phase, the **Korcek** mechanism, which transforms γ -keto hydroperoxides into a carboxylic acid and a ketone or an aldehyde, can occur.

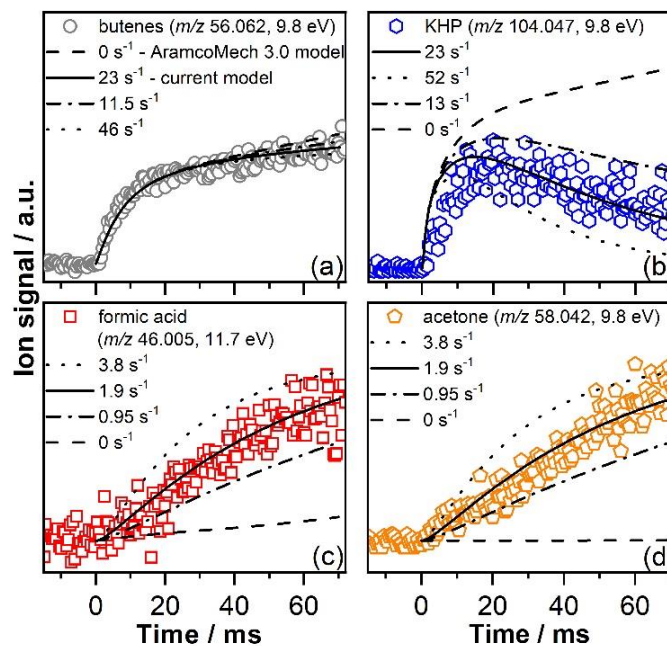
The production of these chemicals via the Korcek mechanism has been suggested to happen under tropospheric conditions and has also been introduced in proposed combustion kinetic reaction mechanisms (Ranzi et al., *Combust. Flame* **162** (2015) 1679-1691; Xie et al., *Combust. Flame* **242** (2022) 112177).

Introduction

Further evidence of the occurrence of that mechanism has been presented recently D₄-butane:



ALS-LBNL data + kinetics fits

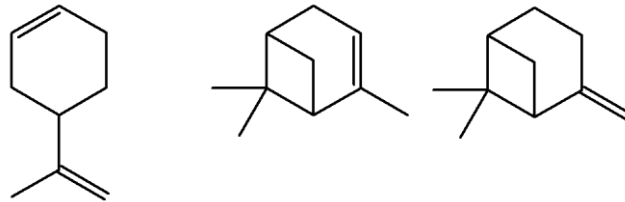


Source: Popolan-Vaida et al. *Angewandte Chemie-Int. Ed.* **61** (2022) 9168-9168.

Introduction

Terpenes' high-energy-density: potential biojet fuels. for greener transportation.

ΔH_c (kcal/mole): 1474 for d-limonene; 1483 for α -pinene; 1485 for β -pinene (*J. Am. Chem. Soc.* 1954, 76, 10, 2669). ΔH_c (BTU/gallon): 132 500 for α -pinene; 132 300 for β -pinene vs. 142 000 for **JP-10** (*Energy Fuels* 2010, 24, 267).



The kinetics of combustion of this class of compounds is poorly known: flame speeds, limited flame structure and impact on ignition have been reported.

Potential formation or **aromatic or polyunsaturated products** from terpenes oxidation?

- We aimed to:
- better characterize the autoxidation products of limonene and α -and β -pinene
 - investigate the formation of aromatics/polyunsaturated products

