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# Application of gas chromatography–cryocondensation–Fourier transform infrared spectroscopy and gas chromatography–mass spectrometry to the identification of gas phase reaction products from the $\alpha$ -pinene/ozone reaction

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Dedicated to Professor Dr. Günther Tölg on the occasion of his 70th birthday

## Abstract

The gas phase reaction of  $\alpha$ -pinene with the atmospheric oxidant ozone was investigated by using the capabilities of both gas chromatography–cryocondensation–Fourier transform infrared spectroscopy (GC–FT-IR) and gas chromatography–mass spectrometry (GC–MS), for the identification of the reaction products formed. The reaction was carried out in a flow reaction chamber from where the compounds were sampled on Tenax-containing adsorption cartridges. The reaction mixture was injected onto the column after thermodesorption and analyzed using both GC–IR and GC–MS. Twenty compounds could be detected, including the reactant  $\alpha$ -pinene and its impurities tricyclene and camphene. Eleven compounds were identified by spectra comparison with either reference data or spectra obtained from commercial standards. Four compounds were tentatively identified from their IR and MS spectra, while from the remaining two compounds the nature of basic functional groups could be established. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Air analysis; Pinenes; Ozone; Volatile organic compounds

## 1. Introduction

The emissions of volatile organic compounds (VOCs) from vegetation – especially isoprene, mono- and sesquiterpenes – are considered to be the

major input of reactive organic carbon into the atmosphere. Current estimations on the world-wide emissions of natural VOCs are ranging between 825 and 1150 Tg carbon per year [1,2]. The global release of anthropogenic VOCs has otherwise been assessed to amount to less than 100 Tg/year [3,4]. Due to the highly reactive character of the biogenic VOCs towards the principal atmospheric oxidizing

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agents, such as ozone,  $\text{NO}_3$  and OH radicals, they are rapidly transformed into a series of organic oxidation products. The chemistry of both the primary released natural VOCs and their oxidation products significantly influences gas and particle phase processes in the troposphere. For instance, the formation of ground-level ozone can be strongly affected by biogenic VOCs and their contribution has to be considered when anthropogenic VOCs and  $\text{NO}_x$  emission regulations are aiming at a reduction of tropospheric ozone concentrations. Furthermore, oxidation products of biogenic VOCs can undergo gas-to-particle conversion and therefore contribute to the atmospheric particle phase. Although several investigations on the aerosol formation process from biogenic VOCs were carried out in the past [5–9], the chemical pathways leading to condensable species under atmospheric conditions are far from being understood.

One of the reasons for the incomplete understanding of the atmospheric fate of biogenic VOCs is the lack of knowledge about the chemical nature of individual products formed in reactions with atmospheric oxidants. In order to develop atmospheric chemistry models which include the degradation schemes of biogenic VOCs, ideally the whole product spectrum has to be elucidated and incorporated into respective models. The identification of a wide range of products can give valuable insight into the detailed chemical mechanisms of biogenic VOC oxidation. Therefore, the aim of this paper is to describe the combined application of two GC techniques with selective detection to thoroughly characterize the products formed in the  $\alpha$ -pinene/ozone reaction.

Mass spectrometry (MS) has long been known to be an efficient detection and identification technique in environmental chemistry and in combination with gas chromatography (GC) the method of choice for the analysis of complex mixtures of volatile compounds. However, although very sensitive, GC–MS suffers shortcomings when certain groups of substances have to be identified. For instance, very often the molecular ion of a compound is not detected, because the energy from electron impact ionisation (EI) is too high and causes intensive fragmentation.

Even with the softer chemical ionisation (CI) molecular ions are not necessarily produced from

individual compounds. Especially for the identification of oxygen-containing, cyclic or polycyclic organic molecules, such as typical oxidation products of biogenic VOCs, fragmentation and rearrangement of the analyte ions reduce the usability of the mass spectra for deducing structural elements.

In contrast, infrared (IR) spectroscopy is a method capable to obtain valuable analytical information about functional groups, especially with oxygen containing molecules. The sensitivity of infrared spectroscopy is often questioned, but since the introduction of the gas chromatography–cryocondensation–Fourier transform infrared spectroscopy (GC–FT-IR) technique by Haeffner et al. [10] it is suitable for analysis of samples containing semi-volatile compounds [11,12] even if the analytes are present in the low pg range. Therefore, an analytical approach was chosen using two detection techniques, IR spectroscopy and MS coupled to GC, in order to identify unknown compounds and receive information on the pathways of the  $\alpha$ -pinene degradation.

## 2. Experimental

### 2.1. Materials

The chemicals were purchased from the following suppliers: hexane (LiChrosolv grade), acetone and methanol (analytical reagent grade) from Merck (Darmstadt, Germany);  $\alpha$ -pinene,  $\alpha$ -hydroxypinane,  $\alpha$ -pinene oxide, dimethyldichlorosilane, Tenax TA (60–80 mesh) from Sigma–Aldrich (Deisenhofen, Germany).

### 2.2. Instrumental

For GC–cryocondensation–FT-IR measurements a Bio-Rad FTS-60-A interferometer equipped with a Tracer unit (Digilab Division, Krefeld, Germany) and a Fisons gas chromatograph series 8060 (Mainz, Germany) were used. The GC system was equipped with a laboratory-built thermodesorption injector [13] connected to a DB-5 column (J&W Scientific, Fisons; 60 m  $\times$  0.25 mm I.D., film thickness 0.25  $\mu\text{m}$ ) and the original liquid injector connected to a BPX-5 column (SGE Deutschland, Weiterstadt, Germany; 50 m  $\times$  0.22 mm I.D., film thickness 0.25  $\mu\text{m}$ ) as

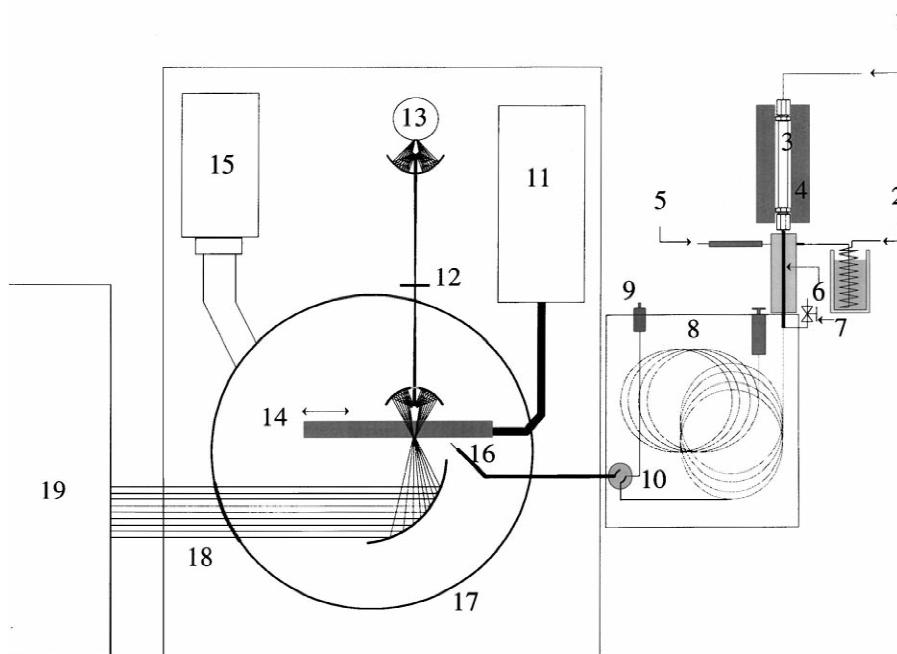


Fig. 1. GC–cryocondensation–FT-IR system. 1=He flow, 2=cold nitrogen, 3=sample tube, 4=heating brackets, 5=hot nitrogen, 6=GL tubing (cryofocussing), 7=split valve, 8=GC system with two columns, 9=FID system, 10=four-way valve, 11=liquid nitrogen container, 12=aperture, 13=MCT detector, 14=ZnSe slide, 15=turbo pump, 16=transferline with tip, 17=vacuum chamber, 18=IR beam, 19=interferometer.

shown in Fig. 1. Both columns were connected to a pneumatically actuated four-way valve (Valco, GAT Analysentechnik, Berlin, Germany), located inside the GC oven, which allows the flame ionization detection (FID) system as well as the Tracer unit to be used as detection devices for both columns.

