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Gas-phase terpene oxidation products: a review

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Abstract

Terpenes are emitted in large quantities from vegetation into the troposphere, where they react readily with ozone, OH and NO₃ radicals leading to a number of oxidation products. The current knowledge about gas-phase terpene oxidation products is reviewed. Their formation and decomposition pathways, their products and their relevance for the troposphere, and their chemical analysis are discussed. Data on oxidation kinetics, and product yields is presented for 23 terpenes and 65 oxidation products. A total of 84 references are quoted. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Monoterpenes; Sesquiterpenes; Troposphere; OH; NO₃; Ozone

1. Introduction

Terpenes are organic compounds of biogenic origin whose structure may be divided into isoprene units. The more volatile mono- (C₁₀) and sesquiterpenes (C₁₅) are emitted in large quantities from the vegetation (Rasmussen, 1972; Zimmermann et al., 1978; Isaksen and Hov, 1987; Guenther et al., 1995). Due to their structural characteristics — they are mostly unsaturated hydrocarbons with one or more C=C-double bonds — terpenes may react to a high extent with atmospheric constituents such as ozone, nitrate and hydroxyl radicals leading to various oxidation products. Terpenes have been considered as important precursors in photochemical ozone formation (Trainer et al., 1987; Jacob and Wofsy, 1988) and secondary organic aerosol production (Went, 1960; Andreae and Crutzen, 1997).

Over the past two decades the reactions of terpenes in the gas-phase have received great attention. Emphasis has been put on the identification and quantification of the reaction products and on the determination of rate constants towards various reactive species, e.g. ozone (O₃), hydroxyl (OH) and nitrate (NO₃) radicals that are ubiquitous in the troposphere. In this article an attempt is made to review current knowledge on the formation, properties and reactions of the *products* from the gas-phase oxidation of terpenes. Various oxidation mechanisms and the possible environmental significance of these products will be discussed.

More recently, interest has focused on the quantification of the aerosol formed during (simulated) atmospheric oxidation of terpenes (Pandis et al., 1991; Kotzias et al., 1993; Lahaniati et al., 1997; Hoffmann et al., 1997a). Only limited information is available on the chemical composition of the produced aerosol. Although it may therefore seem too early to derive definite conclusions on the chemistry of terpene reaction products in the aerosol phase, published data on this aspect will be briefly discussed in the present paper. Low molecular weight

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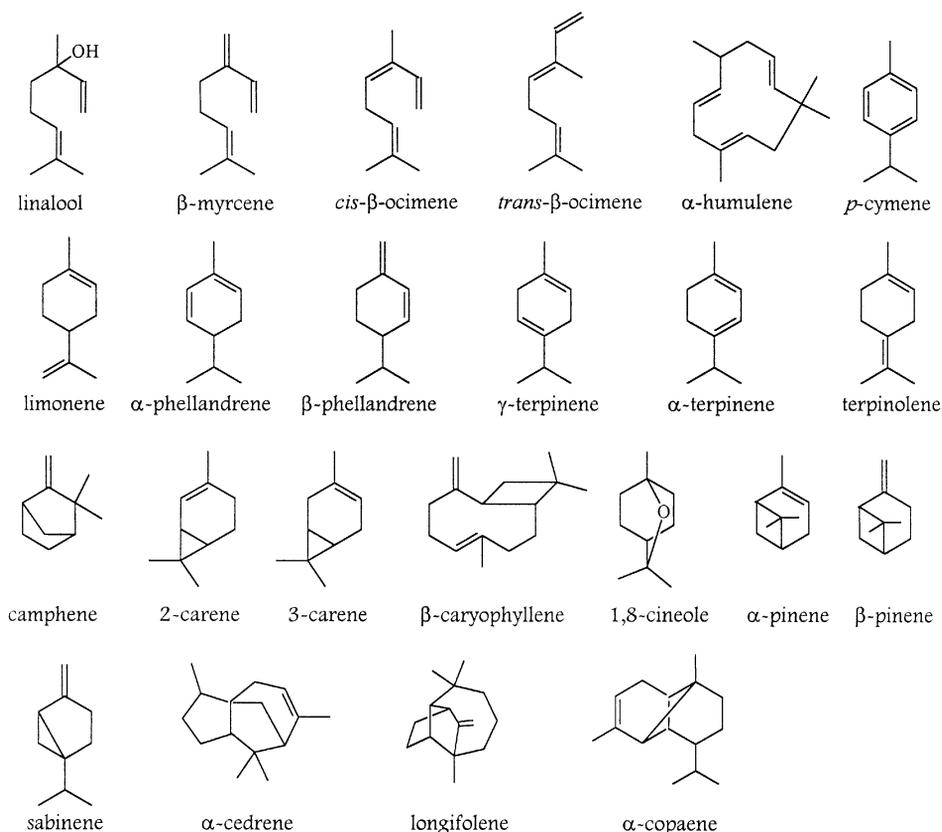


Fig. 1. The chemical structures and names of the terpenes treated in the present review.

aldehydes and carboxylic acids, CO_2 and CO also reported as terpene oxidation products are common products of any organic compound oxidised in the troposphere. The discussion of their chemistry, however, falls beyond the scope of this review. The chemical structures and names of the terpenes treated here are shown in Fig. 1.

2. Reaction pathways for the formation of oxidation products

2.1. General

The kinetics and mechanisms of the OH, O_3 , and NO_3 reactions with simple alkenes, cycloalkenes and conjugated dienes under tropospheric conditions have been thoroughly studied and recently reviewed by Atkinson (1994, 1997). It is fair to conclude, that the kinetics and mechanisms of the alkene/OH reactions are well understood but that work still needs to be done for alkene reactions with NO_3 and in particular with O_3 . For terpenes the situation is even more complex. There are not many mechanistic studies which have been carried out

directly with terpenes. Thus, the chemist is left with no other choice than to regard terpenes as alkenes (e.g. β -pinene, camphene), cycloalkenes (e.g. α -pinene, 3-carene), and dienes (e.g. β -phellandrene, α -terpinene) or as a combination of these classes (e.g. limonene, ocimene). Owing to the specific attack of O_3 on the $\text{C}=\text{C}$ double bond(s), generalisations drawn from ozonolysis of simple alkenes may to a large extent be applicable also for terpenes. However, for reaction with NO_3 and OH radicals, the number of possible reaction products from a terpene is higher than from simple alkenes, cycloalkenes and conjugated dienes.

Besides addition to a $\text{C}=\text{C}$ double bond, abstraction of a hydrogen atom from any of the CH groups in the alkyl backbone of the terpene is also possible. For OH radicals hydrogen abstraction may play a non-negligible role and has in one case been reported to account for up to 15–20% of the initial attack (Paulson and Seinfeld, 1992). There are two characteristic features that distinguish terpenes from the hydrocarbons usually studied:

- The presence of substituted skeletons like the *p*-menthane skeleton of the monocyclic terpenes and the 2,6-dimethyloctadiene backbone of acyclic monoterpenes.

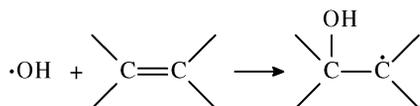
- The presence of highly strained rings like in 3-carene and sabinene (three-member); α -pinene, β -pinene, β -caryophyllene, and α -copaene (four-member); and camphene, α -cedrene and longifolene (five-member).

These features open for alternative reaction pathways such as intramolecular rearrangements which may lead to formation of unexpected compounds such as, e.g. camphene from isoborneol (Wagner–Meerwein rearrangement. For a review of rearrangements in bicyclic systems see March (1992)). Thus, even though the basic reactions of the terpenes and their oxidation products are the same as for the simpler alkenes, it must be kept in mind that the chemistry is far more complex. A brief description of the basic alkene reactions relevant for the formation of terpene oxidation products will be given in the following sections.

2.2. OH radical reactions

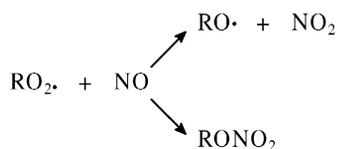
The key species present in the troposphere is the OH radical, which reacts with almost all compounds emitted therein. The C=C double bonds usually present in terpenes render them highly reactive towards this species. The half-life of terpenes in the troposphere due to this reaction is varying between 30 min and 4 h. Rate constants measured for the reaction of OH radicals with terpenes are listed in Table 1.