2 Methods

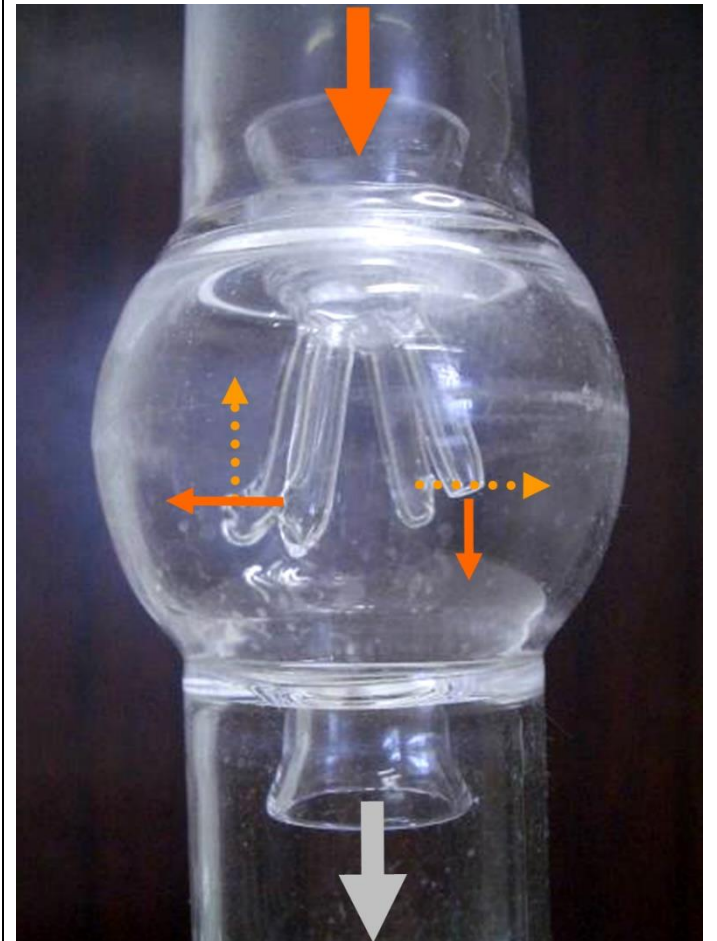
2.1 JSR Experiments

A fused silica JSR (42 mL) was used.

The fuels were pumped using a HPLC pump with an online degasser. The fuels were delivered to a vaporizer assembly fed with a flow of N_2 . Fuel- N_2 and O_2 - N_2 flowed separately to the JSR to avoid premature oxidation before reaching the reactor. Mass flow meters were used.

A thermocouple (0.1 mm Pt-Pt/Rh-10%) was moved along the vertical axis of the JSR to verify thermal homogeneity (gradients of < 1 K/cm).

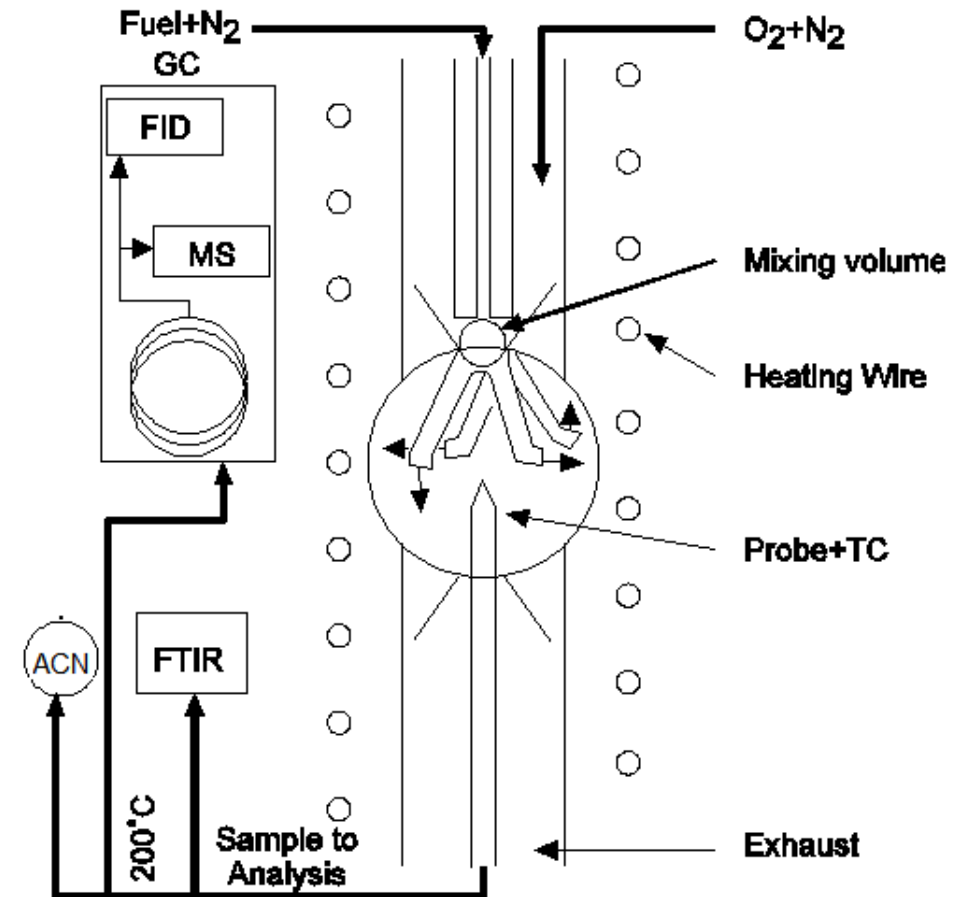
We oxidized **1% of fuel at 1 bar**, in excess of O_2 ($\phi = 0.5$), at a residence time of **1.5 s**, over the T-range **520-680 K**.



