Identification of the oxidation products of the reaction between α-pinene and hydroxyl radicals by gas and high-performance liquid chromatography with mass spectrometric detection

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Abstract

In this paper an identification method is described for determining the degradation products of the reaction of α-pinene with hydroxyl radicals. The study is carried out in a fast-flow reactor equipped with a specially designed microwave cavity (type Surfatron) allowing to operate at pressures up to 100 Torr (1 Torr=133.322 Pa). The semivolatile products are collected on a liquid nitrogen trap (LN_2 trap) and the batch samples are subsequently analysed by GC–MS and HPLC–MS. Some samples were also collected directly on a LpDNPH-cartridge, followed by HPLC–MS analysis. When experiments were carried out at 50 Torr both GC–MS and HPLC–MS measurements showed that campholenealdehyde and pinonaldehyde were identified as condensable oxidation products for the α-pinene/OH reaction, with pinonaldehyde being the main product. Furthermore, the LN_2 trap collection method based on the in situ conversion of aldehydes and ketones to their 2,4-dinitrophenylhydrazone derivatives allowed the determination of formaldehyde, acetaldehyde and acetone. Although formaldehyde and acetone are present in small amounts in blank samples, it could be established that formaldehyde and acetone are also formed in the α-pinene/OH reaction. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since 1970 several studies have shown that a wide variety of volatile non-methane organic compounds (NMOCs) are emitted from vegetation and forests. It has also been shown that on a global scale the biogenic emissions of the NMOCs far exceed the anthropogenic emissions of NMOCs [1–3]. A large portion of these NMOCs can be attributed to isoprene and the monoterpenes. The monoterpenes can react with O_3 and radicals like OH and NO_3. Due to these reactions with ozone, hydroxyl radicals and

nitrate radicals, these hydrocarbons might have an influence on the concentrations of a number of trace gases in the atmosphere on a global scale [4]. These trace gases can be divided into three categories: volatile compounds such as carbon monoxide and carbon dioxide [5–7], semivolatile compounds such as formaldehyde and acetone [8,9] and pinonaldehyde [6,9–11]. In addition biogenic hydrocarbons are known to be involved in the production of atmospheric aerosols [6,12–14].

In order to elucidate the contribution of NMOCs to the composition of the atmosphere, their chemical degradation mechanism is to be incorporated in atmospheric chemistry models [15]. While the kinet-

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ics of the oxidation of isoprene is now very well documented [16] much less is known about the mechanisms and product yields of the oxidation reaction of terpenes such as α-pinene.

Since the overall chemistry in the atmosphere is far too complex to study in situ, experiments are performed on a laboratory scale. To establish the degradation paths and to determine the product yields of the α-pinene/OH reaction, laboratory measurements can be carried out in smog chambers and fast-flow reactors. The disadvantage of smog chambers is the simultaneous occurrence of OH and O_3 reactions, whereas the fast-flow reactor technique has a clean OH radical source. In this way the reaction with hydroxyl radicals can be separated from other primary reactions with ozone or nitrate radicals.

The work presented in this paper identifies some of the products formed in the reaction between α-pinene and hydroxyl radicals in the presence of oxygen using the fast-flow reactor technique. The volatile compounds (CO, CO_2) have already been determined via on-line mass spectrometric analysis [7]. Attention will now be focused on the qualitative determination of the semivolatile organic reaction products (formaldehyde, acetaldehyde, acetone, campholenealdehyde and pinonaldehyde). The paper describes in detail the sampling methods and the analytical procedures to determine these semivolatile products by GC–MS and HPLC–MS.

2. Experimental

2.1. Fast-flow reactor

The fast-flow reactor technique with its clean OH radical source was selected in order to simplify the reaction chemistry. The details of the experimental technique have already been published elsewhere [17,18]. The fast-flow reactor consists of a quartz reactor 70 cm long×2.8 cm I.D. By means of an oil rotary pump with a nominal pump capacity of about 12 $m^3 h^{-1}$, a flow velocity of 3.81 $m s^{-1}$ was obtained with helium as carrier gas. The time scale t_r of the reaction was determined by the position z of the axial inlet probe which is movable along the reactor axis and by the flow velocity v of the

reagents: $t_r = z/v$. In these experiments z was set equal to 16 cm corresponding to a reaction time t_r of 42 ms.

The OH radicals were generated by the titration reaction $H + NO_2 \rightarrow OH + NO$. The H atoms needed for this reaction were produced by a microwave discharge in a H_2–He mixture. In all experiments the H_2 concentration was $1.37 \cdot 10^{13}$ molecules cm^{-3} and the power of the discharge was 100 W (except for the blank where the discharge was turned off). In the past the microwave discharge technique, used to produce hydrogen atoms as precursors for the hydroxyl radicals, could only operate in a pressure range from 0.5 to 12 Torr (1 Torr=133.322 Pa). This limitation was a major drawback of the fast-flow reactor technique since the results had to be extrapolated to much higher pressures to be relevant for atmospheric conditions. This problem has now been solved by installing a specially designed microwave cavity (type Surfatron) which allows to operate at pressures up to 100 Torr. The experiments were carried out at a total pressure of 50 or 100 Torr helium containing 20% oxygen.

Hydroxyl radicals were produced in an upstream zone in the fast-flow reactor by allowing an excess of hydrogen atoms to react with NO_2 in a concentration of $3.62 \cdot 10^{12}$ molecules cm^{-3}. In the downstream zone, addition of α-pinene is carried out by allowing a fraction of the carrier gas helium to flow through a vessel containing the α-pinene resulting in a concentration of α-pinene in the reactor in the range from 10^{12} to 10^{13} molecules cm^{-3}.

2.2. Sampling methods

The semivolatile products were collected over a period of 5–6 h and the batch samples were subsequently analysed by GC–MS and HPLC–MS. Two methods were used to collect these products: a liquid nitrogen trap (LN_2 trap) and a LpDNPH cartridge. Both of these sampling systems were installed at the downstream end of the reactor.

2.2.1. LN_2 trap

A stainless steel cold trap filled with liquid nitrogen was coated with a layer of frozen dichloromethane or a solution consisting of 2,4-dinitro-

phenylhydrazine (2,4-DNPH). The 2,4-DNPH solution is made by mixing 0.1 g of 2,4-DNPH with 0.7 ml diluted H_2SO_4 and adding a mixture of acetonitrile (ACN)–CH_2Cl_2 (DCM) (50:50, v/v) to reach a total volume of 10 ml. The collection is based on the in situ conversion of aldehyde/ketone compounds to their 2,4-dinitrophenylhydrazones, which is the most frequently used procedure for the determination of carbonyls in ambient air [19–25]. After collecting the products for 5–6 h, the residues on the cold wall were dissolved by treating the trap with the same solvent(s) as used for the coating layer.