Spectra were obtained on-the-move by co-adding four scans with a resolution of  $8\text{ cm}^{-1}$ , which resulted in a time resolution of 1 spectrum every 0.8 s.

The analytes can be introduced either by liquid injection or from adsorption tubes by thermodesorption. After separation, the analytes enter the vacuum chamber through a transfer line held at  $250^{\circ}\text{C}$  and are deposited on a ZnSe slide, cooled to  $-180^{\circ}\text{C}$  with liquid nitrogen. ZnSe is transparent in the infrared and allows spectra to be obtained in the transmission mode. The slide is mounted on an electrical stepper motor, and after the deposition the analyte spot is continuously moved into the infrared beam located  $400\text{ }\mu\text{m}$  away. The IR beam is focused on the position of the analyte spot, and is afterwards

directed to an MCT detector for intensity measurements.

GC–MS experiments were carried out with a Dani 6500 gas chromatograph coupled to a Finnigan MAT ITD 700 ion trap mass spectrometer (Finnigan MAT, Bremen, Germany). Separations were accomplished on a BPX-5 column (SGE;  $50\text{ m}\times 0.22\text{ }\mu\text{m}$  I.D., film thickness  $1\text{ }\mu\text{m}$ ). This system was also equipped with a laboratory-built thermodesorption injection system.

### 2.3. Experimental setup

The reaction of  $\alpha$ -pinene and ozone was carried out in a 10 l tube-shaped reaction chamber made of borosilicate glass with an internal diameter of about 10 cm (see Fig. 2). Synthetic air (purity 5.0; Messer, Berlin, Germany) with a total flow of 60 l/h was purified by a hydrocarbon trap (Supelco, Bad Homburg, Germany). The gas stream was then divided into three different paths. The main stream (50 l/h) entered the reaction chamber through a needle valve

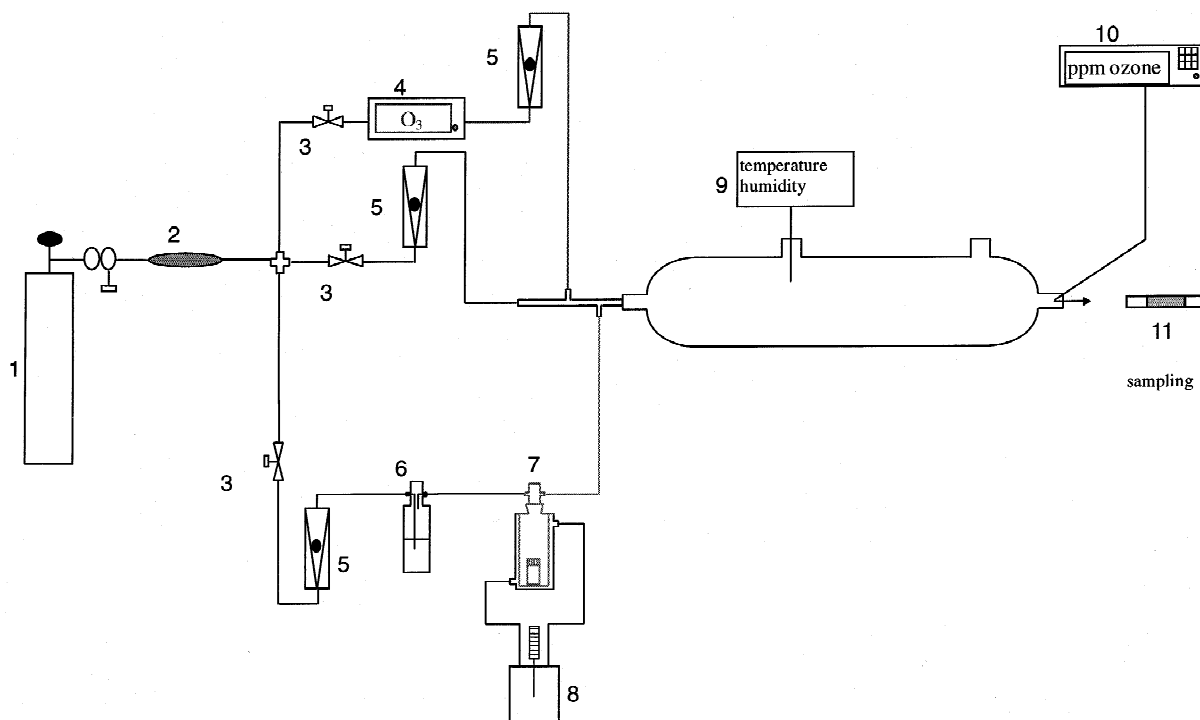


Fig. 2. Reaction chamber. 1=Synthetic air, 2=hydrocarbon trap, 3=needle valve, 4=ozone generator, 5=flow meter, 6=wash bottle, 7=test gas generator, sample vial, 8=thermostat, 9=hygro- and thermometer, 10=ozone analyzer, 11=sampling cartridge.

and a flow meter. The second stream (4 l/h) was led through an ozone generator (Model Peripheral COM; Anseros, Tübingen, Germany). The third stream (6 l/h) was at first humidified using a water filled impinger and then led through a test gas generator to add the hydrocarbon of interest, in this case  $\alpha$ -pinene. The temperature of the test gas generator was maintained at 30°C by a thermostat.

The chamber was wrapped in aluminum foil to prevent a possible influence of diffuse light on the product formation. Temperature and humidity were measured with a Dostmann P560 gauge (Wertheim, Germany), and the ozone concentration was measured with an analyzer (Model Ozomat MP; Anseros) at the inlet and outlet of the chamber. Prior to each experiment, the reaction chamber was cleaned and afterwards flushed with synthetic air for 48 h, and the remaining hydrocarbon level was checked with GC-FID.

#### 2.4. Procedures

The investigations on the gas phase reaction of  $\alpha$ -pinene with ozone were carried out at an ozone concentration of 1 ppm (v/v) (ppmv), while  $\alpha$ -pinene was held constant at 6 ppmv. Blank experiments were carried out with 4 ppmv  $\alpha$ -pinene in the absence of ozone and 3 ppmv ozone without the hydrocarbon. The temperature of the chamber was held at 25°C and the relative humidity at 15%.

The samples were taken using laboratory-built adsorption tubes of 12.5 cm  $\times$  0.6 cm diameter, each filled with 60 mg Tenax TA. The sampling tubes were prepared as described before [14]. The analytes were sampled on the tubes with flow-rates of 8 l/h for 1 min. For analysis with GC-cryocondensation-FT-IR the compounds were thermally desorbed from the Tenax tubes at 250°C and cryotrapped at -110°C within a deactivated glass-lined tube. Afterwards, the

analytes were rapidly vaporized and injected onto the column by heating the cryotrap to 250°C. The temperature of the column was held at 40°C for 3 min and afterwards increased with a rate of 2°C/min to 120°C. Thereafter, the column temperature was increased with a rate of 5°C/min up to 250°C.

The desorption procedure for GC–MS experiments was identical. The separation conditions, however, for the GC–MS analysis were slightly different. The separation started at 37°C for 2 min, then the temperature was increased with a rate of 8°C/min to 200°C and afterwards at 10°C/min to 220°C.

