After washing with dry dichloromethane (10 mL), the compound **1** (0.125 mmol) and a catalytic amount of TEMPO (0.1 mol %) in dry dichloromethane (10 mL) were pumped in a recycle mode under argon for 6 h through the reactor. The reactor system was rinsed with dichloromethane (10 mL) and the combined organic solvents were removed in vacuo and the residue was used for the further reactions without additional purification.

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[8] Under these conditions, gel-type (Amberlite IRA 400) as well as macroporous (Amberlite IRA 900) anion-exchange resins loaded with borohydride anions, both of which are commercially available, behave similarly to the bare monolithic rod and the powdered material, respectively.

[9] Depending on the extent of polymer swelling caused by the solvent used the pressure drop was 10 bar ($3\,\mathrm{mL\,min^{-1}}$) and 28 bar ($10\,\mathrm{mL\,min^{-1}}$), respectively, across a length of the reactor.

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An Analytical Approach for a Comprehensive Study of Organic Aerosols[**]

Wolfgang Schrader,[*] Jutta Geiger,
Markus Godejohann, Bettina Warscheid, and
Thorsten Hoffmann

Since the first scientific explanation of the so-called "blue haze" phenomenon above forests by Went,[1] the formation of natural organic aerosol particles in the atmosphere and their impact on the climate has drawn considerable attention. Airborne particles absorb, reflect, and scatter incoming solar radiation, play an important role in cloud droplet formation, and may even be involved in multiphase atmospheric chemistry.[2]

In recent reports it was established that especially the reaction of mono- and sesquiterpenes with tropospheric ozone contributes to the formation of organic aerosols,[3] however, our knowledge about reaction mechanisms leading to low-volatile products is still limited. Making things difficult is the fact that during the ozonolysis free OH radicals are formed that have to be considered.[4]

However, the initial steps of the terpene ozonolysis in the gas phase corresponds to known mechanisms,[5] exemplified in Scheme 1 for α-pinene **1**, the most abundant single monoterpene released by plants. The first step is the formation of the molozonide **2** that forms reactive Criegee intermediates **3a** and **3b**. Subsequent reactions lead to the formation of several low vapor-pressure products, such as pinonic acid (**4**), pinic acid (**5**), or hydroxy pinonic (**6**) acid which have been identified using mass spectrometric methods.[6] Although possible mechanisms for the generation of these carboxylic products have been suggested,[7] the overall understanding of the reaction mechanisms leading to condensable species is still inadequate.

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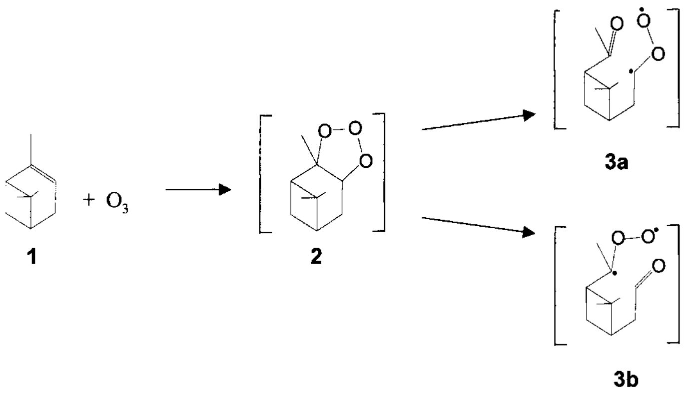
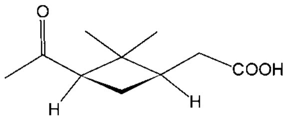


Scheme 1. Reaction pathway of α-pinene oxidation, which leads to the intermediate Criegee biradicals **3**.



