Investigation in the atmospheric simulation chamber CHARME of the ozonolysis of prenol, a VOC used as a biofuel

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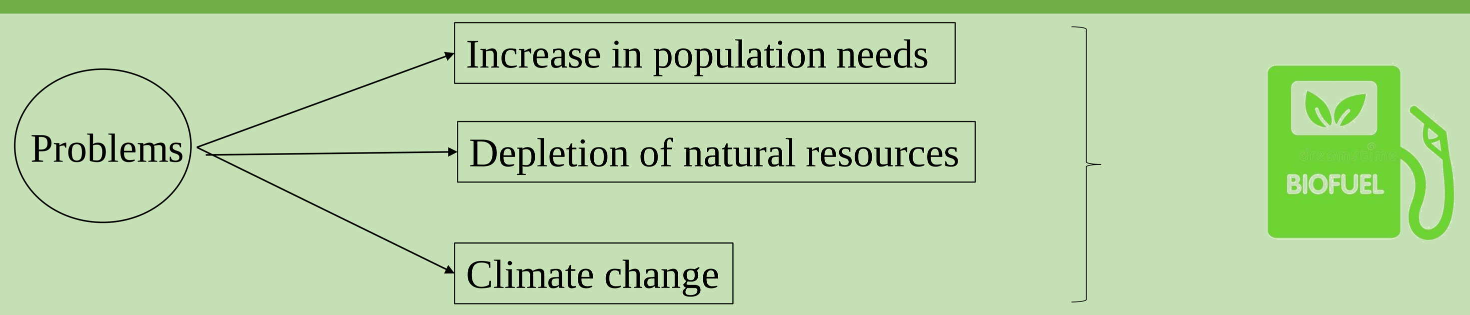
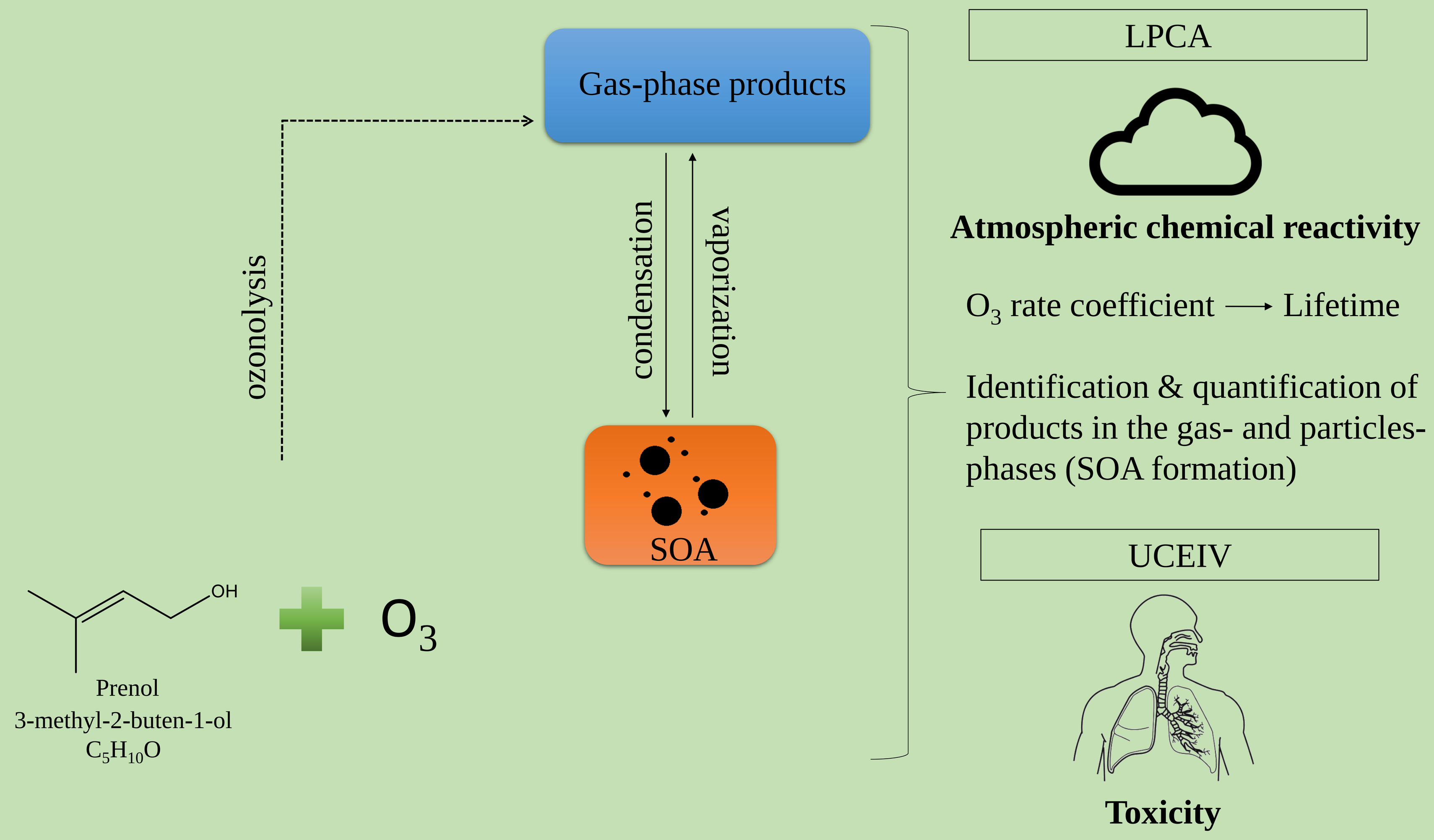
Context