### 3. Results

The first experiments were dedicated to investigate system blanks. Therefore, a series of experiments was carried out with each of the primary reactants that were used later for the investigation of  $\alpha$ -pinene/ozone reaction products. The lowest trace in Fig. 3, for example, shows the result of a blank run of 3 ppmv ozone sampled on Tenax cartridges and measured with GC–cryocondensation–FT-IR.

Here, the GC–IR data are displayed in form of functional group (FG) chromatograms corresponding to the absorption within certain wavenumber ranges, comparable to mass traces in mass spectrometry.

The upper set of chromatograms show the absorption in the region 3050–2750  $\text{cm}^{-1}$ , indicating compounds that contain CH groups. In the bottom set the signals of the C=O-stretching region 1800–1680  $\text{cm}^{-1}$  are shown.

In the experiment of sampling ozone on Tenax practically no blank contributions to the CH region can be seen, while three compounds (marked T1–3) are identified as being the major ozone artifact caused by the adsorption material Tenax.

The blank experiment with pure  $\alpha$ -pinene in synthetic air is displayed in the second trace from bottom in each set of FG chromatograms in Fig. 3. Besides  $\alpha$ -pinene, some minor impurities from the commercial standard were identified as tricyclene (peak 2) and camphene (peak 5).

For identification of the products from the  $\alpha$ -pinene/ozone reaction it was important to exclude the possibility that these compounds would be totally formed on the surface of the adsorption material Tenax during the preconcentration step rather than in the gas phase reaction. Therefore,  $\alpha$ -pinene in synthetic air (6 ppmv, sampled for 1 min) was collected on Tenax-filled sampling cartridges as described above. Afterwards, ozone test gas with a concentration of 180 ppbv – which equals the sampling conditions of the experiments described below – was passed through the same adsorption tube to observe possible reactions between the deposited  $\alpha$ -pinene and the oxidant. The result of this experiment is shown in the second trace from top in Fig. 3. The additional signals that are detectable belong to  $\alpha$ -pinene oxide (7) and pinonaldehyde (19).

The upper trace in Fig. 3 shows the major reaction products resulting from the gas phase reaction of  $\alpha$ -pinene with ozone. Adjusting the flow-rates as described above results in a mean reaction time of ca. 10 min. As can be seen from a comparison of the results with those from the blank runs, none of the peaks, except 19, is found in the blank experiments.

The compounds found as reaction products are shown in Fig. 4. Again, functional group chromatograms of the CH region (top chromatogram) and the C=O region (bottom chromatogram) are used to present the results.

The CH trace clearly shows peak 4 as the major signal, corresponding to unreacted  $\alpha$ -pinene. The C=O chromatogram displays the reaction products containing a carbonyl group as the major functional element from the oxidation. The main reaction product is pinonaldehyde, already detected as such in various reports [7,15]. The assigned peaks were identified by synthetic standards or through spectra comparison with reference data from different spectra libraries, and the identified compounds are listed in Table 1, together with the reference sources as well as with the structures of the compounds.

For verification and support of identification mass spectral investigations were carried out. In Fig. 5 a total ion chromatogram is displayed which shows the same product distribution as the IR traces although the relative intensities of the peaks vary slightly. In this case identification was possible mostly by

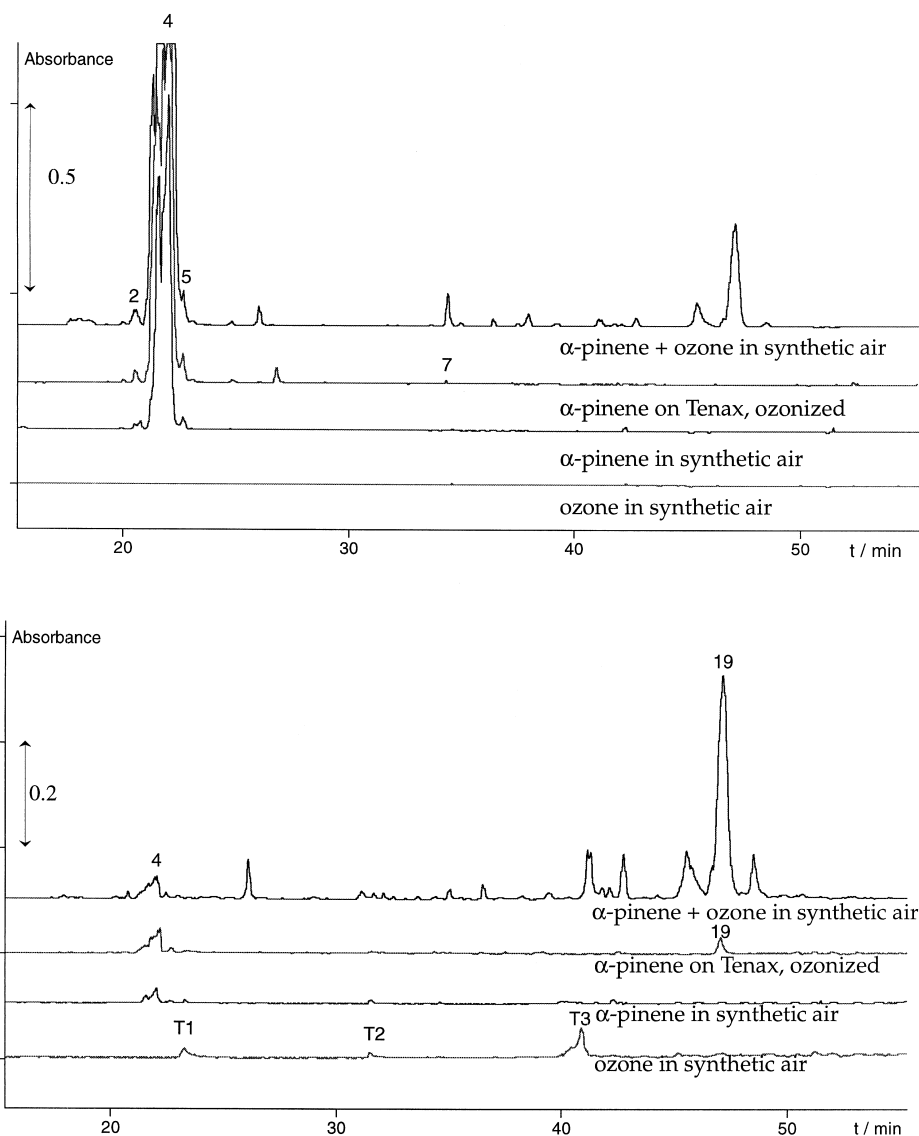


Fig. 3. System blank experiments: upper part: set of functional group chromatograms from CH bands ( $3000\text{--}2750\text{ cm}^{-1}$ ); lower part: set of functional group chromatograms from C=O bands ( $1800\text{--}1680\text{ cm}^{-1}$ ), as described in the text.

spectra comparison with reference data. The assignment of the peaks is the same as the one for the IR signals. The only missing major compound is  $\alpha$ -hydroxypinane (peak 18), which could not be detected with mass spectrometry. Nonetheless, the identification of this product is based on comparison with commercial standard material available.