Addition of OH to the C=C double bond of terpenes is the dominant reaction pathway and leads to the formation of β -hydroxyalkyl radicals:



β -Hydroxyalkyl radicals react rapidly with oxygen forming β -hydroxyalkylperoxy radicals. Terpenes containing conjugated double bonds (e.g. ocimene and α -terpinene) form γ -hydroxy allylic radicals which may isomerize before reacting further.

NO can abstract an oxygen atom from a β -hydroxyalkylperoxy radical leading to a β -hydroxyalkoxy radical, with a small amount of β -hydroxynitrate also being formed. These reactions become significant in polluted atmospheres ([NO] > 30 ppt).



The latter pathway is important for large radicals and is accounting for 14% of the alkylperoxy radical reac-

Table 1

Rate constants k for the reaction of OH and NO₃ radicals and O₃ with terpenes (in units of cm³ molecule⁻¹ s⁻¹)

Terpene	OH ($\times 10^{11}$)	NO ₃ ($\times 10^{14}$)	O ₃ ($\times 10^{18}$)
<i>Acyclic</i>			
Linalool	15.9 ^a	1120 ^a	430 ^a
Myrcene	21.5 ^b	1100 ⁱ	490 ^c
Ocimene	25.2 ^b	2200 ⁱ	560 ^c
<i>Monocyclic</i>			
α -Humulene	29.2 ^d	3500 ^d	11700 ^e
<i>p</i> -Cymene	1.5 ^g	0.099 ^g	< 0.05 ^c
Limonene	17.1 ^e	1220 ^e	210 ^c
α -Phellandrene	31.3 ^e	7300 ^e	2980 ^e
β -Phellandrene	16.8 ^h	800 ^h	47 ^h
α -Terpinene	36.3 ^e	14000 ^e	21100 ^e
γ -Terpinene	17.7 ^e	2900 ^e	140 ^c
Terpinolene	22.5 ^g	9620 ^g	1880 ^e
<i>Bicyclic</i>			
Camphene	5.3 ^f	66 ^f	0.9 ^f
2-Carene	8.0 ^g	2150 ^g	240 ^c
3-Carene	8.8 ^c	910 ^c	37 ^c
β -Caryophyllene	19.7 ^d	1900 ^d	11600 ^e
1,8-Cineole	1.1 ^g	0.017 ^g	< 0.15 ^c
α -Pinene	5.4 ^e	616 ^e	86.6 ^c
β -Pinene	7.9 ^e	251 ^e	15 ^c
Sabinene	11.7 ^f	1010 ^f	86 ^c
<i>Tricyclic</i>			
α -Cedrene	6.7 ^d	820 ^d	27.8 ^c
α -Copaene	9.0 ^d	1600 ^d	158 ^c
Longifolene	4.7 ^d	68 ^d	< 0.7 ^c

^a Atkinson et al. (1995).

^b Atkinson et al. (1986).

^c Atkinson et al. (1990a).

^d Shu and Atkinson (1995).

^e Shu and Atkinson (1994).

^f Atkinson et al. (1990b).

^g Corchnoy and Atkinson (1990).

^h Shorees et al. (1991).

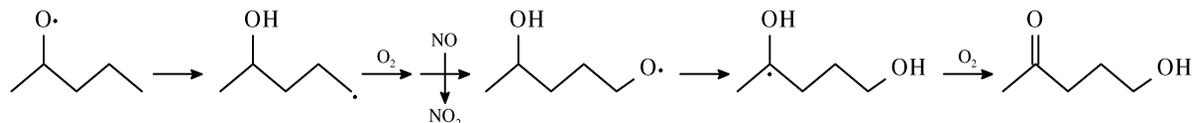
ⁱ Atkinson et al. (1985).

See also review by Atkinson (1997).

tions for isoprene and probably even higher for terpenes (Paulson et al., 1992).

In the troposphere the β -hydroxyalkoxy radical has three possible reaction pathways (Atkinson, 1997): (i) decomposition (ii) isomerisation, and (iii) reaction with molecular oxygen. While the dominant pathway for smaller molecules is decomposition, it is probably not accounting for more than 15% of the terpene radical reactions (Paulson and Seinfeld, 1992). Reaction with O₂ is expected to be even less important than decomposition (Atkinson and Carter, 1991), thus leaving the isomerisation as the main reaction of larger alkoxy radicals. Recent experiments confirm importance of

isomerisation (Eberhard et al., 1995; Kwok et al., 1996). Isomerisation (tautomerisation) proceeds by a 1,5-H shift via a six-membered transition state and is favoured in the order $\text{CH} > \text{CH}_2 > \text{CH}_3$ with a ratio of formed products in the order of approximately 25:10:1, respectively (Eberhard et al., 1995).



In the case of the cyclohexyloxy radical, decomposition has been shown to be an important process (Rowley et al., 1991). Due to the high degree of substitution of the carbon atoms and the sterical limitations imposed by the rings present in terpenes isomerisation is not always possible. This is illustrated in Fig. 2 where the reaction of the alkoxy radical resulting from the OH oxidation of limonene has been taken as an example. If the OH radical attacks in position 2, isomerisation and reaction with O_2 is not possible due to the absence of an H-atom at carbon 1. An H-abstraction from position 4 of the 2-hydroxy cyclohexyloxy radical (A) is only feasible if the oxygen is syn to the H-atom. It is not known if the resulting dihydroxy-cyclohexyloxy radical (B) would give rise to decomposition products.

It should be noticed that with the exception of limonon aldehyde (3-isopropenyl-6-oxo-heptanal) none of the compounds shown in this example have yet been identified. However, they are all very polar and some are not very stable. Besides these products are only expected to be formed in small yields, thus special techniques and care are necessary for their analysis.

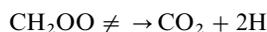
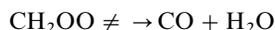
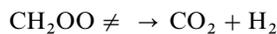
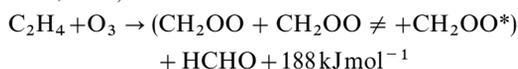
2.3. Ozone reaction

The reaction of ozone with $\text{C}=\text{C}$ double bonds leads to various products of the carbonyl family. The reaction has been well known almost a century and has often been used to localise the position of a double bond in a molecule (Criegee and Wenner, 1949). The ozone attack to the $\text{C}=\text{C}$ double bond leads to the primary ozonide, which is highly unstable and decomposes forming an energy-rich biradical (Criegee intermediate) and a carbonyl. The rate constant of the electrophilic ozone addition strongly depends on the number and nature of the substituents at the $\text{C}=\text{C}$ -double bond (Table 1). The reactivity of terpenes towards ozone is extending over five orders of magnitude leading to half lives in the order of minutes to days.

Due to the highly exothermic nature of the ozone-alkene reaction the Criegee intermediates are in vibrationally (ROO^\ddagger) and electronically (ROO^*) excited

states. Only the collision stabilised Criegee intermediates can participate in further bimolecular reactions, while the rest of the excited species decomposes in a similar way as

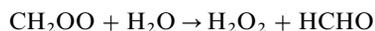
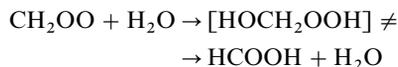
shown for the reaction of ethylene (Hatakeyama and Akimoto, 1994):



For ethylene the ratio between stabilised and excited intermediates is about 2:3 as calculated by Hatakeyama et al. (1984). This ratio, however, depends on the degree of substitution at the double bond and is usually lower with higher substitution due to the increased exothermic character of the reaction.

Decomposition of the excited Criegee intermediates leads to formation of radicals, among which, the OH radical. Hence, ozone/alkene reactions act as a source of radicals in the troposphere, which is particularly important in the absence of sunlight. The OH radical yields appear higher for internal than for terminal and conjugated $\text{C}=\text{C}$ -double-bonds (Atkinson et al., 1992; Atkinson and Aschmann, 1993).

