Smog Chamber Studies of Particle Formation from the Oxidation of Terpenes

Jens Hjorth, European Commission, TP 272, Environment Institute, JRC-Ispra, I-21020 Ispra (VA), Italy

Important aspects of the current research on atmospheric aerosols have recently been highlighted by Andreae and Crutzen (1997). The authors state that secondary organic aerosols, formed by the oxidation of VOCs emitted from biogenic sources, probably account for a significant fraction of the particulate matter in rural and remote continental air masses. Monoterpenes ($C_{10}H_{16}$), which constitute one of the main fractions of the biogenic VOCs, have since long been recognized as potential precursors of secondary organic aerosol in the atmosphere (Went, 1960). Aerosol yields from 5 - 100 % have been measured in laboratory and environmental chamber studies, e.g. Hatakeyama et al. (1989); Hoffmann et al. (1997); Kamens et al. (1999); Pandis et al. (1991); Schuetzle and Rasmussen (1978); Zhang et al., (1992), depending on the experimental conditions and on the species investigated. The present study aims at providing more information on aerosol yields from terpene oxidation and on the main chemical components in the particles.

Experimental

Studies of aerosol formation were carried out in a large outdoor smog chamber (EUPHORE, Valencia, Spain) as well as in large Teflon bags and in a smaller (480 L) chamber facility in Ispra, Italy. The study was mainly focussed on α-pinene, β-pinene and limonene. The EUPHORE facility comprehends two hemispheric outdoor smog chambers, each with a diameter of ~ 9 m and a volume of ~180 m^3, both cooled at the floor. A detailed description of the design and the analytical equipment of EUPHORE has been published by Becker (1996).

The experiments included studies of ozonolysis reactions under dark conditions with terpene concentrations in the range between 10 and 1000 ppbV in dry air, humidified air and with or without addition of cyclohexane as a scavenger for OH radicals. Photo-oxidation of terpenes was studied in EUPHORE by exposing mixtures of terpenes and NOx with initial terpene concentrations of 100 ppbV and initial NOx-concentrations of 20 or 200 ppbV to sunlight. The oxidation of terpenes in air, initiated by OH radicals, was also studied by producing OH via the photolysis of methylnitrite in the chamber facility in Ispra.

The aerosol size distributions presented here were measured by a custom made Vienna-type differential mobility analysis (DMA) system (Winkelmayr et al., 1991) coupled to a condensation nuclei counter (TSI, model 3010). The system measured aerosol size distributions in the range between 7 and 500 nm and was operated in dry-air conditions, thus measuring the size of dry particles.

The hygroscopicity of aerosol particles was measured using a Tandem Differential Mobility Analyser (TDMA) set-up where growth of particle diameter by uptake of water was observed (Virkkula et al., 1999). Aerosol concentrations were corrected for wall-losses based on the observed rate of decrease in particle number concentration at a late stage in the experiments, when particle formation had ceased to take place.

Terpene concentrations were measured by gas chromatography with FID detection. Carbonyl compounds were measured by sampling on DNPH-coated cartridges followed by HPLC measurement of the hydrazones formed. Particles were collected on Teflon filters. The smog-chamber aerosol extracts were analyzed either by GC-MS after derivatisation of carboxylic acids by methylation or by a newly developed HPLC-MS[n] method, which has proved efficient for polar terpene oxidation products (Glasius et al., 1999).