2.2.2. Cartridge

The LpDNPH cartridge (Supelco) is an air sampling device designed for sampling carbonyls in ambient, indoor, and industrial atmospheres [26–30]. Carbonyls were trapped on a high-purity silica adsorbent coated with 2,4-DNPH, where they were converted to the hydrazone derivatives. About 0.1% of the total gas flow in the reactor was drawn through the cartridge. After the collection, the derivatives were eluted from the cartridge with 3 ml ACN.

2.3. Methods of analysis

2.3.1. GC–MS

When the liquid nitrogen trap was coated with DCM, the reaction products collected on the cold wall were dissolved in 100 ml DCM and then analysed by GC–MS. The GC instrument Carlo-Erba (type Vega GC 6000) was equipped with a Chrompack CP-Sil 5 CB capillary column (25 m×0.33 mm I.D., film thickness 1 mm) and an on-column injection system. The flow of the helium carrier gas was ≈ 1.5 cm^3 min^{-1}. After concentration by rotary evaporation at room temperature to about 1 ml, a quantity of 1–2 µl was injected on-column at an oven temperature of 60°C. After elution of the solvent the oven temperature was raised at a rate of 8°C min^{-1} to 200°C. For all experiments electron impact (EI) spectra were recorded on an HP-5989A quadrupole mass spectrometer using an ion source temperature of 250°C and an electron energy of 70 eV. The temperature of the interface between the GC and the MS was 180°C. The collected compounds were identified by comparing the GC–MS results with published GC–MS [31] and mass spectral data [32].

2.3.2. HPLC–MS

When the collection was based on the conversion of carbonyl compounds to their 2,4-dinitrophenylhydrazones, the carbonyl 2,4-DNPH derivatives were analyzed using a HPLC–MS system equipped with atmospheric pressure chemical ionization (APCI; Micromass Quattro II). The negative ion mode was selected for the measurements [25]. The scan range of the MS was from 150 to 600 for the determination of m/z values. The APCI probe temperature and the source temperature were 300 and 80°C, respectively. The cone was set at 22 V. The 2,4-DNPH solutions were separated on a cc Nucleosil 100 C_{18} column (250 mm×3 mm I.D., 5 µm particles) using the Hewlett-Packard 1100 HPLC instrument. Separations were carried out at 35°C using the following mobile phase gradient: from ACN–water (5:95) to ACN–water (84:16) in 50 min followed by 10 min isocratic elution. The eluent flow-rate was 0.6 ml/min. and the sample volume injected was 10 µl using a Rheodyne injector. Both diode array detection (DAD) and mass spectrometry (MS) for total ion current (TIC) were available as detection methods. The DAD was set at a wavelength of 360 nm. The mass spectrum corresponding to each peak in the TIC chromatogram was compared with spectra of reference materials which were obtained from commercial sources or by synthesis.

When collection experiments are repeated under the same conditions, retention times can vary within a few percentages, but the relative positions remain the same. When related to the pinonaldehyde peak, the other peak heights do not change more than 5% for each of the experiments.

2.4. Reagents

The reagents supplied as gas mixtures were: NO_2 (0.1%) in helium (Oxhydrique), H_2 (0.1%) in helium (Praxair), O_2 with a purity of 99.998% (Air Liquide), He with a purity of 99.995% (Air Liquide). The reagent α-pinene in the liquid phase was from Aldrich with a purity of 98%. The solvents used

were acetonitrile HPLC grade (Biosolve) and di-chloromethane analytical-reagent grade (Merck). 2,4-DNPH was recrystallized from ethanol, rinsed with ethanol and dried in a desiccator and analyzed by HPLC for possible carbonyl impurities. Formalde-hyde–, acetaldehyde– and acetone–2,4-DNPH with a purity of 99% were obtained from Supelco. Cam-pholenealdehyde– and pinonaldehyde–2,4-DNPH were synthesized according to the method described by Grosjean [23].

3. Results and discussion

In order to determine the oxidation products of the α-pinene/OH reaction, the collected samples were analysed by GC–MS or HPLC–MS depending on the collection method.

3.1. GC–MS analysis

As described before, a first collection method consists of sampling the products on an LN$_2$ trap coated with dichloromethane. The reaction products collected on the cold wall were dissolved in DCM and then analysed by GC–MS. In the past collection experiments were carried out at a total pressure of 2 Torr [7,33]. Campholenealdehyde was the most important product, followed by pinonaldehyde and a number of less important products such as limonene, pinol, α-pineneoxide, pinocarveol, pinocamphone, verbenone, *trans*-carveol, carvone and car-votanacetone.

When the experiments were now carried out at higher pressures (50 and 100 Torr) unreacted α-pinene, campholenealdehyde and pinonaldehyde were identified, with pinonaldehyde being the most
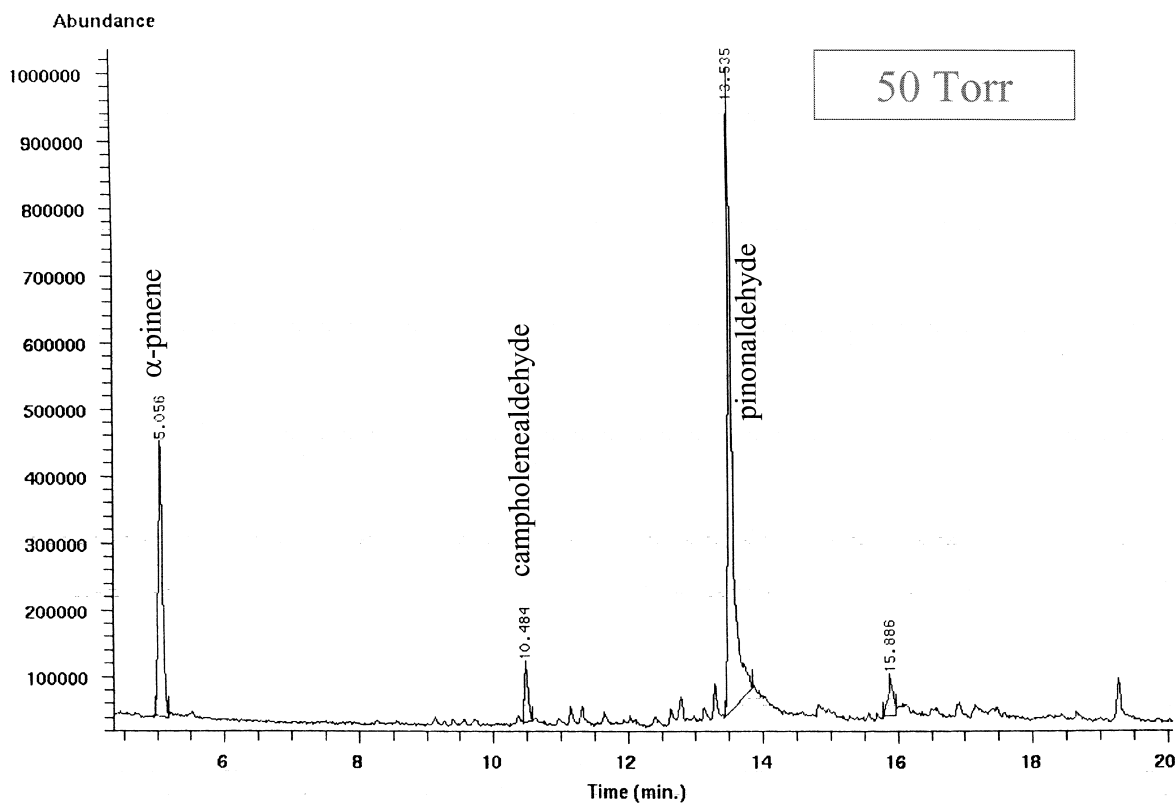