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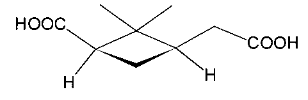

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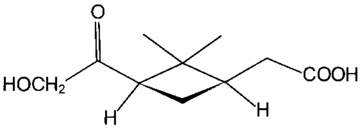

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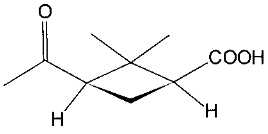

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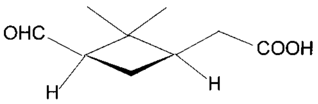

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For a better understanding of the natural aerosol formation processes, ideally the complete set of products should be known. Since synthetic standards are not readily available, the most promising approach to reach this goal is the linking of sophisticated analytical techniques, such as the coupling of liquid chromatography (LC) to three different spectroscopic methods, namely nuclear magnetic resonance (NMR) spectroscopy,[8] mass spectrometry (MS), and infrared (IR) spectroscopy.[9]

The LC/NMR coupling, although not the most sensitive method, clearly allows direct structural information about compounds to be obtained. In Figures 1 and 2 the results of an LC/NMR/MS experiment are presented. This online experiment is made possible through the combination of both a mass spectrometer and NMR spectrometer with a gradient high-pressure liquid chromatography (HPLC) system. The flow coming from the LC is divided into two flows in the ratio 1:20. The larger flow is introduced into a flow cell of the NMR spectrometer, the smaller part is used to obtain corresponding MS or MS^n data. NMR scans can be obtained either in the on-flow mode, which means a continuous flow through the NMR

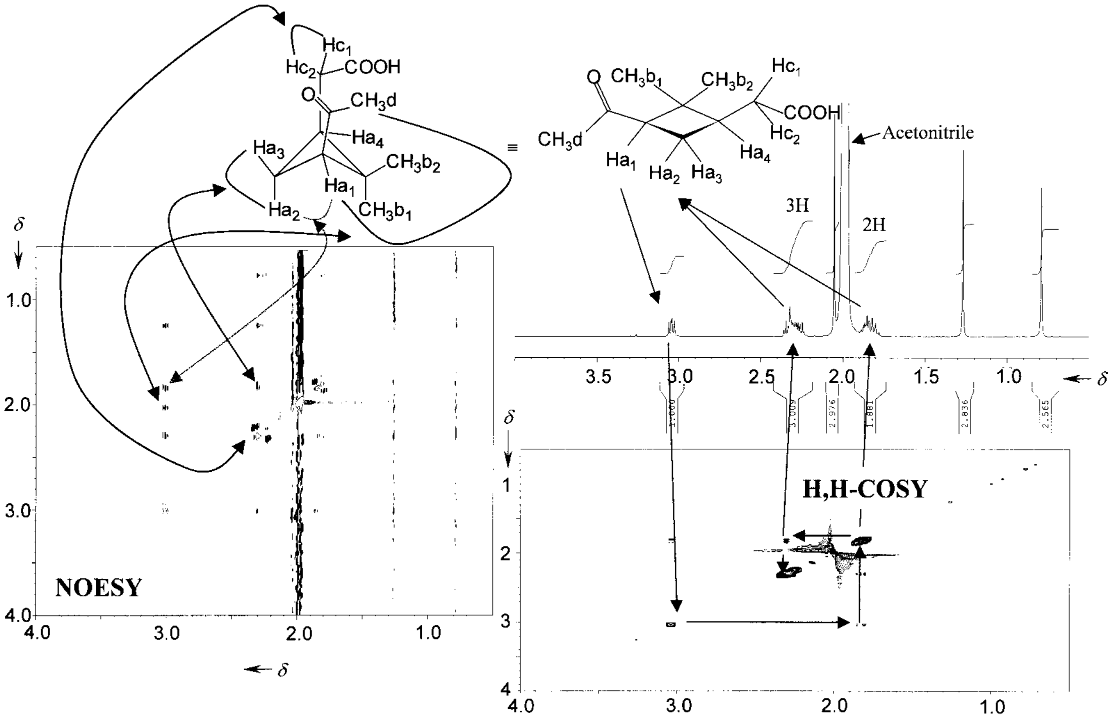

Figure 1. NMR spectra from *cis*-pinonic acid (**4**), obtained from an online experiment after LC separation; assignment of the signals using 1D, 2D NOESY (nuclear overhauser enhancement spectroscopy) and 2D COSY (correlated spectroscopy). Integration of the 1D ^{1}H NMR signal in combination with the corresponding 2D COSY shows that signals Ha$_2$–Ha$_4$ and signals Hc$_1$ and Hc$_2$ (in total 5 protons) resonate at two positions around $\delta = 1.8$ and 2.3 (the correlation caused by J coupling between Ha$_1$ and Ha$_2$/Ha$_3$ is indicated in the figure by arrows). The 2D NOESY spectrum indicates correlations caused by dipole cross-relaxation between nuclei in a close spatial relationship. Some of the correlations not amenable to J-coupling spectroscopy are indicated.