Aerosol yields

Aerosol mass concentrations were estimated by assuming a density of 1 g/cm^3 for the particles that were formed. Aerosol yields were found to increase with increasing aerosol volume, as illustrated in Fig. 1 for the case of α-pinene. This observation is in qualitative

agreement with theoretical work on the partitioning of semi-volatile organic species between the gas phase and a condensed organic matter phase (Odum et al., 1996; Pankow, 1994),

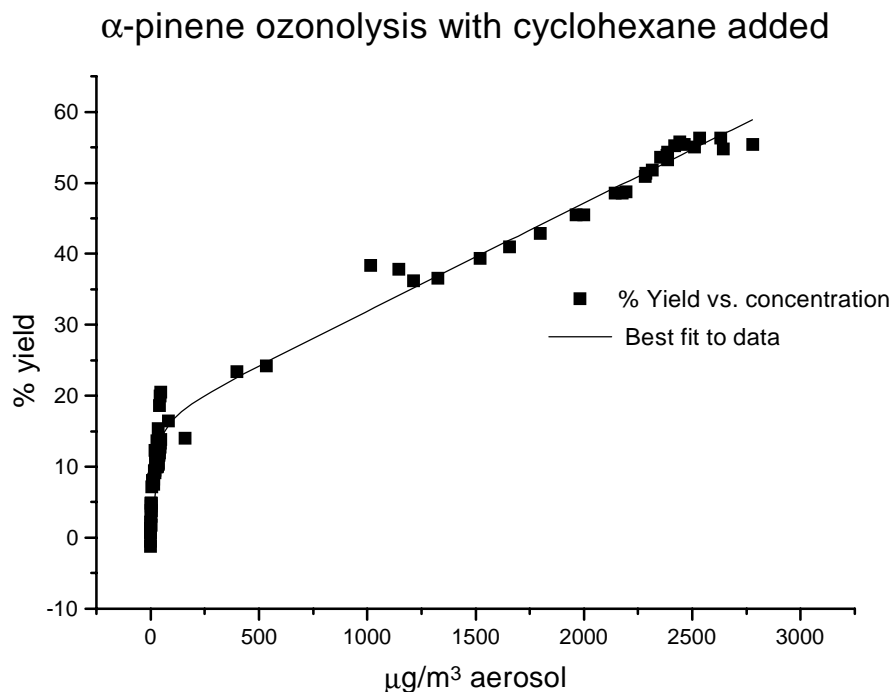## α-pinene ozonolysis with cyclohexane added

Fig. 1. Measured aerosol yields vs. measured aerosol concentrations compared to curve obtained by applying a best fit of the unknown parameter in Equation I.

which indicates that the concentration dependence of the aerosol yield in a situation with equilibrium partitioning between the gas and particle phase can be expressed by the equation

(I) $Y = \Sigma Y_i = M\Sigma(\alpha_i K_{om,i})/(1+K_{om,i}M)$,

where Y is the total aerosol yield, Y_i is the aerosol yield of species i , M is the absorbing organic aerosol mass concentration, α_i is the total yield of species i. $K_{om,i}$ is the partitioning coefficient for species i, which depends on its vapour pressure, its activity coefficient in the condensed organic phase and on its molecular weight when the aerosol yield is expressed on a weight-basis as it is in this work. $K_{om,i}$ $(m^3/\mu g)$ is defined as $c_{i\,aer}/(M\,c_{i\,g})$, where $c_{i\,aer}$ and $c_{i\,g}$ are the aerosol and gas phase concentrations $(\mu g\,/m^3)$ of species i. $K_{om,i}$ also depends on the temperature, but the relatively small temperature variations (around 293 K) within these experiments had no evident influence on the aerosol yields.

By applying a best fit to the unknown parameters in Equation I, an estimate of the aerosol yields (on a mass-basis) under realistic, ambient conditions could be made. For an initial aerosol concentration (M) of 2 $\mu g/m^3$ the following yields could be calculated: α-pinene 3.3 %, β-pinene 1.8 %, and limonene 2.7 %. For an initial aerosol concentration of M = 10 $\mu g/m^3$, the following values were calculated: α-pinene 8.7 %, β-pinene 6.4 % and limonene: 10.6 %.

The aerosol yields that were measured in this study may be compared to results presented in the literature, e.g. to the recent, comprehensive study by Hoffmann et al. (1997). The aerosol yields from the ozonolysis of α- and β-pinene reported in this study seem to be somewhat higher than those found in the present study, when results obtained under similar conditions are compared.

