



ALKANE AUTOXIDATION AND AEROSOL FORMATION: NEW INSIGHTS FROM COMBUSTION ENGINES TO THE ATMOSPHERE

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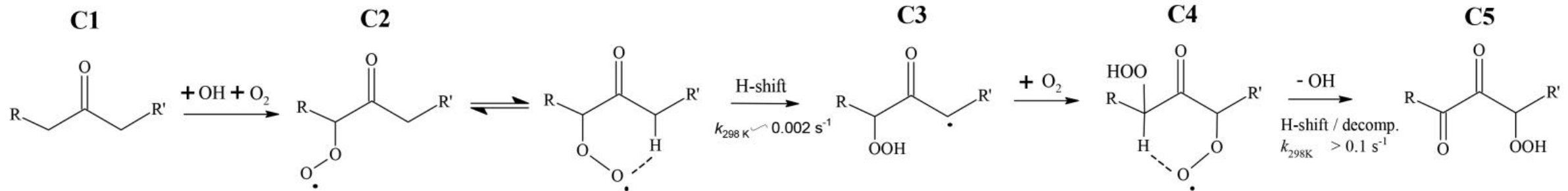
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BACKGROUND AUTOXIDATION

Bianchi F, *et al.* (2019) Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol. *Chem. Rev.* 119(6):3472-3509.



- Autoxidation: H-shifts in peroxy radicals (RO₂) allowing O₂ addition to reform a new RO₂ (C2-C4 above)
 - Recently found to be an important pathway in atmospheric VOC degradation
 - Reported effective H-shift rates at room temperature up to $\sim 1\text{ s}^{-1}$ in favorable structures, making it competitive with bimolecular reactions, unless in very polluted (high-NO) areas
- Multi-step autoxidation can form “highly oxygenated organic molecules”, HOM (*Ehn et al., 2014*)
 - HOM defined here as atmospherically relevant autoxidation products with >5 O-atoms (*Bianchi et al., 2019*)
 - Reported molar HOM yields up to a few percent, and high HOM yields often correlate with high SOA yields
- *But what are the known requirements for HOM formation?*



BACKGROUND

HOM FORMATION REQUIREMENTS


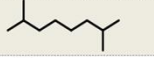



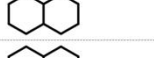
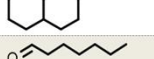



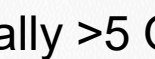
- HOM formation, and autoxidation in general, typically requires suitable functional groups (e.g. carbonyls) to make H-shifts more favorable
 - Alternatively, very high temperatures, as in combustion engines, greatly enhance autoxidation
- Though at variable yields, HOM have been observed from nearly all studied systems
 - At least: monoterpenes + OH/O₃/NO₃, sesquiterpenes + O₃, isoprene + OH, and aromatics + OH
 - Only one important atmospheric VOC group left mostly unstudied: **alkanes**
- Based on the above HOM formation requirements, alkanes should not form any HOM under atmospheric conditions. Or?
- Alkanes often have high SOA yields, sometimes even greatly increasing with NO_x. Certainly autoxidation and HOM cannot be involved. Or?
→ *Someone should look into this! (So that is what we did)*



METHODS

LABORATORY STUDIES

- Alkane oxidation was studied using chemical ionization mass spectrometry (CIMS) in different flow reactors
 - CIMS (CI-API-TOF, Jokinen et al., 2012)
 - Using NO_3^- as reagent ion: selective towards only the most oxygenated species, typically >5 O-atoms
 - Using protonated ethylamine: selective towards almost all oxygenated species, typically >2 O-atoms
 - Experiments (see table)
 - JSR = Jet-stirred reactor in oven (~300-520 K), using NO_3^- CIMS
 - UHEL = Helsinki flow reactor, ~300 K, using NO_3^- CIMS
 - TROPOS = free-jet flow reactor (T. Berndt), ~300 K, using ethylamine CIMS
- Linear alkanes, cycloalkanes, and "oxygenated alkanes" were probed