The stabilised Criegee intermediates may react with water molecules under tropospheric conditions producing organic acids. The reaction proceeds via unstable hydroxyalkyl-hydroperoxides (HOCH_2OOH). In addition, in a side-reaction aldehydes and hydrogen peroxide can be formed (Hatakeyama and Akimoto, 1994; Gäb et al., 1985):



Galloway et al. (1982) reported that organic acids formed according to these reaction schemes may contribute up to 65% to the acidity of rain water in remote areas. Finally, the decomposition of the primary ozonide can also lead to the formation of epoxides which may yield up to 5% (Atkinson et al., 1994). For a more detailed discussion of O_3 -alkene reaction mechanisms see Harrison and Murphy (1996), Grosjean and Grosjean (1997), and Horie and Moortgat (1998).

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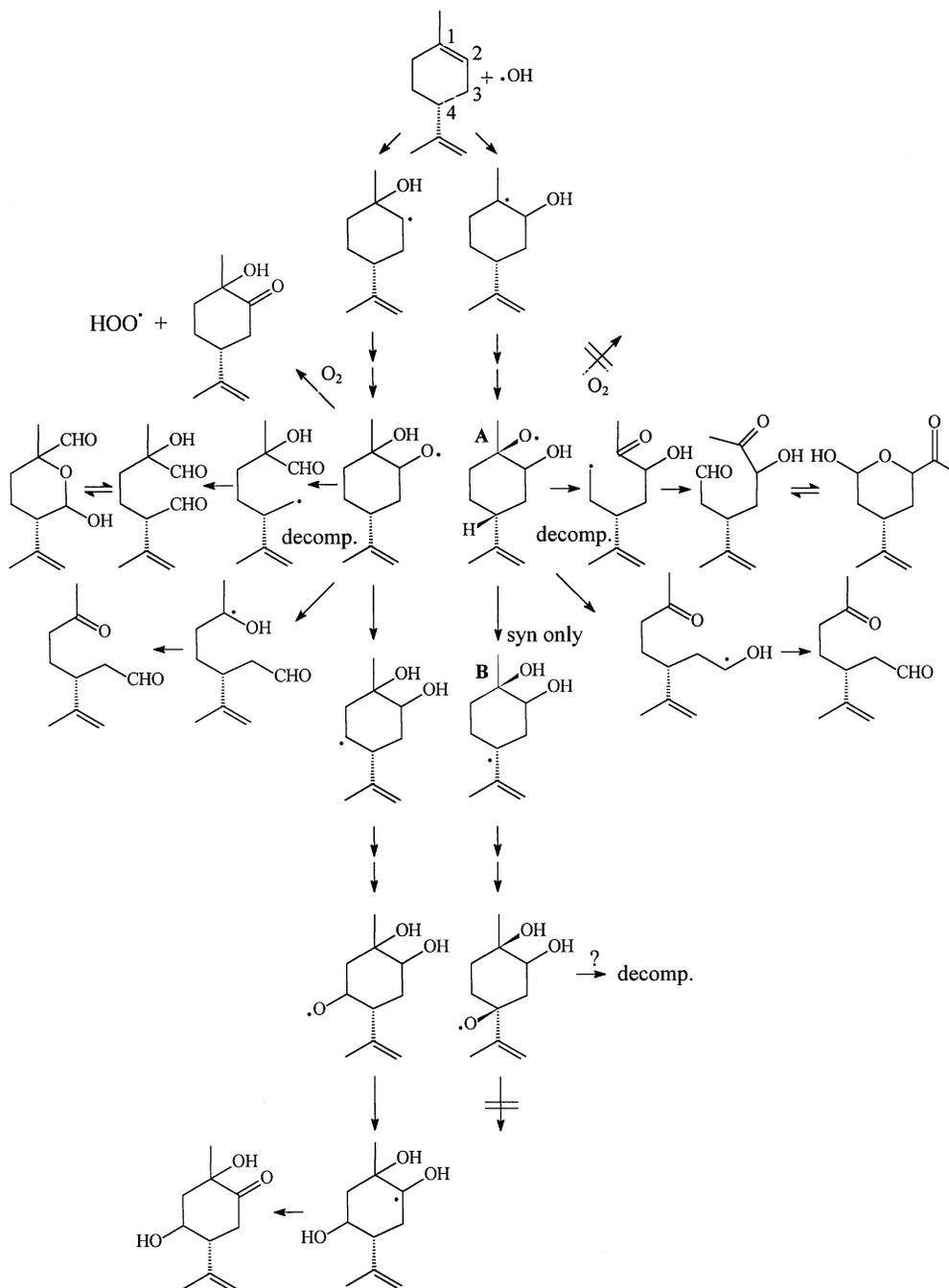


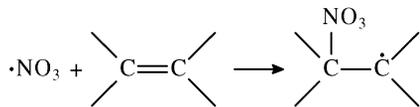
Fig. 2. Oxidation of limonene by OH radicals with possible isomerisation and decomposition pathways.

2.4. NO_3 radical reactions

While the OH radical is the most important oxidising species in the troposphere during daytime, the NO_3 rad-

ical, formed by reaction of O_3 with NO_2 , is the most important oxidising species at night. The half-life of terpenes in the troposphere due to this reaction is varying between 4 min and 18 h. Two kinds of initial steps can be

envisaged: hydrogen abstraction and addition to unsaturated bonds, the latter reaction being more relevant for terpenes. The electrophilic NO_3 radical attacks at the double bond forming a radical adduct intermediate:



As seen for the OH radical, also for NO_3 less substituted carbon atoms are preferentially attacked. The resulting β -nitroalkyl radical reacts rapidly with oxygen forming a β -nitroalkylperoxy radical, which can react with NO forming a β -nitroalkoxy radical or dinitrate. In the absence of NO β -nitroalkylperoxy radical in the troposphere may react with available HO_2 or RO_2 radicals to form nitratoperoxides, nitrocarbonyls and nitroalcohols. The nitrate radical chemistry of simple alkenes, cycloalkenes and conjugated dienes in general and of terpenes in particular is not fully investigated. More studies are required to elucidate the reaction mechanisms for these compounds. However, experimental difficulties are large due to the very low stability of the nitrated products. It is possible that with modern analytical techniques such as direct inlet atmospheric pressure mass-spectrometry (API-MS/MS) the future will bring more data in this field (see next section).

3. Gas-phase terpene reaction products

3.1. General

In the following an overview will be given on the gas-phase terpene reaction products published to date. The data is ordered according to the ring number of the parent terpene and is listed in alphabetical order. Terpenes which have not been encountered in emission studies or are not naturally occurring will not be considered. Recently, a systematic nomenclature has been proposed for terpene oxidation products (Larsen et al., 1998). These names have been adopted in the present paper. For products which are not covered by this nomenclature, acronyms have been chosen. The overview does not claim to be exhaustive — in some cases compounds have even intentionally been left out when their identification was not regarded as sure, for instance when IR was used for their tentative identification without authentic reference standards for confirmation. However, the authors hope that the thorough search of electronic data bases such as Chemical Abstracts and the running study of current literature on air chemistry has avoided unintentional exclusion of important material.

3.2. Analysis of terpene oxidation products

The terpene oxidation products identified so far are mainly carbonyls and carboxylic acids, but as appears in the following chapters also alcohols, epoxides, esters, nitrates and peroxy nitrates have been found as minor products. As an analytical tool on-line FT-IR — albeit not very sensitive — is particularly suited for detection of aldehydes, ketones, nitrates and peroxy nitrates, which shows distinct bands in the spectra. The main advantage of FT-IR is its fast scanning time which facilitates kinetic studies. Chromatographic techniques have been widely used on-line (GC-FID) as well off-line (GC-FID, GC-MS, HPLC). The presence of polar functional groups can cause difficulties in the chromatographic system, making derivatisation necessary. For carbonyls numerous methods exist (Vairavamurthy et al., 1992), derivatisation with 2,4-dinitrophenylhydrazine being the standard one used. Very interesting for the identification of unknown carbonyls via GC-MS is the derivatisation with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (Yu et al., 1995; Lahaniati et al., 1998). For carboxylic acids and alcohols silylation, methylation and acetylation can be used (Shu et al., 1997; Christoffersen et al., 1998). But in general, these derivatisation techniques have not been employed very frequently which may be one of the reasons for the mass balances in product studies being below 50%.