A comparison between aerosol yields obtained by photo-oxidation experiments and ozonolysis experiments showed significantly lower aerosol yields from photo-oxidation,

suggesting that the OH radical reaction, gives significantly lower aerosol yields than ozonolysis. This observation is illustrated in Fig. 2, which also shows a comparison between the aerosol yields from the ozonolysis reaction, performed under different conditions. Concerning the comparison between photooxidation and ozonolysis it should, however, be noticed, that the ozonolysis was studied in the absence of NO_x, while NO_x (particularly NO) certainly will influence the degradation pathways of the terpenes in the photo-oxidation runs. Thus also the influence of $[NO_x]$ on aerosol formation may be a reason for the differences observed between the ozonolysis and photo-oxidation experiments.

Application of the tandem-DMA set-up to the study of the hygroscopic growth of terpene-derived aerosol from ozonolysis as well as photooxidation experimental runs proved that these were only slightly hygroscopic (Virkkula et al., 1999). The experiments were initiated by introducing an ammonium sulphate seed aerosol. The hygroscopic growth factor (i.e. (particle diameter in humid air)/(particle diameter in dry air)) was approximately 1.5 for
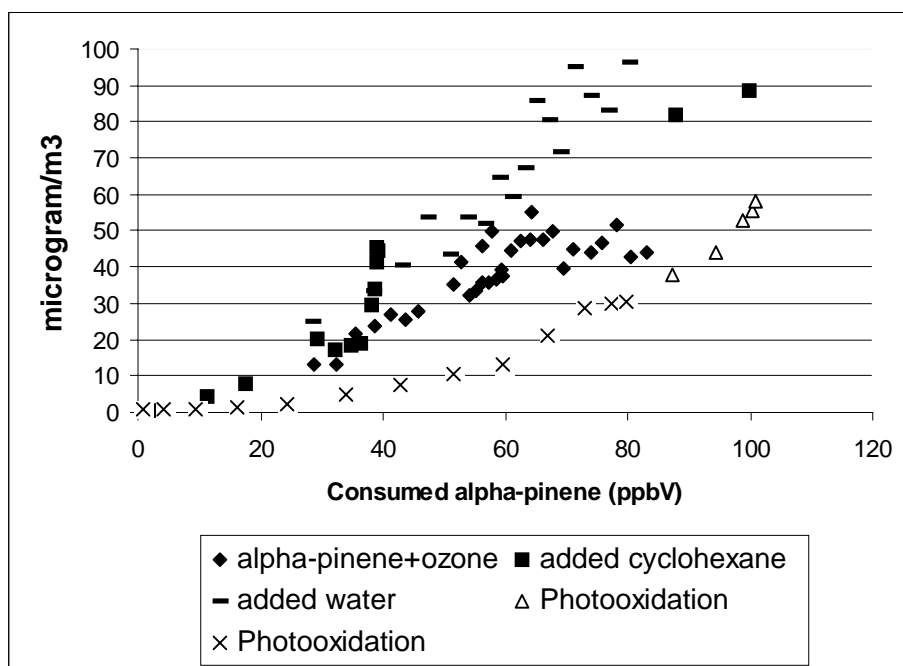

Fig. 2. Aerosol formation from ozonolysis in dry air, ozonolysis with added water, ozonolysis in dry air with cyclohexane added as an OH scavenger and in two photo-oxidation experiments (initial NO_x was 20 ppbV).

the ammonium sulphate aerosol at 84 % RH. As the oxidation of terpenes took place and the oxidation products were condensing on the seed particles, the growth factor decreased to around 1.10. No significant differences between the different terpenes and the different reaction conditions (ozonolysis versus photo-oxidation) could be observed.

Chemical analysis of aerosols.

