

# Particle- and gas-phase analysis of carbonyl compounds formed during monoterpene ozonolysis in chamber studies



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## Introduction

- The emission of biogenic volatile organic compounds (BVOC) exceeds those of anthropogenic compounds by a factor of  $\sim 10$  [Lamb *et al.*, 1993].
- Important constituents of BVOCs are the  $C_{10}H_{16}$  monoterpenes.
- The atmospheric degradation of monoterpenes, which includes reactions with  $O_3$ ,  $NO_3$  and OH radicals, leads to multifunctional oxidation products with lower vapor pressure.
- Condensation and coagulation processes of these oxidation products lead to particle formation and growth.
- Hence, monoterpenes play an important role in the formation of secondary organic aerosol (SOA).
- Carbonyl compounds are formed during the tropospheric degradation of monoterpenes.
- These first generation oxidation products are important intermediates through monoterpene oxidation.
- Due to their semivolatile nature, carbonyl compounds partition between the gas- and particle-phases.
- The knowledge on both gaseous and particulate products is important for better understanding of the mechanism of oxidation processes and the formation of SOA.
- Aerosol chamber studies are particularly suitable as the initial experimental conditions such as RH, T and HC concentration can be controlled.

## Experimental

- The aerosol chamber at the IfT is made of Teflon with a cylindrical geometry.
- The volume is  $19\text{ m}^3$  with a surface/volume ratio of  $2.1\text{ m}^{-1}$ .

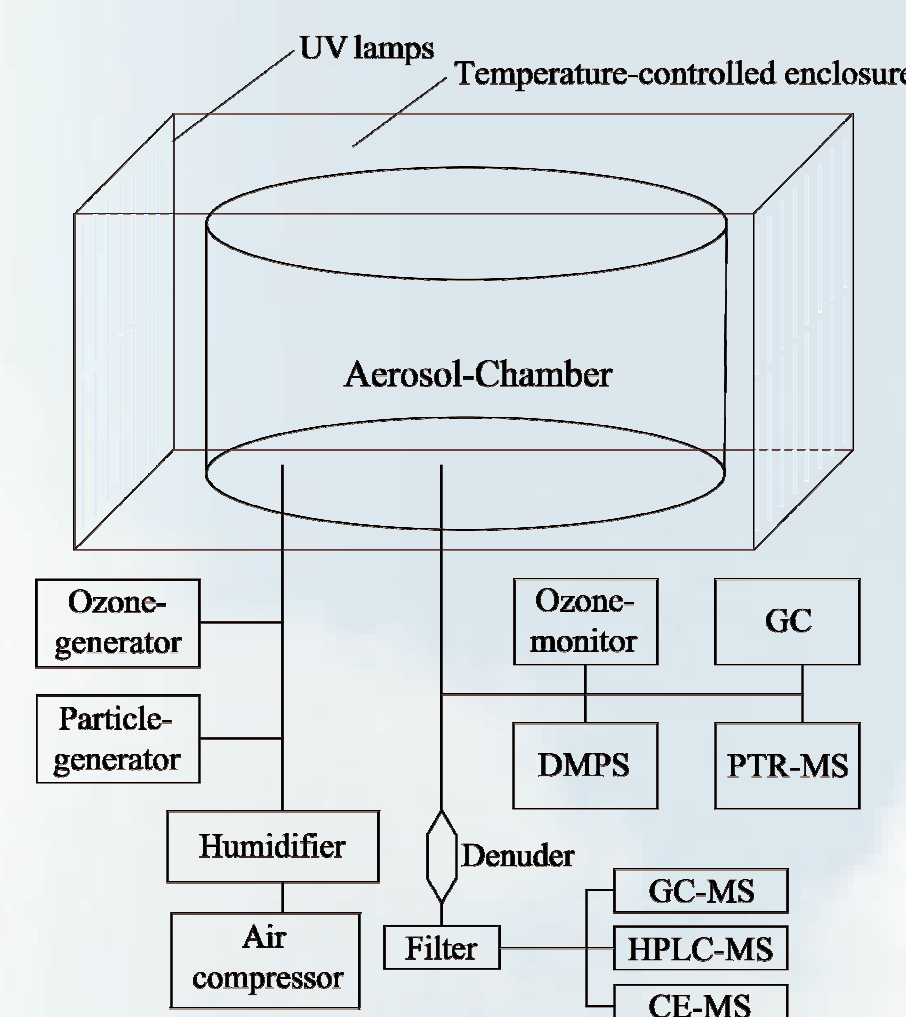


Fig. 1: Diagram of the gas- and aerosol-phase instrumentation of the IfT aerosol chamber



