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IBOOT : Impact of Biogenic emissions on Organic aerosols and Oxidants in the Troposphere

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

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PROJECT WEBSITE(S): <http://www.oma.be/TROPO/IBOOT/Home.html>

ACRONYMS, ABBREVIATIONS AND UNITS

APCI+: positive mode of Atmospheric pressure chemical ionization source
APPI: Atmospheric pressure photospray ionization
BOREAM: Biogenic compounds Oxidation and Related Aerosol formation Model
BVOC: Biogenic Volatile Organic Compound
CI: Criegee Intermediate
CID: Collision induced dissociation
CID-ESI-: fragmentation pattern mass spectrum generated from an isolated anion formed from negative mode of Electrospray ionization source.
CID-APCI+: fragmentation pattern mass spectrum generated from an isolated cation formed from the positive mode of APCI ionization source.
CTM: Chemistry/Transport Model
DBE: Double bond equivalent
DFT: Density functional theory
 E_b : Barrier height (kcal mol^{-1})
ESI-: negative mode of Electrospray ionization source
FTIR: Fourier Transform infrared
HMPH: Hydroxy methyl hydroperoxide
HPLC: High pressure liquid chromatography
LC-MS-MS-TOF: Liquid chromatography coupled to tandem mass spectrometer with TOF
MCM: Master Chemical Mechanism
MS-MS: Tandem mass spectrometry
NMVOC: Non-methane volatile organic compound
PTR-MS: Proton transfer reaction mass spectrometer, which depends on gas phase ion-molecule proton transfer reaction as a principle of ionization.
RRKM-ME: Rice-Ramsperger-Kassel-Markus rate theory combined with master equation analyses
SMPS: Scanning mobility particle sizer
SAR: Structure-Activity Relationship
SOA: Secondary organic aerosol
TOF: Time of flight mass spectrometric analyzer
Triple Quad TOF system: a hybrid mass spectrometric analyzer, which consists of three successive linear quadrupoles connected orthogonally to a TOF analyzer through ion pulser with ion mirror (reflectron) to increase the resolution
TST: Transition State Theory
UT: Upper troposphere
X-HP1-C1: A peroxidic oxidation product with nominal mass X generated from hydroperoxide channel 1 of Criegee Intermediate C1.
X-NP-HP1-C1: A non-peroxidic oxidation product generated through hydroperoxide channel HP1 of Criegee Intermediate C1.
X-HP2-C1: A peroxidic oxidation product with nominal mass X generated from hydroperoxide channel 2 of Criegee Intermediate C1.
X-HP-C2: A peroxidic oxidation product with nominal mass X generated from hydroperoxide channel of Criegee Intermediate C2.
X-E-C2: Oxidation product with nominal mass X generated through the ester channel of Criegee Intermediate C2
ZPVE: Zero point vibrational energy

1. INTRODUCTION

1.1 Context

The biosphere emits large amounts of reactive gases having a profound environmental impact. Pollutants generated from their oxidation include ozone and aerosols, which are key players in air quality and climate change. They influence also the oxidizing capacity of the atmosphere, through their impact on the hydroxyl radical. The non-methane volatile organic compounds (NMVOCs) are primarily biogenic (BVOCs). Although the general lines of their oxidation mechanisms are believed to be well-known, and processes involved in the formation of Secondary Organic Aerosols (SOA) have been identified, recent findings suggest that the current models and mechanisms are incomplete. In particular, it is now recognized that detailed BVOC degradation mechanisms validated by carefully designed laboratory experiments are required in order to reliably extrapolate the impact of BVOCs in the atmosphere. Such mechanisms are still lacking for important BVOC classes, like the monoterpenes (C₁₀H₁₆) and sesquiterpenes (C₁₅H₂₄). Furthermore, the current gas/aerosol partitioning models appear to be unable to match the aerosol yields from laboratory experiments, possibly because of unaccounted processes such as polymer and oligomer formation. In spite of their probable high relevance in the troposphere, their impact is still unknown. Finally, the loss mechanisms of important oxygenated compounds are still very uncertain upper tropospheric conditions. For example, the reactions of carbonyl compounds with HO₂ are potentially significant in this region, a finding of importance for the budget of radicals and ozone.

1.2 Objectives and expected outcomes

We propose to conduct laboratory, theoretical and modelling investigations aiming at reducing the large uncertainties associated with the impact of biogenic volatile organic compounds emissions in the atmosphere. Our general objective is to establish the photochemical degradation mechanism and aerosol formation potential of several mono- and sesquiterpenes. Our specific objectives are the following:

- 1) Experimental determination of the composition and yields of the organic aerosol formed in the ozonolysis of the sesquiterpenes β -caryophyllene and α -humulene in atmospheric conditions (MPI). The influence of (i) H₂O and other Criegee-Intermediate scavengers (HCOOH and HCHO), (ii) different OH-radical scavengers, (iii) temperature (between 275 and 305 K) will be investigated in order to help clarify the reaction mechanism. Polymer/oligomer formation and the CCN activity of aerosols from mono- and sesquiterpene + ozone reaction will be determined.
- 2) Development of predictive tools for mechanism building, based on advanced theoretical calculations (KULeuven). These tools are needed to estimate the reaction parameters in a given class from the available data for individual compounds.
- 3) Gas-phase mechanism development for (i) the oxidation of α - and β -pinene by OH, and (ii) the ozonolysis of α -pinene, β -caryophyllene and α -humulene (all partners). The formation of key low-volatility compounds should be elucidated. Reduced mechanisms will be derived for implementation in atmospheric models. These mechanisms will be validated against laboratory results obtained under various conditions.
- 4) Gas/particle partitioning model development (IASB-BIRA), including the determination of the vapour pressures, activity coefficients and solubilities of the products. The role of aqueous phase chemistry and inorganic salts will be represented, since they might favour heterogeneous reactions enhancing the aerosol yields. The partitioning module coupled to the gas-phase oxidation model will be evaluated against laboratory results.
- 5) Study of the reactions of oxygenated compounds (e.g. acetic acid, hydroxyacetone, glycolaldehyde, glyoxal, nopinone) with OH and/or HO₂ in the conditions of the upper troposphere (KULeuven).
- 6) Assessment of the global impact of terpenes on the budget of oxidants and aerosols, using a global CTM (IASB-BIRA). The modelled organic aerosol will be validated against field measurements.
- 7) Valorization and dissemination (all), including (i) a website for Structure-Activity Relationships (ii) a workshop on mechanism development, in collaboration with BIOSOL, and (iii) data submission to international databases (e.g. within ACCENT).

2. CONFORMITY WITH THE INITIAL PLANNING

2.1 Workplan

WP1 Good conformity with the plan for the laboratory investigations of β -caryophyllene ozonolysis (Tasks 1.1 – 1.3). Work on α -humulene will start in the 2nd half of 2007. Oligomer formation (Task 1.4) was investigated in the ozonolysis of simpler compounds, and will be investigated in the ozonolysis of mono- and sesqui-terpenes in the coming months.

WP2 Good conformity with the plan for the development of theoretical tools, in particular for alkoxy radical decomposition (Task 2.1.1), OH addition reactions on (poly)alkenes (Task 2.2.1). Work on isomerization reactions of alkoxy radicals (2.1.2), NO₃ addition reactions on (poly)alkenes (2.2.2) and H-abstraction reactions (2.4) has started, and will be continued.

WP3 Good conformity with plan regarding the development of the β -pinene + OH mechanism (Task 3.1.1). In addition to the original plan, an important update of the α -pinene + OH mechanism has been realized. Work on α -pinene, β -pinene and β -humulene ozonolysis (Task 3.2.1) has started, and will be continued. Preliminary ozonolysis mechanisms have been used in box model studies simulating α -pinene photooxidation experiments (Task 3.3.1) and β -caryophyllene ozonolysis experiments (3.3.3)

WP4 Good conformity with the plan for the organic aerosol model development (Task 4.2.1) and its validation through simulations of laboratory experiments (Task 4.3.1). Prediction methods for Henry's law solubilities (4.1.2) and activity coefficients (4.1.3) will be developed in the 2nd half of 2007.

WP5 Good conformity with the plan regarding the reaction of oxygenates with OH (Task 4.5.1) and the carbonyl + HO₂ reactions (Task 4.5.2), task which will be continued.

WP6 Global modeling of terpene oxidation and organic aerosol formation has not started yet, although preliminary reduced mechanisms of α -pinene oxidation have been already developed and tested in a global model (Task 6.1). This work will really start after completion of the on-going developments on the α -pinene ozonolysis mechanism.

WP7 Valorization: The work conducted within IBOOT is described in a large number of publications in international journals. Others are submitted or in preparation. In addition to the planned activities, the complete α -pinene oxidation mechanism developed within IBOOT and used in the box model studies has been published on a web site at BIRA. The website for Structure-Activity-Relationships (SARs) is currently under full development. Regarding Task 7.3 (submission to databases), most, if not all existing databases are focused on experimental results. Given the lack of suitable database, we now aim to promote the IBOOT website as a main, widely accessible repository for our theoretical results; dissemination of the information is in this way aided by the automatic inclusion in internet search engines. The workshop on mechanism development (Task 7.2) could not be held in 2007. Opportunities will be sought to organize it in spring/summer of 2008.

2.2 Use of the resource

Person-months since the start of the contract (15/12/2005) till 31/07/2007 :

Partner 1 (IASB-BIRA) : 19 months

Partner 2 (KULeuven) : 18 months

3. COLLABORATION AND SYNERGY WITHIN THE NETWORK

Collaboration between the partners is an essential feature of the IBOOT project. Besides the IBOOT project meetings (held once per year), discussions and information exchange are made through email and telephone conversations.

A primary objective of the project is the development of chemical mechanisms for biogenic terpenes, and the estimation of their impact on the atmospheric composition. In order to reach this goal, the contribution of the KULeuven team (development of theoretical tools for reaction classes, advanced theoretical calculations for key reactions) is to provide the essential building blocks for the construction of the overall mechanisms implemented in a box model at IASB-BIRA. Frequent exchanges of information are needed in order to ensure the completeness and up-to-date status of these mechanisms. Comparisons of the box model results with laboratory experiments provide an indispensable validation. The box model (coupled to a gas/aerosol partitioning module) will be also used in order to design reduced chemical mechanism for use in 3-dimensional atmospheric models. At this stage of the project, the monoterpene α -pinene is the only compound for which a detailed mechanism has been developed and tested using the box model. The α -pinene mechanism in its current state (available at www.oma.be/TROPO/boream/boreammodel), including 5000 reactions and 1300 species, is a major result of the collaboration between the Leuven and IASB-BIRA teams. In the second phase of the IBOOT project, mechanisms for the sesquiterpenes β -caryophyllene and α -humulene will be also developed. The experimental findings of the MPI-Mainz group for these compounds will provide essential constraints for this development. Many products of β -caryophyllene ozonolysis could be detected in the laboratory at MPI-Mainz, and pathways explaining these products have been proposed, awaiting confirmation (and further refinements) from theoretical investigations. The aerosol yield measurements will be also used in IASB-BIRA for validation of the multiphase (gas/aerosol) model. The polymer/oligomer formation studies at MPI will be also important for the proposed aerosol modeling work at IASB-BIRA.

