

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

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Introduction

Terrestrial vegetation releases a great variety of volatile organic compounds (VOC) into the atmosphere. Monoterpenes, like myrcene, contribute significantly to this global biogenic VOC emission. In the atmosphere, monoterpenes rapidly undergo oxidation reactions by OH radicals (mainly during the daytime), NO₃ radicals (mainly during the nighttime) and O₃ to form multifunctional oxidation products. The products of these reactions are likely to be of low volatility and hence might lead to secondary organic aerosol (SOA) formation. Because of the huge influence of particulate organic compounds on thermodynamic, microphysical and chemical properties a quantitative description of the impact of organic compounds to aerosol formation and modification

is needed.

Myrcene is one of the major monoterpenes in the emission of coniferous forests. Typically myrcene represents 2-10 % of total monoterpene emission depending on the tree species (Geron *et al.*, 2000; Raisanen *et al.*, 2009). In the present study, we report results from a series of chamber experiments performed in the LEAK chamber at TROPOS in which 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 have been measured.

Experimental

Aerosol Chamber Experiments

The experiments were performed in the TROPOS indoor chamber LEAK. The chamber has a volume of 19 m³. The chamber is equipped with analyzers for ozone, NO and NO₂, sensors for temperature and humidity. The mixing ratios of Myrcene and the formed gas-phase products were monitored using a PTR-MS. Seed particles were produced by nebulizing a solution of 0.03M/0.05M (NH₄)₂SO₄/H₂SO₄. Particle size distributions were monitored using a differential mobility particle sizer (DMPS) system. Three sets of experiments were performed for myrcene oxidation: i) ozonolysis with carbon monoxide (CO) as an OH scavenger (Myrcene/O₃/CO), ii) ozonolysis without a scavenger (Myrcene/O₃) and iii) photo-oxidation experiments (Myrcene/OH/NO).

Analytical Method and Sample Preparation

After each experiment 1.8 m³ of chamber air was sampled using a denuder-filter device. DNPH (2,4-dinitrophenylhydrazine) coated denuders were used to enable the collection and identification of formed gas phase carbonylic compounds. Denuder as well as filter extracts were analyzed by HPLC/ESI-TOFMS.

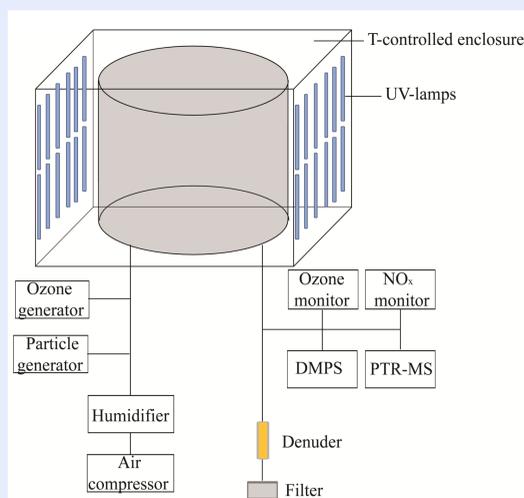


Figure 1. Block diagram of gas- and particle phase instrumentation of the TROPOS aerosol chamber LEAK

Table 1. Initial conditions of the myrcene chamber experiments and summary of the results

Experiment	T °C	RH %	O ₃ ppb	NO ppb	NO ₂ ppb	HC ppb	ΔHC ppb	ΔHC μg/m ³	ΔMSOA μg/m ³	Y	Reference
Myrcene/O ₃ /CO	20	50	26	-	-	30	19	106	-	-	this work
Myrcene/O ₃ /CO	20	50	36	-	-	52	29	161	2	0.01	this work
Myrcene/O ₃ /CO	22	45	76	-	-	89	58	322	4	0.01	this work
Myrcene/O ₃ /Cyclohexane	20	6.7	300	-	-	-100	98	554	61	0.11	Lee et al., (2006b)
Myrcene/O ₃	21	50	23	-	-	30	20	111	22	0.20	this work
Myrcene/O ₃	21	50	15	-	-	22	12	67	10	0.15	this work
Myrcene/O ₃	21	50	83	-	-	118	92	511	103	0.20	this work
Myrcene/OH/NO	20	50	-	50	-	30	25	139	40	0.29	this work
Myrcene/OH/NO	19	50	-	47	-	22	19	106	39	0.37	this work
Myrcene/HONO/UV	21	53	-	40	80	-	112	633	272	0.43	Lee et al., (2006a)
Myrcene/Propene/NOx/UV	38	5	-	23.5	21.5	-	9.8	52	3.5	0.07	Griffin et al., (1999)
Myrcene/Propene/NOx/UV	39	5	-	117.9	79.9	-	77.5	412	57.5	0.17	Griffin et al., (1999)