Fig. 1. GC–MS chromatogram at a total pressure of 50 Torr. Initial concentrations: $[C_{10}H_{16}]=3.83\cdot10^{12}$, $[H_2]=1.37\cdot10^{13}$, $[NO_2]=3.63\cdot10^{12}$, $[O_2]=3.24\cdot10^{17}$ each expressed in molecules cm^{-3}. The reaction time $t_r=42$ ms, collection time $t_c=381$ min. Collection method: LN$_2$ trap coated with DCM.
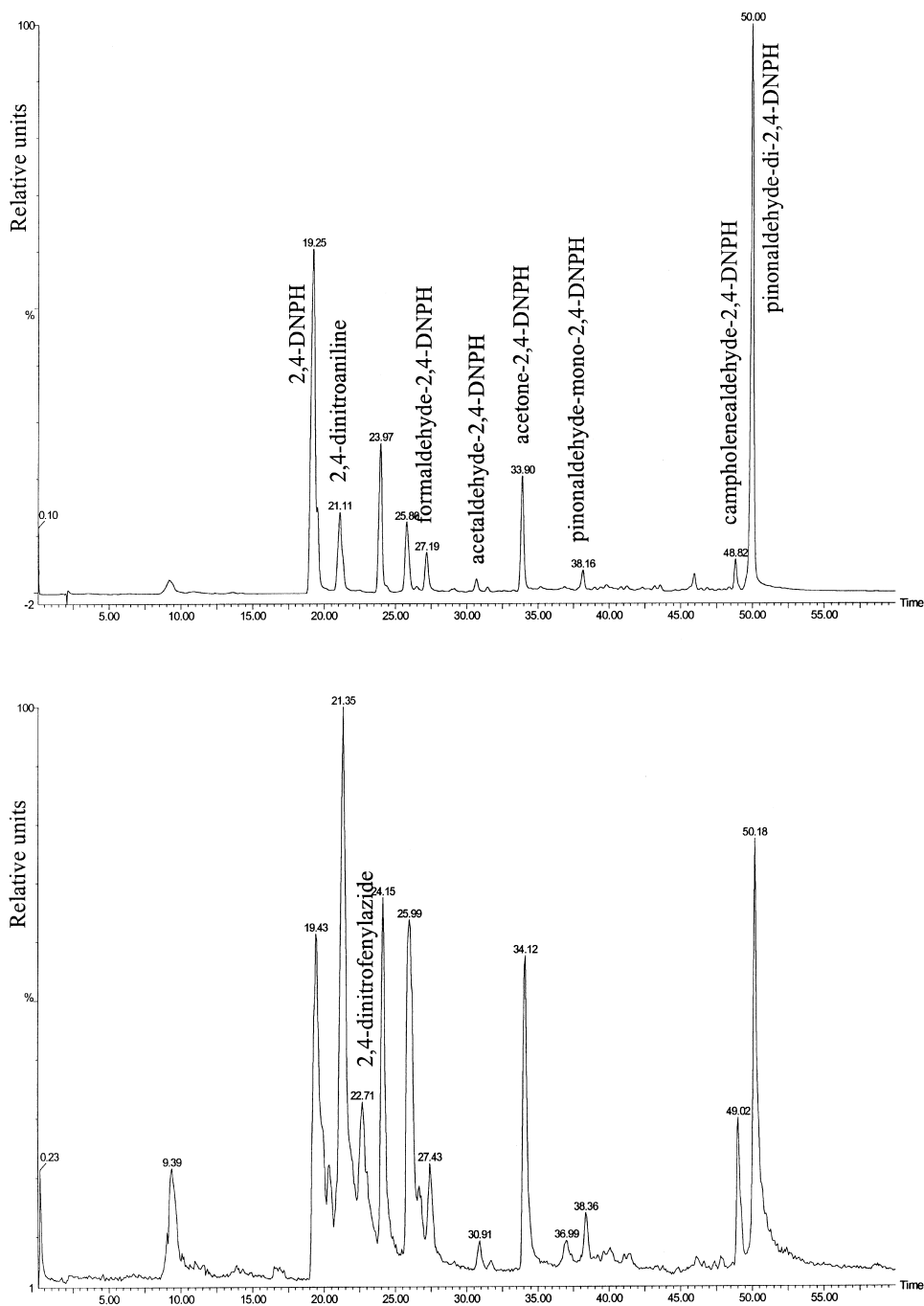
Fig. 2. HPLC chromatogram at a total pressure of 50 Torr. Initial concentrations: $[C_{10}H_{16}]=5.13\cdot10^{12}$, $[H_2]=1.37\cdot10^{13}$, $[NO_2]=3.62\cdot10^{12}$, $[O_2]=3.24\cdot10^{17}$ each expressed in molecules