



ELSEVIER

Journal of Chromatography A, 915 (2001) 75–83

JOURNAL OF  
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

# Determination of the oxidation products of the reaction between $\alpha$ -pinene and hydroxyl radicals by high-performance liquid chromatography

Inge Vanhees, Viviane Van den Bergh\*, Raf Schildermans, René De Boer,  
Frans Compernelle, Chris Vinckier

*Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium*

Received 20 November 2000; received in revised form 13 February 2001; accepted 13 February 2001

## Abstract

In this paper a method is described for determining and quantifying the degradation products of the reaction of  $\alpha$ -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 semi-volatile products are collected on a liquid nitrogen trap (LN<sub>2</sub> trap) coated with a 2,4-dinitrophenylhydrazine (2,4-DNPH) solution and the batch samples are subsequently analyzed by HPLC. In order to perform quantitative measurements the batch samples contained two internal standards: benzaldehyde–2,4-DNPH and tolualdehyde–2,4-DNPH. In the experiments carried out at 50 Torr and 100 Torr, HPLC measurements showed that the semi-volatile products formaldehyde, acetaldehyde, acetone, campholenealdehyde and pinonaldehyde could be quantified as oxidation products for the  $\alpha$ -pinene/OH reaction, with pinonaldehyde being the main product. Assuming that all these five oxidation products have the same collection efficiency on the LN<sub>2</sub> trap, one arrives at the following relative product yields (expressed in mol %) at 50 and 100 Torr, respectively: 9.7 $\pm$ 0.7 and 6 $\pm$ 5 for formaldehyde; 1.1 $\pm$ 0.1 and 0.9 $\pm$ 0.5 for acetaldehyde; 16 $\pm$ 1 and 6 $\pm$ 2 for acetone; 11 $\pm$ 2 and 5.5 $\pm$ 0.7 for campholenealdehyde; 63 $\pm$ 3 and 82 $\pm$ 7 for pinonaldehyde. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Oxidation; Derivatization, LC; Pinenes; Dinitrophenylhydrazine; Carbonyl compounds; Acetone; Volatile organic compounds

## 1. Introduction

A wide variety of volatile non-methane organic compounds (NMOCs) are emitted from vegetation and forests. On a global scale the biogenic emissions of the NMOCs far exceed the anthropogenic emis-

sions of NMOCs [1–3] with a large contribution from isoprene and the monoterpenes. Since monoterpenes can react 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], semi-volatile compounds such as formaldehyde, acetone [8,9] and pinonaldehyde [6,9–11]. In addition biogenic hydrocarbons are

\*Corresponding author. Tel.: +32-16-327-373; fax: +32-16-327-992.

*E-mail address:* viviane.vandenbergh@chem.kuleuven.ac.be (V. Van den Bergh).

known to be involved in the production of atmospheric aerosols ([6,12–16] and references therein).

Since the overall chemistry in the atmosphere is far too complex to study in situ, experiments must be performed on a laboratory scale. To establish the degradation paths and to determine the product yields of the  $\alpha$ -pinene/OH reaction, measurements were carried out in a fast-flow reactor with 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 quantifies some of the products formed in the reaction between  $\alpha$ -pinene and hydroxyl radicals in the presence of oxygen using the fast-flow reactor technique. The volatile compounds (CO, CO<sub>2</sub>) have been determined via on-line mass spectrometric analysis [7]. The semi-volatile organic reaction products (formaldehyde, acetaldehyde, acetone, campholenealdehyde and pinonaldehyde) have already been identified using the derivatization of carbonyls to 2,4-dinitrophenylhydrazone derivatives as has been described in our earlier work [17]. In this paper, the attention is focused on the *quantitative* determination of these product yields. The sampling method and the analytical procedure to determine these semi-volatile products quantitatively, will be described in detail.

## 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 were already published elsewhere [18,19]. The fast-flow reactor consists of a quartz reactor with an internal diameter of 2.8 cm and a length of 70 cm. By means of an oil rotary pump with a nominal pump capacity of about 12 m<sup>3</sup>/h, a flow velocity of 3.81 m/s 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 experi-

ments  $z$  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  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ . The H atoms needed for this reaction were produced by a microwave discharge in a H<sub>2</sub>/He mixture. In all experiments the H<sub>2</sub> concentration was  $1.37 \cdot 10^{13}$  molecules cm<sup>-3</sup> 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<sub>2</sub> in a concentration of  $3.62 \cdot 10^{12}$  molecules cm<sup>-3</sup>. In the downstream zone, addition of  $\alpha$ -pinene is carried out by allowing a fraction of the carrier gas helium to flow through a vessel containing the  $\alpha$ -pinene resulting in a concentration of  $\alpha$ -pinene in the reactor in the range from  $10^{12}$  to  $10^{13}$  molecules cm<sup>-3</sup>. The amount of  $\alpha$ -pinene consumed was determined by the mass difference before and after the experiments.