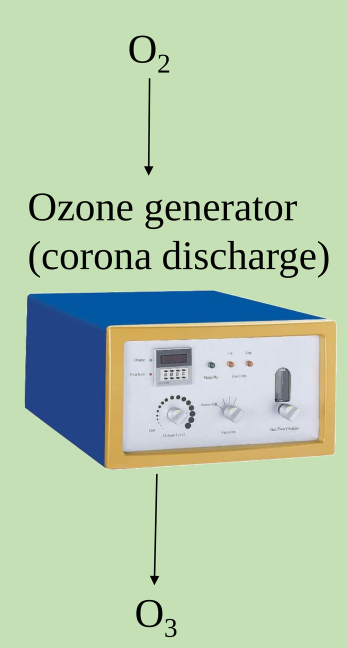


- Advantages of biofuels: renewable energy and contribute to reduce CO_2 emissions
- **First generation biofuels** (also known as conventional biofuels) **derived from edible biomass**
- **Second generation biofuels derived from non-edible biomass**
- Advantages of 2nd generation biofuels over 1st generation: no effect on food balance (Kowalski et al., 2022)
- **Prenol** is a promising **2nd generation biofuel** obtained from lignocellulose (Nascimento et al., 2022)
- Several studies have been performed on **prenol reactivity** with atmospheric oxidants: OH radicals (Mohamad et al., 2022) and Cl atoms (Welz et al., 2015).