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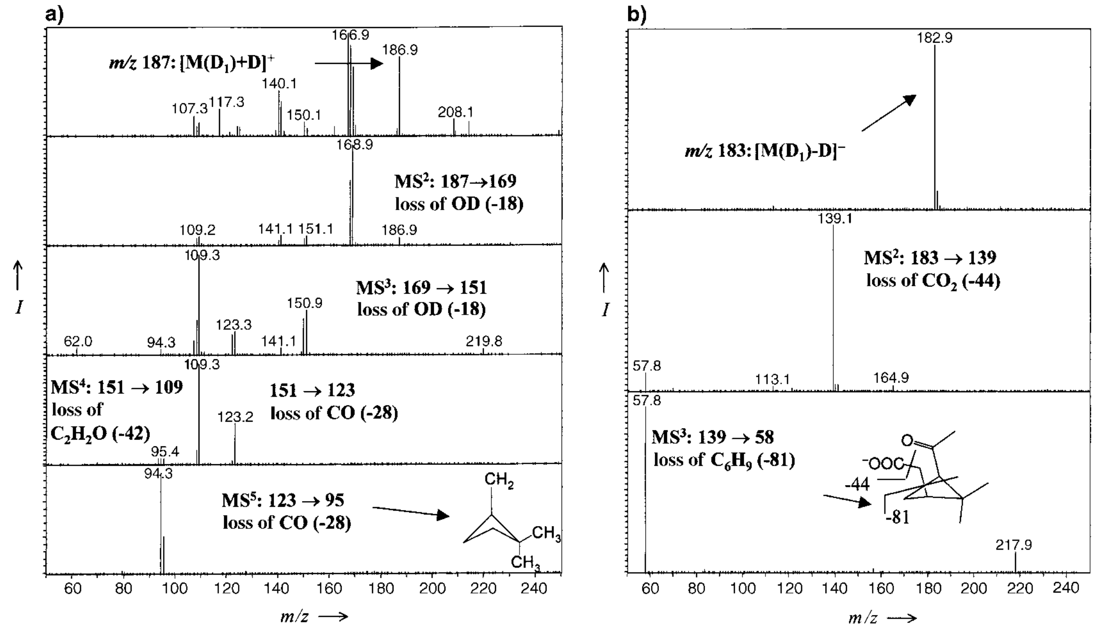


Figure 2. MS spectra from pinonic acid (**4**); $[M] = 184$; $[M(D_1) - D]^- = 183$; online LC/NMR/MS experiment. a) Positive ion MS^n spectra ($n = 1-5$) and b) Negative ion MS^n spectra ($n = 1-3$), the proposed fragmentation is shown.

probehead while the spectrometer constantly aquires one-dimensional (1D) proton spectra or in the loop-storage mode, in which fractions are stored in capillaries (loops) during the chromatography, the probes are then transfered to the NMR and mass spectrometers. This set up allows MS^5 spectra of **4** to be obtained in the positive mode and even MS^3 data in the negative mode (Figure 2).

In addition to the important structural information about reaction products, NMR spectroscopy allows the *cis* and *trans* isomers of ozonolysis products from the α-pinene/ozone reaction to be distinguished on the basis of the singlet resonance signal of the methyl protons (Figure 3). The Hb_1 and Hb_2 signals of the methyl groups of *cis*-pinic acid (**5**) are widely separated, while the difference between the corresponding signals of the *trans* isomer is rather small. However, in contrast to the results of recent field measurements,[10] only *cis* isomers were found as reaction products when the reaction was performed in the absence of light in the laboratory.

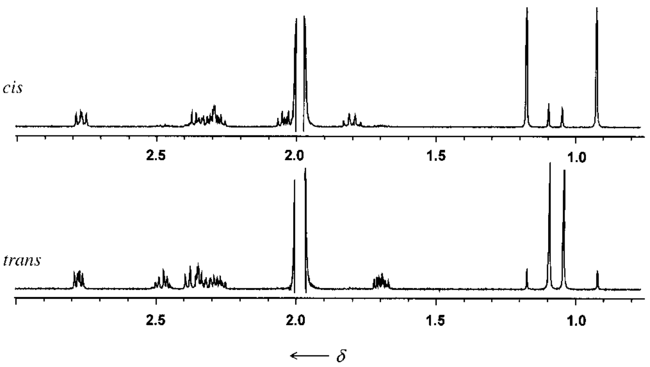


Figure 3. NMR spectra of *cis*-pinic acid (top) below *trans*-pinic acid (**5**) (bottom), with in each case traces of other isomers.