Fig. 2: The aerosol chamber surrounded by UV lamps

Table 1: Experimental information

	$\alpha$ -pinene	$\beta$ -pinene
Chamber experiment		
Initial HC concentration [ppb]	100	102
Consumed HC concentration [ppb]	59	19
$O_3$ [ppb]	60	60
RH [%]	$\sim 50$	$\sim 50$
T [°C]	$21 \pm 1$	$21 \pm 1$
Reaction time [h]	2.5	2.5
Sampling time [h]	1	1
Seed particle	5mM $NH_4HSO_4$	5mM $NH_4HSO_4$



Fig. 3: Denuder coated with XAD-4 and DNPH

- Ozonolysis experiments were carried out with  $\alpha$ -pinene and  $\beta$ -pinene in the presence of ammonium bisulfate seed particles.

- A combined denuder/PTFE filter technique was used to sample the formed carbonyl compounds from both the gas- and particle-phases.

- The combined use of the sorbent XAD-4 and the derivatization reagent 2,4-dinitrophenylhydrazine (DNPH) on the denuder enables us an in-situ derivatization of the gas-phase carbonyl compounds.

- The particle-phase products were analyzed after filter extraction with methanol, followed by an off-line derivatization method with DNPH.

- The derivatization with DNPH forms stable hydrazones, which were afterwards purified with a solid phase extraction (SPE) method using the Oasis HLB cartridges (10mg adsorbent/1ml).

- The derivatives were characterized with an HPLC/ESI-TOFMS (High Performance Liquid Chromatography/Electrospray Ionization Time-of-Flight Mass Spectrometry) technique.

- Pinonaldehyde, one of the major ozonolysis product from  $\alpha$ -pinene, and nopinone, the most abundant ozonolysis product from  $\beta$ -pinene, were quantified with synthesized standard compounds.

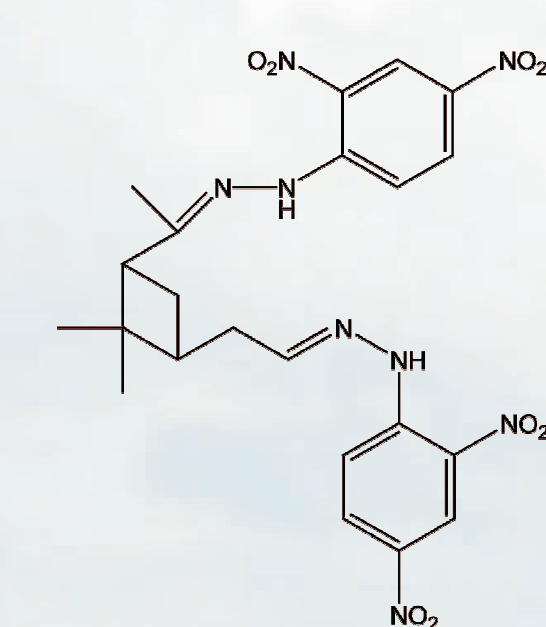


Fig. 4: Pinonaldehyde-2,4-DNPH

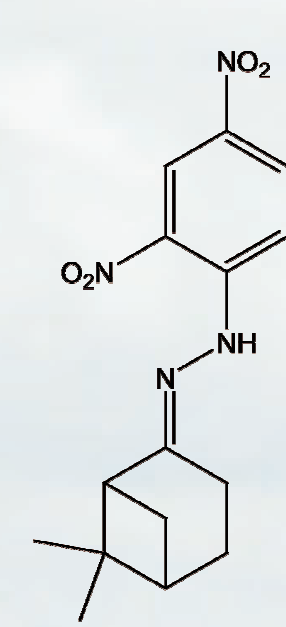


Fig. 5: Nopinone-2,4-DNPH

## Results and Discussion

- Figures 6 and 7 show the extracted ion chromatograms from the identification of carbonyl compounds in the gas- and particle-phases.