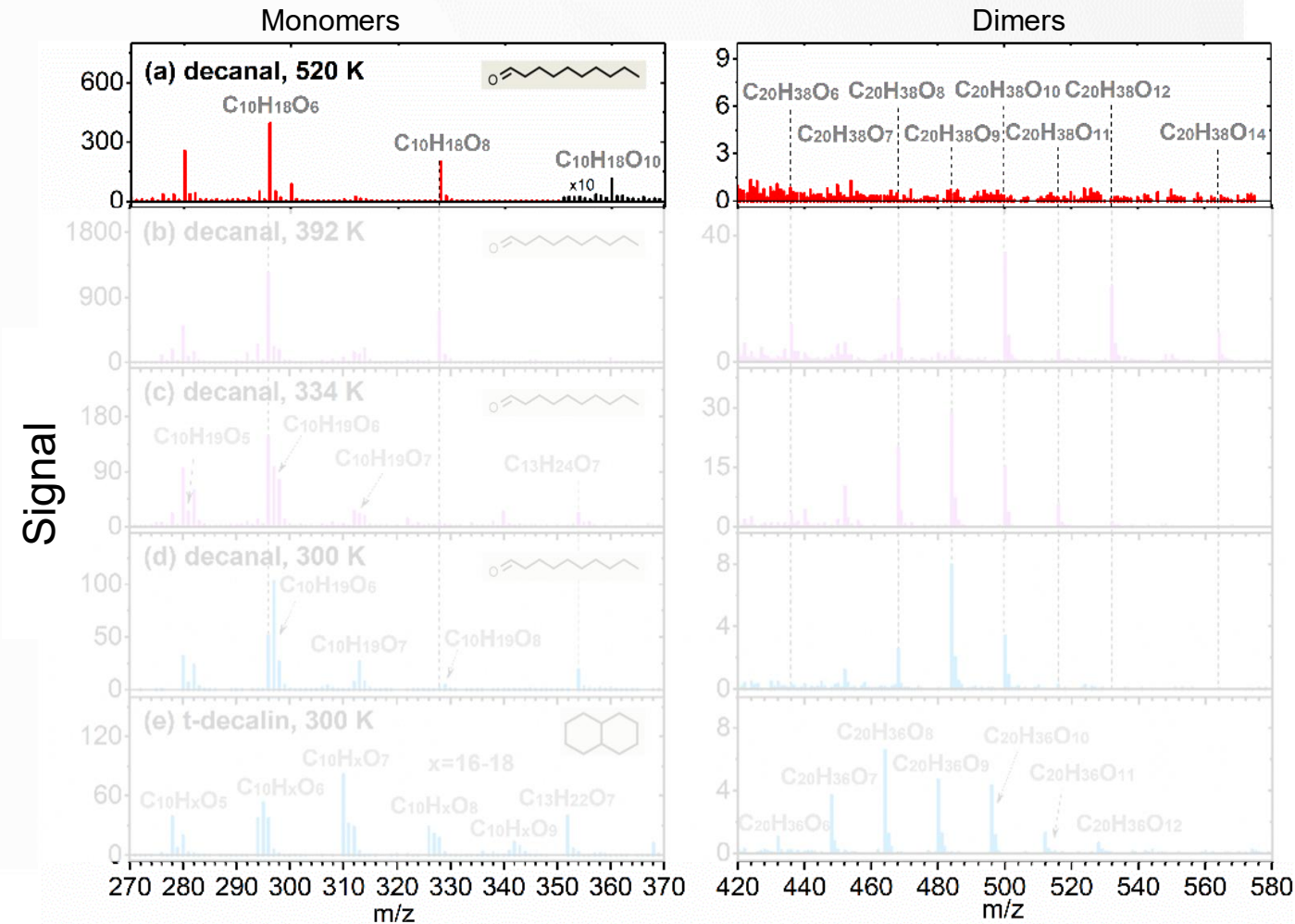
Class	Name	Formula	structure	JSR	UHEL	TROPOS
alkane	<u>n</u> -decane	$\text{C}_{10}\text{H}_{22}$		x	x	x
	2,7-dimethyloctane	$\text{C}_{10}\text{H}_{22}$		x	x	
	cyclohexane	C_6H_{12}				x
cycloalkane	methylcyclohexane	C_7H_{14}			x	
	<u>n</u> -butylcyclohexane	$\text{C}_{10}\text{H}_{20}$		x	x	
	cis-decalin	$\text{C}_{10}\text{H}_{18}$			x	x
	trans-decalin	$\text{C}_{10}\text{H}_{18}$			x	x
oxygenate	heptanal	$\text{C}_7\text{H}_{14}\text{O}$			x	
	decanal	$\text{C}_{10}\text{H}_{20}\text{O}$		x	x	
	1-decanol	$\text{C}_{10}\text{H}_{22}\text{O}$			x	
	2-decanone	$\text{C}_{10}\text{H}_{20}\text{O}$		x		



