# A kinetic investigation on the gas-phase reaction of ozone with four sesquiterpenes

Stefanie Richters, Hartmut Herrmann, Torsten Berndt

Leibniz Institute for Tropospheric Research, TROPOS, Leipzig, Germany

contact: richters@tropos.de

TROPOS
Leibniz Institute for Tropospheric Research

Member of the
Leibniz Association

## Motivation

Sesquiterpenes ($C_{15}H_{24}$, SQT) are emitted by plants with a global emission rate of about 15 million tons per year (Seinfeld and Pankow, 2003). They are possibly an important source of secondary organic aerosol (SOA) but their oxidation processes are scarcely examined.

This study focusses on the kinetics of the reaction of $O_3$ with four atmospherically relevant SQT: β-caryophyllene (β-Car), α-humulene (α-Hum), α-cedrene (α-Ced) and isolongifolene (i-Lon).

Up to now there are only two studies available in the literature describing kinetic measurements of the ozonolysis of a series of SQT, (Shu and Atkinson, 1994; Ghalaieny et al., 2012). As a result of these studies the rate coefficients of the $O_3$ reaction with β-Car and α-Hum differ by three orders of magnitude making a reinvestigation necessary.



β-Caryophyllene          α-Humulene          α-Cedrene          Isolongifolene
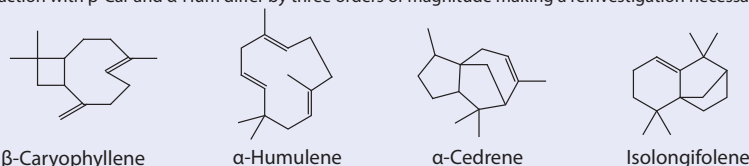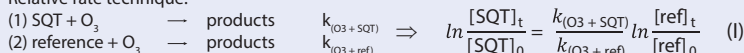
## Experimental setup

Flow tube
- Length: 300 cm, 15 cm inner diameter
- Carrier gas: purified air (99.9999999 vol%)
- Atmospheric pressure
- Temperature: 295 K
- Flow: 5 - 20 l $min^{-1}$ (STP), residence time: 150 - 600 s
- Reactant concentrations:
   [sesquiterpene] = $1 \cdot 10^{11}$ molecules $cm^{-3}$
   $[O_3]$ = (1 - 400) $\cdot 10^{11}$ molecules $cm^{-3}$
   [reference] = (2 - 8) $\cdot 10^{10}$ molecules $cm^{-3}$
   1. Method: $[i\text{-}C_4H_8]$ = $3.7 \cdot 10^{15}$ molecules $cm^{-3}$
   2. Method: $[C_3H_8]$ = (1.2 - 2.5) $\cdot 10^{15}$ molecules $cm^{-3}$
- Detection methods:
   Proton Transfer Reaction - Mass Spectrometry (PTR-MS):
      sampling from centre flow a short capillary directly connected to the drift tube
   Gas chromatography - mass spectrometry coupling (GC-MS):
      Agilent, GC 6890 with MSD 5973; separation column: HP-5MS 19091S-433
      prefocussing device: cryo trap (LN2 temperature) with flash heating for injection
      detection: EI-Q-MS; detection limit: $5 \cdot 10^9$ molecules $cm^{-3}$

## Experimental approach - methods and relative rate technique

1. Method:
- Adjustment of the $O_3$ profile in the tube by high concentrations of i-$C_4H_8$ in order to get negligible $O_3$ concentrations at the sampling point
- Sampling with cryo enrichment followed by GC-MS detection
- Addition of low concentrations of sesquiterpene and reference ((2-10) $\cdot 10^{10}$ molecules $cm^{-3}$)

2. Method:
- $O_3$ present at the sampling point
- Detection with PTR-MS: nearly instantaneous detection after sampling
- Low concentrations of sesquiterpene and reference ((2-10) $\cdot 10^{10}$ molecules $cm^{-3}$)
- $C_3H_8$ addition to scavenge > 95 % of the formed OH radicals

Relative rate technique:
(1) SQT + $O_3$ $\longrightarrow$ products
(2) reference + $O_3$ $\longrightarrow$ products

$$\frac{k_{(O3+SQT)}}{k_{(O3+ref)}} \Rightarrow ln\frac{[SQT]_t}{[SQT]_0} = \frac{k_{(O3+SQT)}}{k_{(O3+ref)}} ln\frac{[ref]_t}{[ref]_0} \quad (I)$$

## Results and Discussion
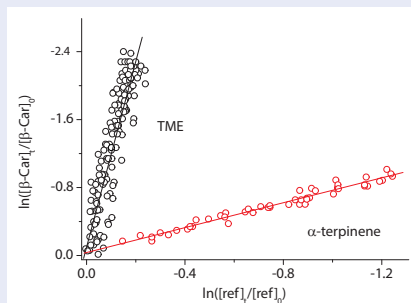
### Relative kinetic experiments with two different methods at 295 K



Figure 1: Experimental data of the reaction of $O_3$ with β-caryophyllene (β-Car) relative to a reference (ref) reaction plotted according to Eq. (I). Red circles: reference: α-terpinene, method 1; Black circles: reference: 2,3-dimethyl-2-butene (TME), method 2.
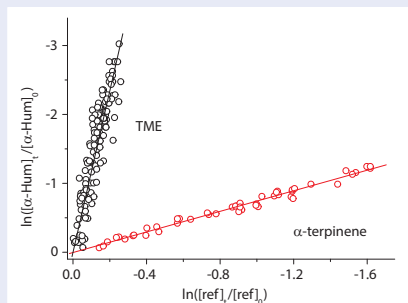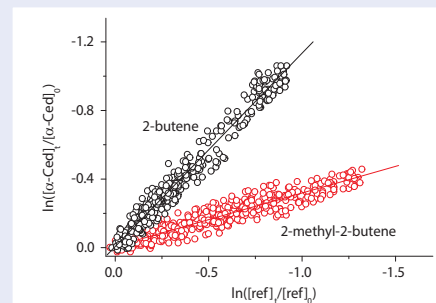
Figure 2: Experimental data of the reaction of $O_3$ with α-humulene (α-Hum) relative to a reference (ref) reaction plotted according to Eq. (I). Red circles: reference: α-terpinene, method 1; Black circles: reference: 2,3-dimethyl-2-butene (TME), method 2.