cm^{-3}. The reaction time $t_r=42$ ms, collection time $t_c=335$ min. Collection method: LN$_2$ trap coated with 2,4-DNPH solution. (upper chromatogram=DAD, 360 nm; lower chromatogram=TIC). Time scale in min.
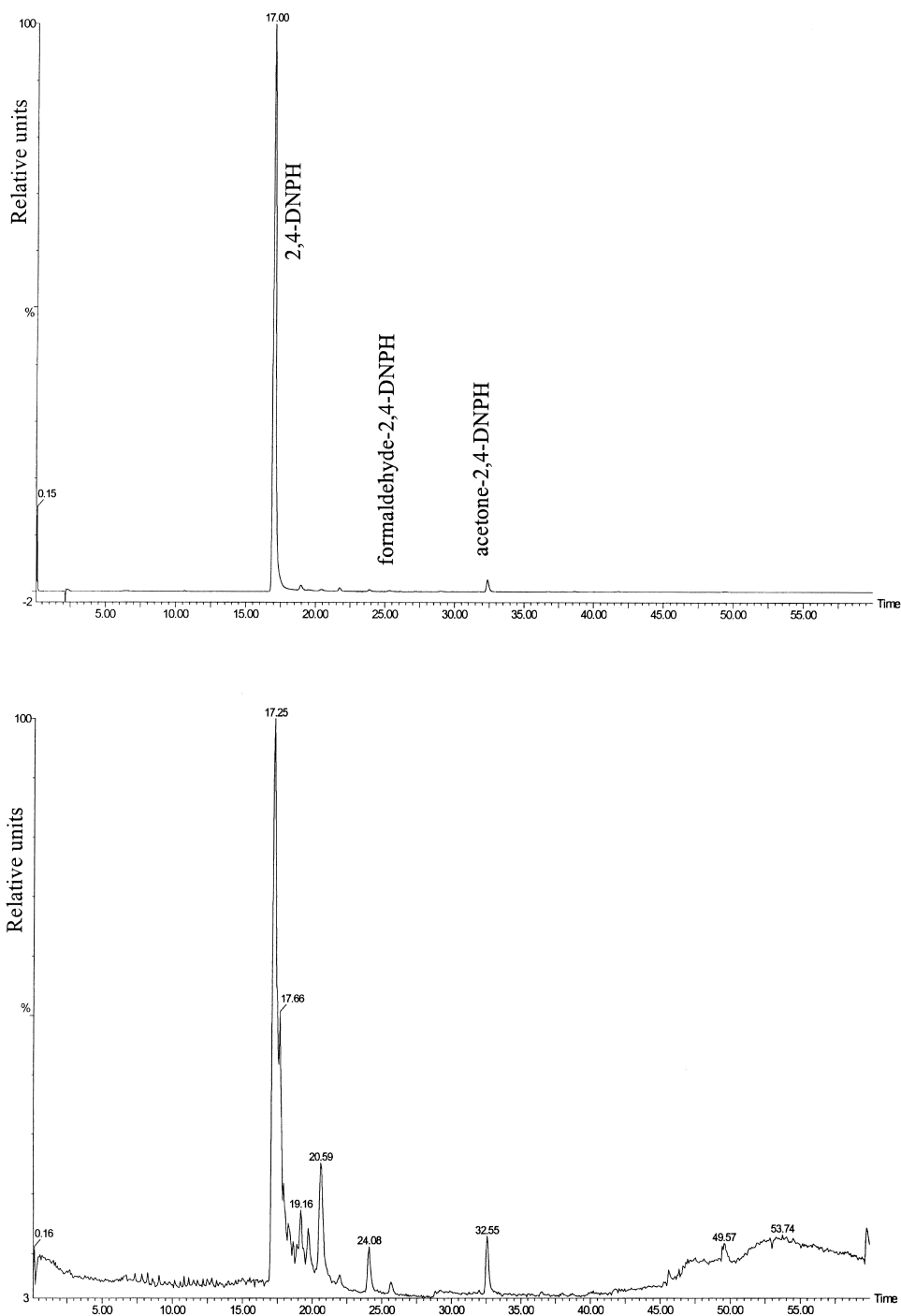
Fig. 3. HPLC chromatogram (blank) at a total pressure of 50 Torr. Initial concentrations: $[C_{10}H_{16}] = 0$, $[H_2] = 1.37 \cdot 10^{13}$, $[NO_2] = 0$, $[O_2] = 3.24 \cdot 10^{17}$ each expressed in molecules cm^{-3}, microwave discharge turned off. The reaction time $t_r = 42$ ms, collection time $t_c = 330$ min. Collection method: LN$_2$ trap coated with 