



Gas-phase products and secondary organic aerosol formation from the ozonolysis and photooxidation of myrcene



Olaf Böge^a, Anke Mutzel^a, Yoshiteru Iinuma^a, Pasi Yli-Pirilä^b, Ariane Kahnt^a, Jorma Joutsensaari^b, Hartmut Herrmann^{a,*}

^a Leibniz-Institut für Troposphärenforschung (TROPOS), Permoserstr. 15, D-04318 Leipzig, Germany

^b Department of Applied Physics, University of Eastern Finland, P.O. Box 1627, FI-70211 Kuopio, Finland

HIGHLIGHTS

- The ozone and OH-radical and reactions with myrcene have been studied in an aerosol chamber.
- The formation of hydroxyacetone from the ozonolysis of myrcene has been observed.
- This suggests a formation of hydroxyacetone directly from the (excited) Criegee radical (dimethyl carbonyl oxide).
- SOA yields ranged from 0 to 0.01 (ozonolysis in presence of CO) to 0.39 (myrcene OH radical reaction).
- Terpenylic acid was found in the SOA samples collected from OH radical initiated reaction of myrcene.

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ABSTRACT

In this study, the ozone and OH-radical reactions of myrcene were investigated in an aerosol chamber (at 292–295 K and 50% relative humidity) to examine the gas-phase oxidation products and secondary organic aerosol (SOA) formation. The ozone reaction studies were performed in the presence and absence of CO, which serves as an OH radical scavenger. In the photooxidation experiments OH radicals were generated by photolysis of methyl nitrite. The ozonolysis of myrcene in the presence of CO resulted in a substantial yield of 4-vinyl-4-pentenal (55.3%), measured as m/z 111 plus m/z 93 using proton transfer reaction-mass spectrometry (PTR-MS) and confirmed unambiguously as $C_7H_{10}O$ by denuder measurements and HPLC/ESI-TOFMS analysis of its 2,4-dinitrophenylhydrazine (DNPH) derivative. Additionally, the formation of two different organic dicarbonyls with m/z 113 and a molecular formula of $C_6H_8O_2$ were observed (2.1%). The yields of these dicarbonyls were higher in the ozonolysis experiments without an OH scavenger (5.4%) and even higher (13.8%) in the myrcene OH radical reaction. The formation of hydroxyacetone as a direct product of the myrcene reaction with ozone with a molar yield of 17.6% was also observed. The particle size distribution and volume concentrations were monitored and facilitated the calculation of SOA yields, which ranged from 0 to 0.01 (ozonolysis in the presence of CO) to 0.39 (myrcene OH radical reaction). Terpenylic acid was found in the SOA samples collected from the ozonolysis of myrcene in the absence of an OH scavenger and the OH radical-initiated reaction of myrcene but not in samples collected from the ozonolysis in the presence of CO as an OH radical scavenger, suggesting that terpenylic acid formation involves the reaction of myrcene with an OH radical. A reaction mechanism describing the formation of terpenylic acid is proposed.

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1. Introduction

Substantial amounts of biogenic volatile organic compounds (BVOCs) are emitted to the troposphere, primarily by terrestrial vegetation. The total nonmethane BVOC emissions are estimated to

be 1150 TgC yr⁻¹, exceeding the anthropogenic emissions by as much as an order of magnitude (Guenther et al., 1995; Middleton, 1995). Together with isoprene, monoterpenes contribute substantially to the global VOC burden. In the atmosphere, monoterpenes rapidly undergo oxidation reactions by OH radicals (mainly during the day), NO₃ radicals (mainly at night) and O₃ to form multi-functional oxidation products (Atkinson and Arey, 2003). The products of these reactions are likely to be of low volatility and hence may lead to particle formation, as reviewed by Kanakidou

* Corresponding author. Tel.: +49 341 2717 7023.

E-mail address: herrmann@tropos.de (H. Herrmann).

et al. (2005) and Hallquist et al. (2009). Because of the huge influence of particulate organic compounds on thermodynamic, microphysical and chemical properties, a quantitative description of the impact of organic compounds on aerosol formation and modification is needed (Turpin et al., 2000). For example, boreal forests emit sufficiently large amounts of BVOCs which likely influence the radiative budget and cloud condensation nuclei formation through the formation of climate-relevant secondary organic aerosol (SOA) (Tunved et al., 2006; Spracklen et al., 2008).

To date, a number of studies have proposed the atmospheric oxidation mechanisms of monoterpenes (Hatakeyama et al., 1989; Arey et al., 1990; Hakola et al., 1994; Hallquist et al., 1999; Yu et al., 1999; Larsen et al., 2001; Lee et al., 2006a, 2006b), although a significant fraction of the carbon mass in both the gas and particle phases cannot be attributed to the oxidation products proposed in these mechanisms (Calogirou et al., 1999; Atkinson and Arey, 2003; Goldstein and Galbally, 2007).

BVOCs are known to be essential compounds for atmospheric SOA production. However, knowledge regarding SOA composition, sources and chemistry is still extremely limited (Hallquist et al., 2009). The biogenic precursors for SOA production have been the focus of numerous recent studies (Chung and Seinfeld, 2002; Kanakidou et al., 2005; Henze and Seinfeld, 2006; Hallquist et al., 2009). Bottom-up estimates of global SOA production from BVOCs based on laboratory experiments predict total biogenic SOA fluxes of 12–70 Tg yr⁻¹ (Hallquist et al., 2009). Top-down estimates result in higher predicted global SOA fluxes, with a range of 140–910 TgC yr⁻¹ (Goldstein and Galbally, 2007). Based on more recent measurements of the tropospheric aerosol composition, the annual biogenic SOA flux is estimated to be 88 (0–180) TgC (Hallquist et al. 2009). The differences among these SOA flux estimates clearly demonstrate that large uncertainties exist in the estimates obtained from chamber experiments and field measurements.