#### 4. Discussion

The investigations on the gas phase reaction between  $\alpha$ -pinene and ozone revealed a number of components that were not known yet as reaction products. The results of the blank experiments clearly show that these products are formed through

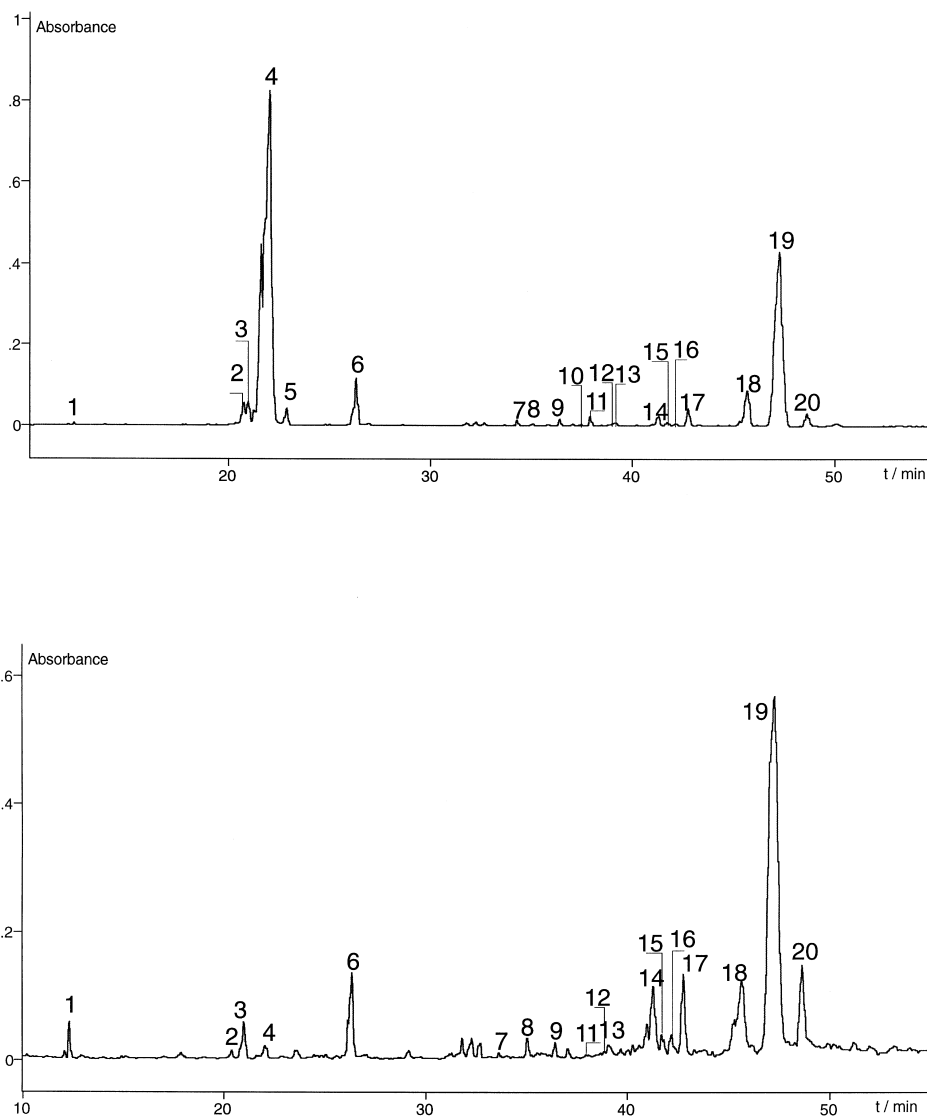


Fig. 4. Reaction product distribution: upper trace: functional group chromatogram from CH bands ( $3000\text{--}2750\text{ cm}^{-1}$ ); lower trace: functional group chromatogram from C=O bands ( $1800\text{--}1680\text{ cm}^{-1}$ ).

the reaction and not on the surface of the sampling cartridges. The only exceptions are  $\alpha$ -pinene oxide and pinonaldehyde, which seemed to be produced in small quantities on Tenax. The blank experiments with an ozone concentration of 3 ppmv show just three minor artifacts, possibly being the result of a reaction of ozone with the adsorption material. These compounds, namely benzaldehyde, acetophenone and

benzoic acid have already been reported as Tenax artifacts [16].

#### 4.1. Known reaction products

Published reports [7,15] dealing with identification of products from the  $\alpha$ -pinene/ozone reaction described pinonaldehyde to be the major compound.

Table 1

Listing of compounds shown in the chromatograms in Figs. 4 and 5 with peak number, retention times from the GC–IR experiment, name of the compound with new tentative identifications in parentheses, molecular structure and references

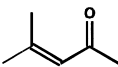
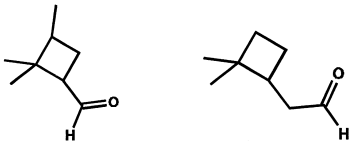
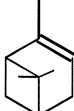
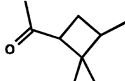
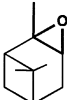
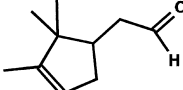
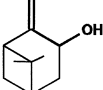



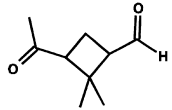
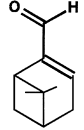
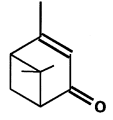
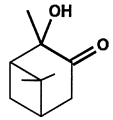
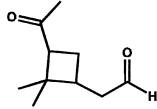
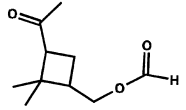
Peak <sup>a</sup>	Retention time (min)	Identified as:	Molecule	Ref.
1	12.07	Isopropylidene acetone		[23]
2	20.80	Tricyclene	Impurity of $\alpha$ -pinene	[24]
3	22.02	Aldehyde 21 [a: (2,2,3-Trimethylcyclobutyl)formaldehyde; b: (2,2-cyclobutyl)acetaldehyde]		
4	22.37	$\alpha$ -Pinene		[24]
5	22.82	Camphene	Impurity of $\alpha$ -pinene	[24]
6	26.11	Ketone 26 [(Acetyl-2,2,3-trimethyl)cyclobutane]		
7	33.64	$\alpha$ -Pinene oxide		[24]
8	35.05	Dicarbonyl	Not identified	
9	36.52	Campholenealdehyde		[23]
10	37.32	<i>trans</i> -Pinocarveol		[24]
11	38.23	<i>trans</i> -Verbenol		[24]
12	38.94	Pinocamphone		[24]
13	39.44	Pinocarvone		[24]



Table 1 (continued)

Peak <sup>a</sup>	Retention time (min)	Identified as:	Molecule	Ref.
14	41.21	Aldehyde 41 (Norpinonaldehyde)		
15	41.77	Myrtenal		[24]
16	42.17	Aldehyde 42	Not identified	
17	42.78	<i>cis</i> -Verbenone		[24]
18	45.56	$\alpha$ -Hydroxypinanone		
19	47.17	Pinonaldehyde		
20	48.54	Carbonyl 48 [(2,2-Dimethyl-3-acetylcyclobutyl)methylformate]		

<sup>a</sup> Peaks are according to the numbers cited in the text.

These findings can be confirmed with this investigation, because the aldehyde was also found as the most prominent product (peak 19). Additionally, isopropylidene acetone, suggested by Yokouchi and Ambe [7] to be a reaction product, was found and identified (1) by spectra comparison.