### 2.2. Sampling method

The semi-volatile products were collected over a period of 5 to 6 h on the LN<sub>2</sub> trap, installed at the downstream end of the reactor, and the batch samples were subsequently analyzed by high-performance liquid chromatography (HPLC). The collection is based on the in situ conversion of aldehyde/ketone compounds to their 2,4-dinitrophenylhydrazone derivatives (Fig. 1), which is the most frequently used method for the determination of carbonyls in ambient air [20–26]. Therefore, the stainless steel cold trap filled with liquid nitrogen was coated with a solution consisting of 2,4-dinitrophenylhydrazine (2,4-

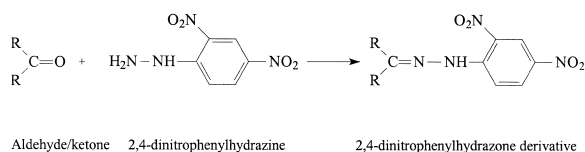


Fig. 1. Reaction mechanism for the derivatization of aldehydes and ketones with 2,4-dinitrophenylhydrazine (in the presence of an acid) to form 2,4-dinitrophenylhydrazone derivatives.

DNPH). The 2,4-DNPH solution was made by mixing 0.1 g of 2,4-DNPH with 0.7 ml diluted H<sub>2</sub>SO<sub>4</sub> and benzaldehyde–2,4-DNPH. Next, a mixture of acetonitrile (ACN)–dichloromethane (DCM) (50:50) was added to reach a total volume of 10 ml, which results in a concentration of 150 µg/ml for benzaldehyde–2,4-DNPH. After collecting the products over a period of 5 to 6 h, the residues on the cold wall were dissolved by treating the trap with a mix of ACN–DCM (50:50), followed by addition of tolualdehyde–2,4-DNPH. The total volume of this solution was 20 ml, containing 75 µg/ml of both benzaldehyde– and tolualdehyde–2,4-DNPH.

Benzaldehyde–2,4-DNPH and tolualdehyde–2,4-DNPH were used as internal standards. They were chosen because their retention time did not overlap with the retention times of the expected reaction products. These two internal standards were needed because treating the trap could result in loss of the coating material. Benzaldehyde–2,4-DNPH was added to the coating solution prior to the coating of the LN<sub>2</sub> trap, whereas tolualdehyde–2,4-DNPH was added to the solution obtained after dissolving the collected residues from the LN<sub>2</sub> trap. Adding these two internal standards in the same concentration allows a correction for possible losses of the first internal standard benzaldehyde–2,4-DNPH. A solution containing benzaldehyde–2,4-DNPH and tolualdehyde–2,4-DNPH both in equal concentrations was analyzed by HPLC in order to derive the ratio of the two peak areas. The resulting value of 0.99 was used to check whether losses of benzaldehyde–2,4-DNPH and the coating occurred during collection experiments or not. Based on this value the loss of the first internal standard benzaldehyde–2,4-DNPH could be calculated. In case the loss of benzaldehyde–2,4-DNPH occurred *after* the collection procedure, it was assumed that the products formed in the α-pinene/OH reaction

were lost to the same extent. However, if during the coating of the LN<sub>2</sub> trap (*before* the collection experiment) some benzaldehyde–2,4-DNPH would be lost an “over” correction is performed.

### 2.3. Method of analysis: HPLC–MS

The carbonyl–2,4-DNPH derivatives were analyzed using HPLC. The identification of these products using HPLC–mass spectrometry (MS) and negative-ion atmospheric pressure chemical ionization [APCI(–)] has already been described in Ref. [17]. The 2,4-DNPH solutions were separated on a cc Nucleosil 100 C<sub>18</sub> 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 flow-rate was 0.6 ml/min and the sample injected was 10 µl using a Rheodyne injector. Both a diode array detection (DAD) and the total ion current (TIC) signal of a triple quadrupole mass spectrometer (Quattro II; Micromass, Manchester, UK) were available as detector. The DAD system was set at a wavelength of 360 nm.

### 2.4. Reagents

The reagents supplied as gas mixtures were: NO<sub>2</sub> (0.1%) in helium (Oxydrique), H<sub>2</sub> (0.1%) in helium (Praxair), O<sub>2</sub> with a purity of 99.998% (L’Air Liquide), He with a purity of 99.995% (L’Air Liquide). The liquid reagent α-pinene (Aldrich) had a purity of 98%. The solvents used were acetonitrile HPLC grade (Biosolve) and dichloromethane (analytical-reagent grade, Merck). 2,4-DNPH was recrystallized from ethanol, rinsed with ethanol and dried in a dessicator and analyzed by HPLC for possible carbonyl impurities. Formaldehyde–, acetaldehyde–, acetone–, benzaldehyde– and tolualdehyde–2,4-DNPH with a purity of 99% were obtained from Supelco. Campholenealdehyde– and pinonaldehyde–di-2,4-DNPH were synthesized according to the method described by Grosjean and Grosjean [24].