4. REPORT OF THE PROGRESS AND IMPLEMENTATION OF THE METHODOLOGY

4.1 Laboratory studies of mono- and sesquiterpenes ozonolysis (Mainz)

4.1.1 Products and reaction mechanism of the reaction of ozone with sesquiterpenes

4.1.1.1 Mass spectrometric characterization of oxidation products from β -caryophyllene

The ozonolysis of β -caryophyllene has been studied in a spherical reactor (570 liter) at atmospheric conditions. The analysis of particulate-phase products by liquid chromatography coupled to mass spectrometry using two different ionisation sources (ESI- and ACPI+) has provided useful insights on the degradation mechanism of β -caryophyllene. Many multifunctional oxidation products could be detected, and structures have been deduced using collision induced fragmentation of molecular ions. For example, an oxocarboxylic acid believed to be formed from the ester channel of a Criegee-Intermediate generated in the first steps of the mechanism has been identified unequivocally. Moreover, the identification of isomers with e.g. molecular weight 252 was accomplished and confirmed by theoretical investigations of the fragmentation pathways. An Electrospray method was developed to ionize not only organic acids but also aldehydes in the negative mode, extending widely the range of oxidation products that can be detected in one analysis step (Kanawati *et al.*, submitted, 2007). Fig. 1 shows the time dependent trace of anions with $m/z=253$. The fragmentation pattern of one parent anion $[M-H]^-$ generated from this neutral species is shown in Figure 2 and reveals the existence of two distinct fragmentation pathways:

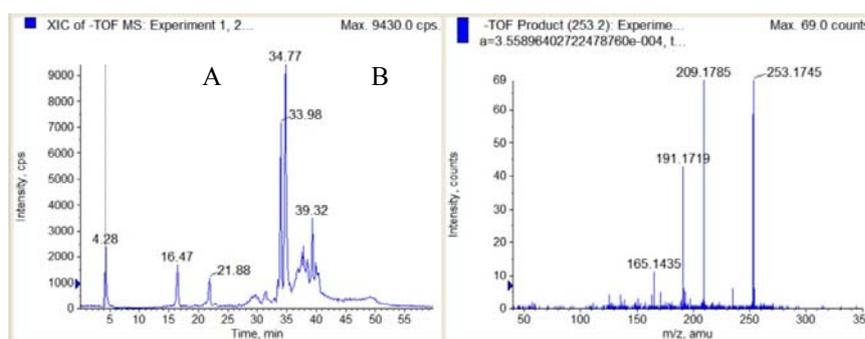
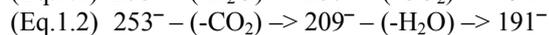
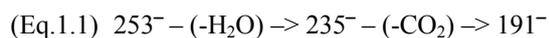


Figure 1: A: Ion chromatogram of m/z 253. B: CID spectrum of the peak at retention time 4.28 min.

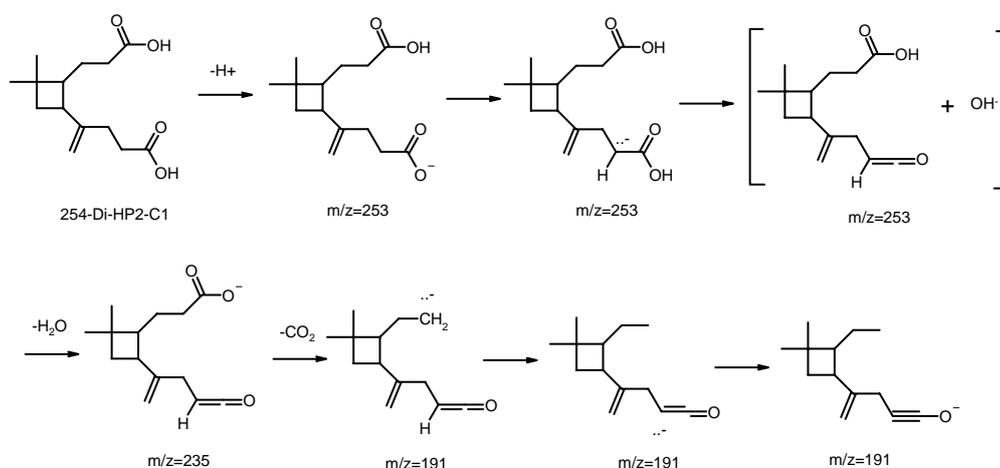


Figure 2: Fragmentation mechanism in agreement with the observed pathway (Eq.1.1).

As seen in Fig. 2, the dicarboxylic acid is deprotonated to yield a carboxylate anion, which can undergo a 1,2- H^+ -shift. The new ion is stabilized by katenization to release an OH^- ion which can form an ion-neutral complex with the ketene. Proton abstraction from the other carboxyl group by the OH^- eliminates water and forms another carboxylate anion. The new anion (primary fragment ion) can release CO_2 and the negative charge moves to the lower carbon chain to form a stable deprotonated

ketene (secondary fragment ion). This ion is very stable due to electron delocalization. Extensive CID and DFT studies have been performed to elucidate the unusual gas phase ion fragmentation mechanisms of some small oxocarboxylic acids (*Kanawati et al.*, manuscripts in preparation). They confirm water elimination from mono and oxocarboxylic acids (*Römpp et al.*, 2006). Both pathways (Eq. 1.1 and 1.2) can be observed experimentally, if excess internal energy is available. Proposed mechanisms for all observed CID fragmentation pathways of parent anions that correspond to the identified oxidation products were investigated and discussed in detail in a manuscript (*Kanawati et al.*, submitted, 2007).

4.1.1.2 Identified oxidation products from β -caryophyllene ozonolysis

The observed products from aerosol samples of β -caryophyllene ozonolysis with reactant ratio β -caryophyllene to ozone of 1.5 to 1 are shown in Fig. 3. Under this condition only the more reactive internal double bond is oxidized.

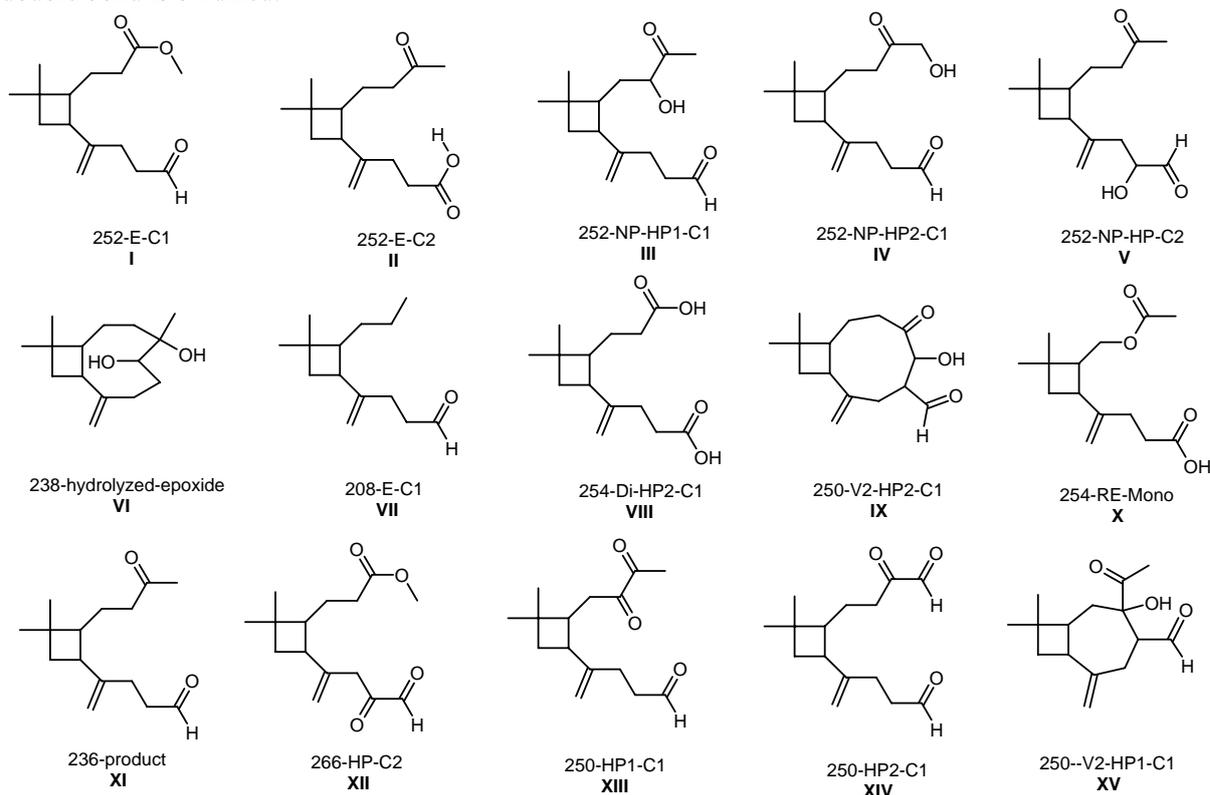


Figure 3: Oxidation products from β -caryophyllene ozonolysis with excess β -caryophyllene.

Possible rearrangements of the Criegee-Intermediates from β -caryophyllene ozonolysis are the ester and hydroperoxide channels. Several rearrangements and degradation products of the Criegee-Intermediates formed through the ester and hydroperoxide channels are shown in Figs. 4 and 5, respectively.

