On the potential use of highly oxygenated organic molecules (HOMs) as indicators for ozone formation sensitivity

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Introduction

- Ozone (O_3) protects lives from harm of solar ultraviolet (UV) radiation in the stratosphere but is toxic in the troposphere [1].
- Tropospheric O_3 is a key oxidant, and source of other oxidants, for various volatile organic compounds (VOCs) [2].
- Recently, highly oxygenated organic molecules (HOMs) were identified as a new compound group formed from oxidation of many VOCs, making up a significant source of secondary organic aerosol (SOA) [3], [4].
- The pathways forming HOMs involve autoxidation of peroxy radicals (RO_2), formed in many VOC oxidation reactions.
- RO_2 + NO, followed by NO_2 photolysis, is a net source for O_3 [5]. It also affects HOM distributions by competing with other bimolecular reactions.
- **Thus, we aim to assess whether HOM ratios can function as a real-time indicator for O_3 formation sensitivity.**

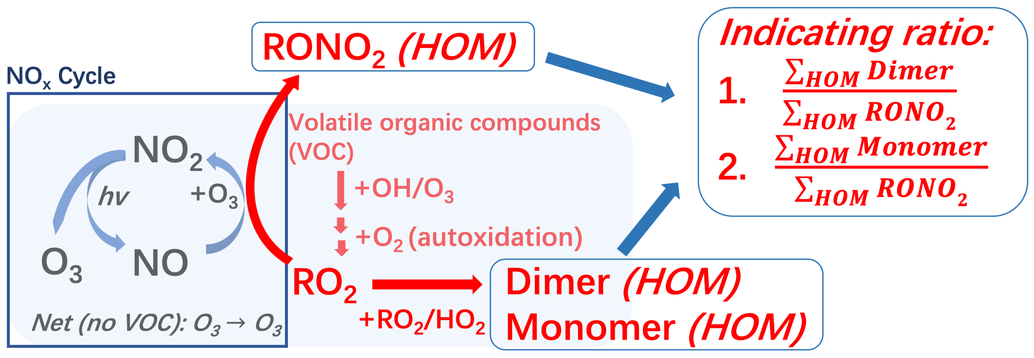

Fig.1 A sketch of the intrinsic connection between HOM and O_3 formation.

Methods

Experiments:

- Monoterpene oxidation experiments, conducted in the COALA chamber [6] (2 m^3).
- "Steady-state mode" [7], [8] with continuous flow: each stage of experiments lasted around 3 times the residence time.
- Input: O_3, α-pinene, NO_2, and UV light (400 nm).

Instrumentation:

1. NO_3-CIMS [9] (nitrate-adduct Chemical Ionization Mass Spectrometer): online measurements of HOMs.
2. PTR (Proton Transfer Reaction Time-of-Flight mass spectrometer): online measurements of α-pinene.
3. NO-NO_2 and O_3 analyzers: online NO_x and O_3 measurements.

Model:

- A simple 0-D box model was constructed to exclusively simulate the concentrations of O_3 and its precursors, NO_x and α-pinene, and to generate O_3 isopleth diagrams. It was also used to determine NO_2 photolysis rates.

Conclusions

- Due to the intrinsic connection between the formation pathways of O_3 and HOMs, the ratio of HOM dimers or non-nitrate monomers to HOM organic nitrates could be used to determine O_3 formation regimes (either VOC- or NO_x- limited).
- Given the fast formation and short lifetimes of HOMs, the HOM-based indicating ratios can describe the O_3 formation in real time.
- Despite the success of our approach in this simple laboratory system, the applicability to the much more complex atmosphere remains to be determined.

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Main results

- Both indicating ratios ($\frac{\sum HOM_{Di}}{\sum HOM_{ON,O>8}}$, $\frac{\sum HOM_{Mono,O>8}}{\sum HOM_{ON,O>8}}$) correspond with changes in O_3 concentrations expectedly, suggesting a possible O_3 formation sensitivity (Fig.2). Moreover, the model worked well.
- Model and experimental results (Fig. 3): HOM ratios can qualitatively predict O_3 formation regimes (either VOC- or NO_x- limited).