RESULTS 1

AUTOXIDATION AT DIFFERENT TEMPERATURES

- Experiments mapping products from 520K down to 300K
- Decanal, 520 K, JSR
 - Oxidation initiated by O_2 and OH
 - Up to five O_2 additions observed!
 - First observation of third O_2 addition a recent PNAS paper (Wang et al., 2017)
 - No dimer accretion products
 - Instrumental issue? ROOR not stable at 520 K? Unimolec. termination too fast?

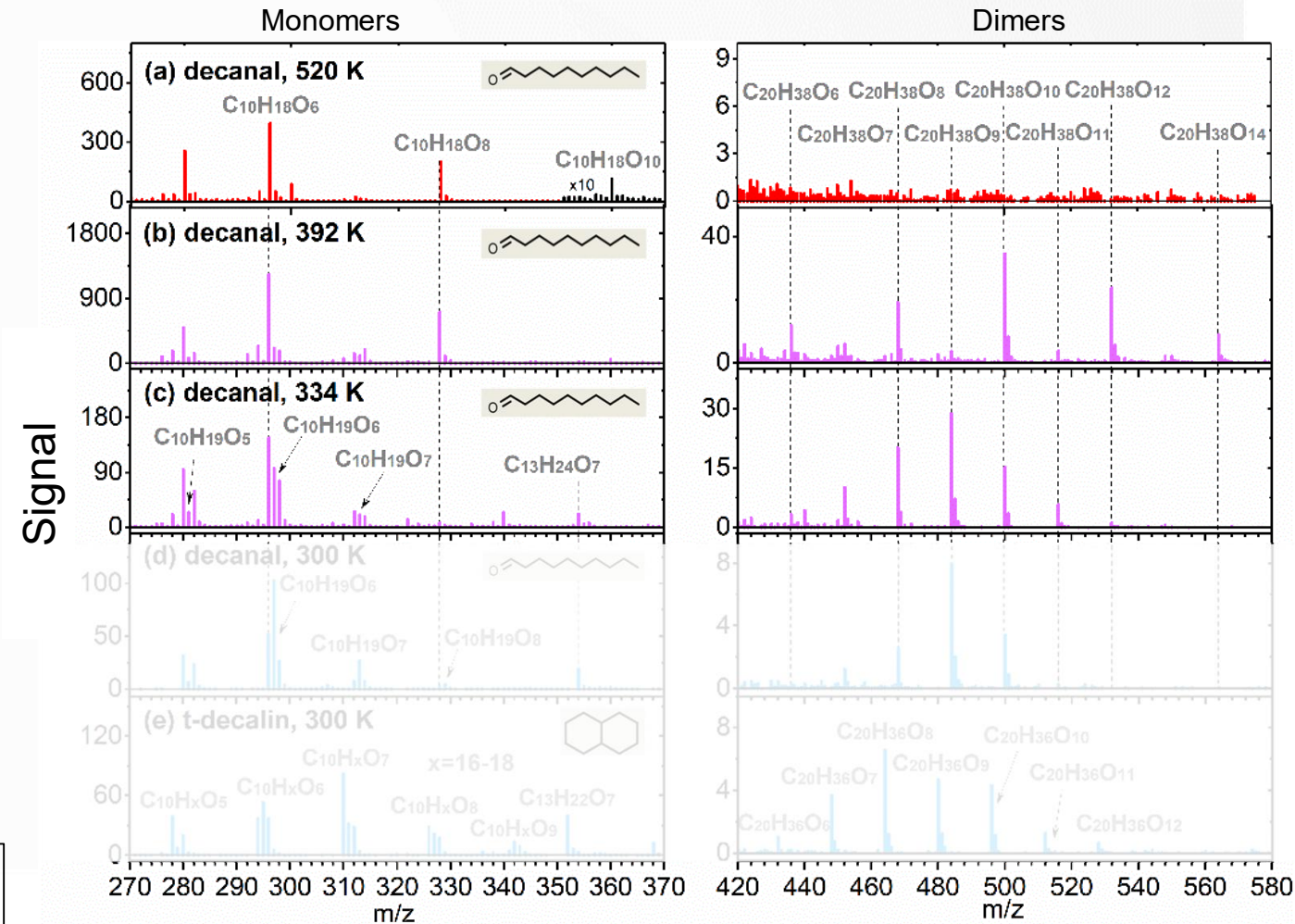
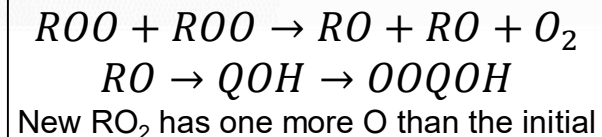




