Aerosol Formation in Gas-Phase Monoterpene Ozonolysis at Near-Atmospheric Concentration

A contribution to subproject CMD

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Introduction

Large amounts of terpenes are globally emitted (Zimmerman *et al.*, 1978; Guenther *et al.*, 1995) and the gas-to-particle conversion upon atmospheric degradation is suspected to form a main fraction of the secondary organic aerosol (SOA). Estimates range from 30 to 270 Tg y^{-1} SOA compared to 140 Tg y^{-1} anthropogenic and 90 Tg y^{-1} biogenic sulfate (Andreae and Crutzen, 1997). For more accurate estimates, the understanding of the gas-phase mechanisms as well as the aerosol formation processes has to be improved. Results from smog chamber experiments (Hoffmann *et al.*, 1997a) indicate, that the terpene-ozone reaction in the dark yields more aerosol than the processes initiated by photo-oxidation. Most studies were so far performed with initial monoterpene concentrations ranging from 100 ppb to a few ppm, and in the presence of seed aerosol. It was found that the SOA yields increase with increasing organic aerosol mass and therefore the question arises if aerosol formation also occurs at near atmospheric conditions, namely low terpene concentration, and in the absence of seed aerosol. The aim of this study was to examine the range of terpene conversion, which is sufficient to form condensation particles during the ozonolysis of selected monoterpenes. For this purpose a variety of monoterpenes and model compounds was investigated at low initial concentrations (4–50 ppb). Furthermore, in order to examine possible relationships between terpene structure and nucleation rate, which is dependent on the rate of terpene conversion, the different terpenes were also investigated at comparable initial rates. The terpene concentration was kept constant and the initial ozone concentrations varied to achieve roughly the same initial rates for the various terpenes.

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Experimental

Ozonolyses were performed in an evacuable spherical glass reactor (V = 570 L) at 730 Torr and 294 K in synthetic air. Ozone was generated with a Hg Penray lamp placed inside the reactor and the concentration determined by its absorption at 253 nm and, additionally, by FTIR spectroscopy. The reaction was then started by adding a diluted mixture of the monoterpene (0.01–0.05 % in N_2) via a 1.38 L transfer cylinder. The mixing during addition was supported by two stirrers inside the reactor.

Nucleation was monitored with a condensation particle counter (TSI 3010) with a lower size detection limit of a particle diameter of 10 nm. For this diameter the counting efficiency is 0.5. For 20 nm particles the efficiency is roughly 0.95 and approaching 1 for diameters above 50 nm. At the lower size range, the counting efficiency approaches zero for particle diameter below 6 nm. The upper limit of the measurable number concentration lies at 10000 particles/cm^3, therefore the sample air stream had to be diluted with particle-free air to allow measuring of number concentrations up to 3×10^5 particles/cm^3.

Results and discussion

The time profiles of the observed particle concentrations upon ozonolysis of 12 ppb terpene at an initial rate of 1×10^8 molec cm^{-3} s^{-1} are shown in Fig. 1. The influence of the initial rate of terpene conversion and particle concentration is shown in Fig. 2 for β-pinene. Also indicated is the converted β-pinene at the reaction time (t_{nuc}), when first particles become observable.

The small changes in the terpene and ozone concentration at these low rates could not be measured by FTIR. The monoterpene conversion was therefore simulated by FACSIMILE, including the OH reaction, with rate constants and OH radical formation yields reviewed by Atkinson (1997). The reaction time (t_{nuc}) and the maximum total number concentration (N_{max}) for all monoterpenes, as well as the calculated terpene and ozone conversion at t_{nuc} are given in Table 1. All terpenes were shown to form nuclei at terpene conversions between 2 and 4 ppb, which is only an upper limit due to the counting efficiency of the particle counter, therefore it is reasonable to assume that the actual nucleation occurs at much lower terpene conversion.