Figure 3: Experimental data of the reaction of $O_3$ with α-cedrene (α-Ced) relative to a reference (ref) reaction plotted according to Eq. (I). Red circles: reference: 2-methyl-2-butene, method 2; Black circles: reference: 2-butene, method 2.

### Rate coefficients and literature comparison

| Sesquiterpene | T [K] | Reference substance | $\dfrac{k_{(O3+SQT)}}{k_{(O3+ref)}}$ | $k_{(O3+SQT)}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) | Literature |
|---|---|---|---|---|---|
| β-Caryophyllene | 296 | TME, α-Terpinene | | $(1.16 \pm 0.43) \cdot 10^{-14}$ | Shu and Atkinson, 1994 |
| | 366 | TME | | $(5.9 \pm 4.2) \cdot 10^{-17}$ | Ghalaieny et al., 2012 |
| | 295 | TME | $10.9 \pm 0.4$ | $(1.09 \pm 0.22) \cdot 10^{-14}$ | This work |
| | 295 | α-Terpinene | $0.73 \pm 0.02$ | $(1.10 \pm 0.3) \cdot 10^{-14}$ | This work |
| α-Humulene | 296 | TME, α-Terpinene | | $(1.17 \pm 0.45) \cdot 10^{-14}$ | Shu and Atkinson, 1994 |
| | 366 | TME | | $(6.4 \pm 4.2) \cdot 10^{-17}$ | Ghalaieny et al., 2012 |
| | 295 | TME | $11.7 \pm 0.4$ | $(1.17 \pm 0.23) \cdot 10^{-14}$ | This work |
| | 295 | α-Terpinene | $0.75 \pm 0.02$ | $(1.13 \pm 0.3) \cdot 10^{-14}$ | This work |
| α-Cedrene | 296 | cis-2-Butene | | $(2.78 \pm 0.71) \cdot 10^{-17}$ | Shu and Atkinson, 1994 |
| | 366 | TME | | $(3.1 \pm 1.9) \cdot 10^{-17}$ | Ghalaieny et al., 2012 |
| | 295 | 2-Methyl-2-butene | $0.31 \pm 0.01$ | $(1.46 \pm 0.13) \cdot 10^{-16}$ | This work |
| | 295 | cis-2-Butene | $1.13 \pm 0.01$ | $(1.3 \pm 0.2) \cdot 10^{-16}$ | This work |
| Isolongifolene | 366 | TME | | $(2.5 \pm 1.1) \cdot 10^{-17}$ | Ghalaieny et al., 2012 |
| | 298 | | | $(2.6 \pm 0.7) \cdot 10^{-17}$ | Pollmann et al., 2005 |
| | 295 | 2-Methyl-2-butene | | $< 2 \cdot 10^{-17}$ | This work |

The rate coefficients of the reaction of $O_3$ with β-caryophyllene and α-humulene support the literature values from Shu and Atkinson, 1994. However the rate coefficient of the reaction of $O_3$ with α-cedrene is one order of magnitude bigger than literature (Shu and Atkinson, 1994; Ghalaieny et al., 2012). The experiment was carried out the same way as for the other sesquiterpenes.

The rate coefficient of the reaction of $O_3$ with isolongifolene was too low to be obtained with the given setup. Only an upper limit is given. The limit is slightly lower than the literature values (Pollmann et al. 2005; Ghalaieny et al., 2012).

The four structural isomers seem to have very different rate coefficients concerning their reactions with ozone. This cannot be easily explained by the different neighbourhoods of their double bonds.

Ghalaieny et al. (2012) stated particle formation as a possible source of error. We detected very little particle formation that cannot considerably interfere with the measurements (< 120 cm$^3$, with cut-off size: 1.5 nm).

## References

M. Ghalaieny et al., PCCP, 14, 6596-6602, 2012.
J. Pollmann et al., Envir. Sci. Techn. 39, 9620-9629, 2005.
J. H. Seinfeld and J. F. Pankow, Annu. Rev. Phys. Chem., 54, 121–140, 2003.
Y. Shu and R. Atkinson., Int. J. Chem. Kin, 26, 1193-1205, 1994.

## Summary

- Relative rate coefficients are determined for four sesquiterpenes reaction with two different methods and PTR-MS and GC-MS detection
- The rate coefficients of the reaction of $O_3$ with β-caryophyllene and α-humulene agree well with the results from a study by Shu and Atkinson, 1994. They are in clear disagreement with the recommendations by Ghalaieny et al., 2012 . These high rate coefficients lead to very short atmospheric lifetimes of the two sesquiterpenes of about two minutes regarding the reaction with $O_3$ ($[O_3] = 7 \cdot 10^{11}$ molecules cm$^{-3}$)
- The rate coefficient of the reaction of $O_3$ with α-cedrene is one order of magnitude higher than literature data by Shu and Atkinson, 1994 and Ghalaieny et al., 2012 and needs further investigation
- For the reaction of $O_3$ with isolongifolene only an upper limit is given which is slightly lower than the results from studies by Ghalaieny et al., 2012 and Pollmann et al., 2005