RESULTS 1

AUTOOXIDATION AT DIFFERENT TEMPERATURES

- Decanal, 392 K, JSR:
 - Oxidation by OH formed from tetramethyl ethylene (TME) + ozone
 - Monomers similar to 520 K case
 - Dimers now visible, separated by O_2 , just as monomers
- Decanal, 334 K, JSR:
 - Oxidation by OH from TME+ O_3
 - Products slightly less oxygenated
 - Radicals now also observed ($C_{10}H_{19}O_x$)
 - C_{13} are accretion products from decanal- RO_2 + TME- RO_2
 - O_2 pattern gone
 - Suggests alkoxy radical (RO) steps involved?

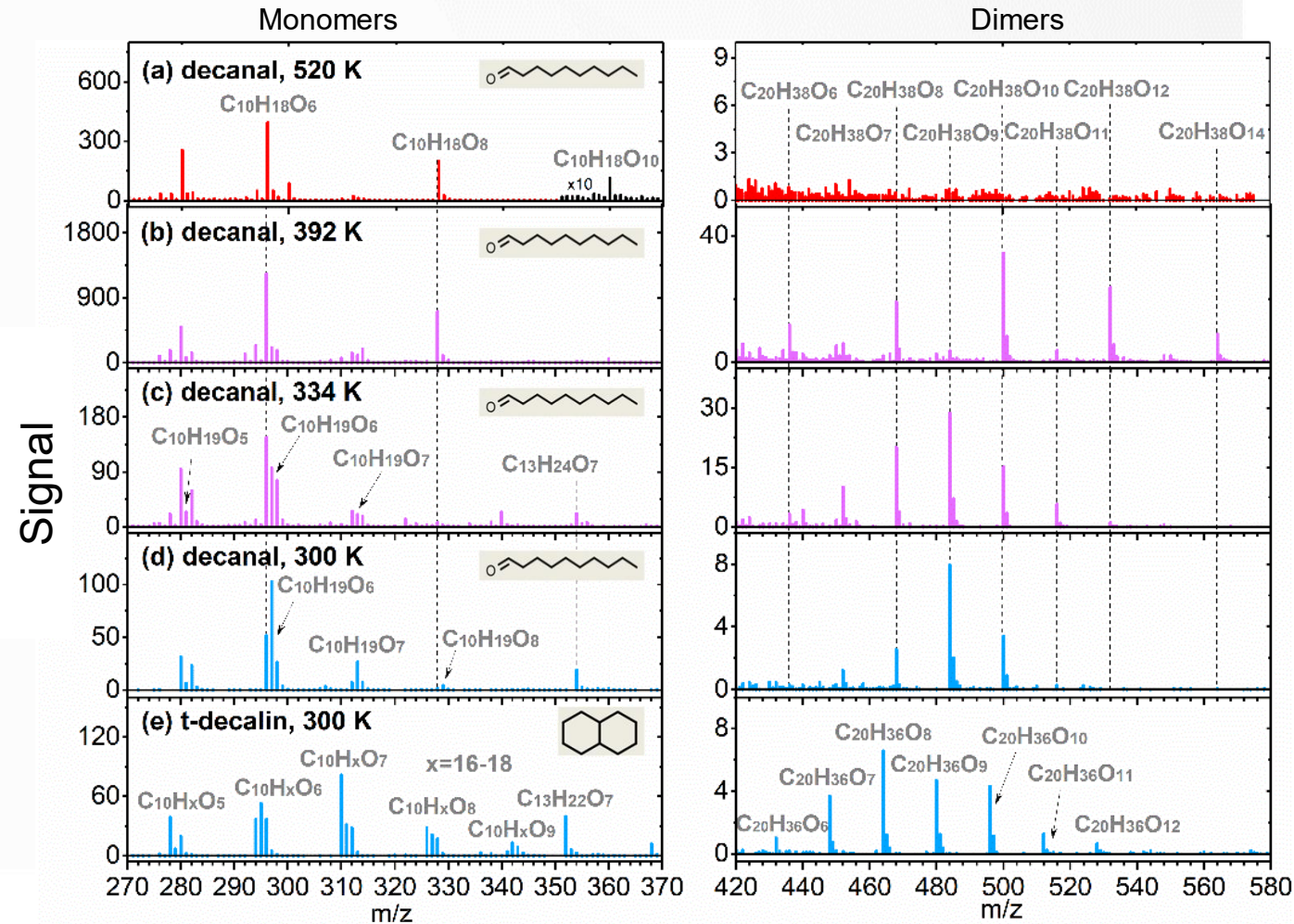




RESULTS 1

AUTOOXIDATION AT DIFFERENT TEMPERATURES

- Decanal, 300 K, UHEL flow reactor:
 - Oxidation by OH from TME+O₃
 - Still high oxidation levels!
 - Similar to 334 K, but slightly less oxygenated
 - Decalin**, 300 K, UHEL flow reactor :
 - Oxidation by OH from TME+O₃
 - Also high oxidation levels!
- (In all cases ~10 ppm VOC, meaning negligible potential for multiple OH reactions to take place)
- HOM are observed at room temperature, both from a cycloalkane and an aldehyde
 - But at what yields?*