#### 4.2. Thermal rearrangement of reaction products

$\alpha$ -Pinene oxide (7) has been reported to be a reaction product of  $\alpha$ -pinene ozonolysis in the liquid phase [17] and most recently also in the gas phase [18]. Again, this observation can be confirmed with the present work. However, during GC experiments with the standard compound it appeared that the amount of  $\alpha$ -pinene oxide was not observed in the

expected intensity, and additional peaks could be detected. These peaks were subsequently identified as campholenealdehyde (9) and pinocamphone (12). It was assumed that  $\alpha$ -pinene oxide undergoes a rearrangement during the experiment within the heated GC system [20]. Therefore, an additional experiment was carried out, where 1  $\mu$ l of the compound in *n*-hexane was injected (concentration = 40  $\mu$ g/ $\mu$ l) at different injection temperatures (160, 180 and 200°C). The results are shown in Table 2. They indicate that the amount of  $\alpha$ -pinene oxide detected by FID depends on the temperature of the injection system. The lower the temperature the higher the intensity of peak 7, while the intensities of the peaks of campholenealdehyde and pinocamphone decreased. Vice versa, the higher the injection tem-

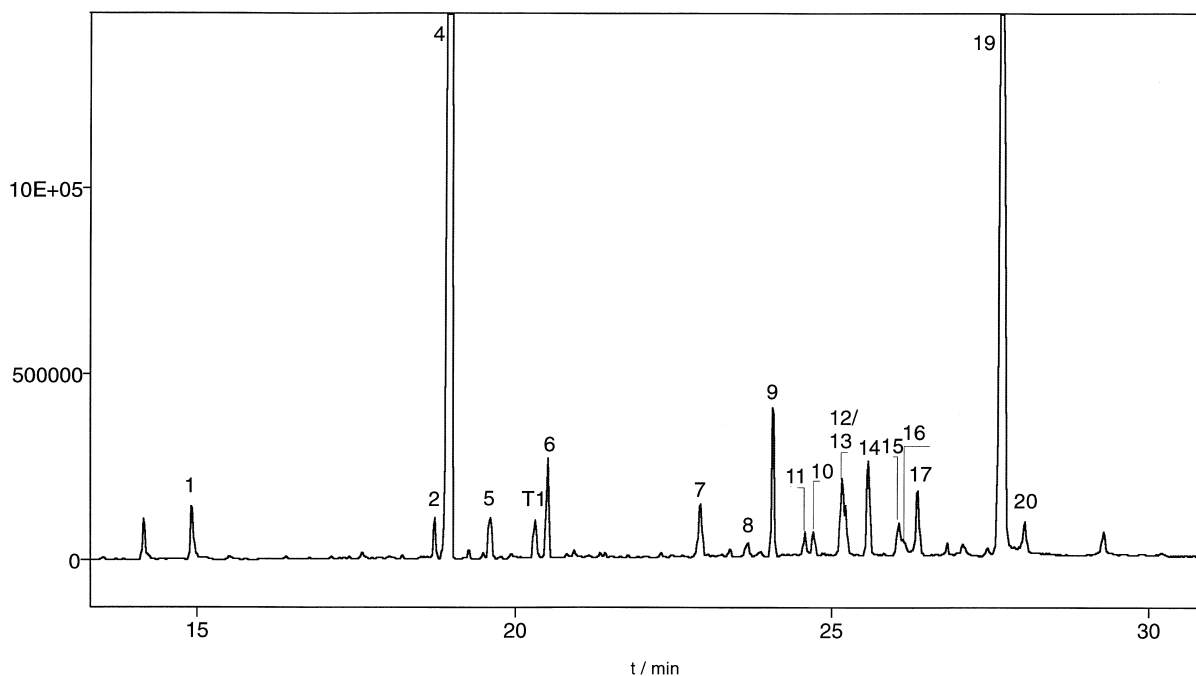


Fig. 5. Total ion chromatogram of reaction products: mass spectrometric identification.

perature, the lower was the intensity of the  $\alpha$ -pinene oxide peak. From these results it was concluded that  $\alpha$ -pinene oxide is thermally labile and rearranges under the applied conditions to campholenealdehyde and pinocamphone, and the latter are artifacts rather than reaction products from the gas phase oxidation of  $\alpha$ -pinene.

#### 4.3. Products newly identified by spectra comparison

In addition to the already known reaction products some compounds were detected, that have not been identified before.

These compounds include two unsaturated alcohols, that were identified as *trans*-verbenol (11) and *trans*-pinocarveol (10). While for the formation of verbenol the  $\alpha$ -position to the double bond in  $\alpha$ -pinene is oxidized, the double bond itself remains unaffected. Interestingly, the formation of *trans*-pinocarveol requires a shift from an endo-, as in  $\alpha$ -pinene, to an exocyclic double bond. The structures of the ketones formed, namely *cis*-verbenone and pinocarvone, resemble those of the alcohols from which they are derived through further oxidation.

One compound was identified as myrtenal. This compound has been detected before in emission

Table 2

Injection of  $\alpha$ -pinene oxide at different injection temperatures of a GC-FID system; concentration=40  $\mu\text{g}/\mu\text{l}$   $\alpha$ -pinene oxide in *n*-hexane, injection volume=1  $\mu\text{l}$ , FID temperature: 250°C, GC program as described in the experimental section

Injection temperature (°C)	Peak area		
	$\alpha$ -Pinene oxide	Campholenealdehyde	Pinocamphone
160	13 760	39 859	22 873
180	5256	40 973	23 314
200	1101	48 911	26 936

experiments [13]. The oxidation occurs at the methyl group next to the double bond of  $\alpha$ -pinene.

One product with two functional groups was observed and identified as  $\alpha$ -hydroxypinanone, which contains both a hydroxy- and a keto group (see Table 1). Although  $\alpha$ -hydroxypinanone could not be detected by mass spectrometry, it was clearly identified through comparison with the IR spectrum of the commercial standard compound.

#### 4.4. Tentative identification of unknown compounds without reference data

For some of the compounds no reference data could be found in existing spectra libraries. However, using both infrared and mass spectra tentative identifications were possible for some of them. The IR and MS spectra of the compound leading to peak 14 are shown in Fig. 6. The infrared spectrum in the lower trace clearly shows this substance to be an aldehyde because of the C=O double bond frequency at  $1705\text{ cm}^{-1}$  and the CH-stretching doublet-band of the CHO group at  $2837$  and  $2734\text{ cm}^{-1}$  caused by a Fermi resonance. These two bands identify the substance as an aliphatic aldehyde. In addition to the  $\text{CH}_3$  stretching,  $\text{CH}_3$ -,  $\text{CH}_2$ - and CH-deformation bands at  $2964$ ,  $1467$ ,  $1374$  and  $1352\text{ cm}^{-1}$ , respectively, a deformation band of a dimethyl group  $-\text{CR}(\text{CH}_3)_2$  could be found at  $1185\text{ cm}^{-1}$ .

Within the mass spectrum of aldehyde 41 no molecular ion could be identified, but several fragments allow an interpretation. The peak at  $m/z$  139 is likely to result from a loss of a methyl group ( $\text{M}-15$ )<sup>+</sup>, while  $m/z$  125 and  $m/z$  111 could be interpreted as a loss of CHO and  $\text{CH}_3\text{CO}$  fragments, respectively. The dominant peak in the mass spectrum is  $m/z$  83, corresponding to the  $\text{C}_4$ -ring system with two methyl groups attached. Therefore, although the molecular ion is not visible, the molecular mass of the aldehyde 41 is assumed to be 154.

From this data the compound can be tentatively identified as nor-pinonaldehyde (structure shown in Table 1), a compound suggested to be one of the reaction products of  $\alpha$ -pinene ozonolysis [8].

The compound responsible for peak 6 produces an intensive infrared spectrum (see Fig. 7, lower trace), which includes a strong  $\text{CH}_3$ -stretching band, while the  $\text{CH}_2$  band is weaker. This substance can be

identified as a ketone resulting from the C=O-stretching vibrations at  $1701\text{ cm}^{-1}$  and the missing characteristic bands of other carbonyl compounds as aldehydes and esters. In addition to the  $\text{CH}_3$ - and  $\text{CH}_2$ -deformation bands at  $1452$  and  $1425\text{ cm}^{-1}$  the tertiary group  $-\text{CR}(\text{CH}_3)_2$  can be derived from the symmetric bending vibrations at  $1382$  and  $1370\text{ cm}^{-1}$  and the stretching band at  $1185\text{ cm}^{-1}$ .

The mass spectrum in Fig. 7, upper part, exhibits an intensive peak at  $m/z$  83, which again can be assigned to a  $\text{C}_4$ -ring system with two additional methyl groups attached. The fragments at  $m/z$  97 and 125 correspond to the  $(\text{M}-\text{CH}_3)^+$  and the  $[\text{M}-\text{C}(\text{CH}_3)=\text{O}]^+$  fragments, respectively. The molecular ion is observed at  $m/z$  140.