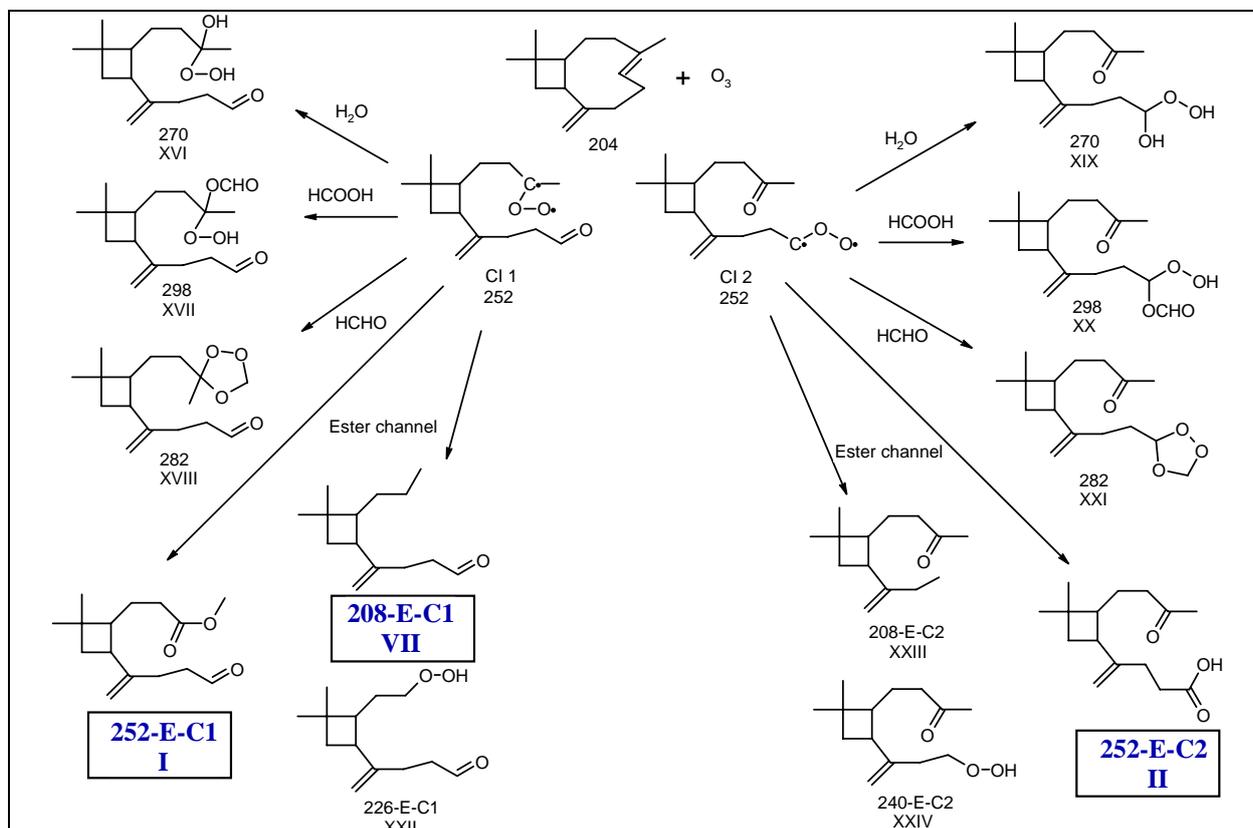


Figure 4: Ester channel of the Criegee-Intermediates. The rectangles indicate observed products.

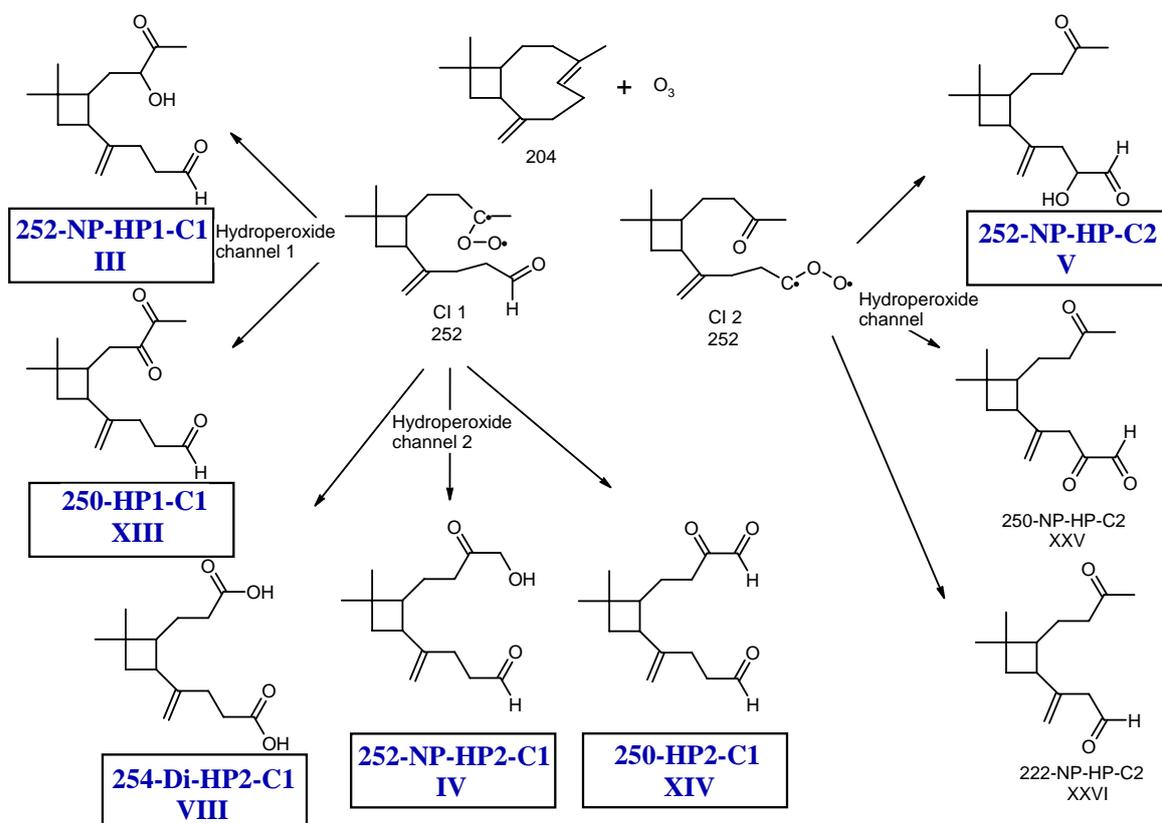


Figure 5: Hydroperoxide channel of the Criegee-Intermediates. The rectangles indicate the observed products.

4.1.1.3 DFT calculations for deprotonation potentials and geometries of identified products

Structures of the most prominent products were optimized by DFT calculations, and the deprotonation potentials from different acidic positions were calculated (*Kanawati et al.*, submitted), to

identify the most probable parent anion for further CID studies. An example is given in Figure 6.

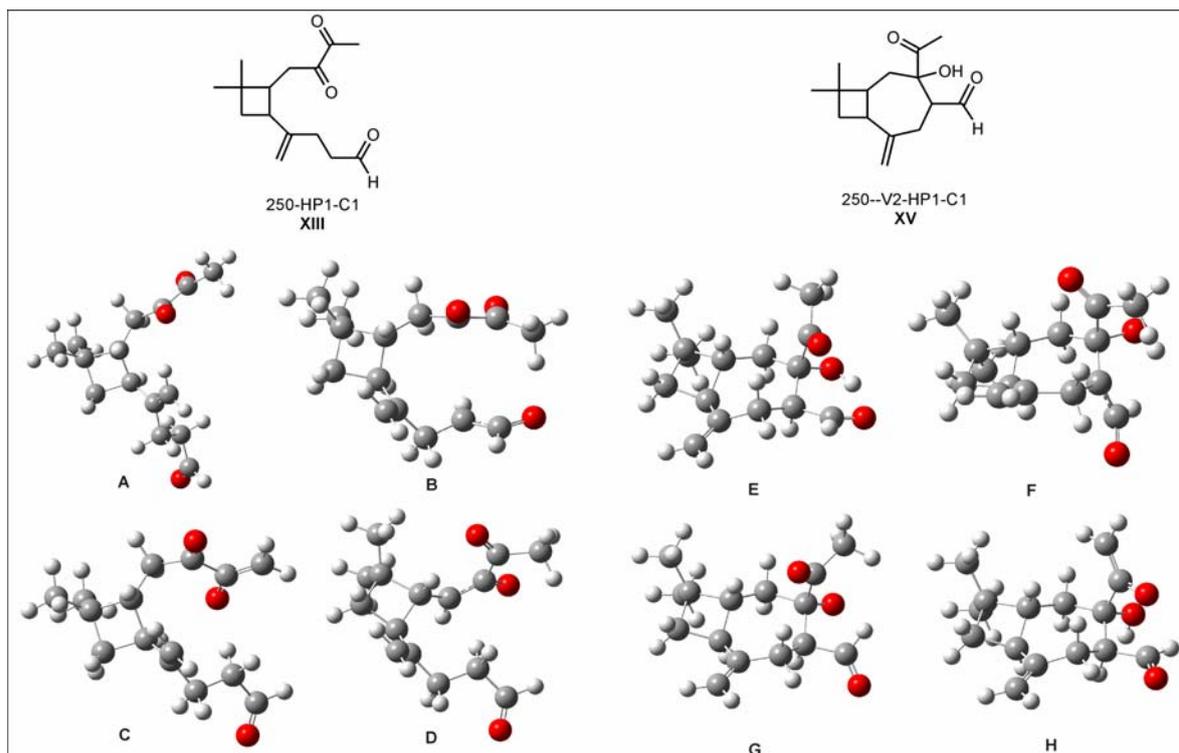


Figure 6: DFT Optimized geometries for **A:** XIII neutral; **B:** XIII deprotonated from α -aldehyde position; **C:** XIII deprotonated from the acetyl moiety; **D:** XIII deprotonated from the internal α -position relative to the dicarbonyl group; **E:** XV neutral; **F:** XV deprotonated from α -aldehydic group; **G:** XV deprotonated from OH group; **H:** XV deprotonated from the acetyl group.

4.1.1.4 OH-radical yields and ozonolysis rate constants

For the determination of OH radical yields, cyclohexane was added as an OH radical scavenger during the ozonolysis experiments. The known reaction products are cyclohexanol (yield 35%) and cyclohexanone (53%). The concentration of cyclohexanone was followed on-line by PTR-MS. Cyclohexanol loses H_2O to yield $m/z=83$ also formed from cyclohexane + O_2^+ in the ion source. For β -caryophyllene the OH yield was $8.5 \pm 1.0\%$ and $21.0 \pm 1.1\%$ for the first and second double bond, respectively. For α -humulene, $10.2 \pm 1.2\%$ for both double bonds. The experimentally determined rate constant for ozone attack on the second (less reactive) exocyclic $\text{C}=\text{C}$ bond in β -caryophyllene was $1.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, i.e. two orders of magnitude less than the rate constant for ozone attack on the first reactive endocyclic $\text{C}=\text{C}$ bond, $1.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constant for the first, second and third ozone attack in α -humulene is 1.17×10^{-14} , 3.6×10^{-16} and $3.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (Herrmann, 2006).