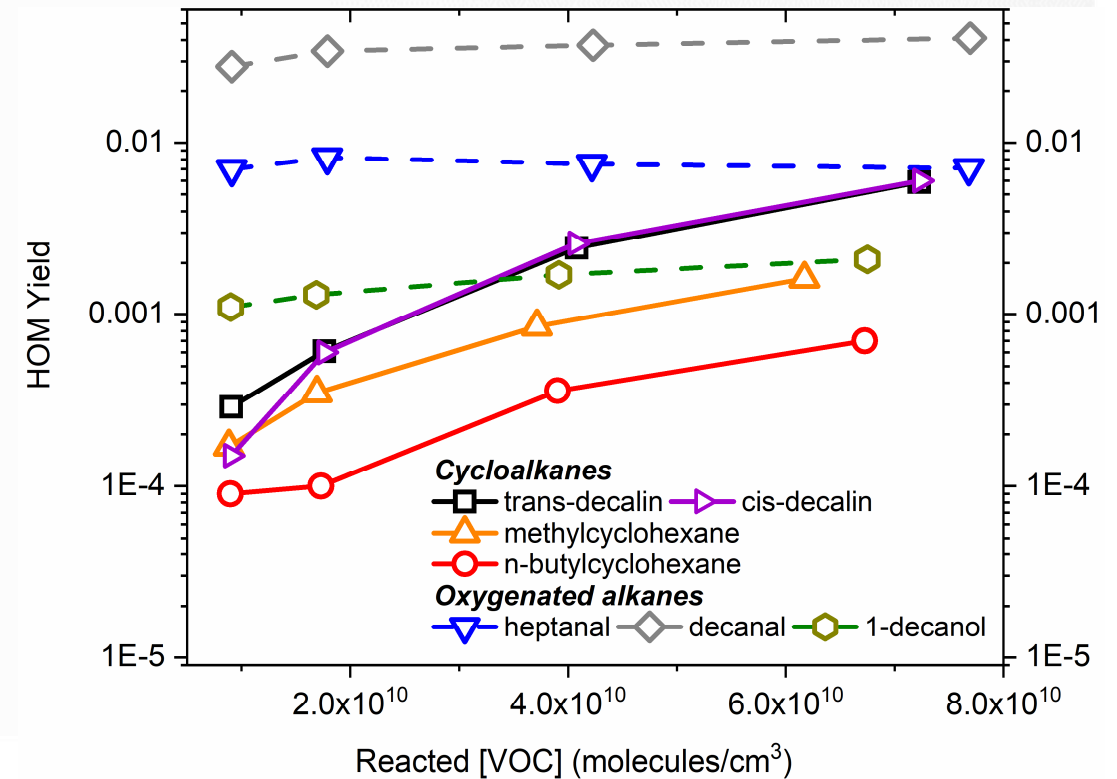




RESULTS 2

ALKANE HOM YIELDS

- Experiments at room temperature in UHEL flow reactor, 3 s reaction time:
 - Oxygenated alkanes: Fairly high HOM yields, moderate increase with reacted VOC
 - Cycloalkanes: Rapidly increasing HOM yields with reacted VOC