Objectives

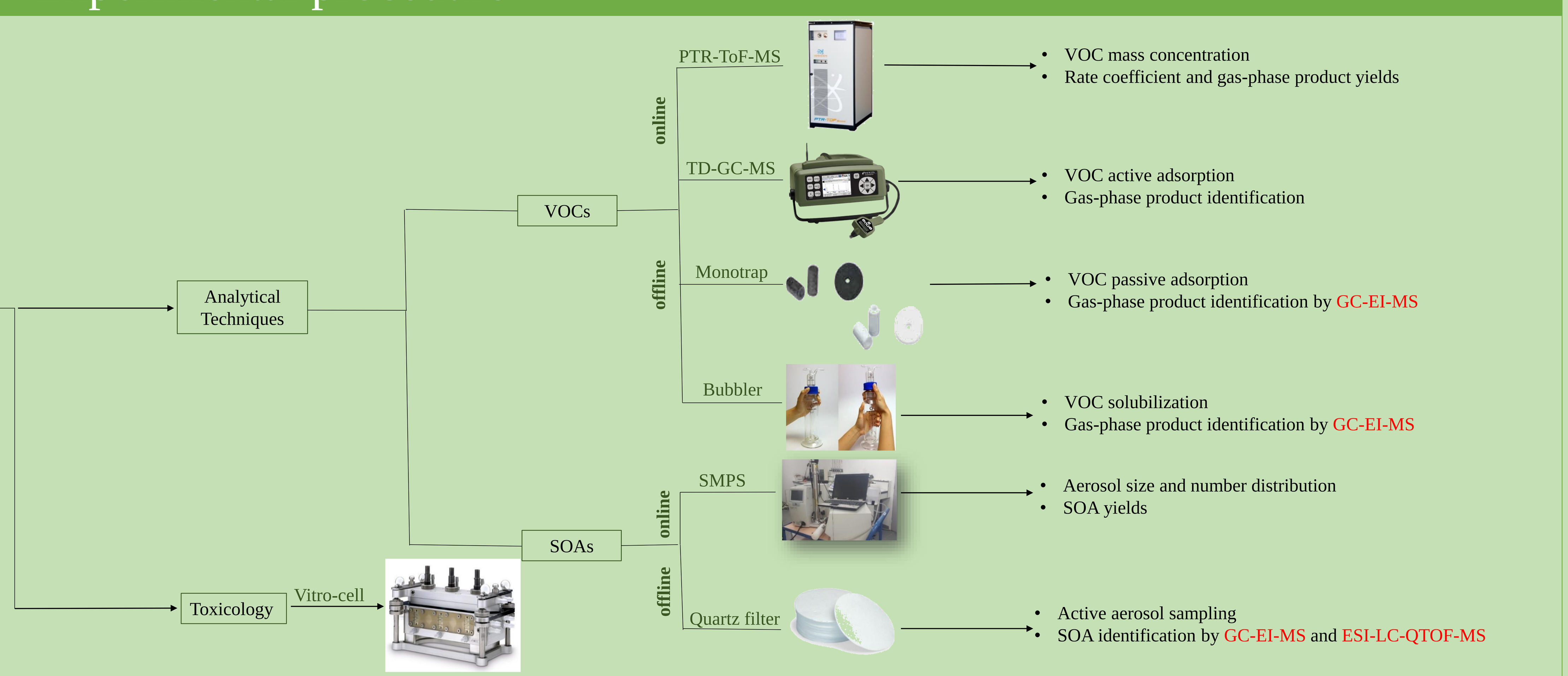


Experimental procedure



Atmospheric simulation chamber CHARME

CHARME characteristics	
Material	Stainless steel (electropolished)
Shape	Cylindrical
Volume	9.2 m³
Temperature	(293±2) K
Pressure	0.1 mbar - P_{atm}



Results

Rate coefficient determination and Lifetime calculation

Pseudo-first order

rate= k[Ozone][prenol]
[ozone] ≥ 10 [prenol]
=> rate =k' [prenol] with k'=k[ozone]

Relative method $\ln\frac{[prenol]_{t=0}}{[prenol]_t} = \frac{k_{prenol+O_3}}{k_{ref+O_3}} \ln\frac{[ref]_{t=0}}{[ref]_t}$

2 references used:
- limonene: k_{O3} = (2.2 ± 0.19)×10⁻¹⁶ cm³.molecule⁻¹.s⁻¹ (IUPAC current recommendation)
- α-pinene: k_{O3} = (9.6 ± 0.15)×10⁻¹⁷ cm³.molecule⁻¹.s⁻¹ (IUPAC current recommendation)