Results

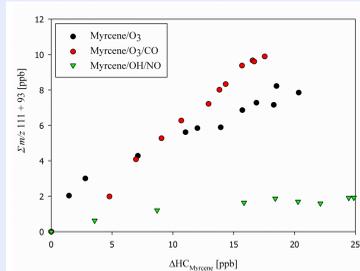


Figure 2. Evolution of *m/z* 111+93 (4-vinyl-4-pentenal) formed during the oxidation of myrcene

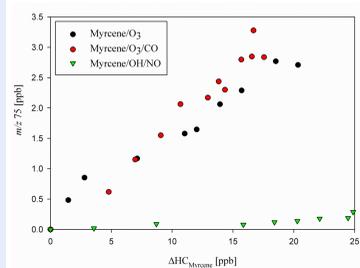


Figure 3. Evolution of *m/z* 75 (hydroxyacetone) formed during the oxidation of myrcene

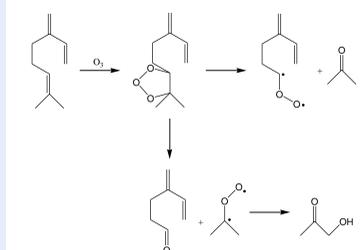


Figure 4. Proposed formation mechanism for 4-vinyl-4-pentenal and hydroxyacetone from the reaction of myrcene and ozone

Gas-Phase Products

Figure 2 shows the formation 4-vinyl-4-pentenal measured as *m/z* 111 plus *m/z* 93 using PTR-MS and confirmed unambiguously as C₇H₁₀O by denuder measurements and HPLC/ESI-TOFMS analysis of its DNPH derivative. The yield of 4-vinyl-4-pentenal was calculated as sum of *m/z* 111 and *m/z* 93, because of the similar change in time, and their 18 amu mass difference, suggesting that *m/z* 93 is a dehydrated fragment of *m/z* 111. The highest yield of 4-vinyl-4-pentenal (53.3 %) was observed in the ozonolysis of myrcene in presence of CO as OH radical scavenger.

An interesting fact from mechanistic point of view is the formation of hydroxyacetone from the ozonolysis of myrcene and not from myrcene OH reaction (Figure 3). This suggests a formation of hydroxyacetone directly from the excited Criegee radical (dimethyl carbonyl oxide). Such a rearrangement of a Criegee radical is different from the currently discussed reaction pathways. The occurrence of hydroxyacetone was confirmed unambiguously by denuder measurements and HPLC/ESI-TOFMS analysis of its DNPH derivative.

SOA Formation

It can be clearly seen in Figure 5 that the ozonolysis of myrcene in the presence of CO as OH radical scavenger produces only a very small amount of SOA. This can easily be explained by the fact that myrcene reacts with O₃ predominantly at the isolated double bond. This leads to the formation of products such as acetone, hydroxyacetone and 4-vinyl-4-pentenal which predominantly exist in the gas-phase. However, myrcene ozonolysis in the presence of OH radicals (reaction without scavenger) leads to a continuous formation of SOA. This is caused by the fast reaction of first generation products with OH radicals and if such first generation products still contain isolated double bonds also O₃ can react with these products. Much enhanced SOA formation was observed in the reaction of myrcene with OH radicals. After an induction period at the beginning of the experiment a pronounced increase in SOA mass can be seen in Figure 5. As stated above, the reactions of first generation products cause this SOA formation.

Terpenylic acid is found in the SOA samples collected from the ozonolysis of myrcene in the absence of an OH scavenger and the photooxidation of myrcene in the presence of NO_x, indicating that terpenylic acid formation likely involves the reaction of myrcene with OH radical. Figure 6 shows the suggested formation mechanisms for terpenylic acid from the reaction of myrcene and OH radical.

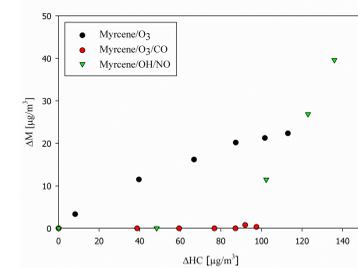


Figure 5. Growth curves obtained from the oxidation of myrcene

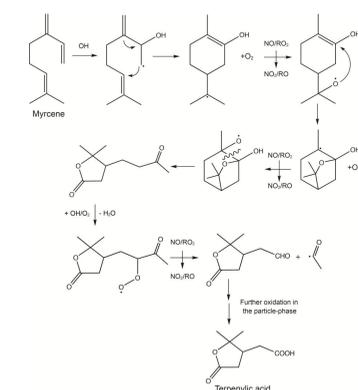


Figure 6. Suggested formation mechanisms for terpenylic acid

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