Nitrates and peroxy nitrates can be analysed by GC-MS or by GC with an electron capture detector (Luxenhofer et al., 1994; Grosjean et al., 1993).

Many errors can arise from sampling problems. Of particular importance for the analysis of terpene oxidation products is the possibility of oxidants to react with the mother terpene or its gas-phase products in the sampling system, producing positive as well as negative artefacts. In contrast to the radicals OH and NO_3 , which are destroyed rapidly on walls and other surfaces in the sample system, ozone can reach the compounds already sampled and cause significant artefacts such as the erroneous identification of gas-phase oxidation products (Calogirou et al., 1996). Helmig (1997) has reviewed ozone removal techniques for the sampling of atmospheric organic trace gases. Recently, a special ozone scavenger based on polyphenylenesulfide has been developed for the sampling of polar volatile organic compounds (Calogirou et al., 1997b). With this scrubber it is possible to analyse terpene oxidation products without artefact from ozone.

In a number of studies smaller aldehydes have been reported as products difficult to explain from the structure of the precursor. It is only recently that Fruekilde et al. (1998) have shown that human skin lipid in contact with ozone leads to the formation of significant amounts of acetone (together with 4-oxopentanal and 6-methyl-5-hepten-2-one). These authors concluded that if care was

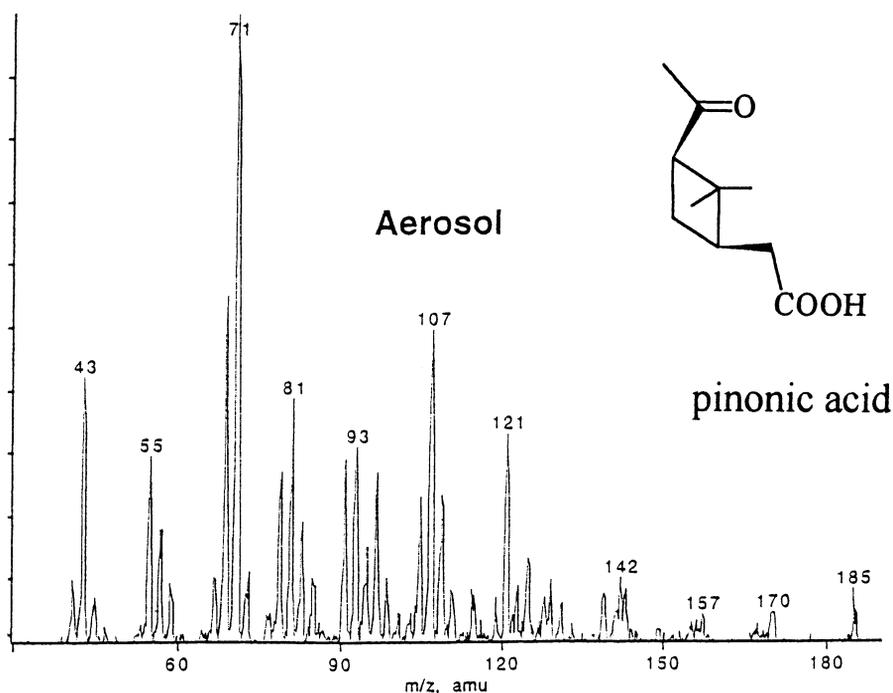


Fig. 3. API-MS/MS spectrum of pinonic acid in a secondary aerosol formed by ozonolysis of α -pinene (see text for explanation). The data is courtesy of Perkin Elmer performed on a PE-Sciex API300.

not taken to avoid skin contact with any material which during an experiment comes into contact with ozone, artefact formation of acetone and other carbonyls cannot be avoided. It is very likely that also the reaction of OH with human skin lipids leads to such artefacts.

From the experimental procedures of most product studies published to date, neither interference from ozone during sampling nor interference from skin-lipid artefacts can be excluded. This fact should be kept in mind when going through the following sections.

A very powerful new method is the direct air sampling by atmospheric pressure ionisation mass spectrometry (API-MS/MS). This technique was first applied to the studies of terpene oxidation by Atkinson et al. (1995) by interfacing a triple quadrupole mass spectrometer directly to a reaction chamber. The feasibility of performing real-time monitoring of gas-phase reactions is owed to the newly developed atmospheric pressure ionisation (API) interfaces for mass spectrometry. An example of the use of API-MS/MS for the detection of pinonic acid in a secondary aerosol formed by ozonolysis of α -pinene is given in Fig. 3. The spectrum has been obtained in the so-called daughter scan mode by locking the first quadrupole on the quasi-molecular ion of pinonic acid ($M+4=185$), collisionally fragmenting these ions in the second quadrupole and scanning the third quadrupole. Comparison with an authentic standard of pinonic acid confirmed the assignment of the spectrum.

The use of liquid chromatography coupled with MS (HPLC-MSⁿ) for the analysis of a variety of ketocarboxylic, hydroxycarboxylic and dicarboxylic acids in secondary aerosols from O₃ and OH oxidation of cyclic monoterpenes has recently been employed in our laboratory (Glasius et al., 1998a, b). It seems to be one of the most promising analytical methods for the study of polar oxidation products.

3.3. Products of acyclic terpenes

3.3.1. Linalool

Linalool (β -isomer) is a terpenoid emitted in large quantities especially during flowering. The formation of 5-methyl-5-vinyl-tetrahydrofuran-2-ol (MVT) as a major linalool oxidation product was firstly observed during the sunlight irradiation of linalool/NO_x mixtures (Compound 1 in Fig. 4, Calogirou et al., 1995). Besides acetone, formaldehyde and acetaldehyde a number of other minor products were tentatively identified such as hydroxy-dialdehydes (**5**, **6**) and hydroxy-carboxylic acids (**4**, **7**). Shu et al. (1997) studied the linalool reaction with O₃, OH and NO₃ radicals and reported molar formation yields for MVT of 0.46 ± 0.11 from the linalool/OH reaction, 0.85 ± 0.14 from the linalool/O₃ reaction and 0.19 ± 0.05 from the linalool/NO₃ reaction. Further yields for acetone of 0.51 ± 0.05 from the linalool/OH reaction, 0.21 ± 0.02 from the linalool/O₃ reaction, and

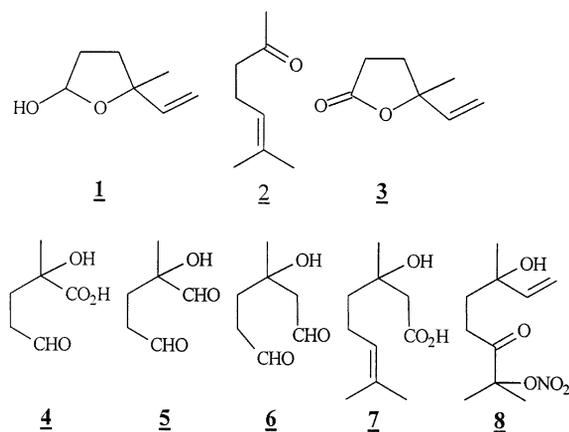


Fig. 4. Products of simulated tropospheric photochemical oxidation of linalool.

0.23 ± 0.05 from the linalool/ NO_3 reaction were reported. 6-Methyl-5-hepten-2-one (MHO, **2**) was formed with a yield of 0.07 ± 0.01 from the linalool/OH reaction. 5-Methyl-5-vinyl-tetrahydrofuran-2-one (**3**) and formaldehyde were formed in yields of 0.13 ± 0.03 and 0.36 ± 0.06 , respectively, from the linalool/ O_3 reaction. Interestingly, also a nitroxy carbonyl (**8**) was tentatively identified from the linalool/ NO_3 reaction.

