Carboxylic Acids in Secondary Aerosols from O_3 and OH Oxidation of Cyclic Monoterpenes

Guest contribution

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Introduction

The ability of terpenes to form secondary organic aerosols (SOA) presents one of the major uncertainties in understanding the impact of terpenes on atmospheric chemistry and photochemical smog formation (Hoffmann *et al.*, 1997). It is generally believed that the formation of oxidation products with considerably lower vapour pressures than the precursor compounds plays an important role in gas-to-particle conversion of terpenes by photochemical oxidation. Until recently, mainly carbonyl compounds have been identified in SOA from gas phase oxidation of terpenes, but carbonyls generally possess relatively high vapour pressures and thus cannot reach super-saturation in order to nucleate homogeneously or condense directly under the experimental conditions used. In order to explain the particle burst observed in most experiments with oxidation of monoterpenes, attention must be turned to secondary products such as carboxylic acids, keto-carboxylic acids, hydroxy ketones, diols and dicarboxylic acids with lower vapour pressures.

Under the framework of the NUCVOC project (ENV4-CT97-0391) smog chamber experiments have been conducted in which a series of cyclic monoterpenes were oxidised by ozone and hydroxyl radicals. The produced carboxylic acids, dicarboxylic acids and keto-carboxylic acids in the particle phase were then identified and quantified.

Experimental details

Ozonolysis and OH oxidation of (+)-α-pinene, (+)-β-pinene, (+)-3-carene, (S)-(-)-limonene, myrtenol and (+)-sabinene was performed in a series of individual experiments at a concentration range of 10–2000 ppb in 600 L Teflon bags (experiments with O_3) and a 480 L Teflon coated Pyrex glass reaction chamber (experiments with OH).

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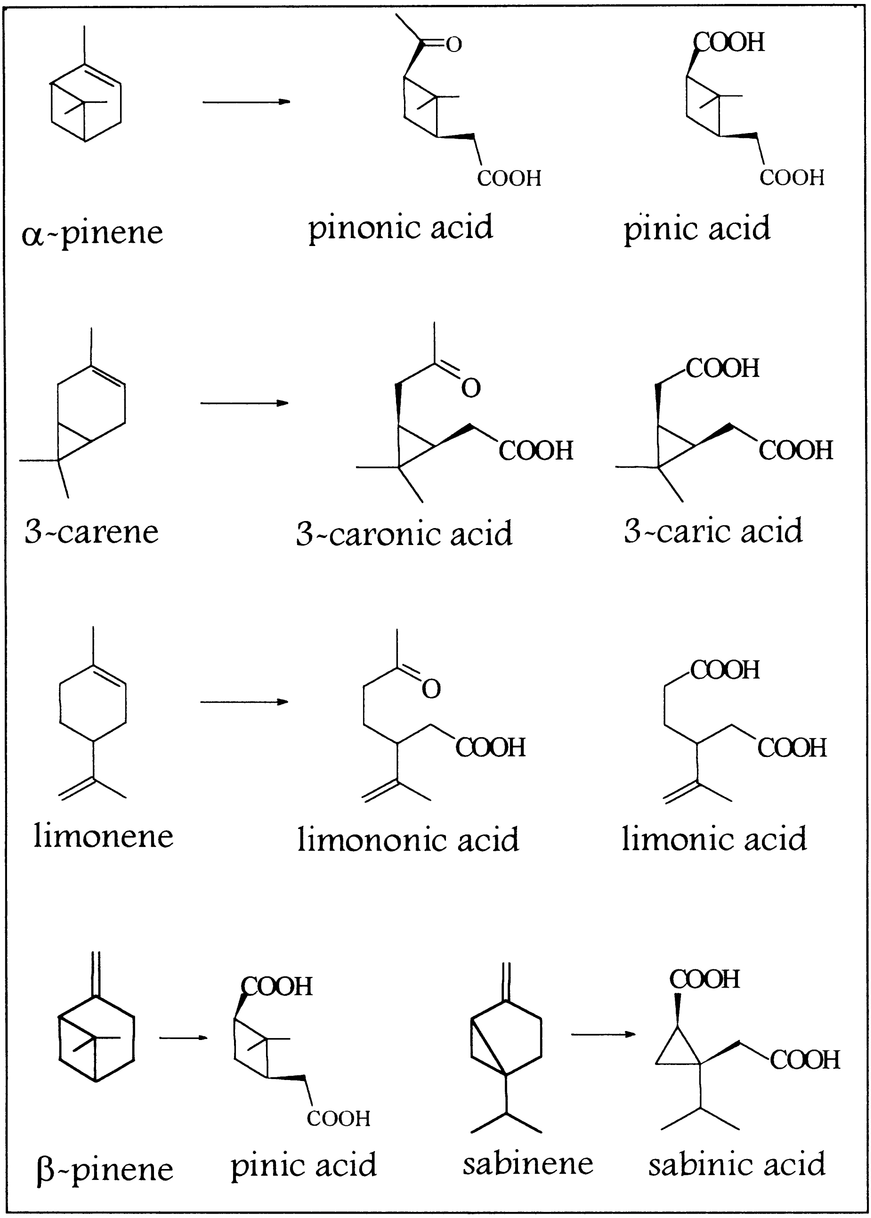

Fig. 1: Main carboxylic acids observed in organic aerosol from O_3 and OH oxidation of the studied monoterpenes.