4.1.2 Determination of aerosol yields from sesquiterpene-ozonolysis

Table 1 lists the aerosol yields of β -caryophyllene ozonolysis from different experiments. Some experiments were performed with formic acid, formaldehyde and water as Criegee-Intermediate scavenger. The yield increases by addition of H_2O and with higher concentration of formic acid. It was suggested that formic acid adds to CI-2 to generate a product $\text{MW}=298$ (XX), which can then undergo a rearrangement to yield the oxocarboxylic acid (II) (Figure 4) and thus increases the aerosol yield.

The aerosol yields are much lower than reported from a photo-oxidation study (Hoffmann *et al.* 1997), but are comparable to the results from Ng *et al.* 2006, who also investigated the dark ozonolysis (see Table 1). They found an initial yield of ca. 11%, when the first double bond is oxidised, and an increase of the yield up to 50% upon ozonolysis of the second double bond (yields are calculated from Fig. 3 in (Ng *et al.* 2006)).

A temperature-controlled flowtube was set up to investigate the temperature dependence of the SOA yield in the ozonolysis of β -pinene (Stenby *et al.*, 2007).

Table 1: Aerosol yields from β -caryophyllene (BC) ozonolysis with and without CI-scavenger.

Experiment	Reacted BC / $\mu\text{g m}^{-3}$	Aerosol / $\mu\text{g m}^{-3}$	Aerosol yield / %	Cl-scavenger / ppm
BC2808	920	50	6	-
BC1608	2340	190	8	-
BC2308	1930	170	9	-
BC1708	2310	230	10	-
BC1618	2010	210	10	-
BC1408	2290	280	12	-
BC2509	1540	270	18	-
BC2908	1540	370	24	-
BC1910	1580	310	19	HCOOH / 0.25
BC1920	2190	460	21	HCOOH / 0.25
BC1810	1900	470	24	HCOOH / 0.5
BC1820	2220	660	30	HCOOH / 0.5
BC1610	1900	620	32	HCOOH / 1
BC2609	2190	820	38	HCOOH / 1
BC0610	1520	620	41	HCOOH / 1
BC0910	2130	180	9	HCHO / 7.8
BC2009	1050	130	12	HCHO / 6.8
BC1310	1620	440	27	H ₂ O / 12800
BC1210	1510	420	28	H ₂ O / 12800

4.1.3 Identification and quantification of H₂O₂ and organic peroxides

1. Indications of the presence of H₂O₂ and organic peroxides were obtained by iodometry.
2. The applicability of LC-MS-MS-TOF for individual peroxide detection was investigated, especially with regard to sample treatment of unstable peroxides, chromatographic separation and ionization method (i.e. ESI and APCI). Samples of *tert*-butyl hydroperoxide, di-*tert*-butyl peroxide, cumene hydroperoxide and peracetic acid were injected in the mass spectrometer. The investigations have shown that both methods are not suitable for peroxide detection.
3. An existing HPLC method for the detection of H₂O₂ and simple α -hydroxy-hydroperoxides was applied for the detection of hydroperoxides from terpenes. In total, 11 experiments were performed, with relative humidity between 50 to 60 %, initial sesquiterpene 400 ppb, and 270, 860 and 1200 ppb of ozone. Preliminary results show that for β -caryophyllene, yields of H₂O₂ were found to be 2 % with excess alkene and 4 % with excess ozone. Moreover, 0.2 % of hydroxymethyl hydroperoxide were formed with excess ozone, while its concentrations were below the quantification limit with excess alkene. Under similar conditions, α -humulene produced 4 times more H₂O₂. The addition of cyclohexane (300 ppm) as OH scavenger did not have any detectable influence on H₂O₂ yields. Samples of organic aerosol showed significant quantities of hydroperoxides, with a relative percentage of long-chain (C₆ to C₁₂) organic hydroperoxides to H₂O₂ of up to 12 %.

4.1.4 Formation of oligomers and polymers from mono- and sesquiterpene-ozonolysis

Based on our recent study (Sadezky *et al.*, 2006), in which oligomeric compounds were found in organic aerosol formed during ozonolysis of enol ethers, we performed similar studies for structurally related small alkenes. Oligomers were identified in the range m/z 200–800, consisting of repetitive chain units having the same elementary composition as the Criegee Intermediates in the ozonolysis reactions. We proposed that these oligomers have the basic structure of an oligoperoxide, $-\text{[CH(R)-O-O]}_n-$, and that such oligoperoxide formation involving CI-like chain units represents a new pathway for organic aerosol and oligomer formation and showed its validity for a range of hydrocarbon alkenes.

4.2 Development of predictive tools for mechanism development (Leuven)

4.2.1 SARs for unimolecular alkoxy radical reactions

The decomposition rate coefficient of alkoxy radicals formed as intermediates in the atmospheric degradation of most hydrocarbons can be well described as $k(T) = A_{\text{TST}} \times \exp(-E_b/kT)$, with $A_{\text{TST}} \approx 1.8 \times 10^{13} \text{ s}^{-1}$ for nearly all alkoxy radicals, and where the barrier height E_b to decomposition depends strongly on the α - and β -substituents on either side of the breaking $^{\bullet}\text{OC}_{\alpha}-\text{C}_{\beta}$ bond.



The quantum chemical methodologies applied to this reaction class include the DFT functionals B3LYP, MPW1K, MPWKIS1K, and B3LYP, and the MP2 ab initio methodology combined with DIDZ, 6-31G(d,p), 6-311++G(2df,2pd), and aug-cc-VTZ basis sets, in combinations limited by our computational resources and selected based on the relative merit of the methodologies. Based on results for over 80 transition states with different combinations of 10 substituents, and pending the finalization of the statistical analysis of our current results and cross-validation against higher-order correlated methods, the impact of α - and β -substituents X on the barrier height for alkoxy radical decomposition can be summarized as follows:

$$E_b / \text{kcal mol}^{-1} = 17.5 + \sum a_x \cdot n_x \cdot X$$

where n_x is the number of substituents of type X on carbon α or β , a_x is the impact of a substituent of type X on the barrier height, and summed over all substituents on carbons α and β . The substituent activities are listed in the table below:

Table 2: Alkoxy decomposition SAR activities of various substituents

α -alkyl : -2.1	β -alkyl : -3.2
α -OH : -8.0	β -OH : -8.0
α -oxo : -12.0	β -oxo : -8.0
α -OR (R=alkyl) : -8.9	β -OR (R=alkyl) : -8.9
α -OOR (R=alkyl): -6.3	β -OOR (R=alkyl): -7.5
α -OOH: -8.2	β -OOH: -9.2
α -ONO ₂ : -3.1	β -ONO ₂ : -2.7
α -ONO : -4.1	β -ONO : -6.2
α =C< (vinoxy): +21.1	β =C< (vinyl): +4.6
α -C=C (vinylketone): -5.0	β -C=C (allyl): -9.6

Compared to earlier work (Peeters *et al.*, 2004) which examined the effect of alkyl-, hydroxy (-OH), and oxo (=O) substituents on the barrier height, the range of substituents was significantly extended to include more oxygen-bearing functionalities, including ethers, hydroperoxides, alkylperoxides, nitrates, and nitrites. This will enable us to predict the reactivity for a much wider range of (oxygenated) intermediates formed in the degradation of the larger biogenic hydrocarbons including terpenes and sesquiterpenes. Also, the effect of vinyl and allyl-substituents was investigated to support work on the degradation mechanism of poly-unsaturated hydrocarbons (including ringed structures) such as isoprene and the terpenoids. Most substituents stabilize the product radical and carbonyl function and reduce the barrier height relative to the non-substituted template molecule ethoxy ($\text{CH}_3-\text{CH}_2\text{O}^{\bullet}$). The only exceptions occur where the α - or β -carbons are involved in a double bond (in addition to the breaking bond). This observation simplifies the degradation mechanisms for some poly-unsaturated hydrocarbons. Systems where the product radicals form a conjugated π -system with the newly formed C=O double bond have a different A-factor by a factor of ~ 2 . A paper is in preparation.

The quantum chemical data on the alkoxy radicals are also the basis for an isomerisation SAR. Due to the ring structure of the H-shift TS, the number of rotamers to consider is significantly less than for the alkoxy radicals themselves, such that the calculations on the decomposition SAR also represent the bulk of the data for the isomerisation SAR.

4.2.2 Site-specific SARs for OH and NO₃ addition on (poly)alkenes

A paper was recently published (Peeters *et al.*, 2007) presenting the site-specific OH-addition on (poly)unsaturated hydrocarbons. The predictions were re-examined against the latest kinetic data recommendation available in the literature. Statistical analyses of preliminary higher-order SAR expressions, e.g. accounting for H-abstraction contributions, were used to identify the source of the residual errors, including dependences on ring strain, competing reaction channels, presence of conjugated

π -systems, and other functionalities. In addition, the hypotheses underlying the SAR were also compared against the mechanistic knowledge from high-level theoretical work in the literature, which is currently viewed as a double-TS approach (Greenwald *et al.* 2005). Finally, direct experimental measurements of the site-specificity of the OH-addition were extensively described.

Summarizing, the site-specific rate of addition can be predicted based on the stability type of the radical formed after addition (see table below); the total rate of addition $k_{\text{tot}} = \sum k_i$ is equal to the sum of addition rates over all addition sites. Isolated double bonds lead to primary, secondary or tertiary product radicals, whereas conjugated double bonds potentially lead to allyl-resonance stabilized product radicals where the rate coefficient $k_{\text{first/second}}$ depends primarily on the first radical site next to the addition site, with an additional effect of the substitution around the second resonance radical site.

Table 3: SAR parameters ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$, 298K) for addition of OH on a (poly)alkene

$k_{\text{prim}} = 0.43$	$k_{\text{sec}} = 3.0$	$k_{\text{tert}} = 5.5$
	$k_{\text{sec/prim}} = 3.0$	$k_{\text{tert/prim}} = 5.7$
	$k_{\text{sec/sec}} = 3.7$	$k_{\text{tert/sec}} = 8.3$
	$k_{\text{sec/tert}} = 5.0$	$k_{\text{tert/tert}} = 9.9$

The SAR predictions for total NO_3 radical addition rates on alkenes are in very good agreement with literature data, except for conjugated alkadienes which are underestimated by about a factor of 3 (linear alkadienes) or 10 (cyclic alkadienes). The reasons for this discrepancy are unclear, but two mechanistic models are currently under investigation using quantum chemical characterizations of the TS. Furthermore, analysis of the residual errors of the SAR predictions versus the experimental data indicates that H-abstraction might be contributing for a small percentage. Literature is being searched for experimental product studies that might provide support for this view. A paper is in preparation.