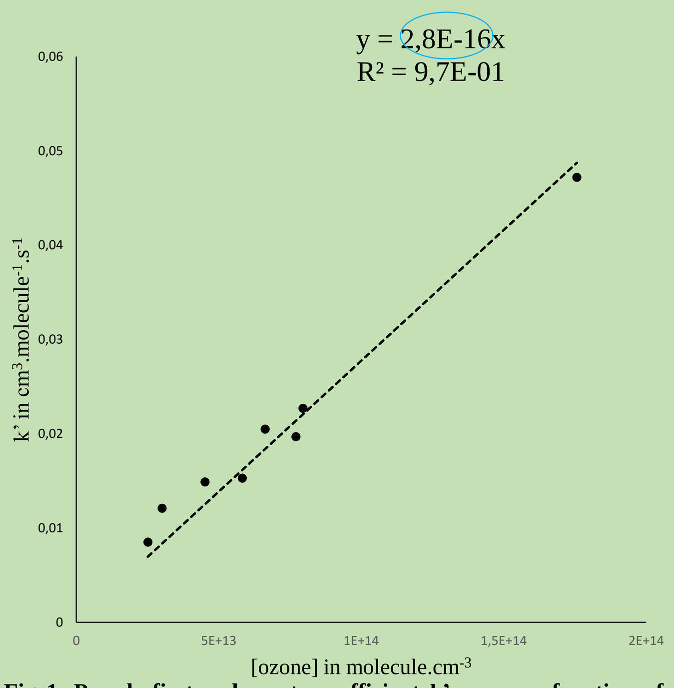


Fig 1. Pseudo-first order rate coefficient k'_{prenol} as a function of the initial ozone concentration (T=293 ± 2K).

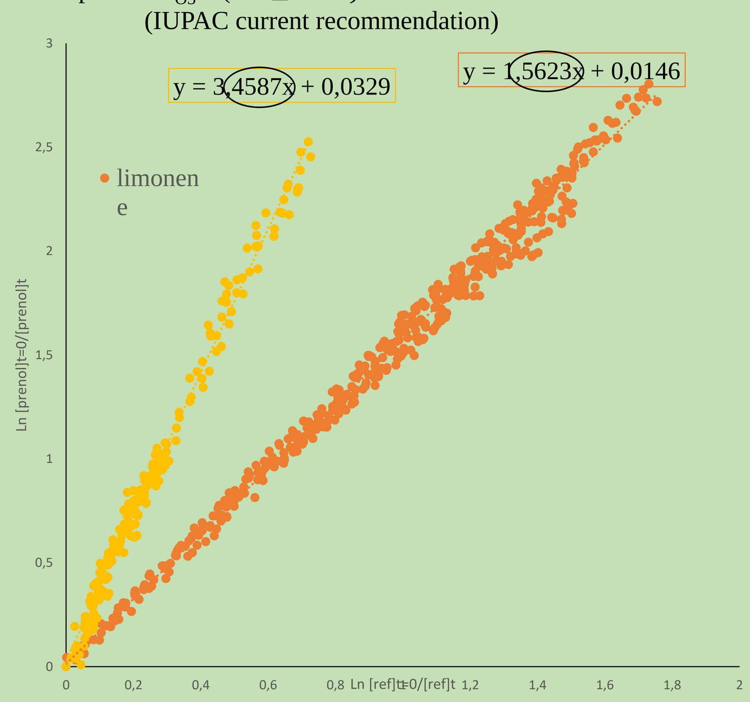


Fig 2. Relative rate plots obtained in the presence of an OH scavenger (1,3,5-trimethylbenzene); (T=293±2 K).

Method	Reference	Rate coefficient × 10⁻¹⁶ (cm³.molecule⁻¹.s⁻¹)	Average rate coefficient × 10⁻¹⁶ (cm³.molecule⁻¹.s⁻¹)	Lifetime with O_3 (in hours)[1]	Lifetime with OH (in hours)[2]	Lifetime with Cl (in hours)[3]
Pseudo-1st order	-	2.8 ± 0.2	3.1 ± 0.5	0.4	10	2.3
Relative	Limonene	3.4±0.3				
	α-pinene	3.3±0.5				

(1)Calculated using $[O_3]$ = 2.46×10¹² molecule.cm⁻³ (100 ppbv; polluted area) (Lin et al., 2001)
(2)Calculated using [OH]= 2× 10¹⁶ molecule.cm⁻³ (Hein et al., Glob.Biogeochen.Cycles, 1997) and $k_{prenol+OH}$ =1.75× 10⁻¹¹ cm³.molecule⁻¹.s⁻¹ (Mohamad et al., 2022)
(3)Calculated using [Cl]= 3×10⁵ molecule.cm⁻³ (Chang et al. , 2004) and $k_{prenol+Cl}$ = 4.02×10⁻¹⁰ cm³.molecule⁻¹.s⁻¹ (Rodriguez et al., 2008)