Calogirou et al. (1998) determined the reaction rate constants of MVT; $k_{\text{OH}} = (7.4 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{NO}_3} = (2.0 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{O}_3} = (3.8 \pm 0.8) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reactions of MHO have been studied (Smith et al., 1996; Grosjean et al., 1996) in reference to its ubiquitous occurrence in the atmosphere (Ciccioli et al., 1993) as a possible product of the heterogeneous ozonolysis of lipids and higher terpenoids at vegetation surfaces (Fruekilde et al., 1998); $k_{\text{OH}} = (1.57 \pm 0.39) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{NO}_3} = (7.5 \pm 3.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{O}_3} =$

$(3.9 \pm 1.5) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Smith et al., 1996); $k_{\text{O}_3} = (394 \pm 40) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Grosjean et al., 1996).

A particular feature of the linalool products is the presence of the OH group. The oxidation of the internal double bond leads to formation of γ -hydroxy acids and γ -hydroxy aldehydes, which exist as a mixture of their cis and trans forms. These compounds have been detected in equilibrium with their cyclic hemiacetal forms (Calogirou, 1997), such as 5-methyl-5-vinyl-tetrahydrofuran-2-ol (from 4-hydroxy-4-methyl-5-hexenal) and possible 5-methyl-5-vinyl-tetrahydrofuran-2-one (from 4-hydroxy-4-methyl-5-hexenoic acid). Other examples of such equilibria are shown in Fig. 5.

The gas-phase reaction of MVT with the OH radical leads to formation of 4-oxopentanal (Calogirou et al., 1998). Also acetaldehyde, and acetone were reported in significant yields although it is not easy to envisage a mechanism which leads to the formation of these small aldehydes. The reaction of MHO with OH radicals and O_3 leads to 4-oxopentanal and acetone with formation yields of 0.59 ± 0.13 and 0.71 ± 0.05 from the OH reaction, and 0.82 ± 0.21 and 0.30 ± 0.05 from the O_3 reaction, respectively (Smith et al., 1996). Grosjean et al. (1996) reported a yield of 0.28 ± 0.02 for acetone from the MHO/ O_3 reaction.

Due to existing parallelisms between MVT and 5-methyl-5-vinyl-tetrahydrofuran-2-one the OH radical reaction of the latter could lead to the formation of 4-oxopentanoic acid. To date this has not been investigated.

3.3.2. Myrcene

Myrcene (β -isomer) has been identified in emission from a number of plants. There are only few data regarding the gas-phase chemistry of myrcene. Succinic acid has been identified from the myrcene/ O_3 reaction in solution (Ruzicka and Stoll, 1924). Recently the formation of

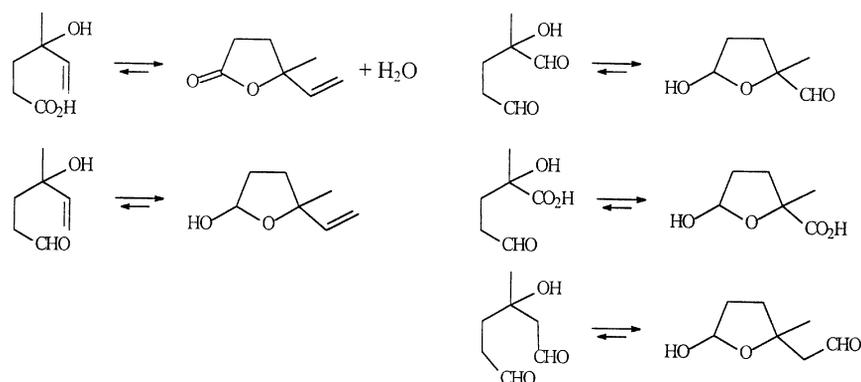


Fig. 5. γ -hydroxy acids and γ -hydroxy aldehydes are important gas-phase oxidation products of linalool and have been found in equilibrium with their cyclic hemiacetal forms.

hydroxyacetone, formaldehyde and acetone in yields of 0.19, 0.26, and 0.29, respectively, was reported from the O_3 reaction (Ruppert et al., 1997).

3.3. Ocimene

Trans- β -ocimene and to a lesser extent *cis*- β -ocimene are emitted by many plants. Methylglyoxal, formaldehyde, malonaldehyde, acetone, acetic acid and malonic acid has been reported from the ocimene/ O_3 reaction in solution (Enklaar, 1908). The formation of 4-methyl-3,5-hexadienal (**9**), methyl-vinyl-ketone and acetone as major oxidation products were observed during sunlight irradiation of ocimene/ NO_x mixtures (Calogirou, 1997). Besides formaldehyde, methylglyoxal and malonaldehyde three higher aldehydes (**10**, **11**, **12**) were tentatively identified in small amounts (Fig. 6).

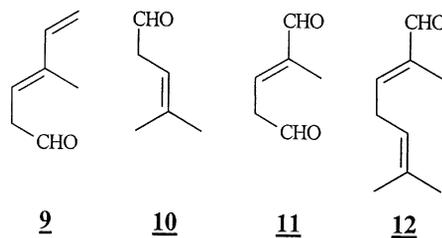


Fig. 6. Aldehydes are major products of photochemical oxidation of ocimene.

3.4. Products of monocyclic terpenes

3.4.1. Limonene

d-Limonene is one of the most common terpenes emitted from plants. Limona ketone (4-acetyl-1-methylcyclohexene, also known as AMCH, **13**, Fig. 7) and limonon aldehyde (3-isopropenyl-6-oxo-heptanal, **14**) have been identified as reaction products from the limonene/ OH reaction (Hakola et al., 1994). The reported yields were 0.20 ± 0.03 for limona ketone and 0.29 ± 0.06 for limonon aldehyde. The latter yield may be underestimated because the authors in lack of better data used the rate constant of acetaldehyde with OH ($k_{OH} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ De Moore et al. (1994), to calculate losses of limonon aldehyde during the measurements.

Limonon aldehyde has been identified as a major reaction product of the limonene/ O_3 reaction (Jay and Stieglitz, 1987; Grosjean, 1993). A number of higher oxidated products were also identified by these authors including keto-limonon aldehyde (3-acetyl-6-oxo-heptanal, **15**) and a decarbonylised analogue (**16**) limononic acid (3-isopropenyl-6-oxo-heptanoic acid, **17**) and keto-limononic acid (3-acetyl-6-oxo-heptanoic acid, **18**). These findings have recently been confirmed by Glasius et al. (1998b).

Atkinson and Aschmann (1993) measured the following rate constants for the reactions of limona ketone: $k_{OH} = (1.29 \pm 0.33) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{NO_3} = (1.05 \pm 0.38) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{O_3} = (1.50 \pm 0.53) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Calogirou et al. (1998) reported on the reaction rate constants of limonon aldehyde; $k_{OH} = (1.1 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{NO_3} = (2.6 \pm 0.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{O_3} = (8.3 \pm 2.2) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Norlimonon aldehyde (2-isopropenyl-5-oxo-hexanal) was identified besides acetaldehyde

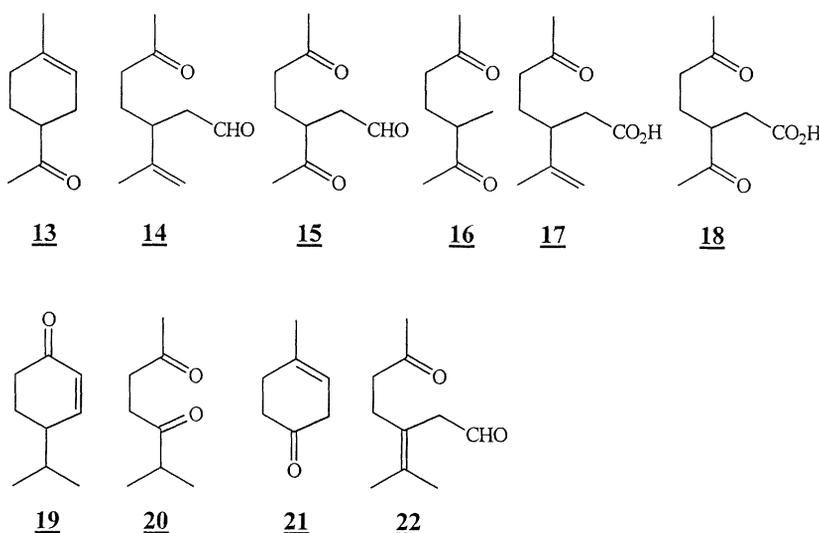


Fig. 7. Ketones, ketoaldehydes, and ketoacids which have been found as gas-phase reaction products of monocyclic monoterpenes with OH radicals and ozone (refer to text).

and acetone as a product of the limonon aldehyde/OH reaction (Calogirou et al., 1998).