The use of a FT-ICR-MS (Fourier-transform ion cyclotron resonance mass spectrometer) allows not only high-resolution mass data to be obtained, but also highly accurate mass determination, which permits the calculation of the respective molecular formula. Surprisingly, the high-resolution mass spectra revealed a higher complexity of the products than anticipated. While mass spectrometric observations with standard resolution suggested only one compound at a certain mass-to-charge ratio, the high-resolution mass spectra indicate that more than one product with the same nominal mass but different elemental composition can contribute to the signal. In the case of α-pinene oxidation products, which can only be composed of C, H, and O, the difference between CH_4 (16.0313) and an oxygen atom (15.994914) can easily be resolved by FT-ICR-MS. Figure 4 shows an example, were a $C_{10}H_{15}O_4$ ion (*m*/*z* 199.09769) is clearly separated from an additional product with a composition of $C_9H_{11}O_5$ (*m*/*z* 199.06133).

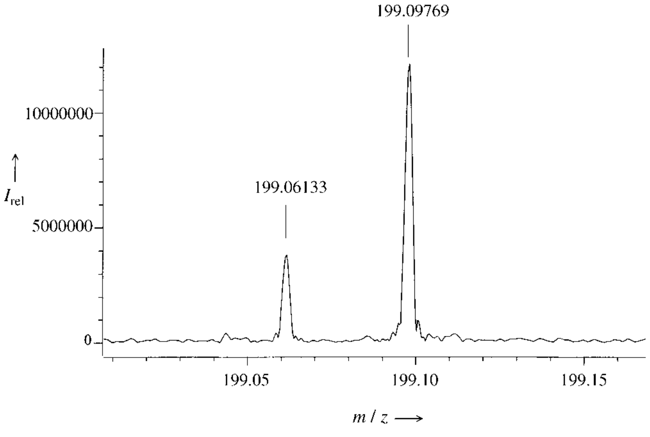
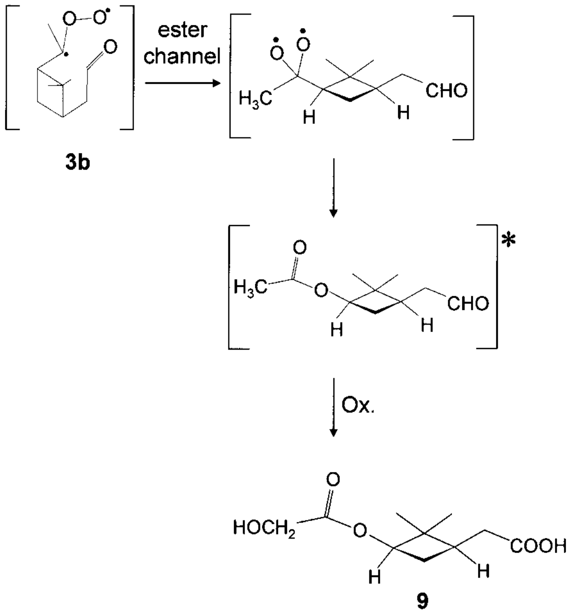


Figure 4. High-resolution mass spectrum of two reaction products at mass *m*/*z* 199.

1433-7851/01/4021-4000 $ 17.50+.50/0

Taking all of the spectrometric data into account a number of new compounds (**7**, **8**) can be identified with a high degree of confidence. For all of the identified compounds, which include the already described products (**4**–**6**), new analytical data could be obtained, that allows them to be included into a reaction scheme of the α-pinene ozonolysis that is based purely on identified compounds. In addition to these compounds, a structural suggestion can be made for an additional product **9** based on MS and IR data. This structure is supported by the ester channel mechanism suggested by Atkinson[11] to be one of the leading mechanisms for the formation of terpene reaction products (Scheme 2).



