Two different methods to investigate the kinetics of the gas-phase reaction of ozone with four sesquiterpenes

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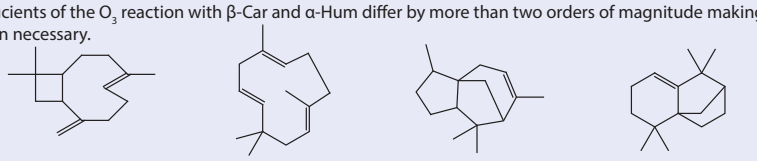
Motivation

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 three studies available in the literature describing kinetic measurements of the ozonolysis of these SQT, (Shu and Atkinson, 1994; Ghalaieny et al., 2012, Pollmann et al., 2008). As a result of these studies the rate coefficients of the O_3 reaction with β-Car and α-Hum differ by more than two orders of magnitude making a reinvestigation necessary.



β-Caryophyllene α-Humulene α-Cedrene Isolongifolene

Experimental setup

- Carrier gas: purified air (99.9999999 vol%)
- Atmospheric pressure
- Temperature: 295 ± 2 K
- Reactant concentrations:
  [sesquiterpene] = (1 - 7) · 10^{11} molecule cm^{-3}
  [O_3] = (1 - 400) · 10^{11} molecule cm^{-3}
  [C_5H_8] = (1.2 - 2.5) · 10^{16} molecule cm^{-3}

Relative method:
- Flow tube length: 300 cm, inner diameter: 15 cm
- Flow: 5 - 20 l min^{-1} (STP), bulk residence time: 150 - 600 s
- Reference substance: 2,3-dimethyl-2-butene (TME); [TME] = 1 · 10^{11} molecule cm^{-3}
- Detection method: Proton Transfer Reaction - Mass Spectrometry (PTR-MS)

Absolute method:
- Stopped-flow experiment
- Cell volume: 5 l
- Detection method: UV spectroscopy, absorption pathlength: 422 cm

Experimental approach - relative rate technique and absolute method

Relative method:
- Detection of SQT and reference substance concentrations by means of PTR-MS
  - nearly instantaneous detection after sampling (short capillary)
- Low concentrations of sesquiterpene and reference ⇒ negligible particle formation
- Only relativ concentrations are necessary

Absolute method - Stopped-flow experiment:
- Detection of the O_3 signal at 254 nm
- Absolute values of initial reactant concentrations are needed
- Numerical solution of the ordinary differential equation system resulting from (3) + (4)
- Estimation of $k_{(O3+SQT)}$ via parameter fitting on $[O_3] = f(t)$

Relative rate technique:

(1) O_3 + SQT ⟶ products; $k_{(O3+SQT)}$

(2) O_3 + reference ⟶ products; $k_{(O3+ref)}$

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

Absolute rate technique:

(3) O_3 ⟶ wall; k_{wall}

(4) O_3 + SQT ⟶ products; $k_{(O3+SQT)}$

Results and Discussion

Relative method:

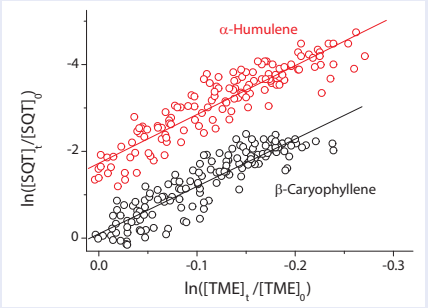


Figure 1: Experimental data of the reaction of O_3 with β-caryophyllene (β-Car) and α-humulene (α-Hum) relative to the reference substance 2,3-dimethyl-2-butene (TME) reaction plotted according to Eq. (I). Red circles: α-Hum (offset: -1.6); Black circles: β-Car

Absolute method:

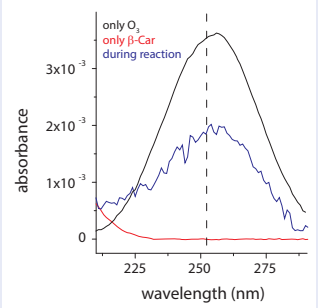
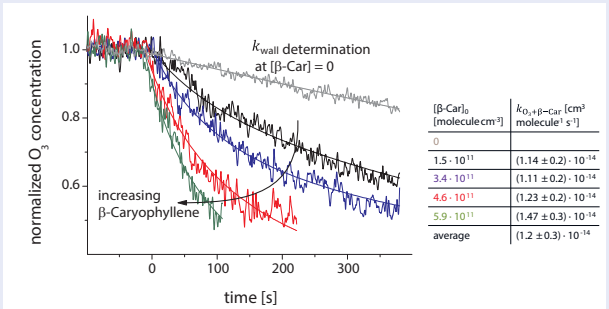


Figure 2: UV spectra of O_3 (black line), β-caryophyllene (β-Car) (red line) and during the reaction of O_3 and β-Car (blue line). β-Car does not absorb at 254 nm (dashed vertical line) and does not influence the O_3 measurement.