4.2.4 H-abstraction from substituted hydrocarbons by OH-radicals

The H-abstraction SAR is the first project in our research group based predominantly on the "Science project" software framework to manage the large amounts of data generated in the quantum chemical computations, and the subsequent verification and incorporation in the SAR. This framework has been mainly developed in the frame of IBOOT, and has reached a sufficient level of maturity to be used in a well-controlled production environment, though SAR-specific modules are still under development. The quantum chemical calculations for the SAR are well under way, and the first results are expected to be published on our website as they are generated during the summer holidays and the last quarter of the year. The preparation of a publication on our preliminary work combined with the first set of data is planned for later this year. The MCM Review Panel has provided us with an updated extensive list of available experimental data on VOC+OH-reaction for use in this Task.

4.3 Development of terpene oxidation mechanisms

4.3.1: OH-initiated oxidation of α - and β -pinene

In a recently submitted publication (Vereecken *et al.*, 2007), we upgraded our earlier explicit mechanism on the OH-initiated oxidation of α -pinene (Peeters *et al.*, 2001), based on very high-level quantum chemical calculations and theoretical-kinetic calculations, showing the importance of H-shift reactions and ring closure reactions versus reactions with NO for certain peroxy-radical intermediates. The newly incorporated chemistry readily explains the formation of some heavy poly-oxygenated reaction products observed in mass spectrometric studies available in the literature, but for which no formation channels were confirmed yet. The predicted formation of hydroperoxides and (hydroxy-)(di-)carbonyl compounds has a profound impact on the predicted SOA formation in the atmospheric OH-, O_3 -, and NO_3 -initiated α -pinene oxidation (see also Sect. 4.4.3). These new developments represent a significant contribution to the current knowledge of SOA precursors, and similar reactions must be considered in the oxidation of all (sesqui)terpenes to ensure correct models.

The reaction of OH radicals with β -pinene can occur on nine sites, of which addition onto the exocyclic double bonded carbon is by far the dominant channel. We also investigated the product distribution of

the most important H-abstraction channel, leading initially to an allyl-resonance stabilized alkyl radical. The subsequent degradation of this radical in atmospheric conditions was examined using a combination of SAR-predictions, quantum chemical calculations, and multi-conformer TST, accounting for variations in NO_x concentrations ranging from the pristine environment up to laboratory oxidation reaction conditions. The results indicate that, for this initiation channel, formation of larger multi-substituted oxygenates should be predominant; acids are expected only in very high NO_x conditions. We also continued work on the dominant addition channel; development is difficult due to extensive branching through multiple competing H-shift and decomposition channels for several of the intermediates.

4.3.2: O₃-initiated oxidation of mono- and sesquiterpenes

The work on SOA formation in α -pinene oxidation described in Sect. 4.3.3 and 4.4.3 incorporates a mechanism for α -pinene ozonolysis which still lacks (theoretically) confirmed routes for the formation of the SOA precursors pinic acid (as well as peroxy-pinic acid) and hydroxy-pinonic acid. Note that we have shown that the currently accepted gas-phase formation routes for pinic acid are not viable, as crucial steps are completely outrun by competing channels (Peeters *et al.*, 2001; Capouet *et al.*, 2007). Novel pathways that hold promise for efficient formation of these acids are now under theoretical investigation; they involve non-traditional peroxy radical reactions, akin to those already shown to be important in the OH-initiated oxidation of α -pinene, and/or as demonstrated by us to explain byproduct formation in the liquid-phase autoxidation of cyclohexane (Hermans *et al.*, 2007).

In order to quantitatively predict all important *first-generation* products of α -pinene ozonolysis, the mechanism of this major process was newly investigated theoretically in great detail, using the B3LYP/6-311++G(3df,3pd) // B3LYP/6-311G(d,p) level of theory, complemented by TST and RRKM-Master Equation statistical-kinetics approaches. A total of ca. 100 minima and 200 transition states have been located and characterized. The computed barriers for the initial O₃-addition to form the *trans*- and *cis*-ozonides, of 1 and 2 kcal/mol, are in line with the experimental Arrhenius activation energy of 1-1.5 kcal/mol; also, the multi-conformer TST-calculated total rate coefficient, $k(T) = 5.6 \times 10^{-24} \times T^{2.9}$ for $T = 200$ -500 K, is in agreement with the experimental data (Khamaganov and Hites, 2001; Atkinson *et al.*, 1982). An important new finding is that the chemically activated *trans*- and *cis*-ozonides – which interconvert rapidly over an energy barrier of only 7 kcal/mol – result in *four* distinct Criegee intermediates (CI) (i.e. *syn*-CI-1, *anti*-CI-1, *syn*-CI-2 and *anti*-CI-2). The reason is that due to their high barriers (of ca. 37 kcal/mol) the *syn/anti* conversions are orders of magnitude slower than the fast 1,4-H shifts or ring-closures which initiate the various hydroperoxide- and ester-channel pathways of the four CI's. The latter routes, leading to the first-generation products (including \cdot OH radicals and pinonic acid), were quantum-chemically investigated in much detail. RRKM-Master Equation analyses on these complex routes, in order to predict quantitatively the product branching ratios, are still in progress.

Work is also in progress on β -pinene ozonolysis. Initial O₃-addition on the exocyclic >C=C< bond faces barriers of 1.9 and 2.3 kcal/mol, to form two primary ozonides (i.e. *trans*- and *cis*-forms), which interconvert rapidly, and decompose mainly to HCHO + a carbonyloxy, in accordance with the experimental observations. Subsequent reactions of the carbonyloxy, i.e. 1,4-H shifts and ring-closures, as well as the reactions leading to various secondary products, including OH radicals, are under investigation.

It was decided to start research on sesquiterpene ozonolysis only in late 2007 or beginning of 2008, pending finalization of the developments on the formation of low-volatility compounds in the α -pinene+OH and +O₃ mechanisms (see above). It is expected that analogous reactions need to be included in the sesquiterpene chemistry. Preliminary work on α -humulene revealed that ozone addition on all three >C=C< sites proceeds without barrier, explaining the high total rate, but also implying a highly complex overall mechanism.

4.3.3: Model simulations of terpene oxidation experiments

The chemical box model describing the OH-oxidation of α -pinene developed in our previous work (Capouet *et al.*, 2004) has been extended to encompass a preliminary ozonolysis mechanism developed at KULeuven, as well as a simple NO₃-initiated oxidation mechanism. In addition, the new pathways proposed by Vereecken *et al.* (2007) (see Sect. 4.3.1) involving a peroxy radical produced in the oxidation of α -pinene by OH and producing low-volatility hydroperoxides has been also included in the mechanism.

Note that a fully explicit terpene oxidation mechanism is out of reach with the current capabilities since the number of reactions which would be required for the explicit oxidation mechanism of a C10 alkene would be prohibitively large (Aumont *et al.*, 2005). However, the impact of the degradation of the primary products might be significant even on the time scale of a laboratory experiment (a few hours). We estimate OH-reaction rates and channels based on SARs by Neeb (2000), modified to account for (i) strain effects due to the 4-membered ring in compounds like pinonaldehyde, based on a theoretical study (Vereecken and Peeters, 2002), and (ii) recent literature data for the abstraction of H atoms adjacent to a carbonyl functionality. Photolysis rates are estimated by treating separately the different functionalities of the molecule, except for keto-nitrates and keto-aldehydes for which experimental data are available.

High-yield compounds of the α -pinene mechanism are treated explicitly in our mechanism, whereas the degradation of minor products (with yields < 5%) is assumed to generate generic peroxy radicals, as described in more detail in Capouet *et al.* (2007). The effects of details in the molecular structure are neglected in this procedure. Volatility classes have been introduced, so that the products of the further reactions of these generic radicals with NO, HO₂ and other RO₂s can partition between the gas and particulate phases. The chemistry of peroxy radicals follows Capouet *et al.* (2004).

The complete α -pinene degradation mechanism has been published in a web page which allows users to explore it in a convenient way (<http://www.oma.be/TROPO/boream/boreammodel/>).

A preliminary β -caryophyllene ozonolysis mechanism has been developed based on similarities with α - and β -pinene, and on laboratory results reported in the literature (Hoffmann *et al.*, 1997, Jaoui *et al.*, 2003) and within IBOOT (WP1), in particular the OH yield from the ozonolysis, the initiation oxidation rates and several tentatively identified products.

4.4 Organic aerosol modeling (IASB-BIRA)

4.4.1 Thermodynamic properties of oxidation products

The vapour pressures of sesquiterpene oxidation products have been determined based on previous work (Capouet and Muller, 2006). The performance of the method is found to be lower against measurements for C10-18 compounds (Yaws, 1994, Helmig *et al.*, 2003, Amelynck, 2006), compared to C_≤10 species, due to limitations of the method for larger compounds, and/or to the larger errors associated with the measurements of low vapour pressures. Further work will be needed to refine these estimates.

4.4.2 Multiphase partitioning model development

The partitioning model follows a kinetic approach (Kamens *et al.*, 1999), with partitioning coefficients evaluated from the vapour pressures, following Pankow (1994). Activity coefficients are taken equal to one at this stage. The coupled gas phase/partitioning model, BOREAM (Biogenic compounds Oxidation and RElated Aerosol formation Model) includes 4000 reactions and 800 species. At this stage, the role of liquid water, inorganic salts and heterogeneous reactions is not considered, except for the formation of high-molecular-weight (HMW) compounds from the reaction of ozone with particle-phase unsaturated organics (Mochida *et al.*, 2006; Zahardis and Petrucci., 2007). Since gas-phase ozone addition to β -caryophyllene occurs mainly at the internal double bond, and ozone addition to the remaining double bond of the primary ozonolysis products is much slower (cf. Sect. 4.1.1.4), these products have a lifetime long enough to partition to the condensed phase. The proposed reaction sequence involves cleavage of the ozonide into aldehydes and Criegee intermediates, which react with carbonyls to produce HMW compounds. The oligomerization limiting factor is the reactive uptake coefficient taken equal to 10⁻³ (Zahardis and Petrucci, 2007). The relevance of these reactions for SOA formation from α -pinene degradation is under investigation.

4.4.3 Validation of aerosol model by simulation of laboratory experiments

About 30 laboratory experiments of α -pinene photooxidation have been modelled, taking their specific conditions into account (actinic flux, initial concentrations, wall losses, temperature, sampling time). Table 4 illustrates the conditions in each series of experiments. The calculated relative contribution of each oxidant to the total sink of α -pinene is also given. OH and O₃ are dominant in Nozière *et al.* and Presto *et al.*, respectively.

