Investigation of Secondary Organic Aerosol Formation in the Hydrocarbon/O_3 Reaction: Implementation of APCI/MS as an Analytical On-Line Technique

A contribution to subprojects CMD and AEROSOL

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Introduction

The atmospheric fate of terpenes is strongly influenced by ozone generated loss processes in the troposphere (Hoffmann *et al.*, 1997). Products formed in the reaction of biogenic volatile organic compounds (VOCs) with ozone are characterised by their low volatility. Therefore, gas-to-particle conversion of these compounds represents an important pathway for the formation of secondary organic aerosol (SOA) (Andreae and Crutzen, 1997; Zhang *et al.*, 1992). A series of investigations are focussed on the determination of the reaction rate constants (Atkinson, 1997). However, the composition of organic aerosols formed in these reactions is poorly understood and reaction mechanisms are far from being elucidated.

In this work on-line APCI / MS is used as an analysis method for gas phase reactions. Therefore, the organic aerosols are directly introduced into the ion source of a mass spectrometer. MS^n experiments can be performed simultaneously to the aerosol formation processes, excluding special sample preparation.

Experimental

Experiments were performed using the Finnigan MAT LCQ ion-trap mass spectrometer, equipped with a modified ion source. The sample flow ($1\ L\ min^{-1}$) was surrounded by a nitrogen sheet flow. The concentrations of the substances in dark reactions with O_3 were adjusted in the ppb range. Ozonolysis were carried out in a 2 L or 10 L reaction vessel at 740 torr total pressure and 294 ± 2 K in synthetic air.

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Results and Discussion

Ozonolysis of α-pinene

On-line APCI/MS analysis of α-pinene–ozone mixture in synthetic air showed the formation of pinonaldehyde (detected in the positive ion mode (M+H = 169)) and of different carboxylic acids such as the ketocarboxylic acid pinonic acid (detected in the negative ion mode (M–H = 183)) as well as some diacids such as pinic acid (M–H = 185) or norpinic acid (M–H = 171). Furthermore, different homomolecular or heteromolecular dimers of the primary formed acids are observed in the mass range between 300–400; For example [(172 + 186)]–H] = 357. These dimers are characterised by a remarkable stability. A typical MS spectrum of particle phase products is illustrated in Fig. 1.

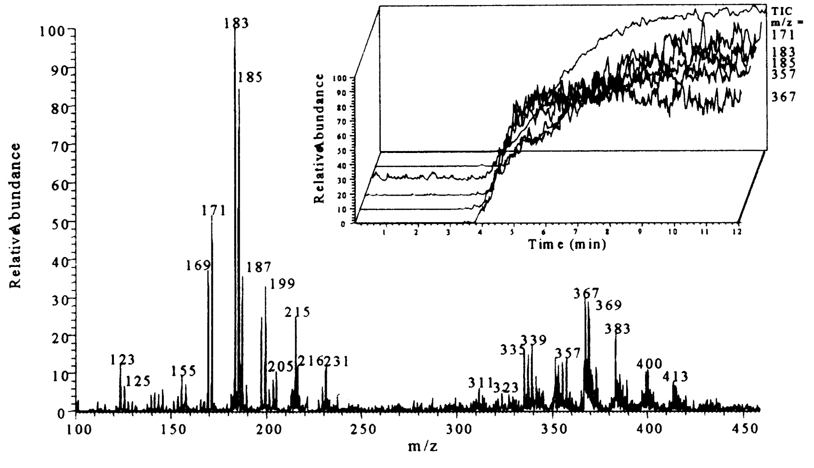

Fig. 1: MS spectrum of the low volatile ozonolysis products of α-pinene and relative abundance of certain product molecular ions (M–H)- as a function of time after the ozone source was switched on.

Ozonolysis of model compounds

The oxidation products of the "model" substances (cyclohexene, 1-methyl-1-cyclohexene, 1,2-dimethyl-1-cyclohexene) were found to have similar functional groups. Therefore, it is likely that similar oxidation pathways are involved as well by α-pinene as by their model compounds. A compilation of the products is given in Table 1.

Since there is a lack of authentic standards, the products written in *italic* are tentatively identified by MS/MS-studies. The remaining compounds are identified by comparison of their MS / MS spectra with reference substances.

Table 1: Compilation of oxidation products of α-pinene and different model substances. The compounds written in *italic* are tentatively identified, the other compounds are verified by comparison of their MS spectra with reference substances.