 - Linear and branched alkanes: No HOM observed
- Could trends be explained by combination of RO and RO₂ isomerization?*
 - I.e. increased reaction rate → increased RO₂ cross reactions → increased RO formation*

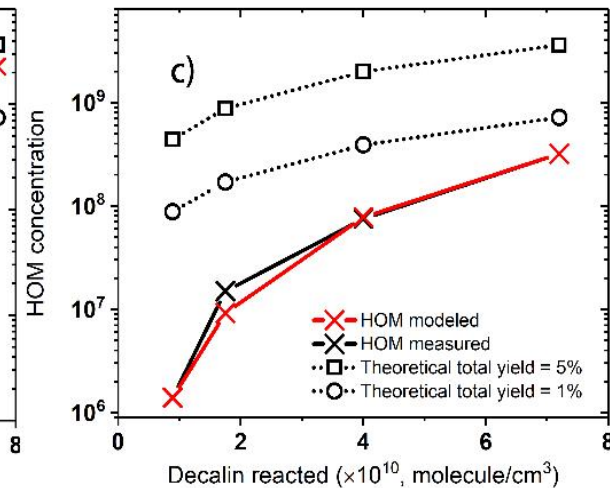
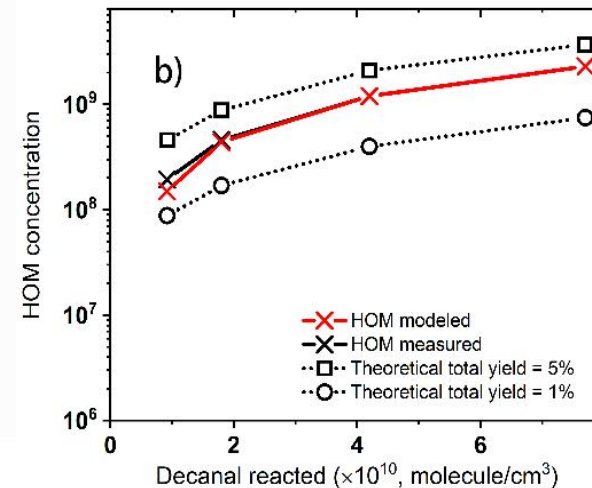
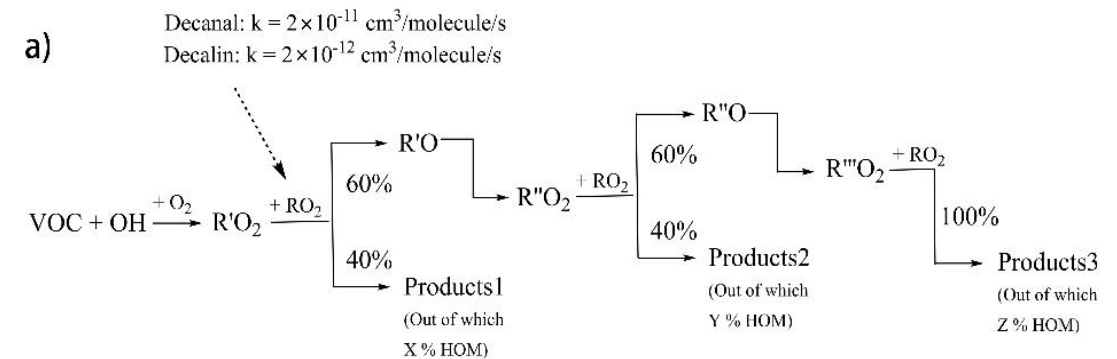