JSR Experimental Set-Up

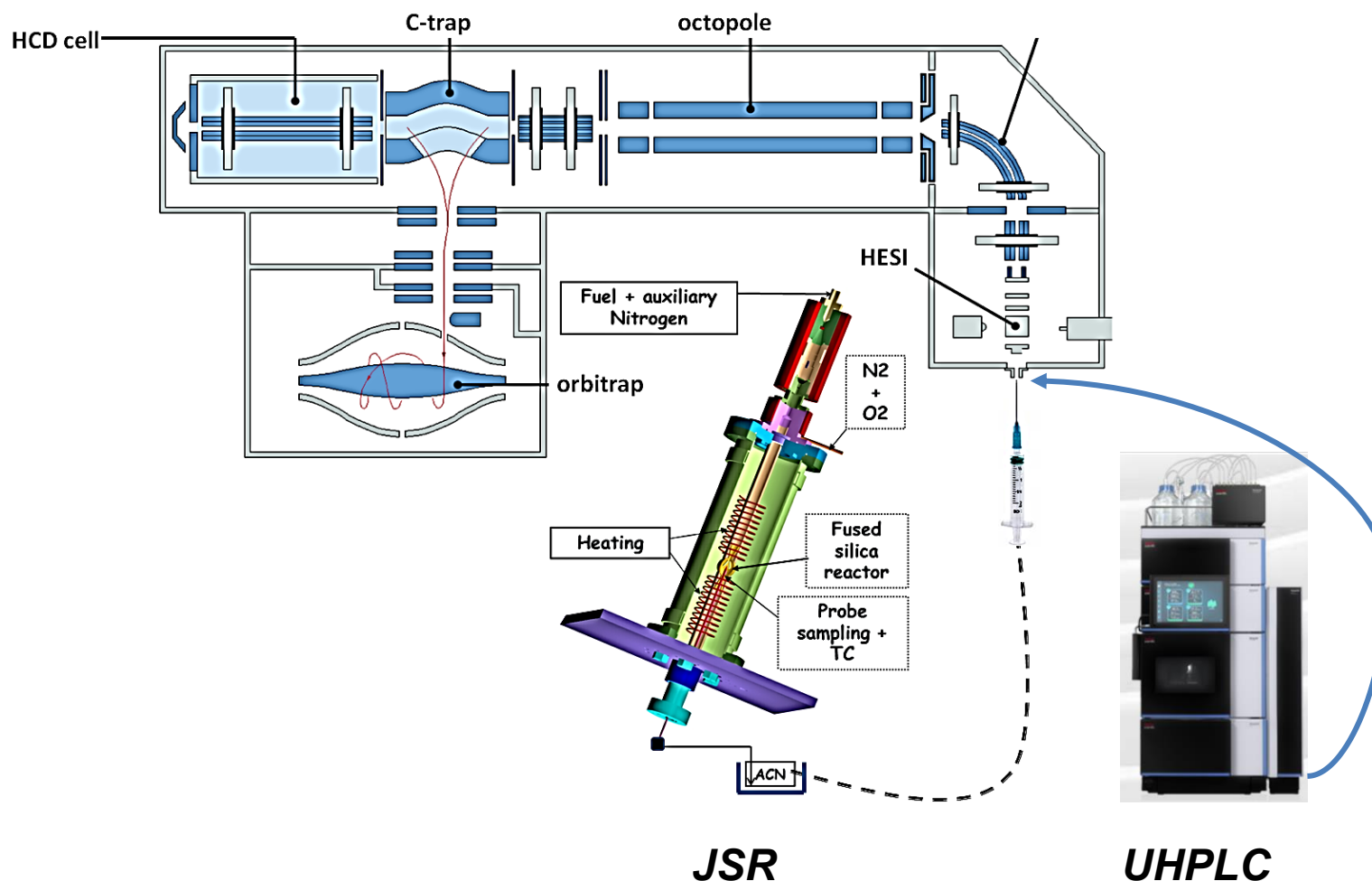
Probe **samples** taken by sonic probe sampling for:

- Trapping in cool acetonitrile, **HPLC-HRMS**.
- on-line **FTIR** analyses



JSR/HRMS Experimental Set-Up

Orbitrap Q-Exactive



- Low-temperature oxidation products were collected by bubbling gas samples for 60 min into 20 mL of UHPLC grade acetonitrile (ACN) maintained at 273 K.

2.2 Chemical analyzes

Mass spectrometry:

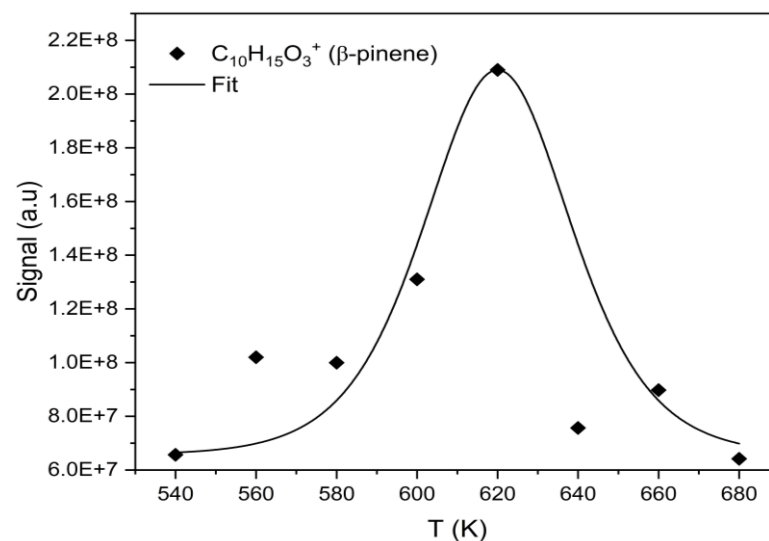
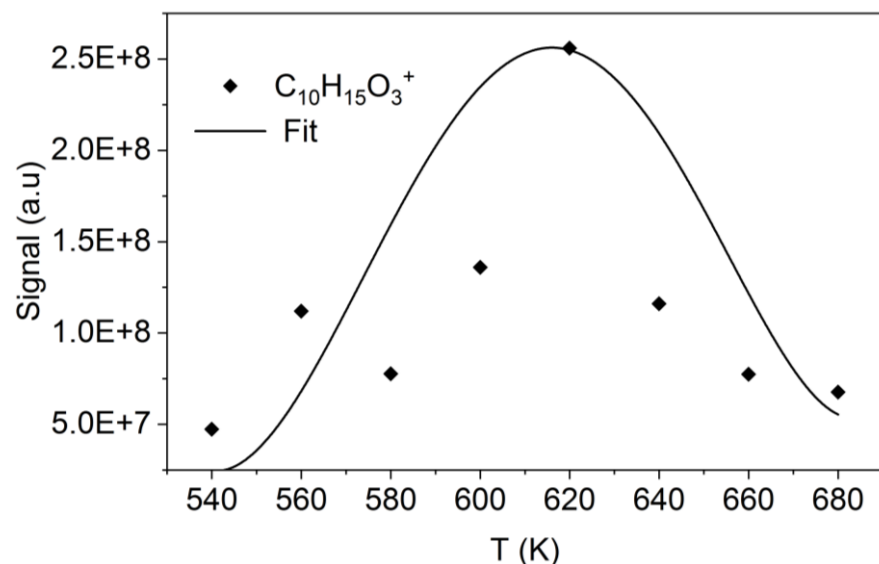
- We conducted flow injection analyses/heated electrospray ionization (FIA/HESI or APCI).
- Reverse-phase ultra-high-performance liquid chromatography (APCI +/-)
- Determination of the chemical structure of oxidation products by MS/MS analyses (HCD 10 eV).

Derivatization and atomic exchange

- 2,4-Dinitrophenylhydrazine used to assess the presence of carbonyl compounds (C=O).
- The fast H/D exchange was used to assess to the presence of a hydroxyl (-OH) or hydroperoxyl (-OOH) groups in oxidation products: 300 μ L of high-purity D₂O added to 1 mL of samples reacting for 20 min.