These data lead to the tentative conclusion that compound ketone 26 is acetyl-2,2,3-trimethylcyclobutane.

The compound detected as peak 3 (see Fig. 8 for spectra) can be clearly assigned to an aldehyde through the infrared spectrum due to the vibrations at  $2726\text{ cm}^{-1}$  in combination with the C=O-stretching vibration of the aldehyde group at  $1720\text{ cm}^{-1}$ . The bands around  $2957$  and  $1467\text{ cm}^{-1}$  belong to CH stretching and deformation frequencies, respectively.

From the MS spectrum a molecular mass of 126 can be taken. The important fragments are at  $m/z$  111 ( $-\text{CH}_3$ ) and at 83 ( $\text{C}_4$ -ring system with two methyl groups).

Considering the spectral data, however, it is possible to suggest two different structures for this molecule, namely (a) (2,2,3-trimethylcyclobutane)formaldehyde and (b) (2,2-dimethylcyclobutyl)acetaldehyde. The spectra can not distinguish between the methyl and the methylene groups in these possible molecules.

The compound causing peak 20 (see Fig. 9) shows a strong carbonyl band at  $1712\text{ cm}^{-1}$ . The signals at  $2960$  and  $2871\text{ cm}^{-1}$  are from CH-stretching vibrations, while their deformation bands are located around  $1463\text{ cm}^{-1}$ . The most interesting band at  $1185\text{ cm}^{-1}$  belongs to a C–O single bond. Because of the intensity and location of this band it can be caused by an ether group or in combination with the carbonyl group by a formate group.

Although the corresponding mass spectrum is difficult to interpret, some basic fragments can be identified. The peak at  $m/z$  169 belongs to a methyl-

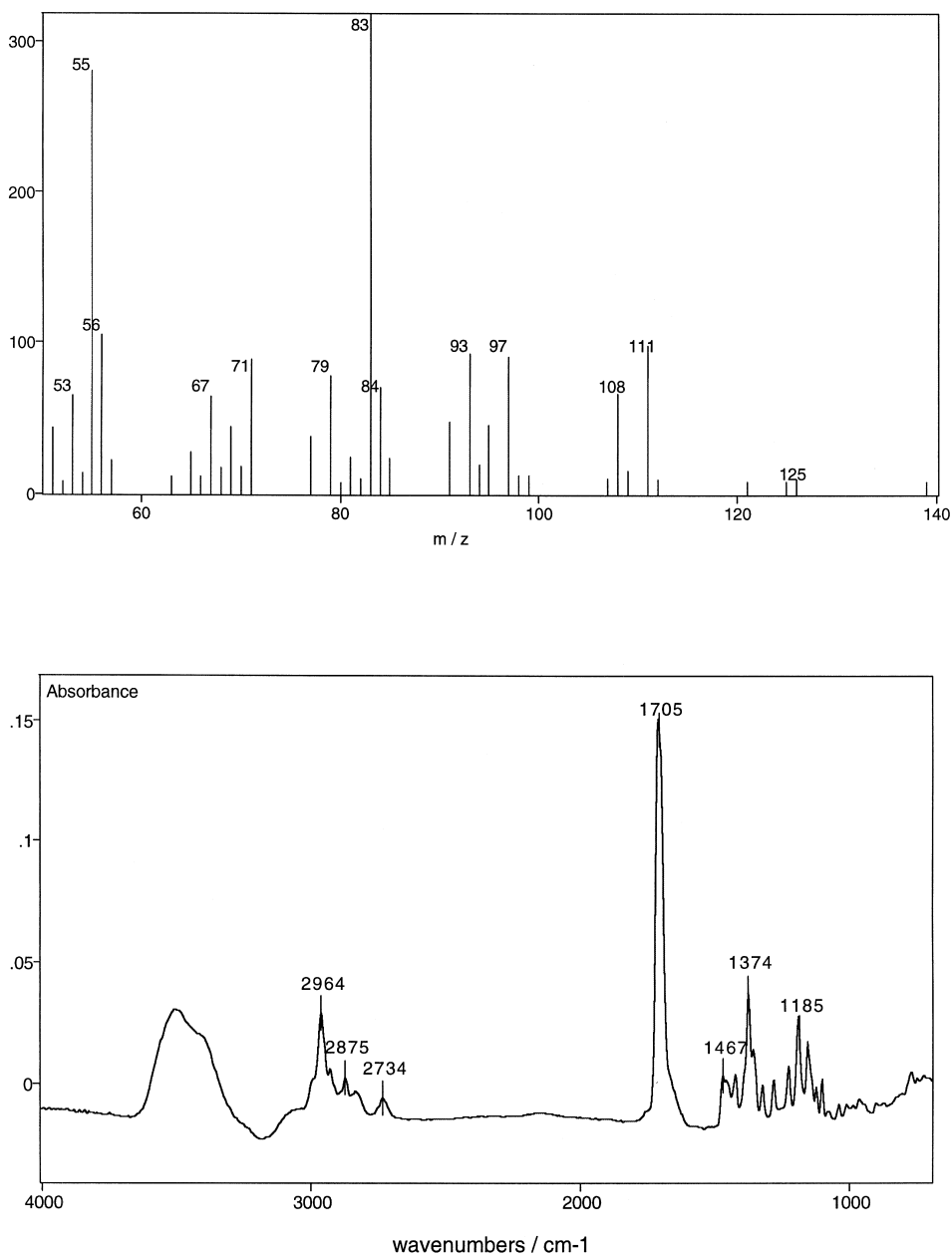


Fig. 6. Spectra from product peak 14: (top) MS spectrum taken from TIC shown in Fig. 5; (bottom) IR spectrum taken from chromatographic run shown in Fig. 4.

fragmentation from the molecular ion. The base peak at 83 again is characteristic for the  $C_4$ -ring system with two methyl groups attached.

Considering the spectra a molecular mass of 184 may be reconstructed and this compound might be [(2,2-dimethyl-3-acetyl)cyclobutyl]methylformate,