## 2.5. Calibration solutions

To perform quantitative measurements, calibration curves were constructed based on the following stock solutions: benzaldehyde–2,4-DNPH (750  $\mu\text{g/ml}$ ); formaldehyde–2,4-DNPH, acetaldehyde–2,4-DNPH and acetone–2,4-DNPH (1000  $\mu\text{g/ml}$ ); campholenealdehyde–2,4-DNPH (740  $\mu\text{g/ml}$ ); pinonaldehyde–di-2,4-DNPH (760  $\mu\text{g/ml}$ ).

Using these stock solutions a number of diluted calibration solutions were prepared, containing 20, 40, 60, 80 and 100  $\mu\text{g/ml}$  formaldehyde–2,4-DNPH, acetaldehyde–2,4-DNPH and acetone–2,4-DNPH. For campholenealdehyde–2,4-DNPH the concentrations were 14.8, 25.9, 37, 62.9, 88.8 and 111  $\mu\text{g/ml}$ . The pinonaldehyde–di-2,4-DNPH calibration solutions contained 114, 190, 304, 418 and 570  $\mu\text{g/ml}$ . In each calibration solution the concentration of benzaldehyde–2,4-DNPH was 75  $\mu\text{g/ml}$ .

## 3. Results and discussion

### 3.1. Collection experiments with two internal standards

A fundamental problem with regard to this work was to find a procedure for collecting semi-volatile components from a high-velocity gas stream passing through a  $\text{LN}_2$  trap under diminished pressure. In preliminary experiments it was found that far better recoveries of  $\alpha$ -pinene were obtained by coating the trap with a suitable frozen solvent, e.g., DCM. Furthermore, this coating procedure also allows for in situ derivatization of carbonyl compounds. The aldehydes and ketones formed in the oxidation reaction of  $\alpha$ -pinene were collected on a  $\text{LN}_2$  trap coated with a solution (10 ml) of 2,4-DNPH in ACN–DCM containing benzaldehyde–2,4-DNPH (150  $\mu\text{g/ml}$ ) as the first internal standard. A quantitative transfer to the cold  $\text{LN}_2$  trap was facilitated by instantaneous freezing out of consecutive layers of the ACN–DCM solution applied to the inner wall of the trap. At the end of the collection experiment, the reaction products collected on the cold wall were recovered by rinsing the frozen solution with further portions of the ACN–DCM solvent mixture, followed by addition of tolualdehyde–2,4-DNPH. This

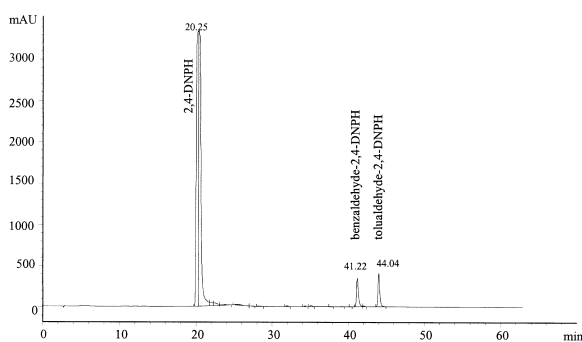


Fig. 2. HPLC chromatogram (blank) at a total pressure of 50 Torr. Initial concentrations:  $[\text{C}_{10}\text{H}_{16}] = 0$ ,  $[\text{H}_2] = 1.37 \cdot 10^{13}$ ,  $[\text{NO}_2] = 0$ ,  $[\text{O}_2] = 3.24 \cdot 10^{17}$  each expressed in molecules  $\text{cm}^{-3}$ , microwave discharge turned off. The reaction time  $t_r = 42$  ms, collection time  $t_c = 170$  min. Collection method:  $\text{LN}_2$  trap coated with 2,4-DNPH solution.

solution containing the two internal standards was further analyzed by HPLC.

First a blank experiment was run without  $\alpha$ -pinene and OH radicals. The resulting HPLC chromatogram in Fig. 2 shows that besides 2,4-DNPH, only the two internal standards were found.