3.4.2. α -Phellandrene

Only the α -phellandrene/ NO_3 reaction has been studied (Berndt et al., 1997). The formation of *p*-cymene in a yield of 0.22 and a few unidentified nitrates were observed.

3.4.3. β -Phellandrene

Phellandra ketone (5-isopropyl-2-cyclohexenone, **19**, Fig. 7) has been identified as reaction product from both the OH radical and O_3 reaction of β -phellandrene (Hakola et al., 1994). Yields of 0.29 ± 0.06 from the O_3 reaction and 0.29 ± 0.07 from OH reaction were reported.

3.4.4. α -Terpinene

6-Methyl-hepta-2,5-dione (**20**, Fig. 7) has been identified from the α -terpinene/ O_3 reaction in solution (van Auwers and Hinterseber, 1915). The formation of *p*-cymene in a yield of 0.06, together with some unidentified nitrates were observed from the α -terpinene/ NO_3 reaction (Berndt et al., 1997).

3.4.5. Terpinolene

The unsaturated ketone 4-methyl-3-cyclohexenone (**21**, Fig. 7) has been identified as a product from both the OH radical and O_3 reaction of terpinolene (Hakola et al., 1994). Yields of 0.26 ± 0.06 from the OH reaction and of 0.40 ± 0.06 from the O_3 reaction were reported. The authors observed small amounts of a second product (molecular weight 168) which is likely to be terpinolenon aldehyde (3-isopropylidene-6-oxo-heptanal) (**22**, Fig. 7) in yields of 0.08 ± 0.02 from the OH reaction.

3.5. Products of bicyclic terpenes

3.5.1. Camphene

Campha ketone (3,3-dimethyl-bicyclo[2.2.1]heptan-2-one, also known as camphenilone, **23**, Fig. 8) and 4,4-dimethyl-3-oxabicyclo[3.2.1]octan-2-one (**25**, Fig. 8) have been identified as major products of the camphene/ O_3 reaction (Jay and Stieglitz, 1987, 1989; Hakola et al., 1994) with formation yields of 0.36 ± 0.06 and 0.2, respectively. Jay and Stieglitz (1987, 1989) also observed the formation of *cis*- and *trans*-camphenylaldehyde (**24**, Fig. 8).

The reaction rate constant of OH radicals with campha ketone has been determined; $k_{\text{OH}} = (5.15 \pm 1.44) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Aschmann, 1993).

3.5.2. 3-Carene

The formation of 3-carene aldehyde (*cis*-2,2-dimethyl-3-(2-oxopropyl)-cyclopropyl-ethanal, **26**, Fig. 8) in a yield

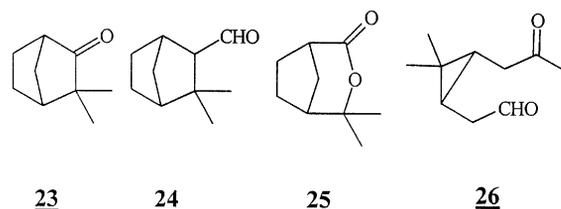


Fig. 8. Major gas-phase reaction products of OH radicals or ozone with camphene (**23–25**) and 3-carene (**26**).

of 0.34 ± 0.08 from the reaction of 3-carene with OH radicals has been observed (Hakola et al., 1994). Only small amounts of this product were encountered from the 3-carene/ O_3 reaction.

The reaction rate constants of 3-carene aldehyde with OH and NO_3 radicals have recently been determined; $k_{\text{OH}} = (1.21 \pm 0.36) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{NO}_3} = (2.71 \pm 0.15) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Hallquist et al., 1997).

3.5.3. β -Caryophyllene

Two ketoaldehydes, namely β -caryophyllon aldehyde (3,3-dimethyl- γ -methylene-2-(3-oxobutyl)-cyclobutyl-butanal, **28**, Fig. 9) and keto- β -caryophyllon aldehyde (3,3-dimethyl- γ -oxo-2-(3-oxobutyl)-cyclobutyl-butanal, **29**) together with formaldehyde have been identified as major products from the β -caryophyllene/ O_3 reaction (Grosjean et al., 1993; Calogirou et al., 1997a). β -Caryophyllene 3-oxide (trans-8-methylene-4,11,11-trimethyl-4-oxa-bicyclo[8.2.0.0^{4,5}]dodecane, **30**) and a number of other high molecular weight products were tentatively identified in small amounts (nor- β -caryophyllon aldehyde, **31**; nor-keto- β -caryophyllon aldehyde, **32**; a diketone, **33**; and β -caryophyllonic acid, **34**; Calogirou et al., 1997a). Furthermore Grosjean et al. (1993) have reported a non-identified compound with the molar weight of 206. This could be β -caryophylla ketone (Larsen et al., 1998).

3.5.4. α -Pinene

α -Pinene is probably the most abundant terpene in the atmosphere. It has been found in forest air in middle and northern Europe, the Mediterranean, north America and Japan, and together with β -pinene it is the most studied terpene. Pinon aldehyde (*cis*-3-acetyl-2,2-dimethyl-cyclobutyl-ethanal, **35**, Fig. 10) has been identified as the major product from the reactions of α -pinene with OH, NO_3 and O_3 (Hull, 1981; Yokouchi and Ambe, 1985; Hatakeyama et al., 1989, 1991; Kotzias et al., 1991; Vinkier et al., 1997; Hakola et al., 1994; Wängberg et al., 1997). The molar yields have been reported to be 0.62 ± 0.04 for the α -pinene/ NO_3 reaction and vary from 0.28 ± 0.05 (Hakola et al., 1994) to 0.56 ± 0.04 (Hatakeyama et al., 1991) for the α -pinene/OH reaction

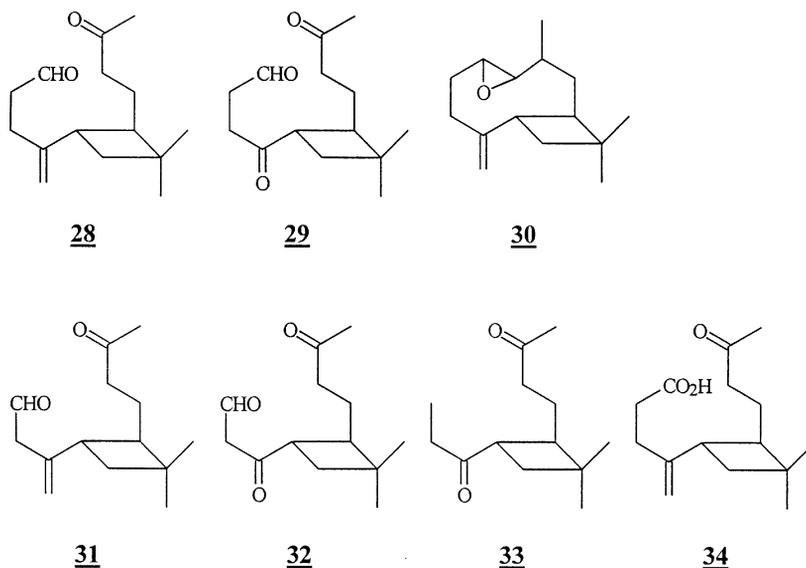


Fig. 9. The most important products of gas-phase ozonolysis of β -caryophyllene.