Scheme 2. Proposed reaction scheme leading to the ozonolysis product **9** from **3b**; in accordance to Atkinson.[11]

The results show that an analytical approach to the investigation of atmospheric relevant organic aerosols by coupling liquid chromatography with mass spectrometry, NMR spectroscopy, and infrared spectroscopy allows valuable information to be obtained about the structure of the reaction products. Even with high-resolution mass spectrometry it is not possible to differentiate between **7** and **8** which have the same composition (empirical formula). But with the structural information from both NMR and MS/MS a characterization is possible.

With this instrumentation we have for the first time tools at hand that are able to give enough information about such a complex and difficult problem as terpene gas-phase oxidation. While NMR spectroscopy allows *cis* and *trans* isomers to be distinguished, in addition the structural information from high-resolution and highly accurate mass determination make it possible to address with precision the formulas of the unknown products.

Experimental Section

Analytical data: NMR: (proton signals are referenced to the acetonitrile ($\delta = 1.93$); MS: accurate mass determination (m/z: accuracy in parentheses; molecular formula in square parentheses corresponds to negatively charged ion).

cis-Pinonic acid (**4**): NMR: Ha$_1$ 2.990 (dd, 1H); Ha$_4$, Hc$_1$, Hc$_2$ 2.187–2.348 (m, 3H); Hd 2.032 (s, 3H);[12] Ha$_2$, Ha$_3$ 1.782–1.905 (m, 2H); Hb$_1$ 1.266 (s, 3H); Hb$_2$ 0.797 (s, 3H); MS: 183.1027330 [$C_{10}H_{15}O_3$] (0.33 ppm); IR: $\tilde{\nu} =$ 2957, 1707, 1369, 1226, 1184, 948 cm^{-1}.

cis-Pinic acid (**5**): NMR: Ha$_1$ 2.769 (dd, 1H); Ha$_4$, Hc$_1$, Hc$_2$ 2.246–2.401 (m, 3H); Ha$_3$ 2.018–2.069 (m, 1H);[12] Ha$_2$ 1.794 (q, 1H); Hb$_1$ 1.167 (s, 3H); Hb$_2$ 0.913 (s, 3H). MS: 185.0819860 [$C_9H_{13}O_4$] (0.29 ppm); IR: $\tilde{\nu} = 2961$, 2657, 1713, 1419, 1246, 935, 740 cm^{-1}.

Hydroxy pinonic acid (**6**): NMR: Ha$_1$ 2.994 (dd, 1H); Ha$_4$, Hc$_1$, Hc$_2$ 2.182–2.370 (m, 3H); Hd$_1$, Hd$_2$ 4.093–4.230 (dd, 2H); Ha$_2$ 1.891 (m, 1H); Ha$_3$ possibly obscured; Hb$_1$ 1.204 (s, 3H); Hb$_2$ 0.787 (s, 3H); MS: 199.0976910 [$C_{10}H_{15}O_4$] (0.54 ppm).

cis-nor-Pinonic acid (**7**): Ha$_1$ 3.100 (dd, 1H); Ha$_4$ 2.886 (dd, 1H); Ha$_2$ 2.352 (q, 1H); H$_d$ 2.090 (s, 3H) (partly obscured by signal of acetonitrile); Ha$_3$ 1.852 (qd, 1H); Hb$_1$ 1.411 (s, 3H); Hb$_2$ 0.868 (s, 3H). MS: 169.0870480 [$C_9H_{13}O_3$] (0.56 ppm).

cis-Pinornalic acid (**8**): NMR: Hd 9.631 (s, 1H); Ha$_1$ 2.817 (t, 1H); Hc$_1$ 2.575 (dd, 1H); Hc$_2$ 2.476 (dd, 1H); Ha$_4$ 2.408 (m, 1H); Ha$_2$ possibly obscured; Ha$_3$ 1.810 (dd, 1H); Hb$_1$ 1.193 (s, 3H); Hb$_2$ 0.917 (s, 3H). MS: 169.0870480 [$C_9H_{13}O_3$] (0.56 ppm).

[Hydroxy acetic acid-((2,2-dimethyl)-*cyclo*-butyl)-ester] acetic acid (**9**): MS: 215.0925990 [$C_{10}H_{15}O_5$] (0.46 ppm); IR: $\tilde{\nu} = 2976$, 1742, 1392, 1275, 1130, 961 cm^{-1}.

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