When  $\alpha$ -pinene was reacting with OH radicals at 50 Torr pinonaldehyde–di-2,4-DNPH ( $t_R = 51.1$  min,  $M_r = 528$ ) was identified as the main product. Other products shown in Fig. 3 are campholenealdehyde–2,4-DNPH ( $t_R = 49.4$  min,  $M_r = 332$ ), formaldehyde–2,4-DNPH ( $t_R = 28.7$  min,  $M_r = 210$ ), acetaldehyde–

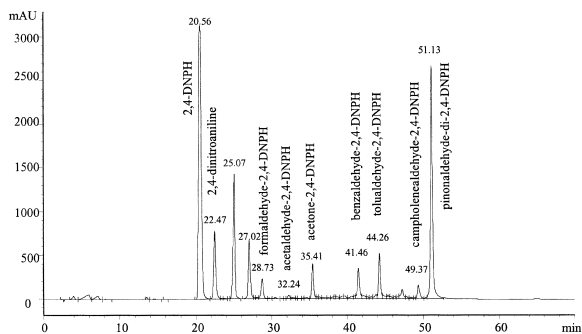


Fig. 3. HPLC chromatogram (DAD, 360 nm) at a total pressure of 50 Torr. Initial concentrations:  $[\text{C}_{10}\text{H}_{16}] = 5.08 \cdot 10^{12}$ ,  $[\text{H}_2] = 1.37 \cdot 10^{13}$ ,  $[\text{NO}_2] = 3.62 \cdot 10^{12}$ ,  $[\text{O}_2] = 3.24 \cdot 10^{17}$  each expressed in molecules  $\text{cm}^{-3}$ . The reaction time  $t_r = 42$  ms, collection time  $t_c = 306$  min. Collection method:  $\text{LN}_2$  trap coated with 2,4-DNPH solution.

2,4-DNPH ( $t_R=32.2$  min,  $M_r=224$ ) and acetone–2,4-DNPH ( $t_R=35.4$  min,  $M_r=238$ ).

Besides these oxidation products, the chromatogram shown in Fig. 3 contains three other peaks: dinitroaniline ( $t_R=22.5$  min) and two unidentified products with  $t_R=25.1$  min and  $t_R=27.0$  min and with a  $(M-H)^+$  value of 182. Because the same peaks are obtained in a blank experiment with OH radicals but in the absence of  $\alpha$ -pinene, it is clear that these products do not result from the  $\alpha$ -pinene/OH reaction. Those peaks are probably formed due to the presence of DNPH.

### 3.2. Quantitative results

The standard solutions described in Section 2.5 were used to construct calibration curves for formaldehyde–, acetaldehyde–, acetone–, campholenealdehyde–2,4-DNPH and pinonaldehyde–di-2,4-DNPH with benzaldehyde–2,4-DNPH as an internal standard (I.S.). To generate these calibration curves the area ratios of the standards  $A_{st}$  to the internal standard  $A_{I.S.}$  were plotted as a function of the concentration ratios  $C_{st}/C_{I.S.}$ , resulting in a relative response factor (RRF) for each of the five products (standards, st):

$$\frac{A_{st}}{A_{I.S.}} = \text{RRF} \cdot \frac{C_{st}}{C_{I.S.}} \quad (1)$$

This RRF value was then used to calculate the unknown concentrations (in  $\mu\text{g/ml}$ ) of the samples  $C_{\text{sample}}$  collected on the  $\text{LN}_2$  trap as is shown in Eq. (2):

$$C_{\text{sample}} = \frac{A_{\text{sample}}}{A_{I.S.}} \cdot \frac{C_{I.S.}}{\text{RRF}} \quad (2)$$

As described in the Experimental section, for each collection the loss of benzaldehyde–2,4-DNPH can be determined by comparing the area ratio of benzaldehyde–2,4-DNPH and tolualdehyde–2,4-DNPH to the same area ratio ( $=0.99$ ) for a standard solution in which both concentrations are the same. In the experiments carried out at 50 and 100 Torr, the amount of benzaldehyde–2,4-DNPH lost varied from a negligibly small amount to at the most 24%. The concentrations calculated for the five reaction products were then corrected accordingly. This pro-

cedure was performed for three collection experiments each at a total reactor pressure of 50 and 100 Torr.

The results are summarized in Table 1, where the concentrations and amounts of both the 2,4-DNPH derivative and the pure compound are given. The concentrations resulting after correction for the loss of benzaldehyde–2,4-DNPH represent the concentration of the 20 ml solution, obtained after rinsing the trap. The actual amount of the hydrazone derivatives on the trap (expressed in mg) is also shown in Table 1. In a next step the corresponding amount of each aldehyde/ketone present on the trap is calculated in mg and mol.