RESULTS 2

ALKANE HOM YIELDS

- A simple kinetic model can reproduce our results if assuming that
 - all detected decanal products have undergone **one RO isomerization step**
 - all detected decalin products have undergone **two RO isomerization steps**
- Without RO steps, increasing trends could not be captured
- *If RO steps important, what does it mean for high-NO_x conditions (where alkanes normally found)?*

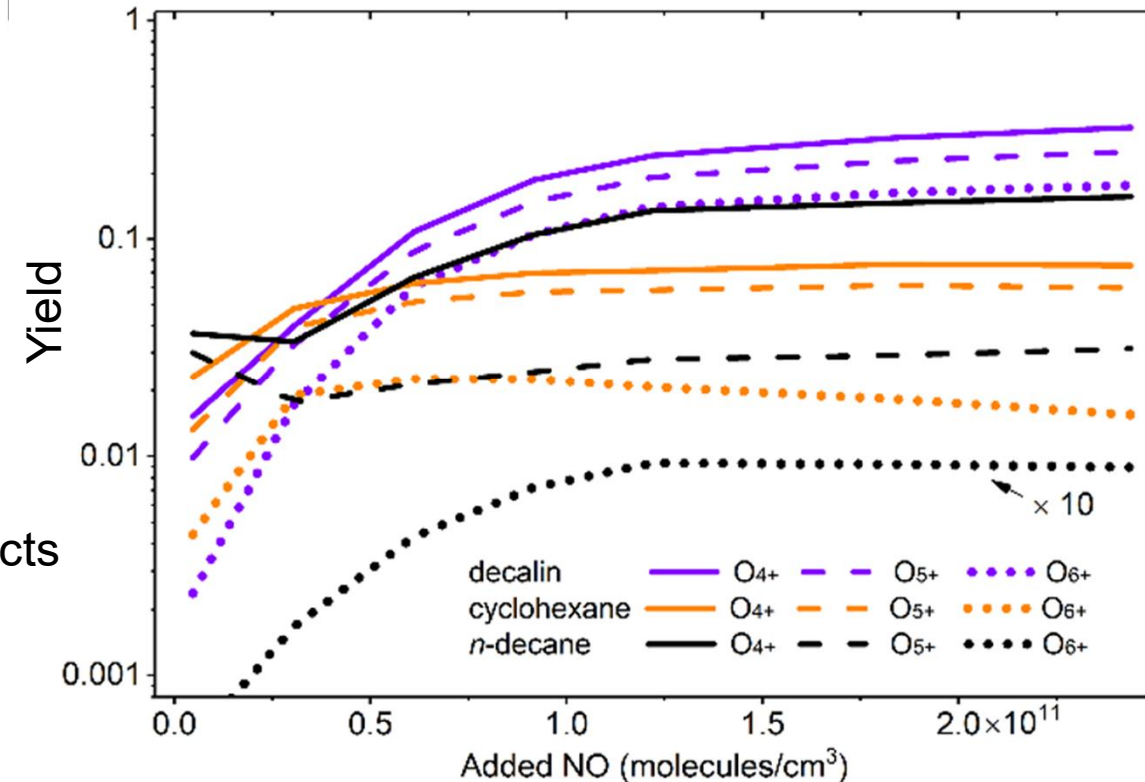




RESULTS 2

ALKANE HOM YIELDS WITH NO

- In TROPOS flow reactor, alkane + OH at different [NO], reaction time 8 s, ethylamine CIMS:
 - Dotted lines (O_{6+}) resemble earlier HOM yields, but now yields also for O_{4+} and O_{5+} products included
 - At low NO (~ 1 ppb): Yield increase due to increased oxidation rates
 - At high NO (nearly 10 ppb):
 - Decalin HOM yields nearly 20 %!
 - Decane HOM yield low, but abundant O_4 and O_5 products
 - No clear indication of autooxidation being outcompeted!





IMPLICATIONS 1

ALKANES AND SOA

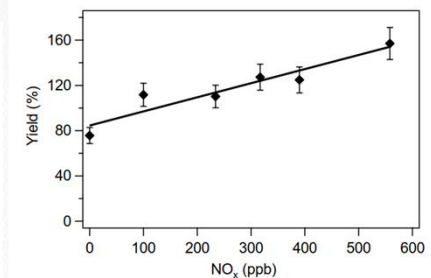
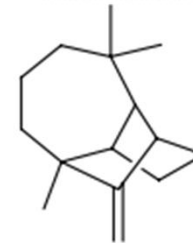
- For most monoterpenes, HOM and SOA yields decrease with NO. For alkanes, SOA known to be high even at high NO. Now we show that this is true also for autoxidation products.
 - Or at least that multi-step isomerization of RO and/or RO₂ is more common than thought
 - “Autoxidation” formally limited to RO₂ isomerization