Table 4: Typical conditions in the laboratory experiments simulated in this work. ΔHC is the amount of reacted α -pinene, T is temperature, $J(\text{NO}_2)$ is the photolysis frequency of NO_2 . The 4th column indicates the relative contribution of the oxidants (OH , O_3 , NO_3) to the total sink of α -pinene. More information on the experimental setups and results can be found in *Capouet et al. (2007)*.

	ΔHC (ppb)	$\Delta\text{HC}/\text{NO}_x$	Oxidants (%) $\text{OH} : \text{O}_3 : \text{NO}_3$	T (K)	$J(\text{NO}_2)$ (10^{-4} s^{-1})
<i>Nozière et al., 1999</i>	900	0.3	100 : 0 : 0	298	3.5 (lamp)
<i>Kamens et al., 2001</i>	980	2.3	42 : 44 : 14	304	35 (sun)
<i>Hoffman et al., 1997</i>	95	0.8	45 : 33 : 22	315	83 (sun)
<i>Takekawa et al., 2003</i>	93	1.8	53 : 42 : 5	283	40 (lamp)
<i>Ng et al., 2006</i>	108	1.1	62 : 22 : 16	293	10 (lamp)
<i>Presto et al., 2005</i>	11	0.5	6 : 82 : 12	295	161 (lamp)

Figure 7 compares modelled and measured SOA yields for the laboratory experiments of α -pinene oxidation (Table 4). In most cases, SOA production is stabilized at the sampling time (1-3 hours after start of experiment). The model generally reproduces the measured yields to within 50%, a remarkable result considering the uncertainties on the vapour pressures and the use of a preliminary ozonolysis mechanism which lacks formation pathways for the most common acids which have been measured (pinic/hydroxy pinonic acid). Objective theoretical grounds are still lacking for the formation mechanisms of these acids, but they currently investigated in Leuven (Sect. 4.3.2). Note that the contribution of generic compounds is small ($\sim 20\%$) at the sampling time for most experiments. Differences in the vapor pressure estimations partly explain the larger SOA yields and the better agreement with the data in our model results, compared to previous modelling studies (*Jenkin, 2004; Chen and Griffin, 2005*). Another explanation is the more explicit treatment adopted in our mechanism for the chemistry of primary products, which generates a large variety of secondary products with different volatilities.

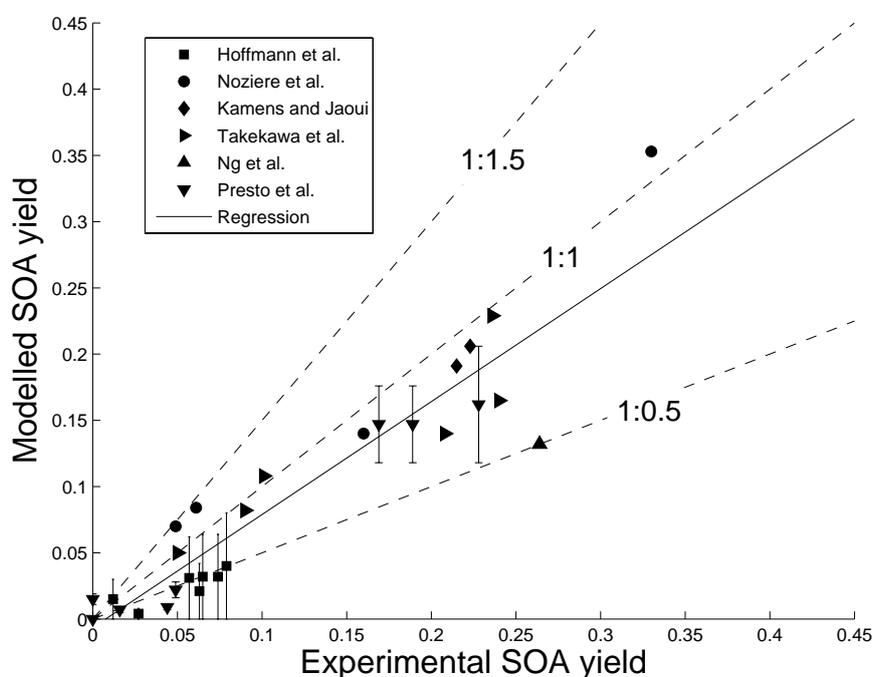


Figure 7. Modelled vs. measured aerosol yields in experiments of α -pinene photooxidation.

However, the comparison of the observed and simulated temporal profiles of SOA formation (Fig. 8) shows that aerosol formation starts systematically later in the model than in the observations. This might be due to the low yields of low-volatility acids in the ozonolysis mechanism, and/or to uncertainties in the vapor pressures of the products.

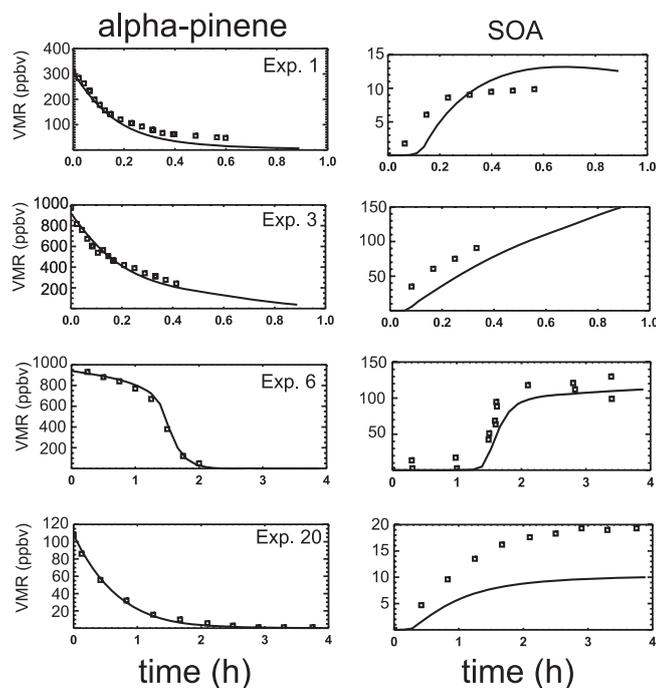


Figure 8. Time-dependent measured (squares) vs simulated (curves) concentrations of α -pinene (left) and SOA (right) in experiments from *Nozière et al.* (1 and 3), *Kamens and Jaoui* (6) and *Ng et al.* (20).

Multifunctional compounds are dominant in the modelled SOA. Hydroperoxides make up a large fraction of SOA in low NO_x conditions. Interestingly, the newly incorporated hydroperoxide compounds formed in the OH-initiated oxidation mechanism of α -pinene (see Sect. 4.3.1) are found to contribute significantly to SOA formation in the *Nozière et al.* experiments conducted in presence of NO_x . The lower vapour pressures of hydroperoxides compared to organic nitrates explain the increase in modelled SOA yields with decreasing NO_x , a result confirmed by the laboratory measurements of *Presto et al.* (2005). The contribution of generic compounds to the modelled SOA is significant, but not dominant in any case. This comforts the treatment adopted in BOREAM for the degradation of primary products. This conclusion would not hold at later times (e.g. after several days) when most gaseous and particulate primary products would have had enough time to be oxidized.

The model calculates that the ozonolysis produces about twice as much aerosol as the oxidation by OH in similar conditions, and the NO_3 -initiated oxidation is negligible, in agreement with *Griffin et al.* (1999). A more extensive discussion of the dependence of the SOA yields on photochemical conditions and temperature is provided in *Capouet et al.* (2007).

Figure 9 shows the aerosol mass formed in function of the reacted β -caryophyllene in the experiments by *Ng et al.*, 2006. The agreement is good, considering the very preliminary nature of the oxidation mechanism. *Ng et al.* have observed that aerosol production continues after complete conversion of the precursor. This feature is not well reproduced by the model, probably because of oversimplification in the chemistry of the highly reactive primary products. Note that the aerosol is mainly formed of unsaturated compounds. The model calculates that the reaction of ozone with particulate-phase compounds has a significant impact on the time scale of the experiments (3 hours).

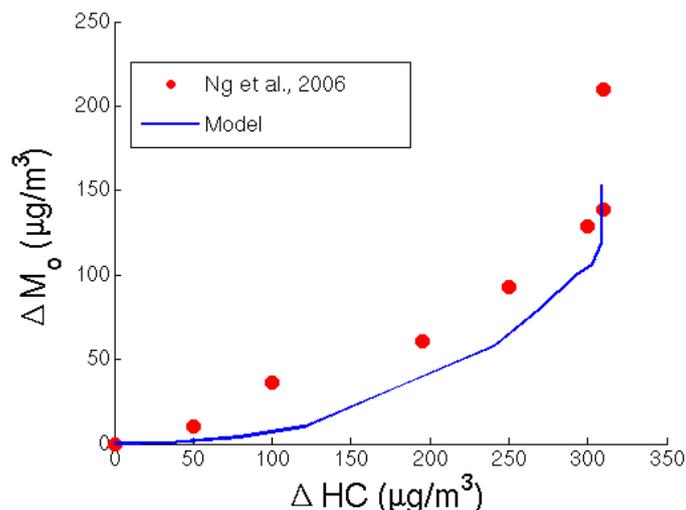


Figure 9. Secondary aerosol mass in function of the reacted β -caryophyllene.

4.5 Impact of oxygenates on the upper troposphere (Leuven)

4.5.1: T,P-dependence of reactions with oxygenates with OH

The reactions of oxygenates with OH are characterized by the formation of H-bonded pre-reactive complexes, affecting the energy of the abstraction transition states (TS); in certain cases this even lowers the abstraction TS to below the energy of the free reactants. Using formal kinetic rate theories supplemented by multi-conformer TST calculations and RRKM-ME analyses, we showed that two regimes exist depending on the energy of the abstraction transition states relative to the initial reactants. For TS above the free reactants, a positive T-dependence is expected, with no pressure dependence. Only at very low temperatures some curvature of the Arrhenius plot can occur due to tunnelling through the barrier; a typical example is the reaction of acetone with OH. For TS below the free reactants, negative temperature dependence is predicted, affected by the energy dependence of the competition between redissociation versus reaction of the pre-reactive complexes, the negative T-dependence of the initial, barrierless H-bond formation, and –to a lesser extent– tunneling. Typical examples include reactions of aldehydes or hydroxy-acetone with OH (Peeters and Vereecken 2006; a full paper is in preparation). Recently we showed that an intermediate regime can exist, provided that the barrier height is within a narrow region just below the energy of the free reactants, leading to a near-T-independence over fairly large T ranges. Experimental work by Crowley et al (MPI-Mainz), in a joint study with us, found glycolaldehyde to exhibit this extraordinary behaviour between at least 240K and 360K (Karunanandan et al., 2007).