Hydroxyl radicals were formed by photolysis of CH_3ONO or H_2O_2 according to standard procedures for our laboratory (Fruekilde *et al.*, 1998). In order to minimise sampling artefacts from residual O_3 excess concentrations of terpenes were used in all experiments. The SOA formed were sampled on 0.5 μm Teflon filters and extracted with CH_2Cl_2. Analysis was done directly by HPLC-MS-MS and after derivatisation with BF_3-methanol, by large volume injection GC-MS (CI and EI) (Christoffersen *et al.*, 1998). The new reaction products in the SOA were tentatively identified from retention data and mass fragmentograms and quantified by comparison with TIC peak areas of pinonic and pinic acid.

Results and discussion

A significant production of SOA was observed in all experiments, and carboxylic acids, dicarboxylic acids and keto-carboxylic acids were observed in molar yields of up to 6 %. Some of the identified acids were pinonic acid (3-acetyl-2,2-dimethyl-cyclobutylethanoic acid) from α-pinene, pinic acid (3-carboxy-2,2-dimethyl-cyclobutylethanoic acid) from α-pinene, β-pinene and myrtenol, 3-caronic acid (2,2-dimethyl-1,3-cyclopropylethanoic acid) and 3-caric acid (2,2-dimethyl-1,3-cyclopropyldiethanoic acid) from 3-carene, sabinic acid (2-carboxy-1-isopropyl-cyclopropylethanoic acid) from sabinene, and limononic acid (3-isopropenyl-6-oxo-heptanoic acid) and limonic acid (3-isopropenyl-hexanedioic acid) from limonene (Fig. 1).

Table 1: Products and yields from oxidation of monoterpenes.

α-pinene	pinic acid	pinonic acid	nor-pinic acid
O_3	0.3 – 2.6 %	0.1 – 0.3 %	trace
OH	0.3 – 0.6 %	0.8 – 1.9 %	trace
limonene	limonic acid	limononic acid	keto-limonic acid
O_3	0.1 – 0.3 %	0.02 – 0.2 %	0.004 – 0.03 %
OH	2.0 – 5.0 %	1.9 – 5.8 %	-
β-pinene	pinic acid	pinonic acid	nor-pinic acid
O_3	0.5 – 5.0 %	-	trace
OH	0.18 – 0.2 %	0.07 – 0.08 %	trace
3-carene	3-caric acid	3-caronic acid	3-nor-caric acid
O_3	0.5 – 5.0 %	0.1 – 0.7 %	0.08 – 0.1 %
sabinene	sabinic acid	pinic acid	nor-pinic acid
O_3	1.1 %	1.4 %	trace

Chemical names have been adopted from Larsen *et al.*, 1998. The carboxylic acids from 3-carene, sabinene and limonene are reported here for the first time.

A number of other products such as the corresponding decarbonylised analogues (*e.g.* norpinic acid) were found in the SOA at lower yields, together with previously observed carbonyl oxidation products such as pinonaldehyde from α-pinene. The results have been described in detail elsewhere (Glasius *et al.*, 1998).

It has been suggested that due to their extremely low vapour pressures many of the acidic reaction products, especially the dicarboxylic acids, found in SOA may play an important role in aerosol condensation and nucleation. In the second phase of the NUCVOC project it is planned to test this hypothesis. In addition, we will synthesise the acidic reaction products in order to confirm their identification.

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References

Christoffersen T.S., J. Hjorth, O. Horie, N.R. Jensen, D. Kotzias, L.L. Molander, P. Neeb, L. Ruppert, R. Winterhalter, A. Virkkula, K. Wirtz, B.R. Larsen; *Atmos. Environ.* **32** (1998) 1657–1661.

Fruekilde, P., J. Hjorth, N.R. Jensen, D. Kotzias, B.R. Larsen; *Atmos. Environ.* (1998) in press.

Glasius, M., M. Lahaniati, A. Calogirou, N.R. Jensen, J. Hjorth, D. Kotzias, B.R. Larsen; *Environ. Sci. Technol.* (1998) submitted.

Hoffmann, T., J.R. Odum, F. Bowman, D. Collins, D. Klockow, R.C. Flagan, J.H. Seinfeld; *J. Atmos. Chem.* **26** (1997) 189–212.

Larsen, B.R., M. Lahaniati, A. Calogirou, D. Kotzias; *Chemosphere* (1998) in press.