- Praske et al., 2017, PNAS: “As a result of policies to reduce emissions of NO_x, autoxidation is now becoming an important pathway for urban photochemistry”
 - Our results suggest that autoxidation may already be highly competitive for some systems, and at lower NO_x, oxidation levels may potentially even decrease.



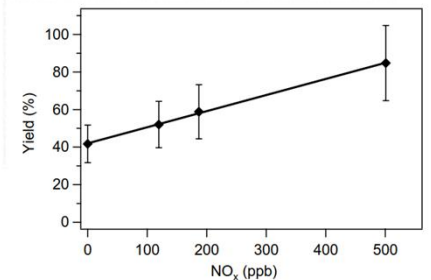
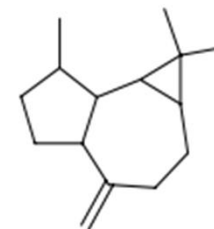
IMPLICATIONS 2 OTHER SYSTEMS

- Our results on alkanes can be extrapolated also to other systems. For example, some sesquiterpenes without endocyclic double bonds (e.g. longifolene and aromadendrene) have shown increased SOA yields with NO_x. (Ng *et al.*, 2007, ACP)
- In particular, saturated cyclic structures seem to greatly enhance autoxidation, as the RO step can break the ring and form a carbonyl-containing RO₂

longifolene



aromadendrene





SUMMARY AND OUTLOOK

- Autoxidation, and non-terminating isomerization reactions in general, produce more highly oxygenated products from alkane oxidation than previously thought
 - Even at very high NO.
 - NO can potentially even enhance the oxidation.
 - Strong implication that autoxidation/isomerization linked to SOA also in alkane oxidation.
- Next step: Direct, concurrent measurements of SOA and HOM from alkane oxidation
 - Would be ongoing right now, if it weren't for COVID shutdown.