2,4-DNPH solution (upper chromatogram = DAD, 360 nm; lower chromatogram = TIC). Time scale in min.
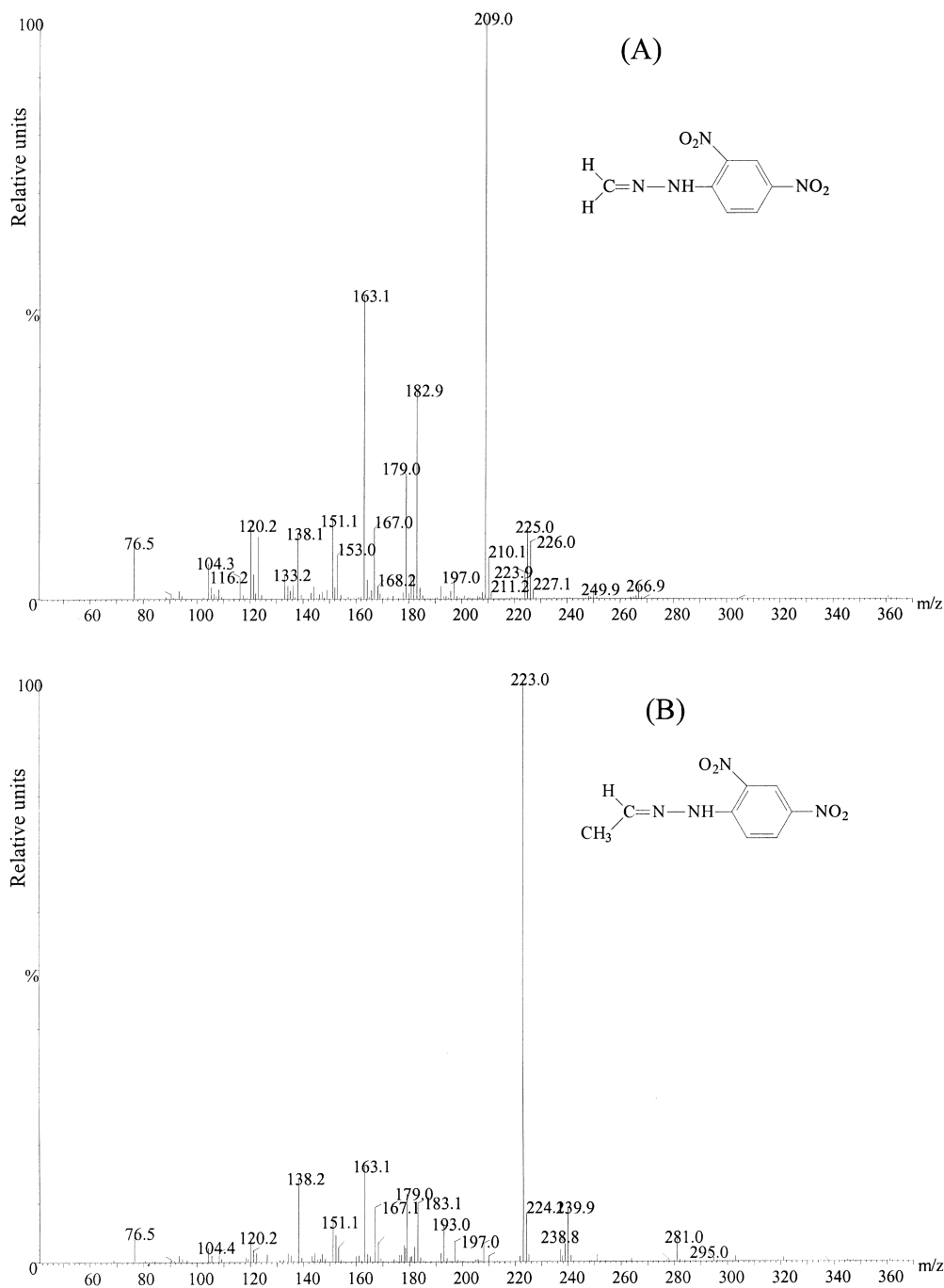
Fig. 4. APCI(−) generated mass spectra of reference materials obtained from commercial sources [(A) formaldehyde-2,4-DNPH, (B) acetaldehyde–2,4-DNPH, (C) acetone–2,4-DNPH] or by synthesis [(D) campholenealdehyde–2,4-DNPH, (E) pinonaldehyde–mono-2,4-DNPH, (F) pinonaldehyde–di-2,4-DNPH)].
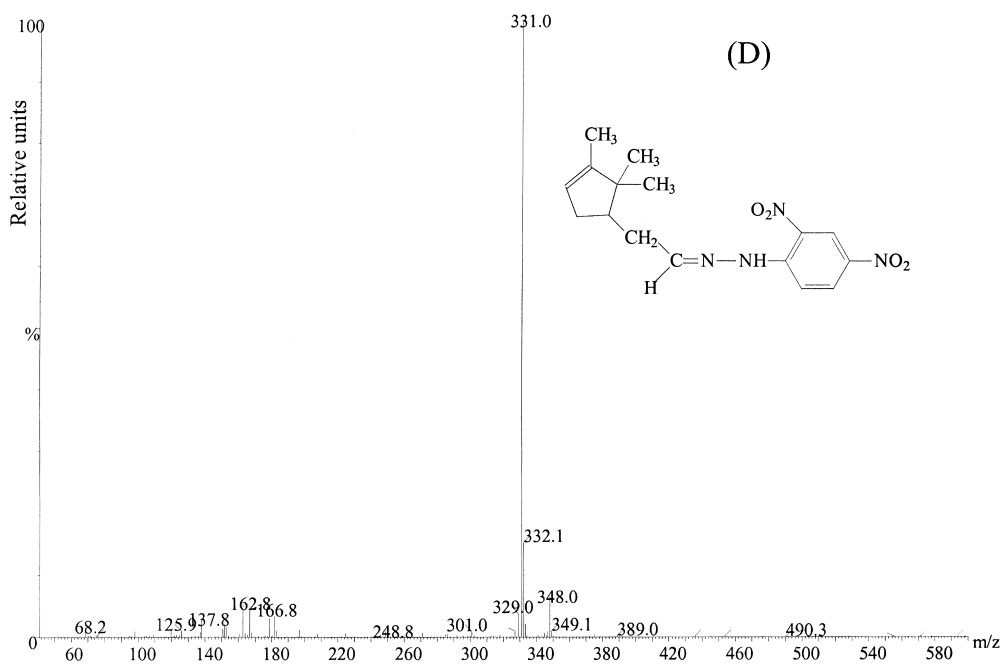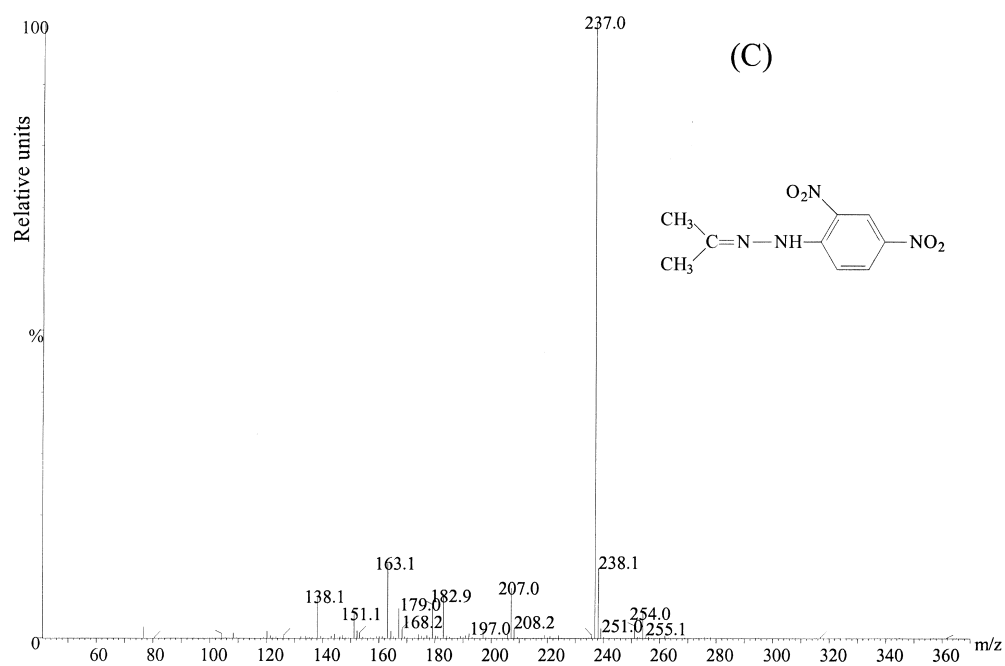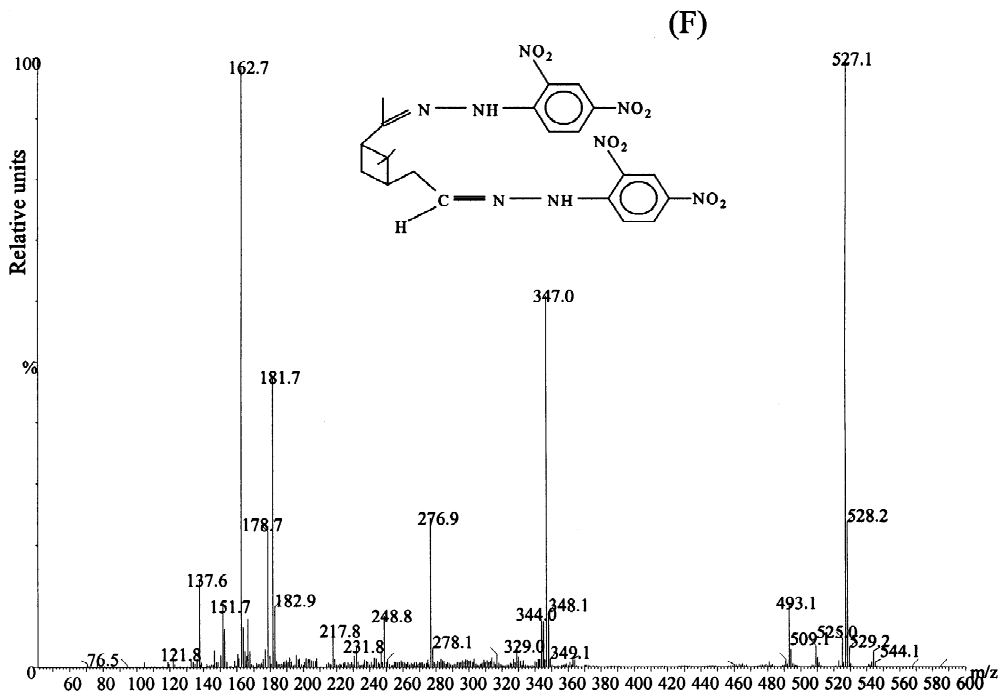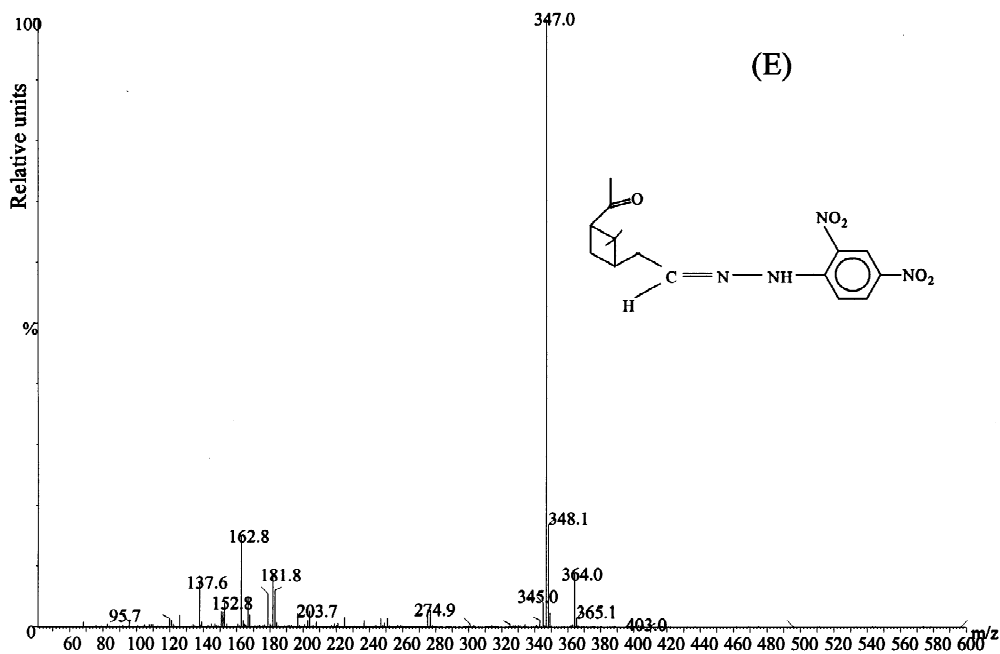
Fig. 4. (*continued*).