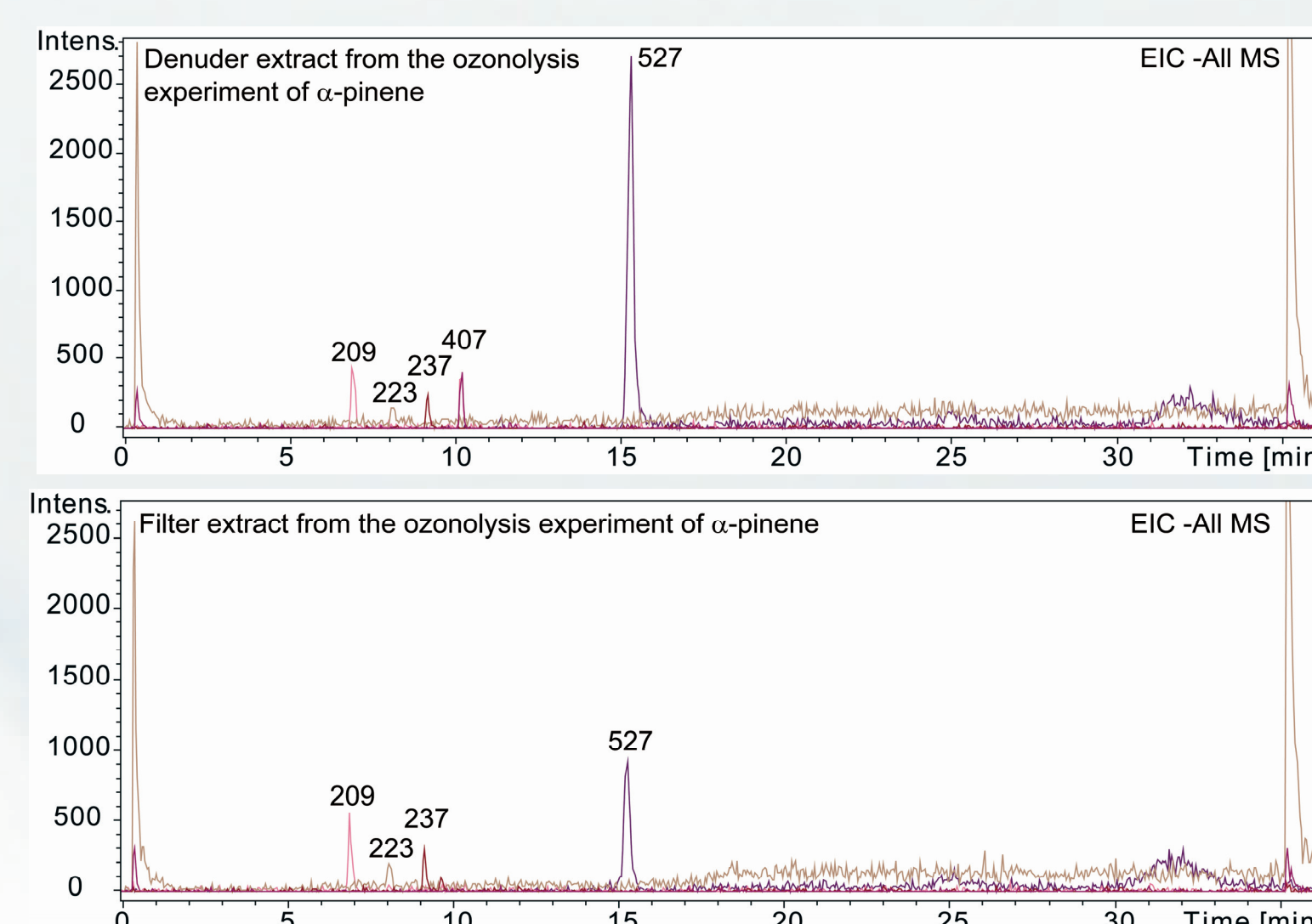


Fig. 6: Extracted ion electropherograms of the HPLC-MS analysis of gas- and particle-phase carbonyl compounds from the ozonolysis of  $\alpha$ -pinene