α-pinene / ozone	1-methyl-1-cyclohexene/ ozone	Cyclohexene / ozone	1,2-dimethyl-1-cyclohexene / ozone
pinonaldehyde $C_{10}H_{16}O_2$; M = 168	*6-oxoheptanal* $C_7H_{12}O_2; M = 128$	n.d.	*2,7-octanedione* $C_8H_{14}O_2; M = 142$
norpinonicacid $C_9H_{14}O_3; M = 170$	*6-oxohexanoicacid* $C_6H_{10}O_3; M = 130$	*6-oxohexanoicacid* $C_6H_{10}O_3; M = 130$	*6-oxohexanoicacid* $C_6H_{10}O_3; M = 130$
norpinicacid $C_8H_{12}O_4; M = 172$	glutaric acid $C_5H_8O_4$; M = 132	n.d.	n.d.
pinonicacid $C_{10}H_{16}O_3$; M = 184	6-oxoheptanoicacid $C_7H_{12}O_3$; M = 144	n.d.	6-oxoheptanoicacid $C_7H_{12}O_3$; M = 144
pinicacid $C_9H_{14}O_4$; M = 186	adipic acid $C_6H_{10}O_4$; M = 146	adipic acid $C_6H_{10}O_4$; M = 146	n.d.

It should be noted that the formation of diacids by the ozone reaction with 1,2-dimethyl-1-cyclohexene could not be observed.

Mechanistic study on the influence of vapour pressure, using $H_2{}^{18}O$.

The mechanism of the gas phase reaction of ozone with α-pinene was investigated using $H_2{}^{18}O$. This reaction led to the formation of pinonaldehyde. Interestingly, one of the two oxygen atoms was labelled (Fig. 2), strongly indicating the reaction of the Criegee intermediate with water vapour.

A possible reaction pathway, which explains the formation of pinonaldehyde, is displayed in Fig. 3.

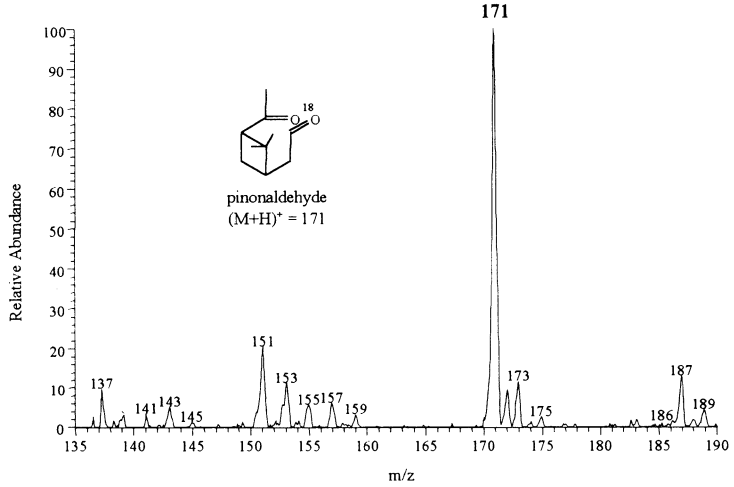

Fig. 2: Section of the MS spectrum with background subtracted $(M + H)^+$ of the α-pinene / ozone / $H_2{}^{18}O$ reaction.

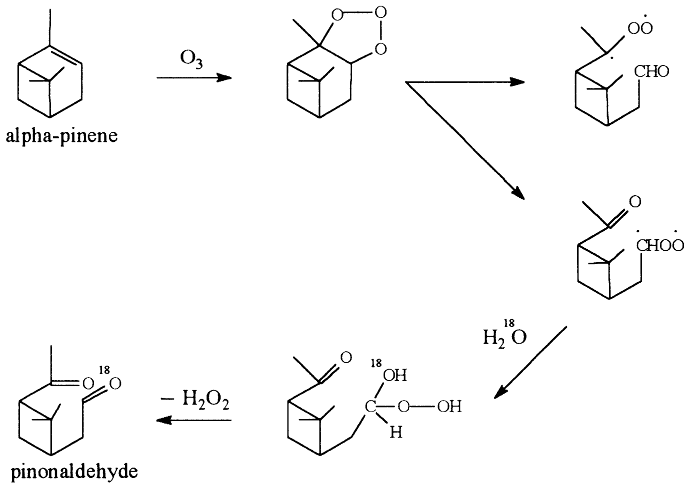

Fig. 3: Expected reaction sequence of the formation of pinonaldehyde investigated by using $H_2{}^{18}O$.

Conclusions

* On-line APCI / MS is a helpful analytical tool to understand organic aerosol formation.
* All investigated compounds seem to follow similar oxidation pathways.
* Ozonolysis leads to the formation of low volatile products, such as multifunctional carboxylic acids.
* Stable dimer formations might be connected with homogeneous nucleation processes of organics.
* Pinonaldehyde results from the reaction of the Criegee intermediate with gas-phase water.

Acknowledgements

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