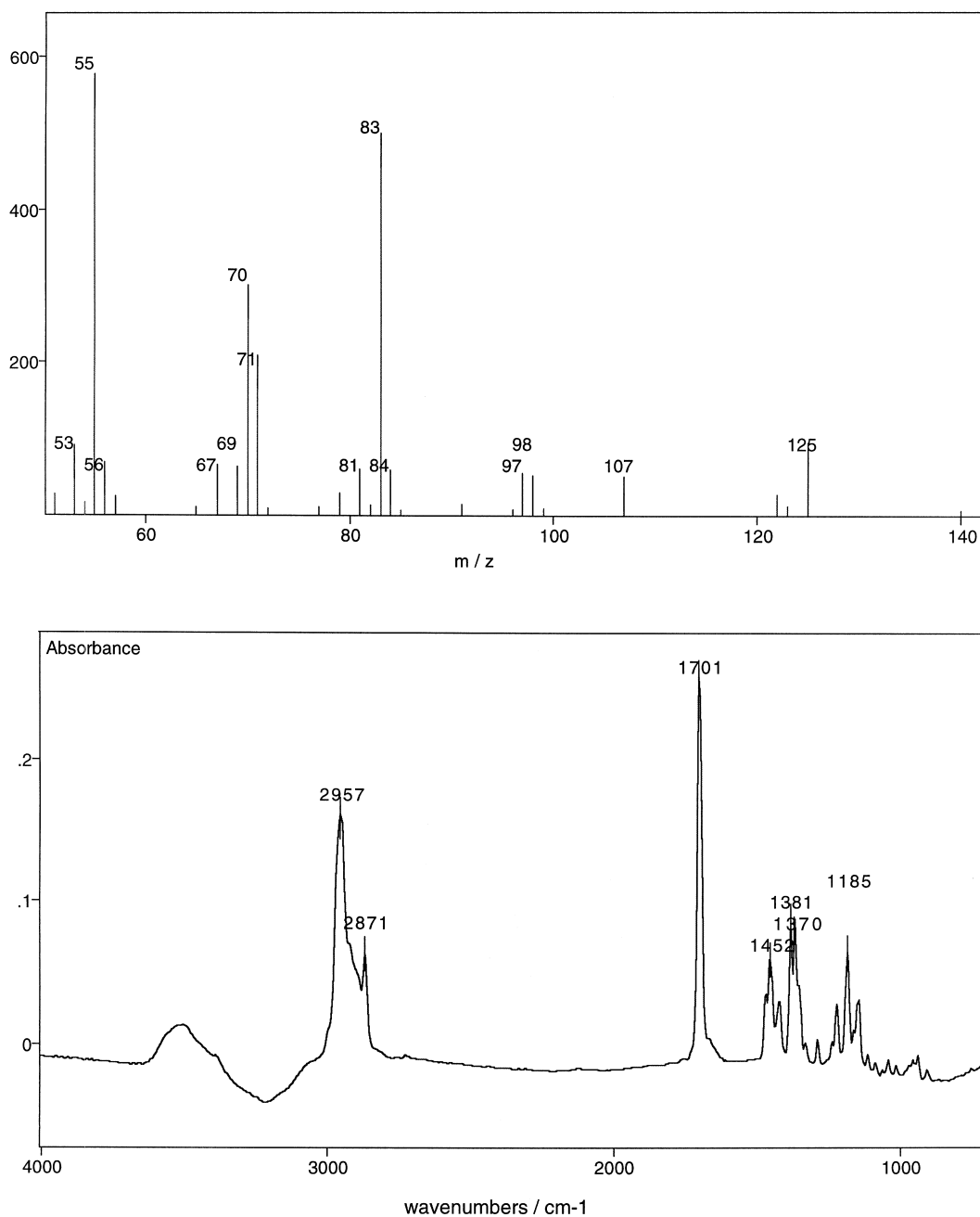


Fig. 7. Spectra from product peak 6: (top) MS spectrum taken from TIC shown in Fig. 5; (bottom) IR spectrum taken from chromatographic run shown in Fig. 4.

which was just recently reported by Yu et al. [19]. The corresponding structure is shown in Table 1 (carbonyl 48).

## 5. Conclusion

The use of the combined capabilities of infrared

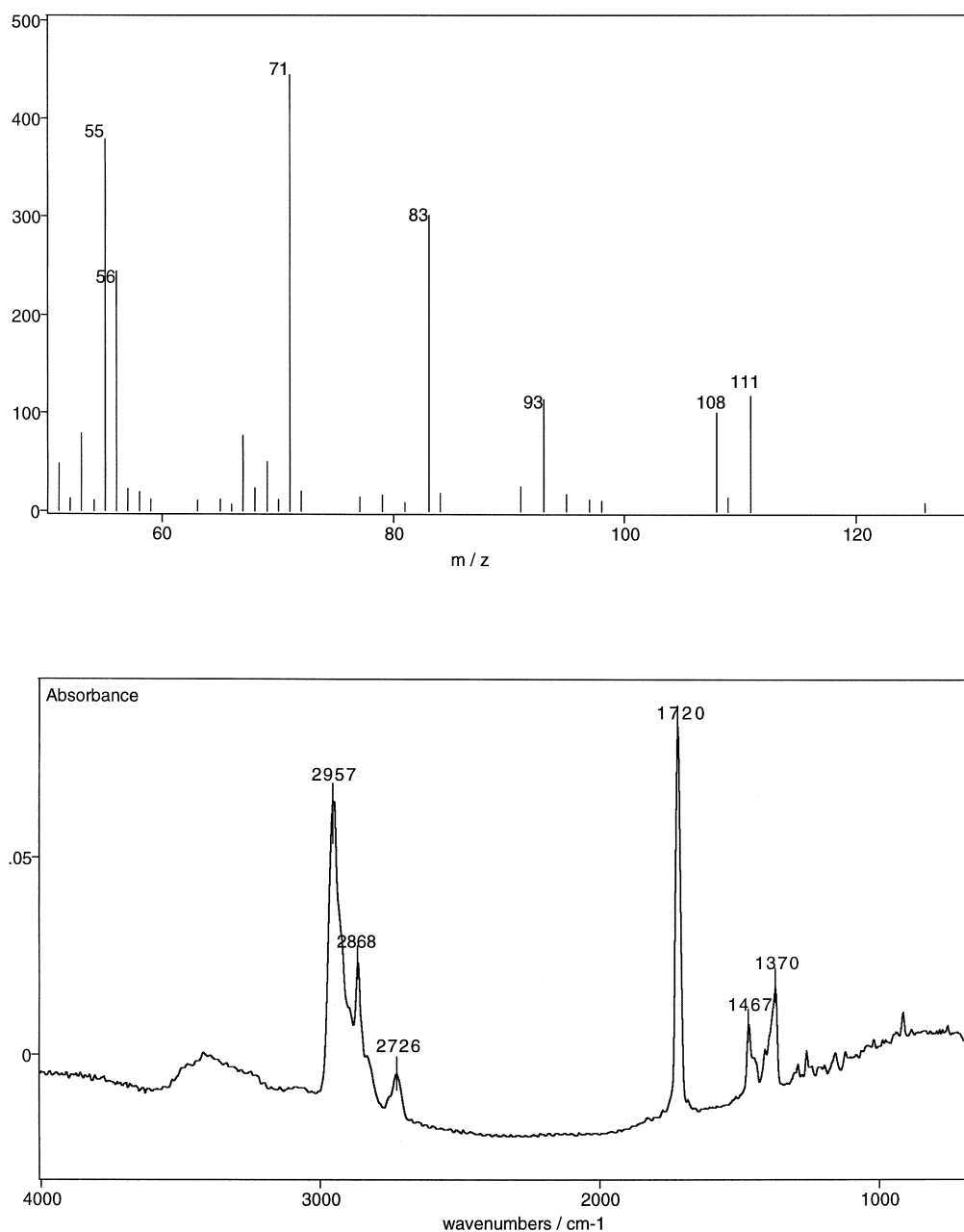


Fig. 8. Spectra from product peak 3: (top) MS spectrum taken from TIC shown in Fig. 5; (bottom) IR spectrum taken from chromatographic run shown in Fig. 4.

spectroscopy and mass spectrometry coupled to gas chromatography allows an in depth investigation of unknown reaction products resulting from the gas

phase reaction of  $\alpha$ -pinene with the atmospheric oxidant ozone. Although the concentrations of  $\alpha$ -pinene and ozone used for these studies are much