[β-Car]0 [molecule cm-3]	kO3+β-Car [cm3 molecule-1 s-1]
0	
1.5 · 10^11	(1.14 ± 0.2) · 10^-14
3.4 · 10^11	(1.11 ± 0.2) · 10^-14
4.6 · 10^11	(1.23 ± 0.2) · 10^-14
5.9 · 10^11	(1.47 ± 0.3) · 10^-14
average	(1.2 ± 0.3) · 10^-14

Figure 3: Experimental data and fitted lines of the reaction of O_3 with β-caryophyllene in a stopped-flow experiment. The O_3 concentration decreases more rapidly with increasing β-caryophyllene concentration. [O_3] = (7.4-9.6) · 10^{11}, [β-Car] = (1.5-5.9) · 10^{11} molecule cm^{-3}. $k_{(O3+SQT)}$ was estimated via parameter fitting on $[O_3] = f(t)$.

Rate coefficients and literature comparison

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 which is slightly lower than the literature values (Pollmann et al. 2005; Ghalaieny et al., 2012).

The results from the absolute method confirm the relative rate coefficient for the reaction of O_3 with β-caryophyllene by Shu and Atkinson and from this work.

The four structural isomers have very different rate coefficients concerning their reactions with ozone. This cannot be easily explained by the different neighbourhood of their double bonds. Ghalaieny et al. (2012) stated particle formation as a possible source of the differences. We detected very little particle formation that cannot considerably interfere with the measurements (< 120 cm^{-3}, cut-off size: d ≤ 1.5 nm).

Sesquiterpene	T [K]	Reference substance	$\frac{k_{(O3+SQT)}}{k_{(O3+ref)}}$	$k_{(O3+SQT)}$ (cm^3 $molecule^{-1}$ s^{-1})	Literature
β-Caryophyllene	296	TME, α-Terpinene		(1.16 ± 0.43) · 10^{-14}	Shu and Atkinson, 1994
	366	TME		(5.9 ± 4.2) · 10^{-17}	Ghalaieny et al., 2012
	295	TME	10.9 ± 0.4	(1.1 ± 0.2) · 10^{-14}	This work
	295	α-Terpinene	0.73 ± 0.02	(1.1 ± 0.3) · 10^{-14}	This work
	295	Absolute method		(1.2 ± 0.3) · 10^{-14}	This work
α-Humulene	296	TME, α-Terpinene		(1.17 ± 0.45) · 10^{-14}	Shu and Atkinson, 1994
	366	TME		(6.4 ± 4.2) · 10^{-17}	Ghalaieny et al., 2012
	295	TME	11.7 ± 0.4	(1.2 ± 0.2) · 10^{-14}	This work
	295	α-Terpinene	0.75 ± 0.02	(1.1 ± 0.3) · 10^{-14}	This work
α-Cedrene	296	cis-2-Butene		(2.78 ± 0.71) · 10^{-17}	Shu and Atkinson, 1994
	366	TME		(3.1 ± 1.9) · 10^{-17}	Ghalaieny et al., 2012
	295	2-Methyl-2-butene	0.31 ± 0.01	(1.5 ± 0.2) · 10^{-16}	This work
	295	cis-2-Butene	1.13 ± 0.01	(1.3 ± 0.2) · 10^{-16}	This work
Isolongifolene	366	TME		(2.5 ± 1.1) · 10^{-17}	Ghalaieny et al., 2012
	298	Other SQT		(2.6 ± 0.7) · 10^{-17}	Pollmann et al., 2005
	295	2-Methyl-2-butene		< 2 · 10^{-17}	This work

References

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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.
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Summary

- Relative rate coefficients are determined for the reaction of O_3 with four sesquiterpenes with a relative and an absolute method with PTR-MS and UV 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 · 10^{11} molecule 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.