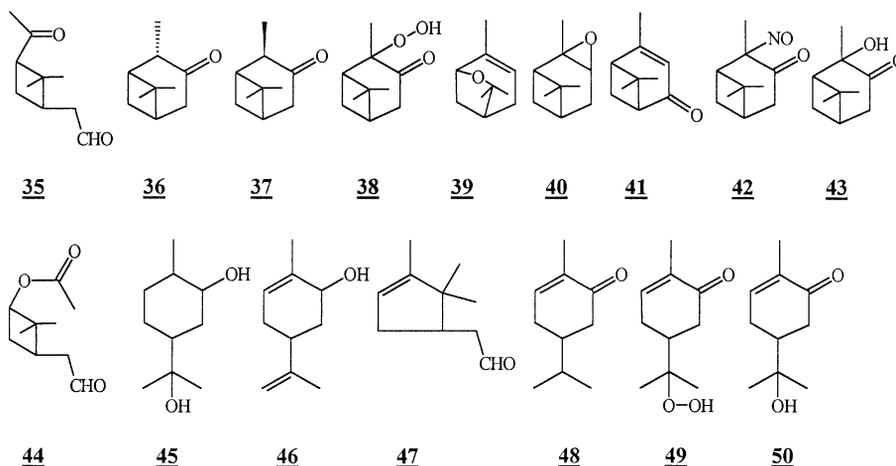


Fig. 10. A broad range of cyclic compounds have been reported from the oxidation of α -pinene by OH and NO_3 radicals and ozone.

and from 0.19 ± 0.04 (Hakola et al. 1994) to 0.51 ± 0.06 (Hatakeyama et al., 1989) for the α -pinene/ O_3 reaction and. Both of the values reported for the α -pinene/OH reaction may be biased due to the experimental methods involved. On the one hand Hakola et al. (1994) used the rate constant of acetaldehyde with OH ($k_{\text{OH}} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ De Moore et al. (1994)) to calculate losses of pinon aldehyde during the measurements which may lead to an underestimation of the yields. On the other hand Hatakeyama et al. (1991) used a method (FT-IR) which tends to overestimate yields due to the contribution of other carbonyls.

A number of other products have been reported. However, it remains unclear if all these products derive from

pure gas-phase reactions or if reactions and rearrangements on surfaces may also have taken place (Hull 1981; Vinckier et al., 1997; Schwartz 1985; Yokouchi and Ambe, 1985). The structures of these compounds (**35–50**) are shown in Fig. 10.

In secondary aerosols formed by the α -pinene/ O_3 reaction a number of carboxylic acids have been identified: pinonic acid (cis-3-acetyl-2,2-dimethyl-cyclobutylethanoic acid, **51**, Fig. 11) in molar yields around 7%, norpinonic acid (cis-3-acetyl-2,2-dimethyl-cyclobutylmethanoic acid, **53**) in molar yields around 0.5% (Hatakeyama et al., 1989); pinic acid (cis-3-carboxy-2,2-dimethyl-cyclobutylethanoic acid, **54**) in molar yields up to 3% (Christoffersen et al., 1998; Hoffmann et al., 1997b)

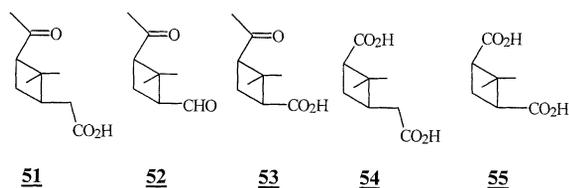


Fig. 11. Reaction products in secondary aerosol formed by the ozonolysis of α -pinene.

and norpinic acid (cis-3-carboxy-2,2-dimethyl-cyclobutylmethanoic acid, **55**) (Hoffmann et al., 1997b).

From the α -pinene/ NO_3 reaction, Jay and Stieglitz (1989) have tentatively identified 1-methyl-2-nitrooxy-4-(2-hydroxy-isopropyl)-cyclohexene (**58**, Fig. 12), pinon aldehyde (**35**, Fig. 10), norpinon aldehyde (3-acetyl-2,2-dimethyl-cyclobutylmethanal, **52**, Fig. 11), and 1-methyl-nitrate-4-(2-2-hydroxy-isopropyl)-cyclohexene, **59**, Fig. 12). Furthermore α -pinene oxide (2,6,6-trimethyl-2-oxabicyclo[3.1.1.0^{2,3}]heptane, **40**, Fig. 10) in yields of 0.03 ± 0.005 , 2-hydroxy-pinanyl-3-nitrate (2-hydroxy-2,6,6-trimethyl-bicyclo[3.1.1]heptanyl-3-nitrate, **57**, Fig. 12) in yields of 0.05 ± 0.004 and 3-oxo-pinanyl-2-nitrate (3-oxo-2,6,6-trimethyl-bicyclo[3.1.1]heptanyl-2-nitrate, **56**, Fig. 12) in yields of 0.05 ± 0.004 were recently identified by Wängberg et al. (1997).

The reactions of pinon aldehyde with O_3 , OH and NO_3 radicals have been studied recently by two groups: $k_{\text{OH}} = (9.1 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{NO}_3} = (5.4 \pm 1.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{O}_3} = (8.9 \pm 1.4) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Glasius et al., 1997); $k_{\text{OH}} = (8.7 \pm 1.14) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{NO}_3} = (2.35 \pm 0.37) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Hallquist et al., 1997); The reported values for k_{OH} are in very good agreement while there is a difference of a factor two for the values of k_{NO_3} . Measuring the absorption cross-sections of pinon aldehyde Hallquist et al. (1997) have calculated a lifetime due to photo-dissociation varying from 3.3 h (1 July, 50°N) to 22 h (1 Jan, 50°N). Reaction with OH radicals seems to be the most important

removal process in the troposphere leading to an estimated lifetime of two hours.

The formation of acetone and norpinon aldehyde (**52**, Fig. 11) from this reaction has been observed (Calogirou et al., 1998). Norpinon aldehyde is expected to have a similar reactivity as pinon aldehyde towards oxidants, thus being the final step before the decomposition of the original pinane carbon skeleton. The corresponding peroxy-nitrate (cis-3-acetyl-2,2-dimethyl-cyclobutyl-acetyl-peroxy-nitrate(**60**, Fig. 12) has been tentatively identified from the pinon aldehyde/ NO_3 reaction (Wängberg et al., 1997).

3.5.5. β -Pinene

Pina ketone (6,6-dimethyl-bicyclo[3.1.1]heptan-2-one, also known as nopinone, **61**, Fig. 13) has been identified as a major product from the reactions of β -pinene with OH and O_3 (Hull, 1981; Jay and Stieglitz, 1987; Hatakeyama et al., 1989, 1991; Kotzias et al., 1991; Grosjean et al., 1993; Hakola et al., 1994). The reported molar yields vary from 0.27 ± 0.04 (Hakola et al., 1994) to 0.79 ± 0.08 (Hatakeyama et al., 1991) for the β -pinene/OH reaction and from 0.22 (Grosjean et al., 1993) and 0.23 ± 0.05 (Hakola et al. 1994) to 0.40 ± 0.02 (Hatakeyama et al., 1991) for the β -pinene/ O_3 reaction. 3-Hydroxy-pina ketone (3-hydroxy-6,6-dimethyl-bicyclo[3.1.1]heptan-2-one, **62**), 3-oxo-pina ketone (6,6-dimethyl-bicyclo[3.1.1]heptan-2,3-dione, **63**), and

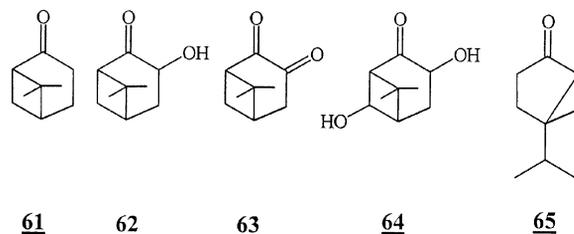


Fig. 13. Ketones and hydroxy-ketones from OH and O_3 oxidation of β -pinene (**61–63**, and sabinene (**65**)) and from OH oxidation of pina ketone (**64**).