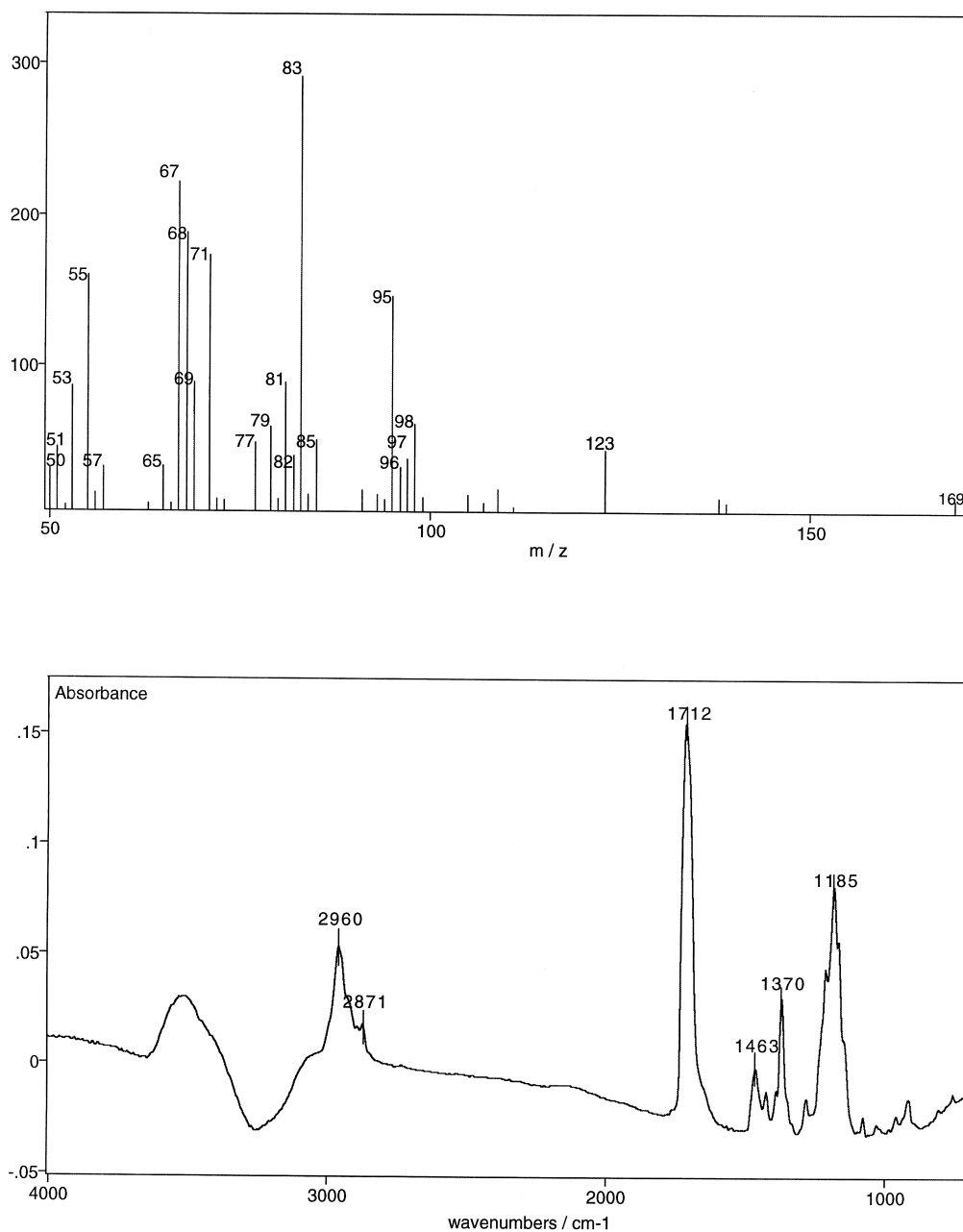


Fig. 9. Spectra from product peak 20: (top) MS spectrum taken from TIC shown in Fig. 5; (bottom) IR spectrum taken from chromatographic run shown in Fig. 4.

higher than the ones usually found in the atmosphere, information obtained about the different substances is considered to be relevant for atmospheric

processes. The investigations have shown that with the GC–cryocondensation–FT-IR instrument it was possible to identify formerly unknown reaction prod-

ucts. While mass spectrometric data sometimes lack detailed structural information, infrared spectrometry often shows distinct differences in the nature of functional groups and allows to identify structural elements.

It has been shown [21,22] that the reaction of ozone with alkenes can produce high yields of OH radicals, and although the experiments that are the subject of the present report were carried out in the dark, it cannot be excluded that some of the products observed were formed by the attack of OH radicals to  $\alpha$ -pinene. Similarly, the influence of water vapor on the product distribution has been ignored during these investigations. Therefore, the results of this paper are intended mainly to evaluate the capabilities of the two analytical techniques applied to the identification of different gas phase products of the  $\alpha$ -pinene ozonolysis, GC–cryocondensation–FT-IR and GC–MS. Further systematic investigations on the reaction pathways and the influences of different environmental conditions (humidity,  $\text{NO}_x$ ) on the product distribution are under way.

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### References

- [1] F. Fehsenfeld, J. Calvert, R. Fall, P. Goldan, A. Guenther, C.N. Hewitt, B. Lamb, S. Liu, M. Trainer, H. Westberg, P. Zimmerman, *Global Biochem. Cycles* 4 (1992) 389–430.
- [2] A. Guenther, C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, *J. Geophys. Res.* 100 (1995) 8873–8892.
- [3] A.M. Hough, C.E. Johnson, *Atmos. Environ.* 25A (1991) 1819–1835.
- [4] J.F. Müller, *J. Geophys. Res.* 97 (1992) 3787–3804.
- [5] T. Hoffmann, J.R. Odum, F. Bowman, D. Collins, D. Klockow, R.C. Flagan, J. Seinfeld, *J. Atmos. Chem.* 26 (1997) 189–222.
- [6] J.R. Odum, T. Hoffmann, F. Bowman, D. Collins, R.C. Flagan, J.H. Seinfeld, *Environ. Sci. Technol.* 30 (1996) 2580–2585.
- [7] Y. Yokouchi, Y. Ambe, *Atmos. Environ.* 19 (1985) 1271–1276.
- [8] S. Hatakeyama, K. Izumi, T. Fukuyama, H. Akimoto, *J. Geophys. Res.* 94 (1989) 13013–13024.
- [9] T. Hoffmann, R. Bandur, U. Marggraf, M. Linscheid, *J. Geophys. Res.* 103 (1998) 25569–25578.
- [10] A.M. Haeffner, K.L. Norton, P.R. Griffith, S. Bourne, R. Curbelo, *Anal. Chem.* 60 (1988) 2441–2444.
- [11] K.L. Norton, A.J. Lange, P.R. Griffiths, *J. High Resolut. Chromatogr.* 14 (1991) 225–229.
- [12] P. Jackson, G. Dent, D. Carter, D.J. Schofield, J.M. Chalmers, T. Visser, M. Vredenburg, *J. High. Resolut. Chromatogr.* 16 (1993) 515–521.
- [13] J. Geiger, T. Hoffmann, J. Kahl, D. Klockow, E.H. Korte, W. Schrader, *Fresenius J. Anal. Chem.* 362 (1998) 148–154.
- [14] T. Hoffmann, *Fresenius J. Anal. Chem.* 351 (1995) 41–47.
- [15] H. Hakola, J. Arey, S.M. Aschmann, R. Atkinson, *J. Atmos. Chem.* 18 (1994) 75–102.
- [16] A. Calogirou, B. Richter Larson, C. Brussol, M. Duane, *Anal. Chem.* 68 (1996) 1499–1506.
- [17] K. Greisbaum, *Tetrahedron* 52 (1996) 1813–1826.
- [18] A. Alvarado, E.C. Tuazon, S.M. Ashmann, R. Atkinson, J. Arey, *J. Geophys. Res.* 103 (1998) 25541–25551.
- [19] J. Yu, D.R. Crocker III, R.J. Griffin, R.C. Flagan, J.H. Seinfeld, *J. Atmos. Chem.* (1999), in press.
- [20] E. Poyals, L.L. Harrell Jr., *J. Am. Chem. Soc.* 77 (1955) 3405–3408.
- [21] S.M. Aschmann, J. Arey, R. Atkinson, *Atmos. Environ.* 30 (1996) 2939–2943.
- [22] A.A. Chew, R. Atkinson, *J. Geophys. Res.* 101 (1996) 28649–28653.
- [23] M. Passlack, W. Bremser, M. Beckmann, H. Wagner, *Infrared Spectral Data*, VCH, Weinheim, New York, 1986.
- [24] P.A. Stadler, *Helv. Chim. Acta* 43 (1960) 1601–1612.