Gas-phase product identification

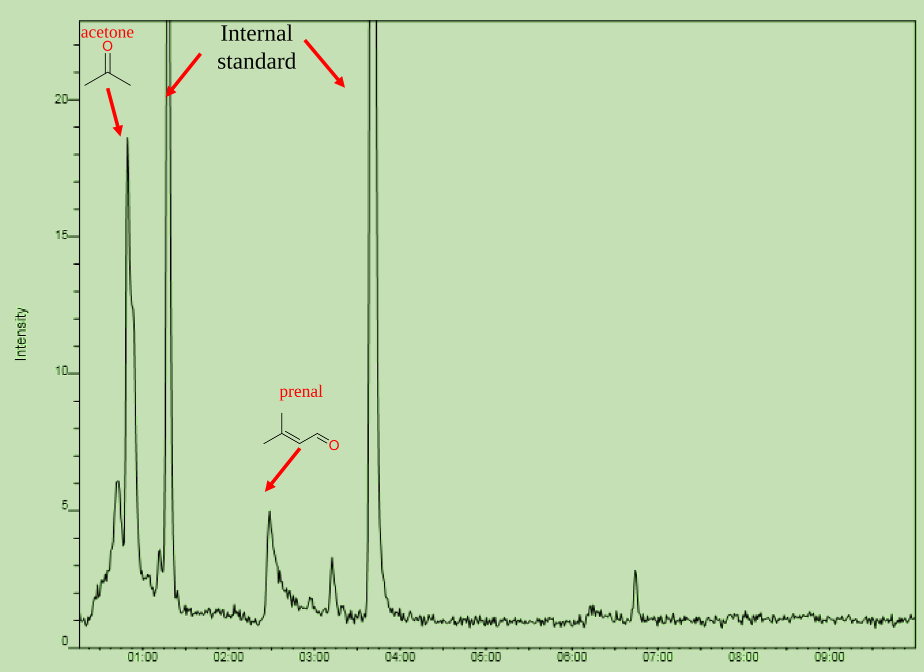


Fig. 3. Characterization of gas-phase oxidation products (TD-GC-MS analysis); Identifications performed with NIST library or peak fragmentation.

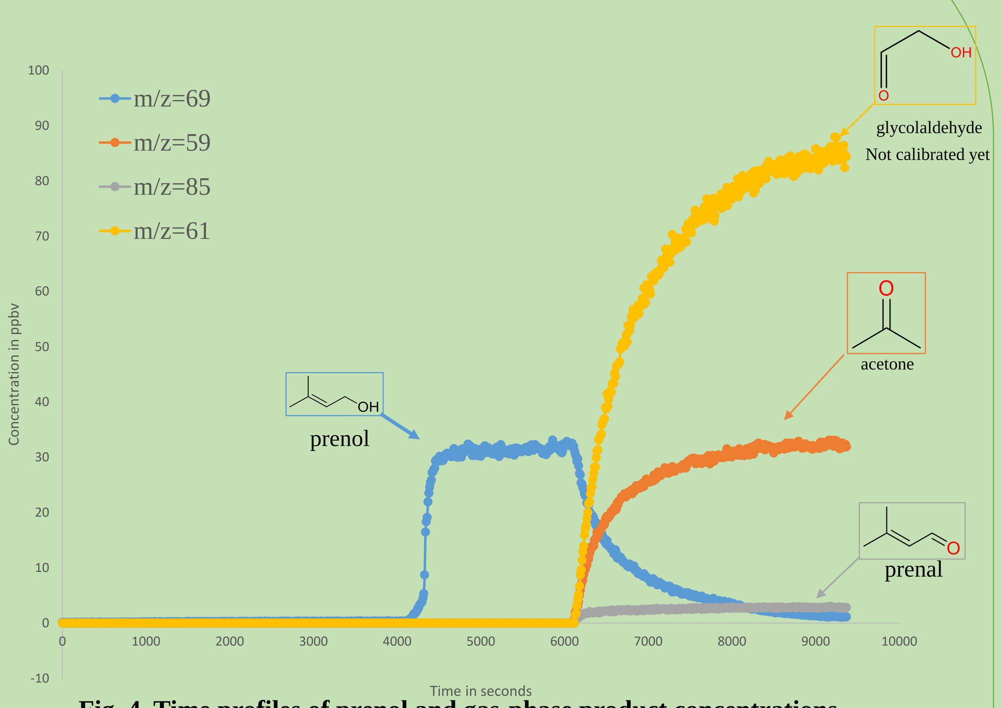


Fig. 4. Time profiles of prenol and gas-phase product concentrations (PTR-ToF-MS analysis).