These first-principle results are fully compatible with all the available experimental literature data on OH-initiated oxidation of partially oxygenated hydrocarbons, and represent the culmination of our theoretical work performed in previous years in the UTOPIHAN project and our collaboration with MPI-Mainz (Dr. J. Crowley).

In a continued experimental investigation of the $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{OH}$ reaction – begun under the PODO II program – we have now measured the branching fraction for the carboxyl-H-abstraction over a temperature range from 300 to 500 K, using the discharge-flow technique combined with molecular beam sampling mass spectrometry, finding this fraction to rapidly decrease from about 65% at 300 K to only some 10% at 500 K. Together with our recent experimental total rate coefficient data over the 300 - 800 K range (Khamaganov et al. 2006), this confirms the gradual transition from a low-T, tunnelling-assisted, acidic-H-abstraction proceeding through an H-bonded complex, to (direct) methyl-H abstraction at high T. New PLP-LIF measurements of the rate coefficients of both the $\text{CH}_3\text{C}(\text{O})\text{OH}$ and $\text{CD}_3\text{C}(\text{O})\text{OD}$ reactions with OH, over the 295 - 800 K range, fully corroborate these views, showing, among others, the much slower tunneling of D as compared to H. A second paper is in preparation.

4.5.2: Reactions of carbonyl-bearing compounds with HO₂-radicals

As a follow-up of our earlier work on the importance of the HO₂-initiated oxidation of formaldehyde

and acetone at the low temperatures of the tropopause (Hermans *et al.*, 2004 and 2005), theoretical studies have been conducted on reactions of the HO₂ radical with major (di-)carbonyl oxidation products of isoprene and terpenes. The rationale is that at these low temperatures the initial α -hydroxy-alkylperoxy adduct is stable enough to undergo subsequent, effective chemical degradation reactions with NO and HO₂. Present theoretical investigations on glyoxal and methylglyoxal have shown that such HO₂-initiated oxidation mechanisms can indeed constitute effective sinks for both these dicarbonyls near the tropopause. One key quantity for such schemes is the energy of the α -hydroxy-alkylperoxy adduct relative to carbonyl + HO₂ reactants; the *ab initio* computed value for methylglyoxal is consistent with earlier laboratory observations at room temperature (Staffelbach *et al.*, 1995). For glyoxal, we identified also a unimolecular pathway of the OCH-CH(OH)OO adduct to OH + CO + HC(O)OH; this route could play some role in laboratory experiments on glyoxal involving HO₂. A paper is to be submitted.

Directly in this context, we have also theoretically investigated the subsequent reactions of α -hydroxy-alkylperoxy adducts with HO₂. The aim was first to rationalize the recent new findings (Jenkin *et al.*, 2007) that the HOCH₂OO + HO₂ reaction also generates both the corresponding HOCH₂O radical and OH radicals, besides the corresponding hydroperoxide and the acid + H₂O. We have characterized the various reaction channels involved, occurring on the triplet and singlet PES surfaces, both proceeding through H-bonded pre-reactive complexes (PRC). Our theoretical study rationalizes all observed products and their branching ratios, and reproduces the experimental absolute magnitude and T-dependence of the rate coefficient (Burrows *et al.*, 1989). We predict rate coefficients at 210 K on both the singlet and triplet PES that are capture limited (i.e. formation of the PRC controls the rate), of order $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. These very high values will even enhance the efficiency of the carbonyl removal initiated by HO₂ near the tropopause, in particular at high HO₂ levels. A paper on HOCH₂OO + HO₂ is to be submitted. Studies of the HO₂ reactions of the α -hydroxy-alkylperoxy adducts from glyoxal and methylglyoxal + HO₂ are still in progress.

WP 7. Valorization and dissemination of results

As already mentioned, the complete α -pinene degradation mechanism has been published in a web page. It will be regularly updated.

4.7.1 Website for Structure-Activity-Relationships

A web site discussing the H-abstraction SAR is currently under development at http://arrhenius.chem.kuleuven.be/~luc/sar_habstr/header.html.

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5. PRELIMINARY CONCLUSIONS AND RECOMMENDATIONS

Structure-Activity Relationships (SARs)

The SAR for OH-addition on (poly)alkenes is now fully published, showing excellent predictive properties while remaining very easy in manual and automated use. It is recommended for use in model construction both for laboratory and atmospheric conditions. The SAR on alkoxy radical decomposition is currently the only available predictive tool spanning such an extensive set of substituents, and hence can aid model construction even if currently some caution is advised for substituents whose activity factors are determined on lower-level or a smaller number of calculations. The website for the H-abstraction SAR is in full development at the moment at http://arrhenius.chem.kuleuven.be/~luc/sar_habstr/header.html.

α -pinene mechanism

The α -pinene+OH oxidation mechanism developed in our previous project (2001-2005) in the context of the SSD program has been updated. Newly discovered reaction sequences cause the formation of low-

volatility multifunctional compounds which we believe can enhance the aerosol formation potential of α -pinene, in particular when OH is the main oxidant. These sequences are supported by hitherto unexplained laboratory measurements. This OH-initiated oxidation mechanism is complemented by preliminary O₃- and NO₃-initiated mechanisms, as well as by a parameterized treatment for the subsequent oxidation of the primary products. The resulting overall oxidation mechanism, published on a web page (www.oma.be/TROPO/boream/boreammodel), is the most comprehensive α -pinene mechanism to date, and will probably be the basis for future updates of the α -pinene mechanism of the Master Chemical Mechanism (MCM) developed at Leeds University in the UK. Note however, that the formation pathways of key low-volatility species in the ozonolysis mechanism (pinic acid and hydroxy pinonic acid) are still lacking, with important consequences regarding aerosol production (see further below). Different pathways proposed by other groups to explain pinic acid formation are much too inefficient to explain the laboratory measurements, according to our calculations. Investigations are currently under way at KULeuven to evaluate other possible routes. The update of the ozonolysis mechanism will be an important priority for IBOOT in the coming months.

β -pinene mechanism

Good progress has been made on the β -pinene+OH oxidation mechanism, with the elucidation of the dominant channels nearing finalization.

Aerosol modelling

Our modelling results for aerosol production from terpenes appear promising, in spite of the preliminary nature of the ozonolysis mechanism used, and the absence of parameterized particle-phase reactions at this stage. In contrast with previous modelling work, the aerosol yields from a large number of photooxidation experiments could be matched by the model, to within ca. 50% in most cases. The inability of the model to reproduce the correct temporal dependence of aerosol production in these experiments probably reflects the lack of formation pathways for key low-volatility compounds, and the uncertainties in the vapor pressures estimates of multifunctional products. The role of these uncertainties is currently under investigation. In addition, the possible role of peroxyhemiacetal formation in the particle phase, as well as the reaction of gas-phase ozone with unsaturated particulate products (e.g. from the newly proposed hydroperoxide products from the α -pinene+OH mechanism, see Vereecken *et al.* (2007)) could have a significant impact (Zahardis and Petrucci, 2007) and are therefore also investigated. Further work will be needed to improve the aerosol partitioning module, in particular regarding the activity coefficients (currently taken equal to one). Finally, confirmation of our model validation by laboratory data will be needed, when updated versions of the ozonolysis mechanism will be available.

β -caryophyllene ozonolysis

The components of the organic aerosol formed from the ozonolysis of β -caryophyllene have been characterized experimentally. A methodology was developed to detect not only carboxylic acids, but also aldehydes. This extends the range of detectable products, since many species theoretically formed from the ester channels of the Criegee Intermediates bear an aldehydic group. The high ionization efficiency of carbonyl groups in APCI+ allowed us to compare the trace of each anion with its corresponding cation, to give complementary information about the identity of the product. In depth analysis of CID spectra of anion-cation pairs led in some cases to unequivocal structural determination. In other cases where chromatographic co-elution was observed, structural determination of important isomeric oxidation products could be achieved. Besides the detected oxo- and dicarboxylic acids, multi-functional isomeric products bearing e.g. aldehydic, carbonyl and hydroxyl groups could be differentiated by examining their CID fragmentation pathways. Fragmentation mechanisms were proposed for the experimentally observed ions in all the CID experiments. Gas phase deprotonation potentials were calculated by DFT to estimate the most thermodynamically favourable deprotonation site for efficient negative ion formation in Electrospray.

The OH-radical yields and rate constants for ozone attack on the double bonds in β -caryophyllene and α -humulene were determined. For β -caryophyllene, the OH yield from the second double bond was twice as large (21 %) as for the first more reactive double bond (8.5 %). For α -humulene, both double bonds gave the same OH yield of 10 %.

The potential applicability of LC-MS-MS-TOF for the detection of standard peroxides was

investigated, with negative results. H_2O_2 and simple α -hydroxy-hydroperoxides could be measured by HPLC. The yields of H_2O_2 were found to be 2 to 4 % for β -caryophyllene, and four times larger for α -humulene. In the aerosol phase also significant quantities of long-chain hydroperoxides (C_6 to C_{12}) were detected, with a relative yield of 12 % compared to H_2O_2 .

Although the detected products in these laboratory experiments do not provide unambiguous information on the precise oxidation pathways occurring in the reactor, their nature will represent useful constraints in the development of oxidation mechanisms using theoretical means, in particular with regard to the fate of the Criegee Intermediates. This development will be made possible by the ongoing advances in the realization of accurate Structure-Activity Relationships for important classes of chemical reactions, as well as by the high-level theoretical calculations aiming at determining the fate of key specific intermediates produced in the degradation of the terpenes.

The aerosol yield from β -caryophyllene ranged from 6 to 24 % in the absence of CI-scavenger, while in the presence of CI-scavenger such as HCOOH , HCHO and H_2O the yield ranged from 9 to 41 %. The SOA yield was also found to depend on aerosol mass.

Oligomer formation involving Criegee Intermediates, first observed in the ozonolysis of a variety of enol ethers, has been shown to occur for small symmetric alkenes in an analogous way. It is proposed that an oligoperoxide with repeating unit $-\text{[CH(R)-O-O]}_n-$ is formed. Future work will elucidate the possible formation of oligomers from sesquiterpene ozonolysis.

Reactions of oxygenates with OH

Our extensive study of the acetic acid + OH reaction is completed. The product and kinetic measurements, including kinetic isotope effects, supported by theoretical analyses, confirm tunneling-assisted acidic-H abstraction in the doubly-hydrogen-bonded pre-reactive complex as the major channel at and below room temperature, switching however to methyl-H abstraction above 500 K. An additional paper is in preparation. Generally, OH reactions with oxygenates are found to proceed through H-bonded complexes. A general theoretical analysis shows that temperature and pressure dependences depend on the energy of the final H-abstraction TS lying above or below the reactant level. A paper is in preparation.