Fig. 4. (*continued*).

important oxidation product. This is illustrated in Fig. 1, where a chromatogram is shown of the products found at 50 Torr. Similar results were obtained at 100 Torr. It should be mentioned here that when the trap is coated with DCM products like formaldehyde, acetaldehyde and acetone are not detected. Although these products can be captured on the LN_2 trap they are lost while evaporating the solvent. This rotary evaporation was required to reduce the solution from approximately 100 ml to 2–3 ml prior to GC injection.

3.2. HPLC–MS analysis

The second collection method is based on the conversion of the aldehydes/ketones to 2,4-dinitrophenylhydrazone derivatives. This is done by either using a LpDNPH cartridge or a collection on a LN_2 trap coated with a 2,4-DNPH solution.

When the LN_2 trap is coated with a layer of a frozen solution of 2,4-DNPH instead of DCM, it is possible to collect all the aldehydes and the ketones formed in the oxidation reaction of α-pinene. Besides pinonaldehyde and campholenealdehyde, this collection method enables the determination of formaldehyde, acetaldehyde and acetone as their 2,4-dinitrophenylhydrazone derivatives. The reaction products collected on the cold wall were dissolved in ACN–DCM and then analyzed by HPLC–MS using APCI in the negative ion mode.

Fig. 2 shows the HPLC chromatogram obtained for the carbonyl-2,4-DNPH derivatives using both the DAD detector (top) and the TIC (bottom). For the reaction at 50 Torr pinonaldehyde was identified as the main product with a retention time $t_R = 50.0$ min. Other products are campholenealdehyde ($t_R = 48.8$ min), formaldehyde ($t_R = 27.2$ min), acetaldehyde ($t_R = 30.9$ min) and acetone ($t_R = 33.9$ min). In blank experiments (without α-pinene) small background signals of formaldehyde and acetone are observed (Fig. 3). However, a comparison with the results shown in Fig. 2 clearly show that formaldehyde and acetone were formed in the reaction of α-pinene with OH radicals with an intensity of about a factor of 10 higher than in the blank experiment.

In Figs. 2 and 3, the total ion chromatogram (bottom) is used for localisation of the components

as compared to the DAD trace. The mass spectrum corresponding to each peak is shown in Fig. 4. The mass spectra generated in the APCI($-$) ion mode display the $(M-H)^-$ ion as the main peak, from which the molecular mass can be derived. These spectra are identical with APCI($-$) spectra of reference materials which were obtained from commercial sources or by synthesis. A summary of the retention times, identified products, $(M-H)^-$ values, and molecular masses is presented in Table 1.

Because the coating procedure on the LN_2 trap with the 2,4-DNPH solution and the subsequent dissolution of the collected sample is rather time consuming, an attempt was made to simplify the collection procedure. Sampling on cartridges [26–30] is often used in systems monitoring the air quality. The LpDNPH cartridge was directly connected to the fast-flow reactor and a fraction of the products could be collected during the experiment. About 0.1% of the total gas flow in the reactor was drawn through the cartridge. After a collection time t_c of 5–6 h, the cartridge was eluted with 3 ml ACN. The eluate containing 2,4-DNPH derivatives was then analyzed by HPLC–MS using APCI in the negative ion mode [25] to identify the peaks in the chromatogram.