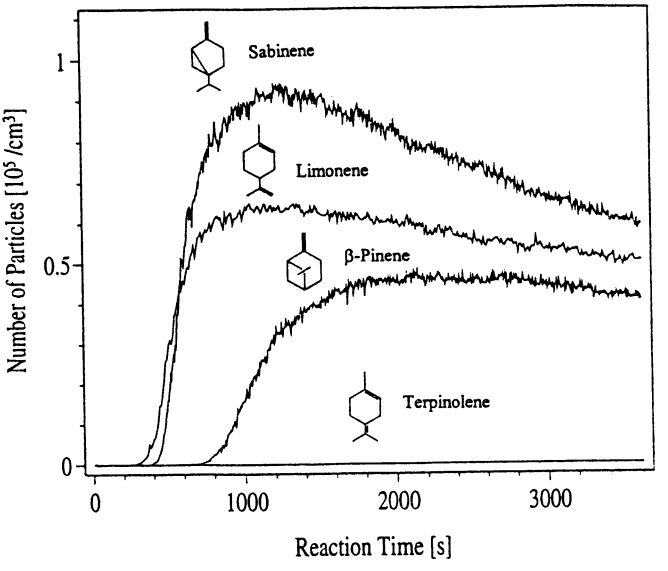

Fig. 1: Temporal profiles of particle numbers in different ozone–monoterpene systems. $[\text{monoterpene}]_0$ = 12 ppb and $[\text{ozone}]_0$ = 17–1000 ppb. The initial ozone concentrations were calculated to obtain an initial rate of 1×10^8 molecule cm^{-3} s^{-1}.

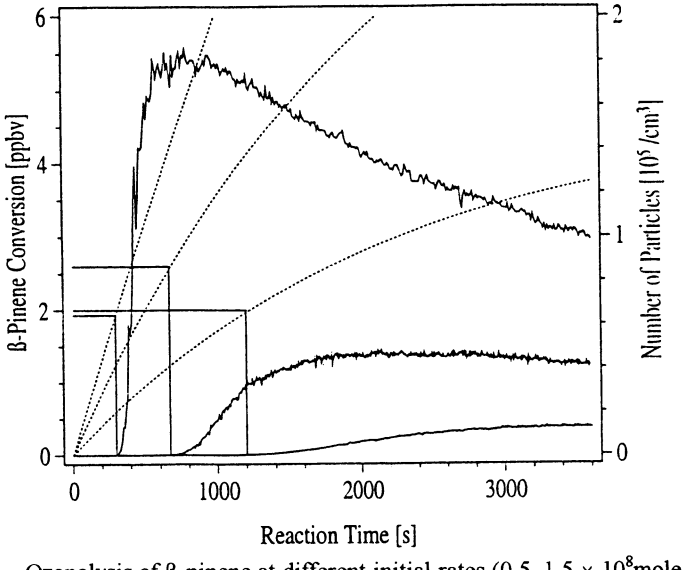

Fig. 2: Ozonolysis of β-pinene at different initial rates ($0.5–1.5 \times 10^8$molecule cm^{-3} s^{-1}). $[\text{ß-pinene}]_0$ = 6–50 ppb and $[\text{ozone}]_0$ = 360–1000 ppb. Solid lines (right axis) represent particle numbers and dashed lines (left axis) represent the calculated (see text) conversion of ß-pinene. Vertical traces indicate the time when particle formation was observed

Table 1.