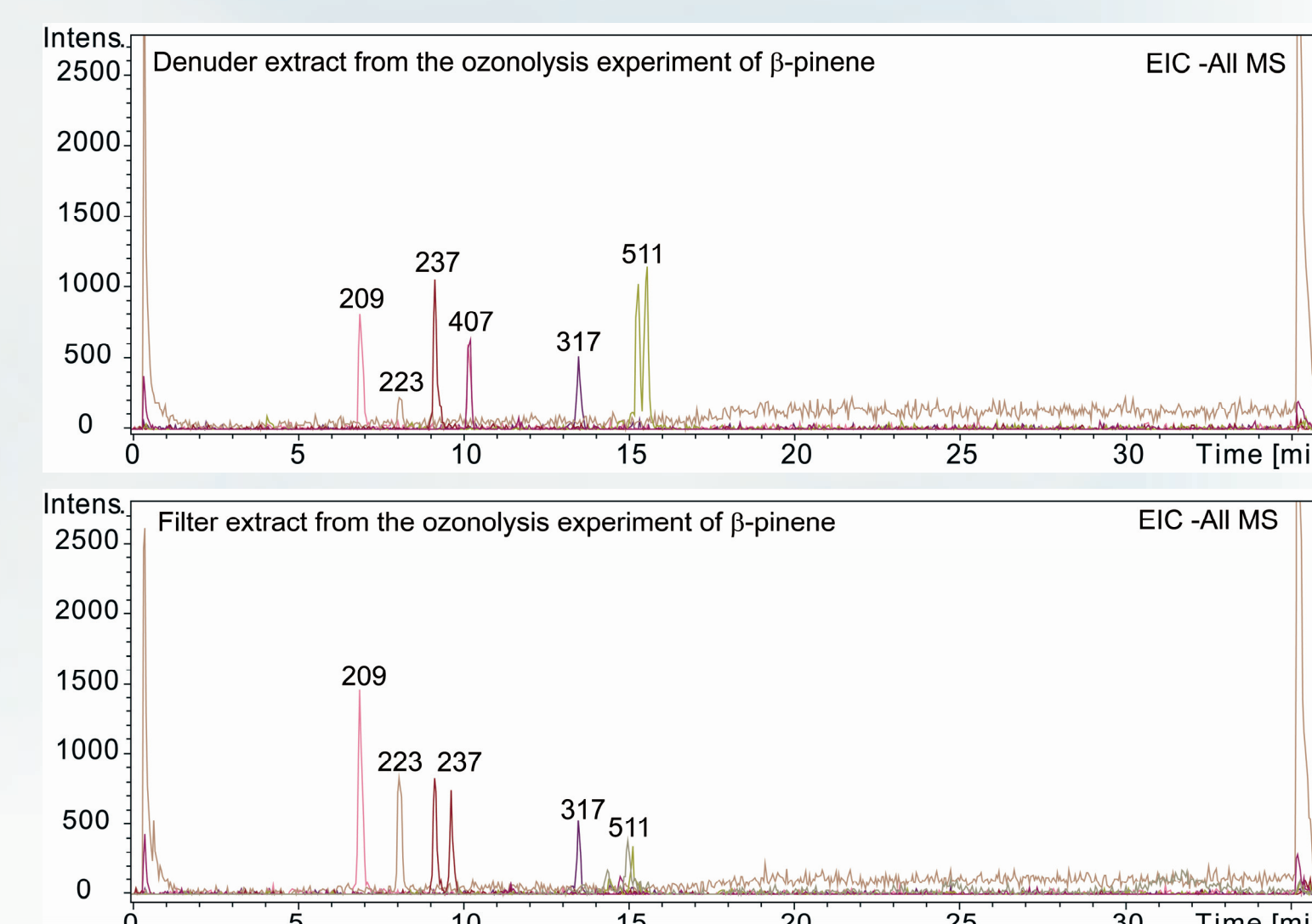


Fig. 7: Extracted ion electropherograms of the HPLC-MS analysis of gas- and particle-phase carbonyl compounds from the ozonolysis of  $\beta$ -pinene

- The identification of the carbonyl-derivatives was based on the determination of the exact chemical formula using the highly sensitive TOFMS.
- Further studies are necessary for the identification of  $m/z$  407.
- Nopinone and pinonaldehyde were positively identified with comparison to the retention time and mass spectra of the derivatized authentic standards.