In Table 2 the amounts of the aldehydes/ketones are related to the amount of  $\alpha$ -pinene consumed in the reaction, resulting in a mass balance (mg %) and a mole balance (mol %). Modeling calculations have shown that, in the experimental conditions used, 23% (at 50 Torr) and 21.8% (at 100 Torr) of the total amount of  $\alpha$ -pinene reacted with OH radicals. The corresponding amount of  $\alpha$ -pinene consumed at 50 and 100 Torr is illustrated in the table. As indicated by the numbers in italics in Table 2, the values of the balances do not reach 100% and the possible reasons will be explained in Section 3.3. Scaling the sum of the five products to 100, product yields expressed in relative units can be calculated for each collection experiment (shown in Table 3).

On the basis of these results the mean value of the product yields can be calculated for formaldehyde–, acetaldehyde–, acetone–, campholenealdehyde–2,4-DNPH and pinonaldehyde–di-2,4-DNPH at 50 and 100 Torr (Table 4). Assuming the same collection efficiency on the  $\text{LN}_2$  trap for all the oxidation products, one can conclude that pinonaldehyde is the most abundant semi-volatile oxidation product, present for 63 mol % at 50 Torr and about 82 mol % at 100 Torr.

### 3.3. Discussion

When collection experiments were carried out at 50 and 100 Torr one sees that formaldehyde, acetaldehyde, acetone, campholenealdehyde and pinonaldehyde were five semi-volatile products formed in the  $\alpha$ -pinene/OH reaction.

At 50 Torr, the product yields of the five oxidation

Table 1

Concentrations  $C_{\text{sample}}$  of the five oxidation products after correction and amounts collected on the trap for both the 2,4-DNPH derivative and the original compound

	Aldehyde/ketone-2,4-DNPH(*)				Aldehyde/ketone			
	50 Torr		100 Torr		50 Torr		100 Torr	
	$C_{\text{sample}}$ (corrected) ( $\mu\text{g/ml}$ )	Amount (mg)	$C_{\text{sample}}$ (corrected) ( $\mu\text{g/ml}$ )	Amount (mg)	Amount (mg)	Amount (mol)	Amount (mg)	Amount (mol)
<i>Experiment 1</i>								
Formaldehyde <sup>a</sup>	35	0.70	71	1.4	0.10	$3.3 \cdot 10^{-6}$	0.20	$6.7 \cdot 10^{-6}$
Acetaldehyde <sup>b</sup>	4.9	0.10	9.6	0.19	0.019	$4.4 \cdot 10^{-7}$	0.038	$8.6 \cdot 10^{-7}$
Acetone <sup>c</sup>	67	1.3	60	1.2	0.33	$5.6 \cdot 10^{-6}$	0.29	$5.0 \cdot 10^{-6}$
Campholenealdehyde <sup>d</sup>	59	1.2	54	1.1	0.54	$3.6 \cdot 10^{-6}$	0.49	$3.2 \cdot 10^{-6}$
Pinonaldehyde <sup>e</sup>	637	13	1126	23	4.1	$2.4 \cdot 10^{-5}$	7.2	$4.3 \cdot 10^{-5}$
<i>Experiment 2</i>								
Formaldehyde <sup>a</sup>	44	0.89	16	0.32	0.13	$4.3 \cdot 10^{-6}$	0.045	$1.5 \cdot 10^{-6}$
Acetaldehyde <sup>b</sup>	5.4	0.11	3.7	0.073	0.021	$4.8 \cdot 10^{-7}$	0.014	$3.3 \cdot 10^{-7}$
Acetone <sup>c</sup>	90	1.8	24	0.47	0.44	$7.6 \cdot 10^{-6}$	0.12	$2.0 \cdot 10^{-6}$
Campholenealdehyde <sup>d</sup>	93	1.9	35	0.71	0.86	$5.7 \cdot 10^{-6}$	0.32	$2.1 \cdot 10^{-6}$
Pinonaldehyde <sup>e</sup>	675	13	1000	20	4.3	$2.6 \cdot 10^{-5}$	6.4	$3.8 \cdot 10^{-5}$
<i>Experiment 3</i>								
Formaldehyde <sup>a</sup>	40	0.81	21	0.43	0.12	$3.9 \cdot 10^{-6}$	0.061	$2.1 \cdot 10^{-6}$
Acetaldehyde <sup>b</sup>	3.9	0.079	3.7	0.074	0.016	$3.5 \cdot 10^{-7}$	0.015	$3.3 \cdot 10^{-7}$
Acetone <sup>c</sup>	67	1.3	34	0.67	0.33	$5.6 \cdot 10^{-6}$	0.16	$2.8 \cdot 10^{-6}$
Campholenealdehyde <sup>d</sup>	61	1.2	63	1.3	0.56	$3.7 \cdot 10^{-6}$	0.57	$3.8 \cdot 10^{-6}$
Pinonaldehyde <sup>e</sup>	631	13	1361	27	4.0	$2.4 \cdot 10^{-5}$	8.7	$5.2 \cdot 10^{-5}$