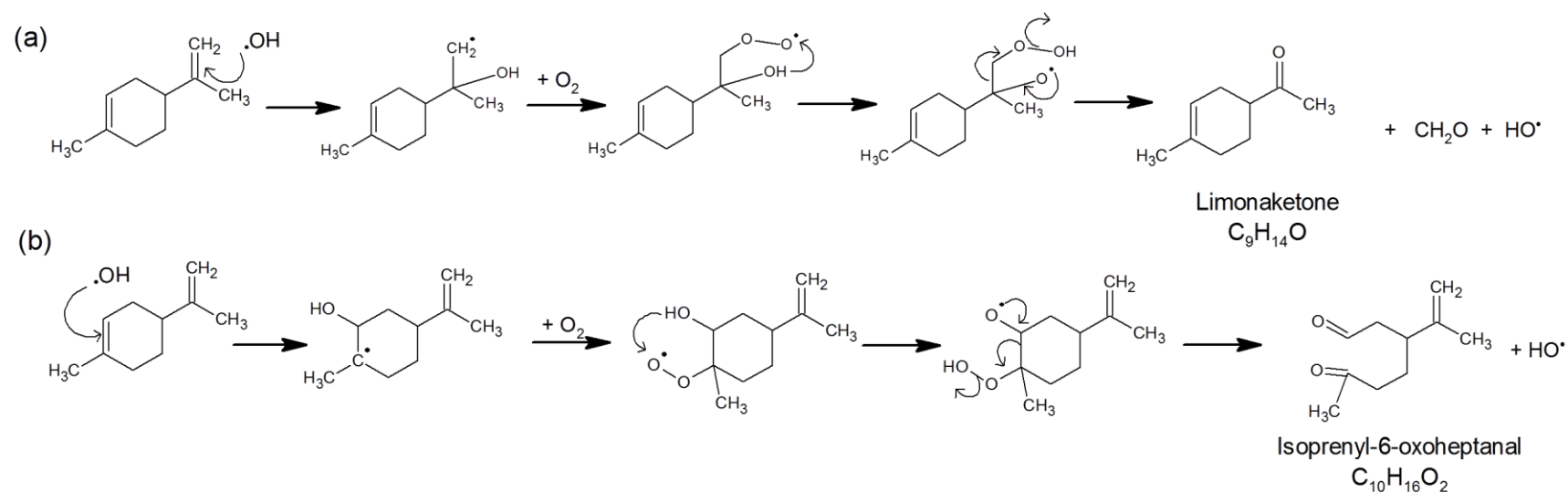
3 Results and Discussion

A broad range of oxidation products ranging from water to highly oxygenated products, containing five and more O-atoms, was detected: $C_7H_{10}O_{4,5}$, $C_8H_{12}O_{2,4}$, $C_8H_{14}O_{2,4}$, $C_9H_{12}O$, $C_9H_{14}O_{1,3-5}$, $C_{10}H_{12}O_2$, $C_{10}H_{14}O_{1-9}$, $C_{10}H_{16}O_{2-5}$, and $C_{10}H_{18}O_6$.



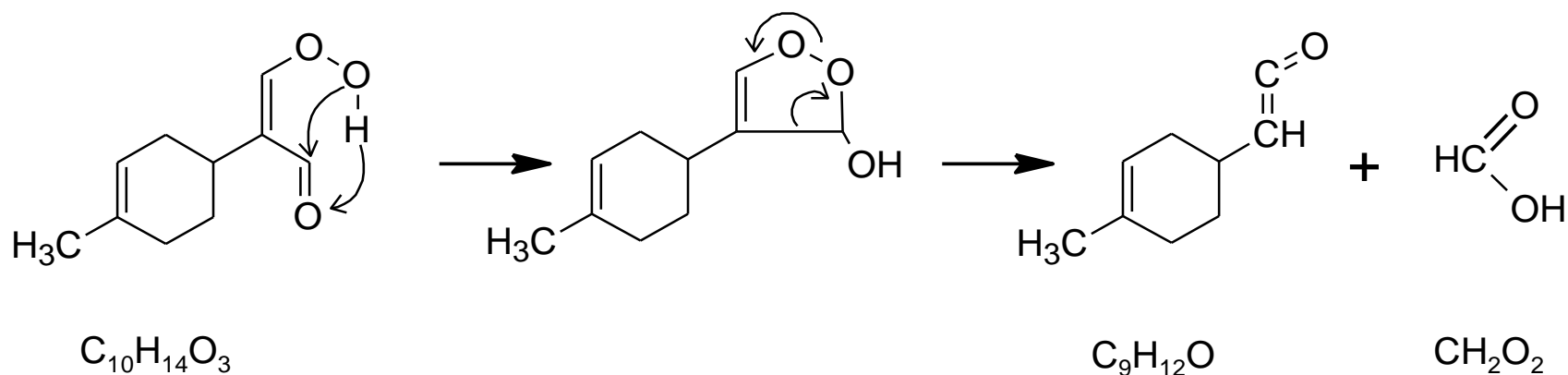
HRMS signal obtained for **limonene** (left) and **β -pinene** (right) products of oxidation. The data for **KHPs** and isomers ($C_{10}H_{14}O_3$) were obtained via FIA and HESI (+), i.e., $C_{10}H_{15}O_3^+$ m/z 183.1015.

Carbonyl compounds from the **Waddington** mechanism on *exo*- and *endo*-double bonds (C=C) were observed as well as their products of further oxidation. The earlier reported (Witkowski *Environ. Sci. Technol.* 52 (2018) 11583-11590) higher reactivity of the *endo* double bond vs the *exo* double bond seems to be confirmed here since higher ion signal ($[M+H]^+$) was obtained for isoprenyl-6-oxoheptanal ($C_{10}H_{17}O_2^+$) than for limonaketone ($C_9H_{15}O^+$).