Myrcene is one of the major monoterpenes in the emissions from coniferous forests. Typically, myrcene represents 2–10% of the total monoterpene emissions, depending on the tree species (Geron et al., 2000; Griffin et al., 1999a; Räisänen et al., 2009). The acyclic structure of myrcene, with three double bonds, provides a high reactivity in the atmospheric oxidation by O₃ as well as with OH and NO₃ radicals (Atkinson and Arey, 2003).

There have been several product studies of the OH radical-initiated and O₃ reactions of myrcene (Ruppert et al., 1999;

Reissell et al., 1999, 2002; Orlando et al., 2000), focusing primarily on the formation of small carbonylic products, such as formaldehyde, acetone and hydroxyacetone, and formic acid. Reissell et al. (2002) also reported the formation of 4-vinyl-4-pentenal. More recently, Lee et al. (2006a, 2006b) studied the SOA yields and gas-phase oxidation products from the ozonolysis and photooxidation of myrcene using the mass-to-charge ratios measured by PTR-MS. They identified protonated 4-vinyl-4-pentenal (mass-to-charge ratio, *m/z* 111) as one of the main gas-phase oxidation products of myrcene ozonolysis. They also reported that the SOA yields from the myrcene OH radical experiments were four times higher than for ozonolysis. SOA formation from myrcene photooxidation has also been reported by Griffin et al. (1999a, 1999b) and Ng et al. (2006).

In the present study, the results from a series of chamber experiments using the gas-phase products and SOA yields obtained from myrcene O₃ reactions with and without an OH radical scavenger as well as from the myrcene OH radical reaction in the presence of NO_x are presented. In addition to the products observed by their *m/z* values, identifications of carbonylic compounds by their 2,4-dinitrophenylhydrazine (DNPH) derivatives have been performed and the result of the analysis of particulate products are presented.

2. Experimental

2.1. Chamber experiments

The chamber experiments were conducted in the aerosol chamber LEAK at the Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany. A description of the chamber and its instrumentation can be found elsewhere (Iinuma et al., 2009). Briefly, the 19 m³ chamber is constructed of flexible Teflon[®] FEP film with aluminum housing and is equipped with a heating and cooling system to maintain a consistent chamber temperature during the experiment (292–295 K). Before each experimental run, the chamber was flushed continuously with purified dry air for at least 18 h.

The experiments conducted in this study are summarized in Table 1. Three types of myrcene oxidation experiments were performed: i) ozonolysis with carbon monoxide (CO) as an OH scavenger (experiments 1–3), ii) ozonolysis without a scavenger (experiments 4–6) and iii) photooxidation (experiments 7–8). Typical time series of myrcene, O₃, NO, NO₂ and the formed SOA

Table 1
The initial conditions of the myrcene chamber experiments and summary of the results obtained from this study and other ozonolysis and photooxidation studies of myrcene.

No.	Experiment	Date	T °C	RH %	O ₃ ppb	NO ppb	NO ₂ ppb	HC ppb	HC:NO _x ppbC ppb ⁻¹	Seed	ΔHC ppb	ΔHC μg m ⁻³	ΔMSOA μg m ⁻³	Y ^a	Reference
1	Myrcene/O ₃ /CO	Dec 8, 2010	20	50	26	–	–	30	–	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	19	106	–	–	This work
2	Myrcene/O ₃ /CO	Dec 9, 2010	20	50	36	–	–	52	–	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	29	161	2	0.01	This work
3	Myrcene/O ₃ /CO	Aug 24, 2010	22	45	76	–	–	89 ^b	–	–	58	322	4	0.01	This work
	Myrcene/O ₃ /cyclohexane		20	6.7	300 ^c	–	–	~100	–	(NH ₄) ₂ SO ₄	98	554	61	0.11	Lee et al. (2006b)
4	Myrcene/O ₃	Dec 6, 2010	21	50	23	–	–	30	–	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	20	111	22	0.20	This work
5	Myrcene/O ₃	Dec 7, 2010	21	50	15	–	–	22	–	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	12	67	10	0.15	This work
6	Myrcene/O ₃	Aug 20, 2010	21	50	83	–	–	118 ^b	–	–	92	511	103	0.20	This work
7	Myrcene/CH ₃ ONO/NO/UV	Dec 13, 2010	20	50	–	50	–	30	6	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	25	139	40	0.29	This work
8	Myrcene/CH ₃ ONO/NO/UV	Dec 14, 2010	19	50	–	47	–	22	5	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	19	106	39	0.37	This work
	Myrcene/HONO/UV		21	53	–	40	80	–	9	(NH ₄) ₂ SO ₄	112	633	272	0.43	Lee et al. (2006a)
	Myrcene/propene/NO _x /UV		38	5	–	23.5	21.5	–	2	(NH ₄) ₂ SO ₄	9.8	52	3.5	0.07	Griffin et al. (1999a,b)
	Myrcene/propene/NO _x /UV		39	5	–	117.9	79.9	–	4	(NH ₄) ₂ SO ₄	77.5	412	57.5	0.17	Griffin et al. (1999a,b)

^a Assuming density 1.25 g cm⁻³.

^b Multiple injections.

^c Estimated from Lee et al. (2006b), 3 times the concentration of parent hydrocarbon.

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