Fig. 5 shows a HPLC–DAD chromatogram. The quantities of the products found are rather low in comparison with the LN_2 trap experiments. Moreover, blank experiments with a cartridge show relatively high background signals of formaldehyde–, acetaldehyde– and acetone–2,4-DNPH. Consequently, the collection procedure on the LN_2 trap will be

Table 1
Retention times t_R, $(M-H)^-$ values and molecular masses M_r of the identified products

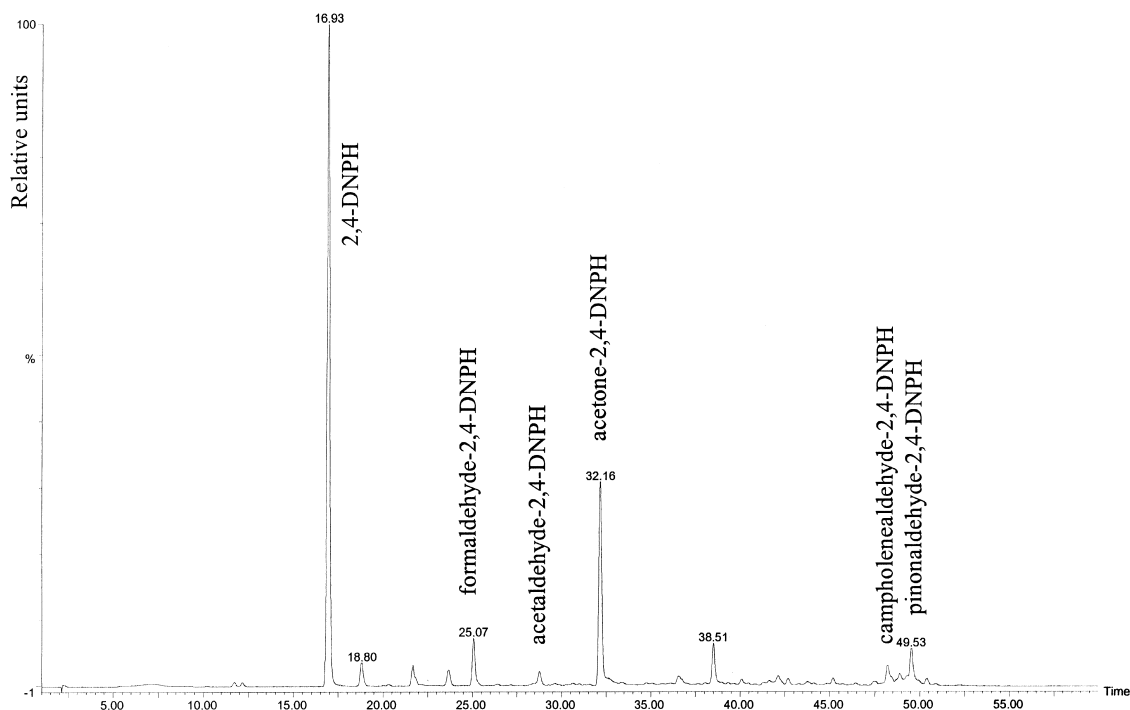| t_R (min)	Product	$(M-H)^-$	M_r
19.3	2,4-DNPH	197	198
27.2	Formaldehyde–2,4-DNPH	209	210
30.9	Acetaldehyde–2,4-DNPH	223	224
33.9	Acetone–2,4-DNPH	237	238
38.2	Pinonaldehyde–mono-2,4-DNPH	347	348
48.8	Camfoleenaldehyde–2,4-DNPH	331	332
50.0	Pinonaldehyde–di-2,4-DNPH	527	528

Fig. 5. HPLC chromatogram (DAD, 360 nm) at a total pressure of 50 Torr. Initial concentrations: $[C_{10}H_{16}] = 5.17 \cdot 10^{12}$, $[H_2] = 1.37 \cdot 10^{13}$, $[NO_2] = 3.62 \cdot 10^{12}$, $[O_2] = 3.24 \cdot 10^{17}$ each expressed in molecules cm^{-3}. The reaction time $t_r = 42$ ms, collection time $t_c = 360$ min. Collection method: LpDNPH cartridge. Time scale in min.

preferred for future quantitative product determination.

3.3. Oxidation products and mechanisms

From the collection experiments and the HPLC–MS analysis described above, the following products were formed in the α-pinene/OH reaction in the presence of oxygen and nitric oxide: formaldehyde, acetaldehyde, acetone, campholenealdehyde and pinonaldehyde.

Formaldehyde and acetone were also identified by Grosjean et al. [8] who used cartridges impregnated with 2,4-DNPH followed by HPLC–MS (CI) detection. Nozière et al. [9] also detected these products but here Fourier transform infrared (FT-IR) was used. The presence of pinonaldehyde was demonstrated by several techniques: GC–MS and GC–FT-IR [11], GC–MS and GC–flame ionisation detection

[10], and FT-IR [6,9]. Up till now acetaldehyde and campholenealdehyde have not been identified as products of the α-pinene/OH reaction under atmospheric conditions.

A reaction mechanism leading to the formation of formaldehyde, acetone, campholenealdehyde and pinonaldehyde is illustrated in Fig. 6. In a first step an OH radical is added to α-pinene. The α-pinene/OH adduct can either react directly with O_2 (**A**) or isomerize (**B,C**). The reaction with O_2 (**A**), followed by O abstraction with NO, results in an α-pinene/OH/O adduct. Next, one pathway (**D**) leads to the formation of formaldehyde and another one (**E**) including a H abstraction, leads to the formation of pinonaldehyde. The isomers of the α-pinene/OH adduct can either lead to the formation of campholenealdehyde (**B**) or react with O_2 and NO, resulting in the formation of acetone (**C**).