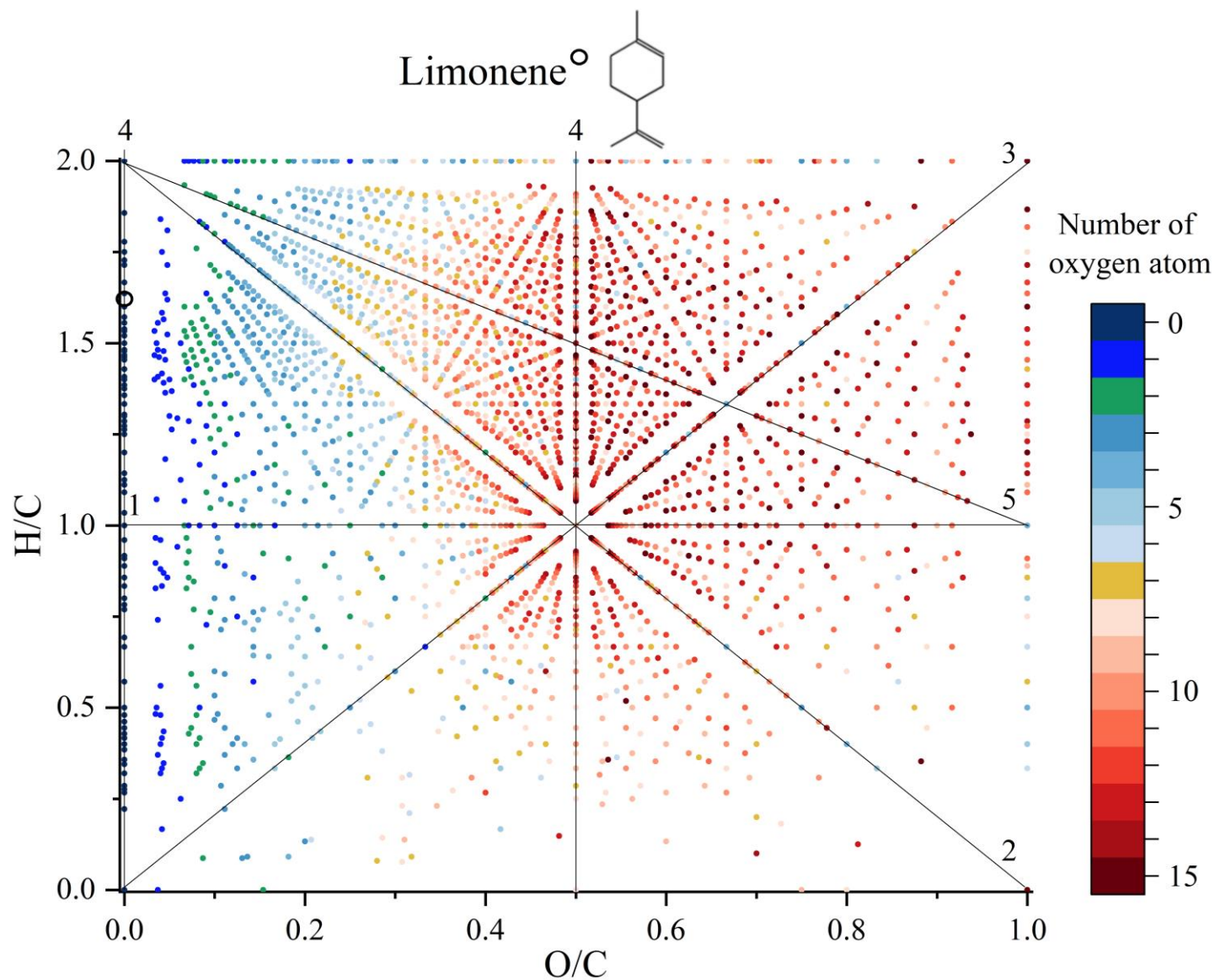
Oxidation of *exo*- (a) and *endo*- (b) cyclic C=C groups in limonene via the **Waddington** mechanism.

Products of the **Korcek** mechanism (carboxylic acids and carbonyls) were also detected. Among the **18 KHPs** deriving from limonene oxidation, **four γ -KHPs isomers** could decompose according to the Korcek mechanism but only one can likely form a cyclic organic peroxide intermediate between the carbonyl and OOH groups, yielding a carbonyl compound, $C_9H_{12}O$, and formic acid, CH_2O_2 by decomposition. Both products were detected in this study.