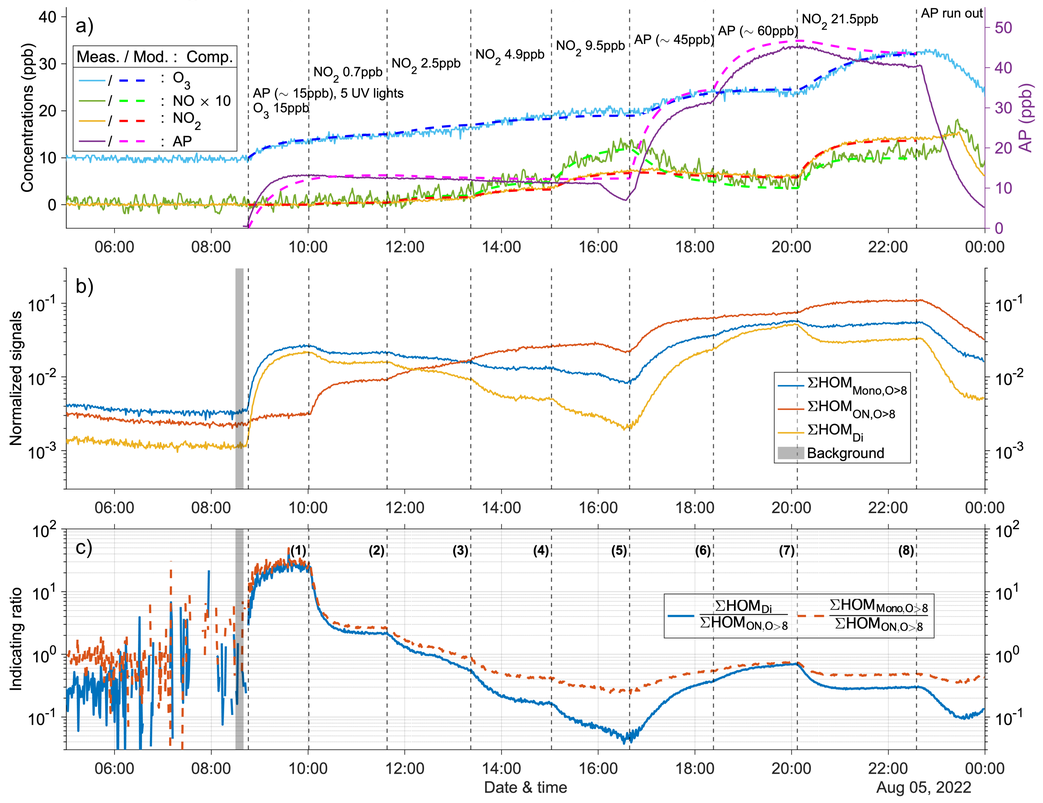

Fig.2 Time series of experiment 2. with 15ppb α-pinene and 15ppb O_3 as initial inputs: a) measured and modeled gas concentrations, b) normalized signals of HOMs, c) indicating ratios.

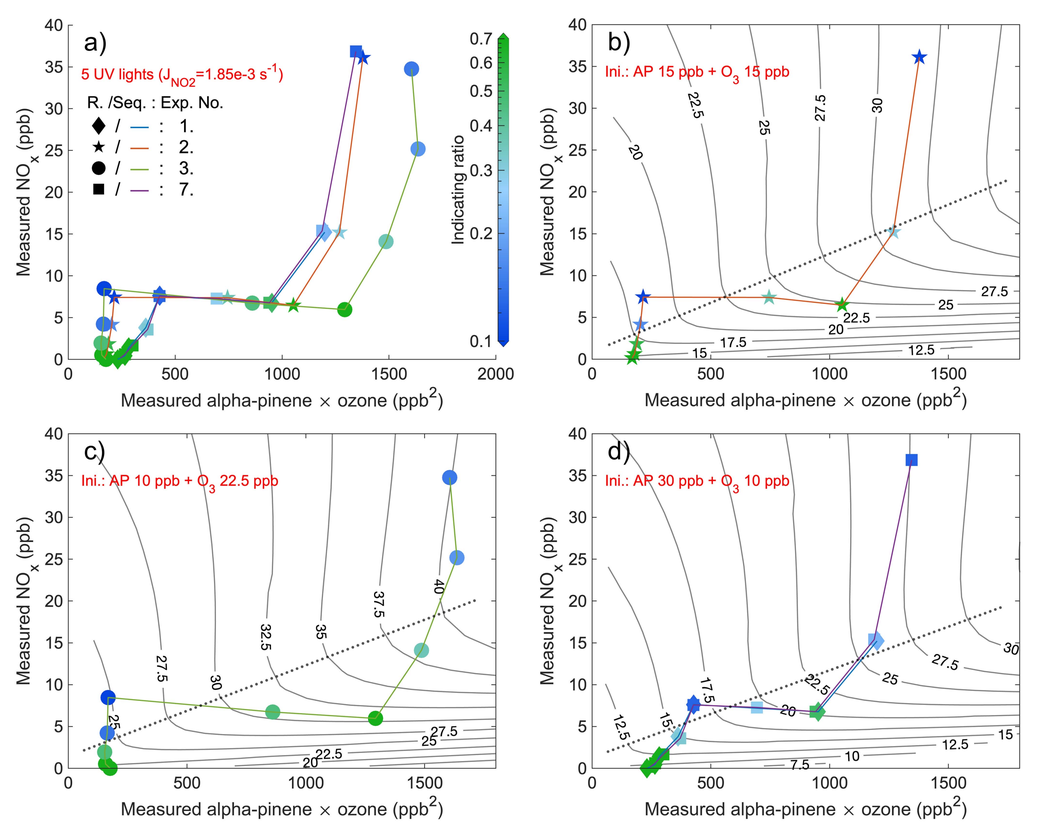

Fig.3 Steady-state indicating ratio $\frac{\sum HOM_{Di}}{\sum HOM_{ON,O>8}}$ of experiments from 4 days with five UV lights. EKMA curves (O_3 isopleths) were simulated by the box model.

Reference

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