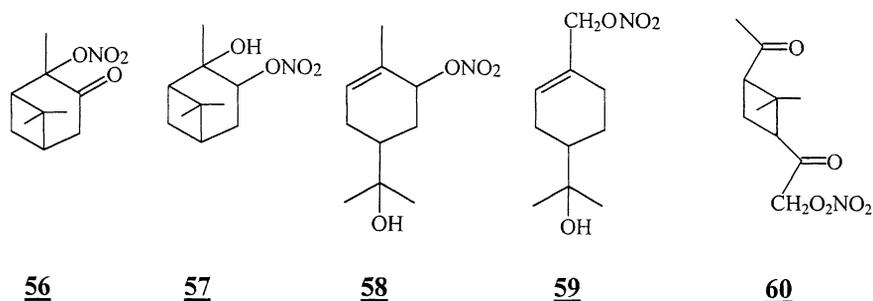


Fig. 12. Organic nitrates identified from the NO_3 radical oxidation of α -pinene and its oxidation product pinon aldehyde.

formaldehyde were also identified (Hull, 1981; Jay and Stieglitz, 1989). Formaldehyde has been found in a yield of 0.54 ± 0.05 (Hatakeyama et al., 1991) from the OH reaction and 0.42 (Grosjean et al., 1993) from the O_3 reaction.

The reactions of pina ketone with O_3 , OH and NO_3 radicals have been studied: $k_{OH} = (1.43 \pm 0.37) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Aschmann, 1993); $k_{OH} = (1.7 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{NO_3} = (1.1 \pm 0.3) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, $k_{O_3} = < 5 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calogirou et al., 1998). Besides the formation of acetone also 3-oxo-pina ketone (**63**), 3-hydroxy-pina ketone (**62**), and 3,7-dihydroxy-pina ketone (3,7-dihydroxy-6,6-dimethyl-bicyclo[3.1.1]-2-heptan-2-one, **64**) from the pina ketone/OH reaction have been observed (Calogirou et al., 1998).

3.5.6. Sabinene

This terpene has not been studied very much and only one oxidation product is known. Sabina ketone (5-isopropyl-bicyclo[3.1.0]hexan-2-one, **65**) is formed in yields of 0.50 ± 0.09 from the O_3 reaction and 0.17 ± 0.03 from the OH reaction of sabinene (Hakola et al., 1994).

3.6. Summarising conclusions

In the previous chapters data has been listed for a large number of individual terpenes and their oxidation products. In the following we will try to summarise these data and draw some general conclusions.

The major terpene oxidation products result from the attack of OH, NO_3 and/or O_3 to the C=C-double-bonds forming carbonyls and carboxylic acids. The current knowledge about the reaction rate constants of

terpene oxidation products is summarised in Table 2. Based on this data lifetime of the compounds in the troposphere have been estimated assuming oxidant concentrations of $[OH] = 0.07 \text{ ppt}$; $[NO_3] = 10 \text{ ppt}$; $[O_3] = 30 \text{ ppb}$. The lifetimes for the major terpene oxidation products are listed in Table 3.

Saturated ketones like pina ketone and campha ketone are much less reactive than their parent terpenes, and are expected to be enriched in ambient air. The rest of the products are more reactive than their parent terpenes. There are only few studies concerning the occurrence of terpene oxidation products in ambient air (Yokouchi and Ambe, 1985; Yokouchi et al., 1987; Satsumabayashi et al., 1990; Helmig and Arey, 1992; Calogirou et al., 1997b). Pina ketone has been identified in ambient air in levels of 70 to 210 ng m^{-3} (Calogirou et al., 1997b) and pinon aldehyde in levels of 2 ng m^{-3} (Yokouchi and Ambe, 1985), 100 ng m^{-3} (Satsumabayashi et al., 1990), and 90 ng m^{-3} (Calogirou et al., 1997b). Since ozone was not scavenged in the majority of these studies the values can contain contributions from artefacts during sampling (Helmig, 1997). MHO has been measured in many areas (Ciccioli et al., 1993a, b, 1996; Helmig et al., 1996), but linalool is not the only source contributing to this compound and it cannot be excluded that artefacts may have contributed to these data (Fruekilde et al., 1998). The formation of MHO results from an attack of the OH radical to the terminal double bond of linalool with subsequent cleavage of hydroxyacetaldehyde and H-atom abstraction. These same mechanism must obviously be the cause of degradation of MVT to 4-oxopentanal. Limonon aldehyde and pinon aldehyde, and presumably other ketoaldehydes, react with OH radicals to form amongst others their corresponding noraldehydes.

Table 2

Rate constants k for the gas-phase reactions of OH and NO_3 radicals and O_3 with terpene oxidation products (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

Oxidation product	OH ($\times 10^{11}$)	NO_3 ($\times 10^{14}$)	O_3 ($\times 10^{18}$)	Parent terpene
MVT	7.4 ^a	2.0 ^a	3.8 ^a	Linalool
MHO	15.7 ^b	750 ^b	390 ^c /394 ^d	Linalool
Limonon aldehyde	11 ^a	26 ^a	8.3 ^a	Limonene
Limona ketone	12.9 ^c	1050 ^c	150 ^c	Limonene
Campha ketone	0.51 ^c	–	–	Camphene
3-Carene aldehyde	12.1 ^f	2.7 ^f	–	3-Carene
Pinon aldehyde	9.1 ^g /8.7 ^f	5.4 ^g /2.4 ^f	0.089 ^g	α -Pinene
Pina ketone	1.7 ^a /1.4 ^c	0.11 ^a	< 0.005 ^a	β -Pinene

^a Calogirou (1998).

^b Fruekilde (1998).

^c Smith (1996).

^d Grosjean (1996).

^e Atkinson and Aschmann (1993).

^f Hallquist (1997).

^g Glasius (1997).

Table 3

Estimated chemical lifetimes of the oxidation products in the troposphere under typical continental conditions: $[\text{OH}] = 0.07 \text{ pt}$; $[\text{NO}_3] = 10 \text{ ppt}$; $[\text{O}_3] = 30 \text{ ppb}$ (in brackets the ratio of lifetime of the terpene oxidation product to the life time of its parent terpene for each oxidant)

Oxidation product	OH (h)	NO ₃	O ₃
MVT	2.3 (2.1)	2 d (560)	4 d (113)
MHO	1.1 (1.0)	9 min (1.5)	1 h (1.1)
Limonon aldehyde	1.6 (1.5)	4 h (53)	2 d (25)
Limona ketone	1.3 (1.3)	6 min (1.3)	2.6h(1.4)
Campha ketone	34 (10)	—	—
3-Caron aldehyde	1.4 (0.7)	42 h (393)	—
Pinon aldehyde	1.9 (0.6)	21/47 h (113/254)	176 d (980)
Pina ketone	10/12 (4.7/5.7)	43 (2270)	> 8 yr

The ketoaldehydes' reactions with NO₃ radicals lead to formation of keto peroxonitrates which may play an important role for transport processes of NO_x in the lower troposphere.

4. Environmental significance of terpene oxidation products

The ozone forming potential of carbonyls is very high (Bowman and Seinfeld, 1994). This means that at high NO_x levels encountered in suburban/semirural areas these compounds will certainly contribute to the formation of ozone. In the update of the US EPA method TO-14 to TO-17 this fact was accounted for by including carbonyl compounds to the list of organic ozone precursors to be monitored (EPA, 1997). Since a large part of the terpene oxidation products are carbonyls their relevance for tropospheric ozone formation is evident.

Pinon aldehyde and 3-caron aldehyde are colourless oils with a vapour pressure of 5.1 and 3.0 Pa at 25°C, respectively (Hallquist et al., 1997). The vapour pressure of pinonic acid and pinic acid have been estimated to be 10⁻² and 1.3 × 10⁻⁵ Pa, respectively (Hull, 1981; Christoffersen et al., 1998). All investigations to date show that terpenes form carboxylic acids, and dicarboxylic acids upon their reaction with ozone (Hull, 1989; Christoffersen et al., 1998; Glasius et al., 1998b), which may be a reason for the formation of secondary aerosols (Pandis et al., 1991; Hoffmann et al., 1997b). Sesquiterpenes have not been studied very much to date. They are expected to show the same chemistry as monoterpenes at even higher reaction rates. They have been found at much higher ambient air concentrations than monoterpenes in the tropics (Hoffmann, 1994). On a global scale, this group of terpenes could be a major source for secondary aerosols of biogenic origin which recently has been estimated to

be as high as 30 to 270 Tg yr⁻¹ (Andreae and Crutzen, 1997). Future research in tropospheric terpene chemistry should include emission studies in this geographical area with more emphasis given to sesquiterpenes.

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