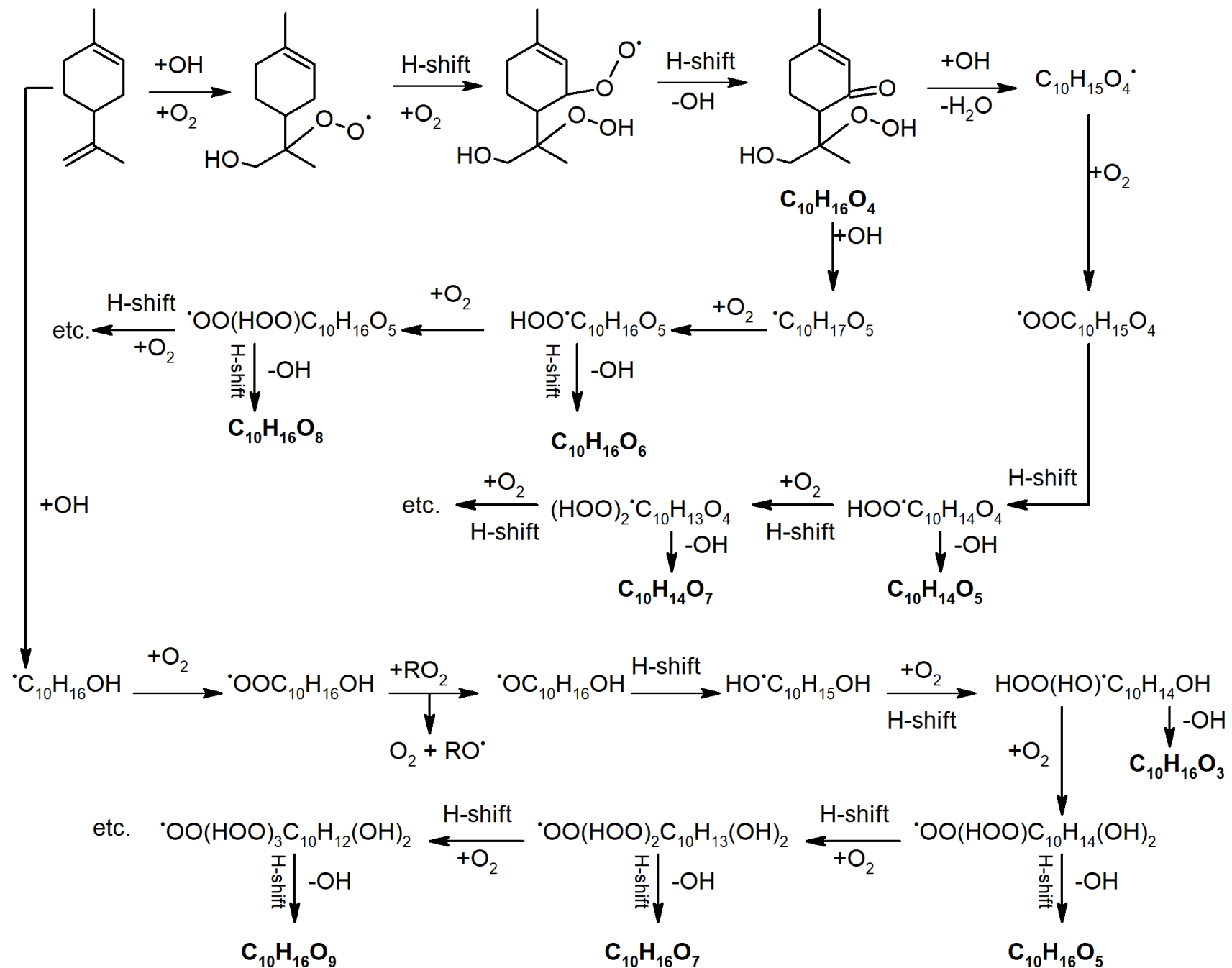


Limonene oxidation: **Korcek** mechanism forming $C_9H_{12}O$ and CH_2O_2 .

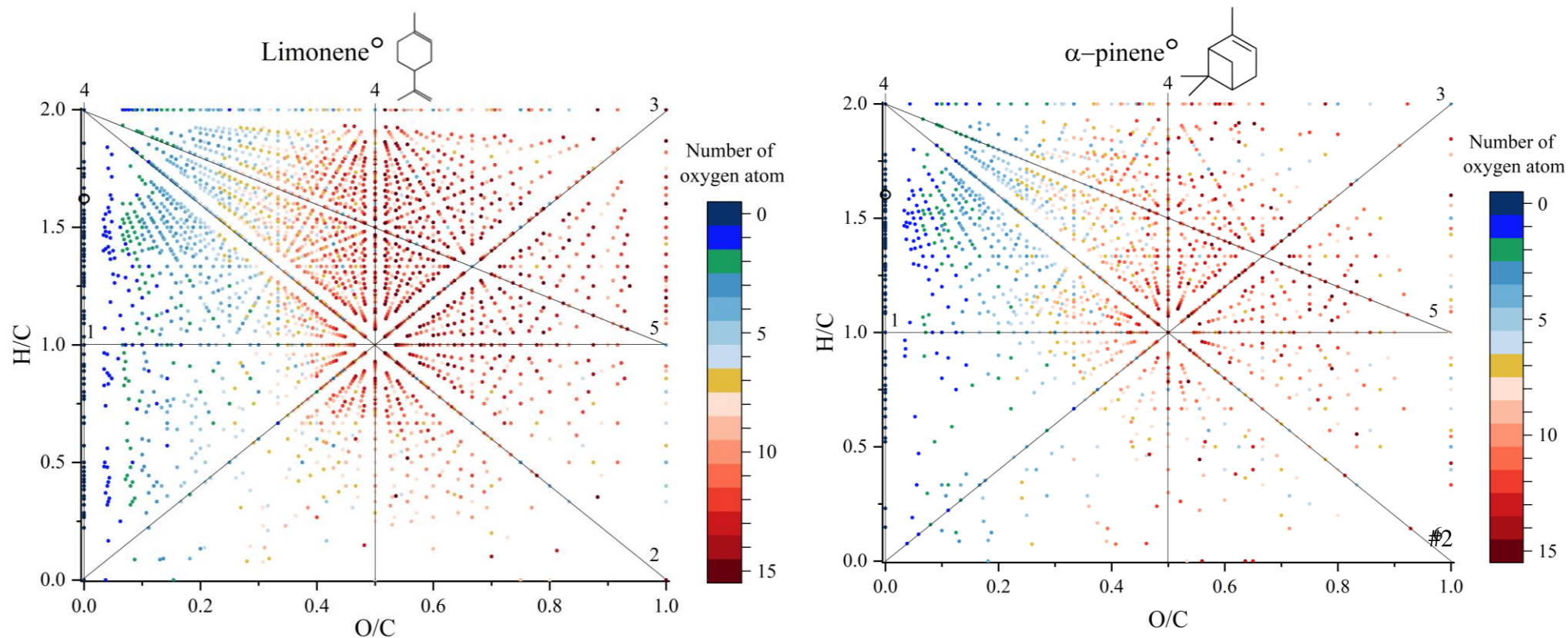
Based on the present identification of **α -pinene** oxidation products: that mechanism occurs also.