Results are shown for three collection experiments at 50 Torr and three at 100 Torr. (\*) pinonaldehyde was characterized as the *bis*-2,4-DNPH derivative. Experimental conditions:  $[\text{O}_2]=3.24 \cdot 10^{17}$  (50 Torr),  $[\text{O}_2]=6.84 \cdot 10^{17}$  (100 Torr),  $[\text{H}_2]=1.37 \cdot 10^{13}$ ,  $[\text{NO}_2]=3.62 \cdot 10^{12}$ ,  $[\alpha\text{-pinene}]\sim 5 \cdot 10^{12}$  (each expressed in molecules  $\text{cm}^{-3}$ ),  $t_r=42$  ms. Molecular masses for the 2,4-DNPH derivative and the original aldehyde/ketone compound are, respectively, <sup>a</sup>210 and 30, <sup>b</sup>224 and 44, <sup>c</sup>238 and 58, <sup>d</sup>332 and 152, <sup>e</sup>528 and 168.

products in relative units (mol %) are: formaldehyde ( $9.7 \pm 0.7$ ), acetaldehyde ( $1.1 \pm 0.1$ ), acetone ( $16 \pm 1$ ), campholenealdehyde ( $11 \pm 2$ ) and pinonaldehyde ( $63 \pm 3$ ). The yields at 100 Torr are (in mol %): formaldehyde ( $6 \pm 5$ ), acetaldehyde ( $0.9 \pm 0.5$ ), acetone ( $6 \pm 2$ ), campholenealdehyde ( $5.5 \pm 0.7$ ) and pinonaldehyde ( $82 \pm 7$ ). The results clearly indicate that at 50 and 100 Torr pinonaldehyde is the main reaction product. In comparison with the results at 50 Torr, the yield of pinonaldehyde is higher at 100 Torr, while the yields of the other products, especially acetone and campholenealdehyde, decrease. A possible explanation for this pressure dependence can be derived from the reaction mechanism proposed in a previous publication [17]. Supposing the initial  $\alpha$ -pinene-OH adduct is more stabilized at higher pressure less isomerization occurs leading to a lower production of acetone and campholenealdehyde.

As shown in Table 2 the resulting mass and mole balances do not reach 100%. This poor balance might be caused by the incomplete capture of the reaction products. The better results at the higher pressure of 100 Torr could be due to the slower diffusion of the products to the outer wall of the cold  $\text{LN}_2$  trap and thus a more efficient trapping. However, other possible explanations for the incomplete carbon balance should also be considered. First one has the possibility of aerosol formation in our flow tube experiments. Nozière et al. [9] reported an aerosol yield of 4% at an initial  $\alpha$ -pinene concentration of  $7.05 \cdot 10^{12}$  molecules  $\text{cm}^{-3}$ . Because the  $\alpha$ -pinene concentration of about  $5 \cdot 10^{12}$  molecules  $\text{cm}^{-3}$  used in our experiments is even slightly smaller, the aerosol contribution is assumed to be lower than 4%. In addition it was stated by Zhang et al. [27] that a possible aerosol precursor such as pinonaldehyde cannot lead to aerosol formation as

Table 2

Mass balance expressed in mg % and mole balance in mol % of the five oxidation products. Results are shown for three collection experiments at 50 Torr and three at 100 Torr

Experiment No. (amount of $\alpha$ -pinene consumed at 50 and 100 Torr, in mg)	$\frac{\text{amount aldehyde/ketone}}{\text{amount } \alpha\text{-pinene consumed}} \cdot 100$			
	50 Torr		100 Torr	
	(mg %)	(mol %)	(mg %)	(mol %)
Experiment 1 (9.13, 10.75)				
Formaldehyde	1.1	5.0	1.9	8.5
Acetaldehyde	0.21	0.66	0.35	1.1
Acetone	3.6	8.4	2.7	6.4
Campholenealdehyde	6.0	5.3	4.6	4.1
Pinonaldehyde	44	36	67	54
	<i>55</i>	<i>55</i>	<i>76</i>	<i>74</i>
Experiment 2 (13.2, 10.58)				
Formaldehyde	0.96	4.4	0.43	2.0
Acetaldehyde	0.16	0.50	0.14	0.42
Acetone	3.3	7.8	1.1	2.6
Campholenealdehyde	6.5	5.8	3.1	2.7
Pinonaldehyde	33	26	60	49
	<i>43</i>	<i>45</i>	<i>65</i>	<i>56</i>
Experiment 3 (11.73, 11.82)				
Formaldehyde	0.98	4.5	0.52	2.4
Acetaldehyde	0.13	0.41	0.12	0.38
Acetone	2.8	6.5	1.4	3.2
Campholenealdehyde	4.8	4.3	4.9	4.3
Pinonaldehyde	34	28	73	59
	<i>43</i>	<i>43</i>	<i>80</i>	<i>70</i>
Average	$47 \pm 7^a$	$48 \pm 6^a$	$74 \pm 8^a$	$67 \pm 9^a$

The values in italics represent the total mass or mole balance. Experimental conditions: see Table 1.