Table 2: List of detected compounds

2,4-DNPH derivatives	MW [g/mol]	Detected $m/z$	RT [min]
Formaldehyde	210.2	209	6.9
Acetone (2 Enantiomers)	238.2	237	9.1 and 9.7
Acetaldehyde	224.2	223	8.1
Nopinone	318.3	317	13.5
Keto-nopinone	512.1	511	15.3 and 15.5
Pinonaldehyde	528.5	527	15.3

- Yields of the major carbonyl products have been determined using the standards and were corrected for the recoveries on the SPE cartridges (66% for pinonaldehyde and 75% for nopinone).
- Tables 3 and 4 summarize the tentatively results from this study and the product yields reported in the literature.

Table 3: Yields of pinonaldehyde from the  $\alpha$ -pinene ozonolysis

	Molar Yield	Reference
Gas-phase	0.31 <sup>a</sup>	This study
	$0.51 \pm 0.06^a$	Hatakeyama <i>et al.</i> (1989)
	$0.19 \pm 0.04$	Hakola <i>et al.</i> (1994)
	$0.143 \pm 0.024$	Alvarado <i>et al.</i> (1998a)
	$0.48 \pm 0.19$	Ruppert <i>et al.</i> (1999)
	$0.06-0.18$	Yu <i>et al.</i> (1999)
	0.23 (dry)	Warscheid and Hoffmann (2001)
	0.53 (RH $\sim$ 60%)	Warscheid and Hoffmann (2001)
	$0.164 \pm 0.029$	Baker <i>et al.</i> (2001)

Particle-phase	0.0004 <sup>a</sup>	This study
	0.003-0.011	Yu <i>et al.</i> (1999)

<sup>a</sup> In the absence of an OH radical scavenger

Table 4: Yields of nopinone from the  $\beta$ -pinene ozonolysis

	Molar Yield	Reference
Gas-phase	0.51 <sup>a</sup>	This study
	$0.40 \pm 0.02^a$	Hatakeyama <i>et al.</i> (1989)
	0.22	Grosjean <i>et al.</i> (1993b)
	$0.23 \pm 0.05$	Hakola <i>et al.</i> (1994)
	$\sim 0.40$	Ruppert <i>et al.</i> (1999)
	0.158-0.170	Yu <i>et al.</i> (1999)
	$0.16 \pm 0.04$ (dry)	Winterhalter <i>et al.</i> (2000)
	0.44 (higher RH) <sup>a</sup>	Winterhalter <i>et al.</i> (2000)
	$0.198-0.212^a$	Jaoui and Kamens (2003)

Particle-phase	0.0004 <sup>a</sup>	This study
	0.060-0.062 <sup>a</sup>	Jaoui and Kamens (2003)

Partitioning coefficient:  $K_i = F_i/A_i M_o$  [Odum *et al.*, 1996]

Table 5: Gas-particle partitioning coefficients

	Partitioning coefficients [m <sup>3</sup> /μg]	Temperature [K]	Reference
Pinonaldehyde	$0.13 \cdot 10^{-4}$	$294 \pm 1$	This study
	$12 \cdot 10^{-4}$	306-308	Yu <i>et al.</i> (1999)
Nopinone	$0.38 \cdot 10^{-4}$	$294 \pm 1$	This study

$F_i$  ... Particle-phase concentration of compound i [ $\mu\text{g}/\text{m}^3$ ]  
 $A_i$  ... Gas-phase concentration of compound i [ $\mu\text{g}/\text{m}^3$ ]  
 $M_o$  ... Total organic mass concentration aerosol [ $\mu\text{g}/\text{m}^3$ ]  
106  $\mu\text{g}/\text{m}^3$  in the  $\alpha$ -pinene experiment ( $p=1\text{ g}/\text{cm}^3$ )  
20  $\mu\text{g}/\text{m}^3$  in the  $\beta$ -pinene experiment ( $p=1\text{ g}/\text{cm}^3$ )

- Lower temperature used for this study is likely reason for the difference in  $K_i$  values (Table 5).

## Conclusions

- The applied in-situ derivatization method for carbonyl compounds with XAD-4 and DNPH-coated denuders and also the off-line derivatization procedure for the particle phase products is suitable for qualitative and quantitative detection.
- The high sensitivity makes the HPLC/ESI-TOFMS method an ideal tool for the analysis of carbonyl compounds from monoterpene oxidation.
- Further characterization is necessary to obtain a better understanding of both gaseous and particulate carbonyl compounds.

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