Van Krevelen plot for **limonene** oxidation (sampled at 640 K) showing the formation of **HOMs** and **unsaturated/aromatic products**.



Formation of polyunsaturated and/or aromatic products:

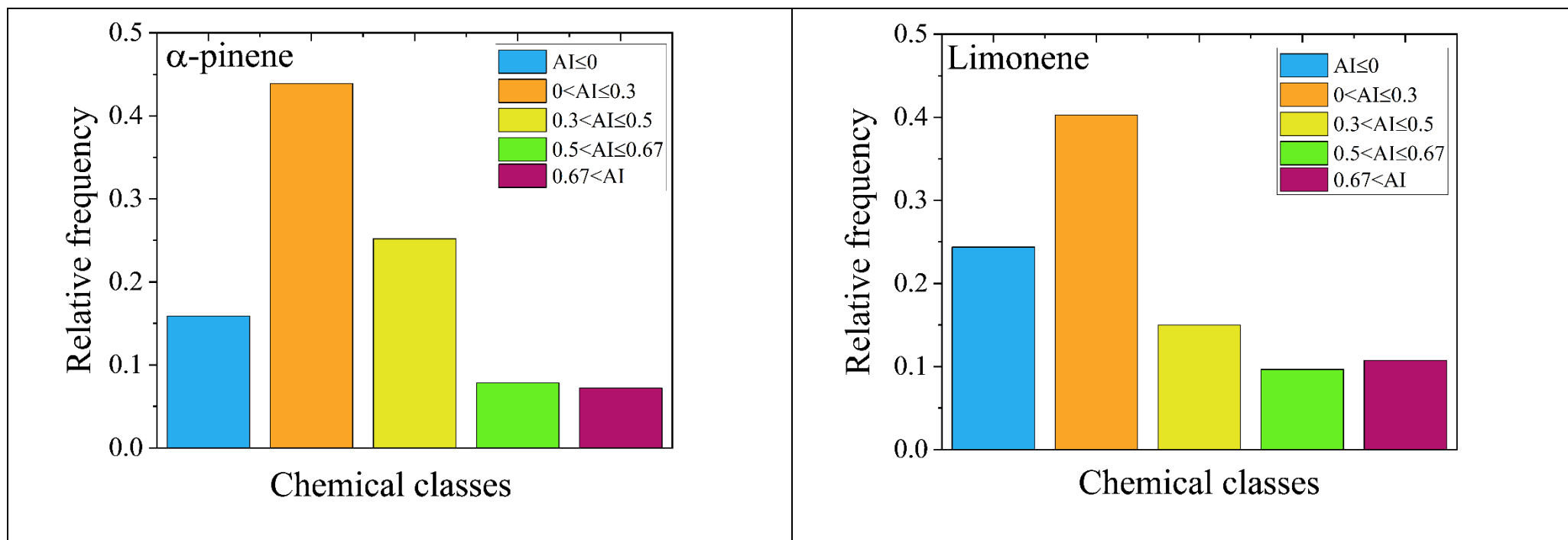


Van Krevelen plot for **limonene** oxidation (sample at 640 K). Van Krevelen plot for **α -pinene** oxidation (sample at 640 K).

Lines indicate 1: oxidation, 2: carbonylation, 3: hydration, 4: dehydrogenation, 5: carboxylation, or reverse processes

VK plots based on HRMS data show the formation of aromatics and polyunsaturated products ($H/C < 0.7$ and $O/C = 0$) is **more important in the case of limonene**.

Aromaticity index (full dataset)



$AI_{\text{mod}} = (1 + C - 0.5 \times O - 0.5 \times H) / (C - 0.5 \times O)$; C, H, and O are the # of atoms in the chemical formulas

Color-coding: Aliphatics; naphthenic/unsaturated; more unsaturated; aromatics; polyaromatics

4 Conclusions

- The low temperature oxidation chemistry is very complex; advanced analytical techniques provided new insights into cool flame chemistry.
- The formation of aromatic and polyunsaturated products observed during the autoxidation of terpenes under cool flame conditions, which was not expected
- Oxidation pathways are numerous and complex and many complex chemical products can be formed.

5 Acknowledgments

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