<sup>a</sup> Standard deviation,  $\sigma$ .

long as its vapor pressure is below its super-saturation level of about  $10^{-4}$  Torr or  $3.2 \cdot 10^{12}$  molecules  $\text{cm}^{-3}$ . Since only 23% of the initial amount of  $\alpha$ -pinene reacts with the OH radicals under our experimental conditions, the concentration of pinonaldehyde formed in the reaction is well below this super-saturation level. A second possible explanation is the production of organic nitrates given the presence of NO in the system, but until now they could not yet be determined in our experiments. In a previous study where the trap was coated with DCM and the batch samples were analyzed with GC–MS [17], organic nitrates were also not observed. Another class of compounds which cannot be detected using the 2,4-DNPH method are substances

without an aldehyde or ketone function. However, the GC–MS analysis of the DCM samples [17] showed that such compounds were not formed in the reaction of  $\alpha$ -pinene with OH radicals. A last possible explanation is the subsequent reaction of pinonaldehyde with OH radicals. However, master chemical mechanism (MCM) [28] model calculations indicate that only rather small amounts of those products could be formed in our experimental conditions since a maximum of 6% of pinonaldehyde could disappear in a subsequent reaction with OH radicals. The calculated mole and mass balances given in this paper have not been corrected for these subsequent reactions of pinonaldehyde.

Formaldehyde and acetone were also identified by

Table 3  
Relative amounts expressed in mg % and mol % of the five oxidation products

	Relative amount of five oxidation products			
	50 Torr		100 Torr	
	(mg %)	(mol %)	(mg %)	(mol %)
Experiment 1				
Formaldehyde	2.0	9.0	2.5	11
Acetaldehyde	0.38	1.2	0.46	1.5
Acetone	6.5	15	3.6	8.6
Campholenealdehyde	10.8	9.7	6.0	5.5
Pinonaldehyde	80	65	88	73
	100	100	100	100
Experiment 2				
Formaldehyde	2.2	9.7	0.66	3.5
Acetaldehyde	0.37	1.1	0.21	0.74
Acetone	7.6	17	1.7	4.6
Campholenealdehyde	15	13	4.7	4.9
Pinonaldehyde	75	59	93	86
	100	100	100	100
Experiment 3				
Formaldehyde	2.3	10	0.65	3.4
Acetaldehyde	0.31	0.94	0.15	0.55
Acetone	6.5	15	1.7	4.7
Campholenealdehyde	11	9.8	6.1	6.2
Pinonaldehyde	80	64	91	85
	100	100	100	100

Results are shown for three collection experiments at 50 Torr and three at 100 Torr. Experimental conditions: see Table 1.

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 ionization detection (FID) [10], and FT-IR [6,9]. Up until now acetal-

dehyde and campholenealdehyde have not been identified as products of the  $\alpha$ -pinene/OH reaction under atmospheric conditions by other research groups.

The presence of pinonaldehyde has been quantified by several research groups [6,9–11,29]. It should be pointed out that Nozière et al. [9] reported a yield for pinonaldehyde of 87%, which is in fairly good agreement with our measurements.

The yields of acetone measured in this study ( $16 \pm 1$  mol % at 50 Torr and  $6 \pm 2$  mol % at 100 Torr) are of the same order of magnitude as the values found in other studies:  $11 \pm 2.7\%$  [30],  $9 \pm 6\%$  [9].

The yields of formaldehyde ( $9.7 \pm 0.7$  mol% at 50 Torr and  $6 \pm 5$  mol % at 100 Torr) are somewhat smaller than the value ( $23 \pm 9\%$ ) recently reported by Nozière et al. [9].

The reaction mechanism presented in Ref. [17] leads to the formation of formaldehyde, acetone,

Table 4  
Product yields expressed in relative units of the five oxidation products

	Relative amount (mol %)	
	50 Torr	100 Torr
Formaldehyde	$9.7 \pm 0.7$	$6 \pm 5$
Acetaldehyde	$1.1 \pm 0.1$	$0.9 \pm 0.5$
Acetone	$16 \pm 1$	$6 \pm 2$
Campholenealdehyde	$11 \pm 2$	$5.5 \pm 0.7$
Pinonaldehyde	$63 \pm 3$	$82 \pm 7$

Experimental conditions: see Table 1.



campholenealdehyde and pinonaldehyde. In addition the MCM model shows that acetone and formaldehyde can also be formed in the subsequent reaction of pinonaldehyde with OH radicals [28]. However, model calculations indicate that only rather small amounts of those products can be formed in our experimental conditions.