Terpene	$Terpene_0$ [ppb]	$Ozone_0$ [ppb]	Inital rate $\times 10^{-8}$molec. $cm^{-3}s^{-1}$	t_{nuc} [s] [a]	Δ Ozone [b] [ppb]	Δ Terpene [c] [ppb]	N_{max} [d] $\times 10^{-3}$ [part./cm^3]
β-Pinene	4	1050	0.4	2000	1.9	2.5	1.2
	6	1025	0.5	1200	2.0	2.6	13
	12	1020	1.0	700	2.4	3.4	46
	12	1400	1.4	340	1.8	2.4	185
	50	370	1.5	300	1.9	2.5	180
Sabinene	4	174	0.3	600	0.8	1.0	38
	12	173	1.0	400	1.6	2.0	93
	12	220	1.3	320	1.6	2.1	102
	12	360	2.1	220	1.8	2.3	135
	50	70	1.7	220	1.5	2.0	250
α-Pinene	40	50	1.0	500	1.9	3.5	24
	50	60	1.5	400	2.3	4.2	30
3-Carene	50	108	1.1	300	1.4	2.7	30
	50	395	4.1	200	3.2	6.4	78
Limonene	12	75	1.0	300	1.2	2.2	64
	43	35	1.7	230	1.6	2.9	96
	50	110	6.2	130	3.2	5.9	260
Terpinolene	12	17	1.6	1000	4.4	8.7	0.15
	50	65	25	180	15	30	105
Methylene-cyclohexane	12	1120	0.9	2200	5	8	0.3
	50	400	1.3	1200	6	9	16
	50	2000	6.6	350	8	13	90
1-Methyl-cyclohexene	50	400	18	300	15	29	4.8
	50	485	22	100	8	15	4.0
Cyclohexene	50	510	11	400	15	30	2.8

[a] reaction time when first particles were observed [b] Δ Ozone = $[Ozone]_0 - [Ozone]$ (t_{nuc})
[c] Δ Terpene = $[Terpene]_0 - [Terpene]$ (t_{nuc}) [d] N_{max} = maximum number of particles/cm^3

Comparing the particle concentration time profiles for the various terpenes at the same initial rate reveals some remarkable differences. Limonene and terpinolene, both structurally related, except for the position of the double bound outside the ring, show very different nucleation rates. Limonene forms much more particles than terpinolene.

The difference could originate from the initial ozone attack, which is mainly endocyclic for limonene, but exocyclic for terpinolene. The endocyclic attack leads to intermediates still with 10 carbon atoms. Among the products, polyfunctional organic acids have been tentativly identified (Schuetzle and Rasmussen, 1978). The ozone attack at the exocyclic double bond of terpinolene yields acetone and a 7 carbon atom Criegee-Intermediate (CI) as well as 4-methyl-cyclohexene-(3)-one and the 3 carbon atom CI. The fragmentation to smaller molecules is accompanied by increasing vapour pressures of the products compared to the 10 carbon atom products from limonene.

The comparision of the results for the different monoterpenes with only one double bond, at initial terpene concentrations of 50 ppb, reveals that the exocyclic terpenes, sabinene and β-pinene, form more nuclei than the endocyclic terpenes, α-pinene and 3-carene. The same kind of structure relationship was observed for the exocyclic methylenecyclohexane and the endocyclic 1-methyl-cyclohexene, where the nucleation is much more pronounced for methylenecyclohexane, despite the fact that the initial rates were much lower.

The majority of the reported terpene-ozonolysis products (Hakola *et al.*, 1994; Hatakeyama *et al.*, 1989; Hull 1981; Palen *et al.*, 1992; Schuetzle and Rasmussen, 1978) are ketones and aldehydes, with vapour pressures far above their atmospheric concentrations. Minor products reported are hydroxycarbonyl and dicarbonyl compounds, whose vapour pressures are considerably lower, but not sufficient for nucleation at atmospheric concentrations. The only products with sufficiently low vapour pressure identified so far, are dicarboxylic acids like pinic acid (formed in α- and β-pinene ozonolysis) (Christoffersen *et al.*, 1998, Hoffmann *et al.*, 1997b) and norpinic acid (from α-pinene) (Hoffmann *et al.*, 1997b).

Conclusions

The observation of particle formation at terpene conversions as low as 2 ppb in this study indicate that this reaction could be a source of the observed formation of new particles in the absence of any sulfur compounds (Marti *et al.*, 1997; Mäkelä *et al.*, 1997). There are many indications now that products with very

low vapour pressure are formed upon ozonolysis of monoterpenes, *e.g.* dicarboxylic acids (Christoffersen *et al.*, 1998, Hoffmann *et al.*, 1997b), which could be the nucleating species.

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