Chemical analyses of particles formed by oxidation of terpenes have been performed and a number of components (particularly organic acids) have been identified. Dicarboxylic acids, such as pinic acid, appear to be a characteristic constituent of terpene-derived aerosol resulting from ozonolysis as well as photo-oxidation (Christoffersen et al., 1997, Glasius et al., 1998). Such compounds were identified as products of α-pinene, β-pinene, limonene, 3-carene and sabinene. The measured yields varied from below 1% up to as much as 6 %, depending on the precursor-terpene and the reaction conditions. Also keto-acids and hydroxy-acids, together with dicarbonyl compounds and hydroxy-dicarbonyl compounds were found to be significant constituents of aerosol particles collected. Dicarboxylic acids were formed

also in the experimental runs where cyclohexane was added as an OH-radical scavenger in ozonolysis experiments, thus demonstrating that there are relevant reaction pathways leading to formation of these species that do not involve OH radical reactions.

References:
Andreae, M.O. and Crutzen, P.J., 1997. Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. Science, 276(5315): 1052-1058.
Becker, K.H., 1996. The European photoreactor EUPHORE.
Christoffersen, T.S. et al., 1998. *cis*-Pinic acid, a possible precursor for organic aerosol formation from ozonolysis of alpha-pinene. Atmos. Environ., 32(10^): 1657-1661.
Glasius, M., Duane, M. and Larsen, B.R., 1999. Determination of polar terpene oxidation products in aerosols by liquid chromatography-ion trap mass spectrometry. J. Chromatography, A 833: 121-135.
Glasius, M. et al., 1998. Carboxylic acids in secondary aerosols from O_3 and OH oxidation of cyclic monoterpenes. In: P.M. Borrell and P. Borrell (Editors), EUROTRAC-2 Symposium 1998, Garmisch-Partenkirchen, Germany.
Hatakeyama, S., Izumi, K., Fukuyama, T. and Akimoto, H., 1989. Reactions of ozone with alpha-pinene and beta-pinene in air: Yields of gaseous and particulate products. Journal of Geophysical Research, 94(D10): 13013-13024.
Hoffmann, T. et al., 1997. Formation of organic aerosols from the oxidation of biogenic hydrocarbons. J. Atmos. Chem., 26: 189-222.
Kamens, R.M., Jang, M., Chien, C.-J. and Leach, K., 1999. Aerosol formation from the reaction of α-pinene and ozone using a gas-phase kinetics-aerosol partitioning model. Environ. Sci. Technol., 33(9): 1430-1438.
Odum, J.R. et al., 1996. Gas/particle partitioning and secondary organic aerosol formation. Environ. Sci. Technol., 30(8): 2580-2585.
Pandis, S.N., Paulson, S.E., Seinfeld, J.H. and Flagan, R.C., 1991. Aerosol formation in the photooxidation of isoprene and ß-Pinene. Atmospheric Environment, 25A(5-6): 997-1008.
Pankow, J.F., 1994. An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. Atmos. Environ., 28(2): 189-93.
Schuetzle, D. and Rasmussen, R.A., 1978. The molecular composition of secondary aerosol particles formed from terpenes. Journal of the Air Pollution Control Association, 28(3): 236-240.
Virkkula, A., van Dingenen, R., Raes, F. and Hjorth, J., 1999. Hygroscopic properties of aerosols formed by oxidation of limonene, α-pinene, and β-pinene. JGR, 104(D3): 3569-3579.
Went, F.W., 1960. Blue hazes in the atmosphere. Nature, 187: 641-643.
Winkelmayr, W., Reischl, G.P., Lindner, A.O. and Berner, A., 1991. A new electromobility spectrometer for the measurement of aerosol size distributions in the size range from 1 to 1000 nm. J. Aerosol Sci., 22: 289-296.
Zhang, S.H., Shaw, M., Seinfeld, J.H. and Flagan, R.C., 1992. Photochemical aerosol formation from alpha -pinene and beta -pinene. Journal of Geophysical Research, 97(D18): 20717-29.