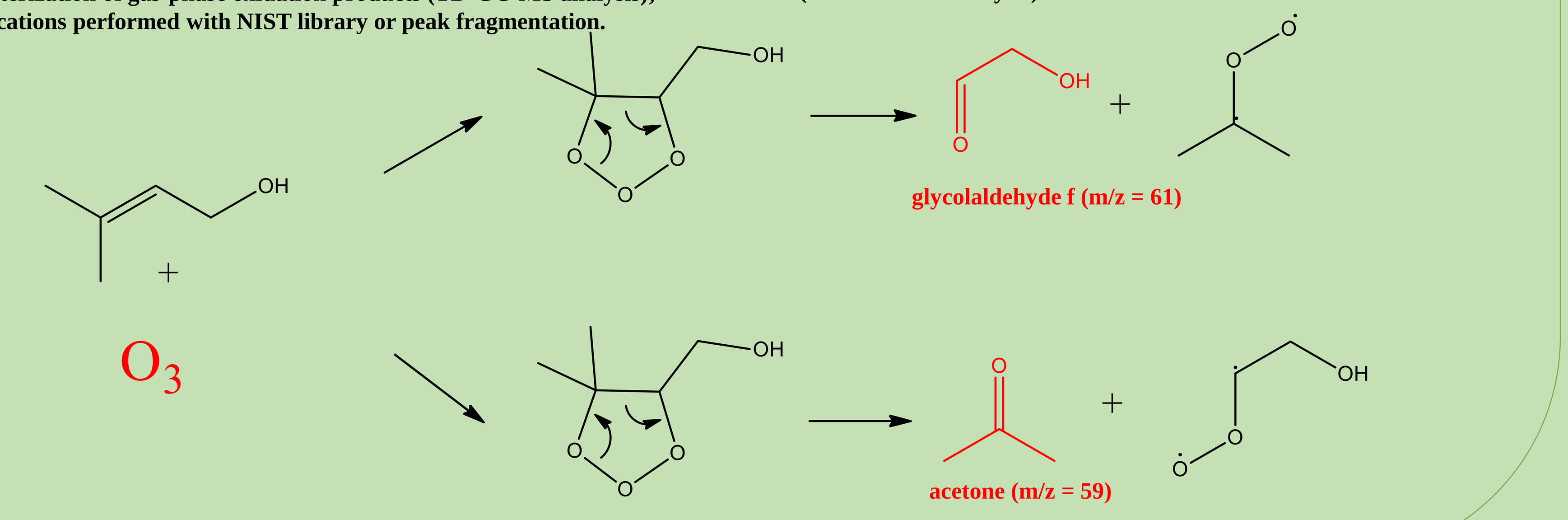


Fig. 5. Chemical mechanism leading to the formation of glycolaldehyde and acetone.

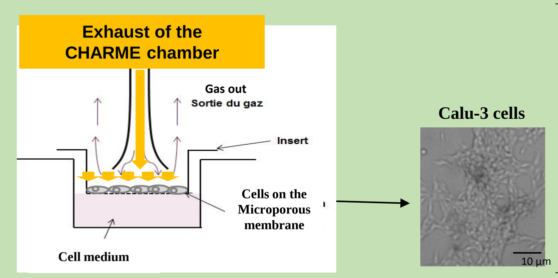
Conclusion

- Rate constant for the ozonolysis reaction of prenol = (3.1 ± 0.5) × 10⁻¹⁶ cm³.molecule⁻¹.s⁻¹
- Ozonolysis of prenol is an important removal pathway in the atmosphere with a lifetime of 0.4 hours
- 3 gas-phase oxidation products were identified: acetone , prenal and glycolaldehyde

Perspectives

- Yields of gas-phase products
- SOA formation potential? Identification + yields

LPCA



Toxicological study

UCEIV

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