## Acknowledgements

This work is financed by the Belgian Ministry of Scientific Policy under the National Impulse Programme Durable Development.

## References

- [1] P.R. Zimmerman, R.B. Chatfield, J. Fishman, P. Crutzen, P.L. Hanst, *Geophys. Res. Lett.* 5 (1978) 679.
- [2] J.F. Müller, *J. Geophys. Res.* 97 (1992) 3787.
- [3] A. Guenther, C.N. Hewith, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, P. Zimmerman, *J. Geophys. Res.* 100 (1995) 8873.
- [4] P. Warneck, in: *Chemistry of the Natural Atmosphere*, Academic Press, San Diego, CA, 1988, p. 158.
- [5] P.L. Hanst, J.W. Spence, E.D. Edney, *Atmos. Environ.* 14 (1980) 1077.
- [6] S. Hatakeyama, K. Izumi, T. Fukuyama, H. Akimoto, *J. Geophys. Res.* 96 (1991) 947.
- [7] C. Vinckier, F. Compernelle, A.M. Saleh, N. Van Hoof, I. Vanhees, *Fresenius Environ. Bull.* 7 (1998) 361.
- [8] D. Grosjean, E. Williams, J. Seinfeld, *Environ. Sci. Technol.* 26 (1992) 1526.
- [9] B. Nozière, I. Barnes, K.H. Becker, *J. Geophys. Res.* 104 (1999) 23645.
- [10] J. Arey, R. Atkinson, S. Aschmann, *J. Geophys. Res.* 95 (1990) 18539.
- [11] H. Hakola, J. Arey, S.M. Aschmann, R. Atkinson, *J. Atmos. Chem.* 18 (1994) 75.
- [12] F.W. Went, *Nature* 167 (1960) 641.
- [13] T. Hoffmann, J.R. Odum, F. Bowman, D. Collins, D. Klockow, R.C. Flagan, J. Seinfeld, *J. Atmos. Chem.* 26 (1997) 189.
- [14] R.J. Griffin, D.R. Cocker III, R.C. Flagan, J.H. Seinfeld, *J. Geophys. Res.* 104 (1999) 3555.
- [15] R.J. Barthelme, S.C. Pryor, *J. Geophys. Res.* 104 (1999) 23657.
- [16] J. Yu, D.R. Cocker III, R.J. Griffin, R.C. Flagan, J.H. Seinfeld, *J. Atmos. Chem.* 34 (1999) 207.
- [17] V. Van den Bergh, I. Vanhees, R. De Boer, F. Compernelle, C. Vinckier, *J. Chromatogr. A* 896 (2000) 135.
- [18] C. Vinckier, N. Van Hoof, in: *Proceedings Eurotrac Symposium*, SPB Academic, The Hague, 1993, p. 652.
- [19] C. Vinckier, N. Van Hoof, *Int. J. Chem. Kin.* 26 (1994) 527.
- [20] E. Grosjean, P.G. Green, D. Grosjean, *Anal. Chem.* 71 (1999) 1851.
- [21] Y. Yacoub, *Proc. Instn. Mech. Engrs.* 213 (1999) 503.
- [22] A. Vairavamurthy, J.M. Roberts, L. Newman, *Atmos. Environ.* 26A (1992) 1965.
- [23] W. Pötter, U. Karst, *Anal. Chem.* 68 (1996) 3354.
- [24] E. Grosjean, D. Grosjean, *Int. J. Environ. Anal. Chem.* 61 (1995) 47.
- [25] D. Grosjean, *Anal. Chem.* 55 (1983) 2436.
- [26] S. Kölliker, M. Oehme, C. Dye, *Anal. Chem.* 70 (1998) 1979.
- [27] S.H. Zhang, M. Shaw, J. Seinfeld, C. Flagan, *J. Geophys. Res.* 97 (1992) 20717.
- [28] M. Pilling, S. Saunders, N. Carslaw, S. Pascoe, M. Jenkin, D. Derwent, <http://cast.nerc.ac.uk/LIBRARY/MCM2/html/main.html>, 1999.
- [29] M. Hallquist, I. Wängberg, E. Ljungström, *Environ. Sci. Technol.* 31 (1997) 3166.
- [30] S.M. Aschmann, A. Reissell, R. Atkinson, J. Arey, *J. Geophys. Res.* 103 (1998) 25553.