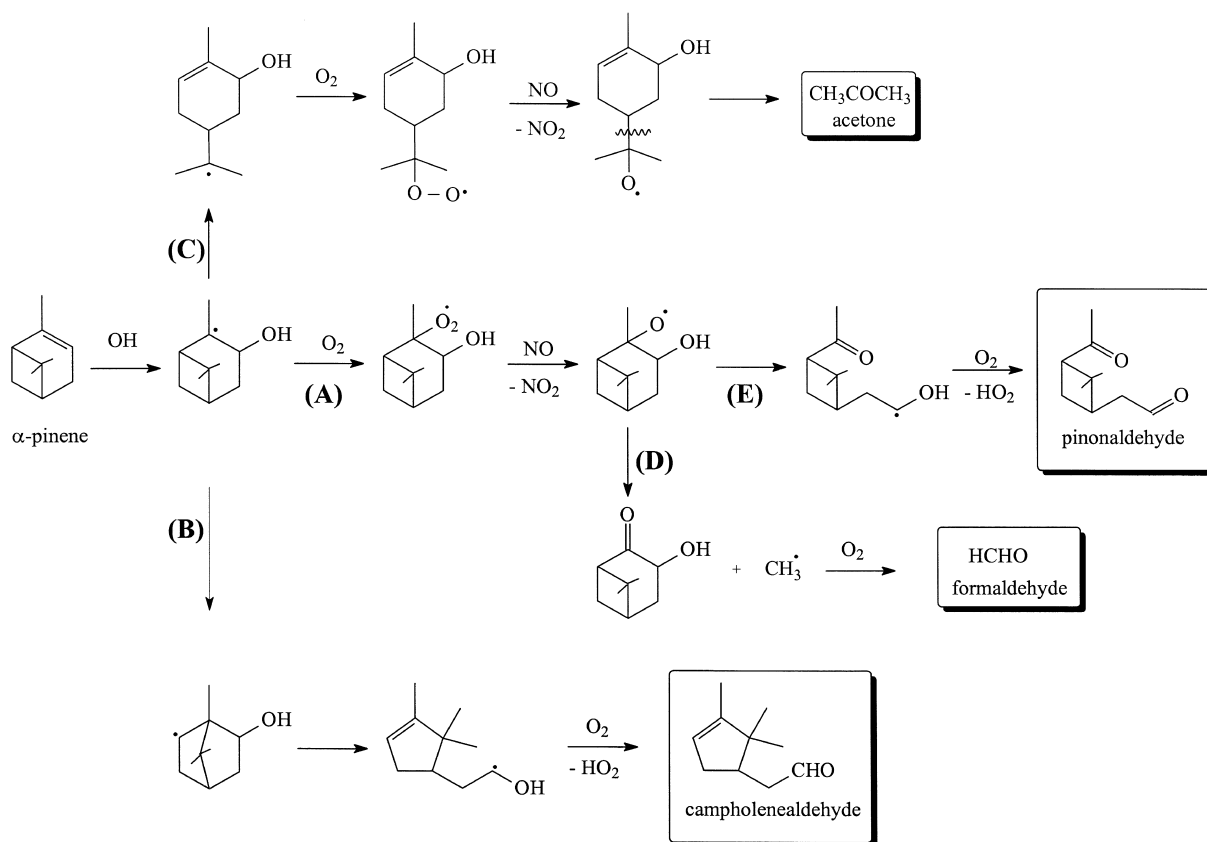Several mechanisms are proposed in the literature

Fig. 6. Mechanism for the reaction between α-pinene and OH: formation of formaldehyde, acetone, campholenealdehyde and pinonal-dehyde.

[9,33–35]. The reaction pathways for formaldehyde, acetone and pinonaldehyde in Fig. 6 are similar to the mechanisms proposed by Nozière [9]. However, the mechanism shown in Fig. 6 does not take into account initial hydrogen abstraction reactions by the OH radical from α-pinene [35,36]. If that path were important, other reaction channels may open up leading to the formation of the observed products.

For acetaldehyde, which has not been identified before as an oxidation product, the mechanisms shown in Fig. 7 are proposed. Acetaldehyde can be formed by tautomerisation of vinylalcohol in an acidic solution. Vinylalcohol could arise as the initial gas-phase product via decomposition of radical X or Y. Because this tautomerisation reaction occurs in solution it is not possible to conclude whether or not acetaldehyde is formed as an oxidation product of the α-pinene/OH reaction in the gas phase. However, if acetaldehyde were to be a real gas phase oxidation product, scheme **B** in Fig. 7 is a possible pathway.

Until now only qualitative results were obtained, but coating the trap with a 2,4-DNPH solution, to which internal standards are added, turns out to be a suitable start for quantitative measurements.
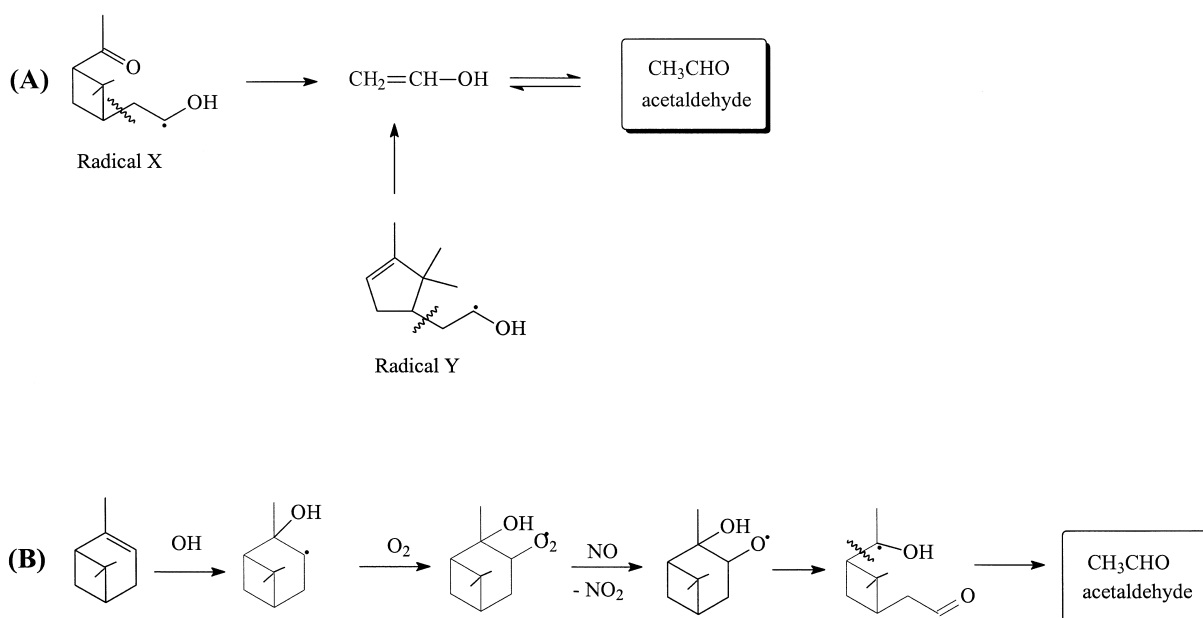
Fig. 7. Mechanism for the reaction between α-pinene and OH: proposed pathways for the formation of acetaldehyde.

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