Reactions of oxygenates with HO_2

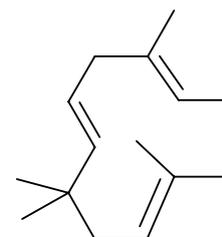
Theoretical work shows that, similar to formaldehyde and acetone, HO_2 -initiated oxidation processes can contribute significantly to removal of glyoxal and methylglyoxal at the low temperatures near the tropopause (applicable only insofar there are local sources of these dicarbonyls). Furthermore, the subsequent reactions of HO_2 with the hydroxyalkylperoxy adduct radicals (from HO_2 + carbonyls) were theoretically confirmed to also proceed via radical-forming channels (mainly OH), and were shown to exhibit a strongly negative T-dependence, such that their rates approach the capture rate constant at tropopause temperatures. A paper is in preparation.

6. PROSPECTS AND PLANNING UNTIL THE END OF PHASE 1

Task 1.1: Products and reaction mechanism of the reaction of ozone with the sesquiterpenes α -humulene and β -caryophyllene

The ozonolysis of β -caryophyllene will be further investigated in order to elucidate the reaction of the stabilized Criegee-Intermediate with H_2O , HCOOH and HCHO , since stabilization appears to be the major channel for the excited Criegee-Intermediate.

Simultaneously, the ozonolysis of α -humulene will be investigated. The oxidation products will be characterized using electrospray and APCI ionization sources. Oxidation products generated through ozonolysis of two and three double bonds will lead to bond breakages yielding C_{10} and C_5 oxidation products, respectively. The chromatographic separation and detection of those products with different backbones will represent a big challenge in the chemical analysis.



Task 1.4: Formation of oligomers and polymers from mono- and sesquiterpene-ozonolysis

Oligomer formation during ageing of aerosol particles or in the presence of acidic seed aerosol increases the aerosol yields. Oligoperoxide formation involving Criegee-Intermediates, first observed in the ozonolysis of enol ethers, was shown to occur for small symmetric alkenes in an analogous way (Herrmann, 2006; Stenby *et al.*, 2007). Therefore the formation of oligomers and polymers from ozonolysis of mono- and sesquiterpenes will be investigated in the presence and absence of seed aerosol. The potentially formed oligomers or polymers will be analyzed by LC-MS-MS-TOF. Specially designed extraction procedures will be developed, since the so far proposed polymers might easily be hydrolyzed upon extraction of the filter samples with water/methanol.

Task 2.1 – 2.4: Development of predictive theoretical tools (SARs)

The main activities in the coming months will be the quantum chemical calculations on the H-abstraction SAR, the finalization of several software modules related to SAR development and automated generation of the SAR website, and migration of the alkoxy decomposition SAR to the ScienceProject software framework..

Task 3.1 – 3.2 Development of oxidation mechanisms for mono- and sesquiterpenes

The new chemistry developed for the α -pinene degradation will also be incorporated into the OH-initiated oxidation mechanism of β -pinene. The theoretical investigations on the ozonolysis mechanisms of α - and β -pinene will be continued. Much attention will be paid thereby to identify formation mechanisms of low-volatility SOA precursors such as pinic acid and hydroxy-pinonic acid. After completion, the ozonolysis of α -humulene will be addressed.

Task 3.3: Mechanism implementation in box model and confrontation with laboratory data

The updates of the α -pinene ozonolysis mechanism (see above) will be implemented in the box model, and their effects on the yields of the products will be estimated.

Task 4.1: Thermodynamic properties of organic oxygenates

A recently proposed update of the UNIFAC method for the estimation of activity coefficients (Erdakos *et al.*, 2006) will be tested and implemented, if found applicable. Since this method currently does not consider the effect of the nitrate and (hydro)peroxide functional groups, the availability of additional data will be determined.

A method will be also developed to estimate the Henry's law solubilities of the stable products in the oxidation of terpenes, based on experimental data (e.g. review of Sander, 1999).

Task 4.2: Multiphase partitioning model development

The activity coefficient calculation module (cf. Task 4.1) will be implemented in the partitioning model. The methodologies proposed by Griffin *et al.* (2003) and other recent model studies for estimating the amount of liquid water in the aerosol will be reviewed and tested. This will allow us in a later step (during Phase 2 of this project) to represent the partitioning of water-soluble oxygenated products of terpene oxidation between the gaseous, organic and aqueous phases.

Task 4.3: Validation of aerosol model by simulation of laboratory experiments

The impact of the model updates (Tasks 3.3 and 4.2) on the simulations of laboratory experiments will be estimated. In addition to the experiments already considered (cf. Section 4 of this Report), ozonolysis experiments in the dark and with OH-scavengers will be used for this comparison, in order to better evaluate the updates in the ozonolysis mechanism.

Task 4.4: Exploratory study of heterogeneous reactions in organic aerosols

The aerosol phase association reactions suggested from experimental investigations, and recently modeled for aerosols formed in the degradation of aromatic compounds (Johnson *et al.*, 2004; 2005) will be implemented in the model, and its impact on the yields and composition of aerosol from α -pinene will be evaluated.

The impact of the reactions of gaseous ozone with unsaturated aerosol products will be investigated based on the ozone-oleic acid studies of Zahardis and Petrucci (2006) and other groups. The formation of high-molecular mass compounds from such reactions will be implemented in the model for the high-yield unsaturated hydroxy-hydroperoxides formed from the reaction of α -pinene with OH.

Task 5.1: Reactions of oxygenates with OH

The experimental and theoretical study of the acetic acid + OH reaction will be finalized, and a third paper on the kinetics and mechanisms of this reaction will be submitted. A general paper will be prepared on the temperature- and pressure dependence of the rate constants of OH + oxygenates reactions proceeding through hydrogen-bonded pre-reactive complexes.

Task 5.2: Reactions of oxygenates with HO₂

A theoretical paper will be submitted on the mechanisms and kinetics of the subsequent reactions between HO₂ radicals and the hydroxyalkylperoxy radicals formed prior by HO₂ addition to carbonyl compounds. Of major importance are the radical forming channels of these reactions, and the high rate coefficients at tropopause temperatures.

7. FOLLOW-UP COMMITTEE

T. Hoffmann has been in regular contact with the team in Mainz. He has provided guidance in particular on the products and mechanism of sesquiterpenes ozonolysis (master Thesis of Frank Hermann).

R. A. Cox is member of the MCM Data Panel, having the mission to discuss the future improvements in the MCM (Master Chemical Mechanism) which is increasingly being acknowledged as the premier link between laboratory data and modeling. During a recent meeting (July 2007) of this Data Panel, which includes L. Vereecken (K.U.Leuven), virtually every aspect of the IBOOT program was touched. Databases of available data were compiled by members of the Data Panel and transferred to Leuven, significantly helping further extension of the SARs. LV proposed the OH-addition SAR for use in the MCM, and the alkoxy decomposition SAR for those compounds not supported in the currently used SAR. Certain reaction classes, e.g. peroxy radical isomerisations, will be incorporated in the MCM, in line with the new chemistry in the updated α -pinene+OH mechanism. Given the excellent results of the α -pinene modeling (BIRA), sections of the BOREAM mechanism are expected to migrate to the MCM.

8. PUBLICATIONS / VALORIZATION

8.1. Publications of the teams

8.1.1. Peer review

R. Karunanandan, D. Hölscher, T.J. Dillon, A. Horowitz, J.N. Crowley, **L. Vereecken, J. Peeters**
Reaction of HO with Glycolaldehyde, HOCH₂CHO: Rate Coefficients (240 - 362 K) and Mechanism
J. Phys. Chem. A, 111, 897-908, 2007.

J. Peeters, W. Boullart, V. Pultau, S. Vandenberk, **L. Vereecken**
Structure-Activity Relationship for the Addition of OH to (poly)Alkenes : Site-specific and Total Rate Constants
J. Phys. Chem. A, 111, 1618-1631, 2007.

S.A. Carl, L. Vereecken, J. Peeters
Kinetic parameters for gas-phase reactions: Experimental and theoretical challenges
Phys. Chem. Chem. Phys., doi:10.1039/b705505f, 2007.

T.J. Dillon, A. Horowitz, D. Hölscher, J.N. Crowley, **L. Vereecken, J. Peeters**
Reaction of HO with Hydroxyacetone (HOCH₂C(O)CH₃): Rate Coefficients (233 - 363 K) and Mechanism
Phys. Chem. Chem. Phys., 8, 236-246, 2006.

V.G. Khamaganov, V. Xuan Bui, **S.A. Carl, J. Peeters**
Absolute Rate Coefficient of the OH + CH₃C(O)OH Reaction at T = 287-802 K. The Two Faces of Pre-reactive H-Bonding
J. Phys. Chem. A, 110, 12852-12859, 2006.

A. Römpp, R. Winterhalter and G. K. Moortgat
Oxodicarboxylic acids in atmospheric aerosol particle
Atmos. Environ., 40, 6848-6862, 2006.

C. Stenby, U. Pöschl, P. Von Hessberg, M. Bilde, O. J. Nielsen and G. K. Moortgat,
Temperature and humidity dependence of secondary aerosol yield from the ozonolysis of β-pinene
Atmos. Chem. Phys. Discuss., 7, 2091-2132, 2007.

A. Sadezky, P. Chaimbault, A. Mellouki, A. Römpp, R. Winterhalter, G. Le Bras and G. K. Moortgat
Formation of secondary organic aerosol and oligomers from the ozonolysis of enol ethers
Atmos. Chem. Phys. Discuss., 6, 5629-5670, 2006.

M. Capouet, J.-F. Müller
A group contribution method for estimating the vapour pressures of alpha-pinene oxidation products,
Atmos. Chem. Phys., 6, 1455-1467, 2006.

Kanawati, B., S. Joniec, R. Winterhalter and G. K. Moortgat
Mass spectrometric characterisation of small oxocarboxylic acids and gas phase ion fragmentation mechanisms studied by Electrospray Triple Quadrupole-MS/MS-TOF system and DFT Theory
J. Mass Spectrom., in press, 2007.

submitted :

T. L. Nguyen, L. Vereecken, J. Peeters
HO₂-initiated oxidation of glyoxal, methylglyoxal and glycolaldehyde in atmospheric and laboratory conditions : a theoretical study
J. Phys. Chem. A, submitted, 2007.

Kanawati, B., F. Herrmann, S. Joniec, R. Winterhalter, and G. K. Moortgat
Mass spectrometric characterisation of β-caryophyllene ozonolysis products in the aerosol studied by Electrospray Triple Quadrupole-MS/MS-TOF system and DFT theory, Rapid Comm. Mass Spectrum, submitted, 2007.

Kanawati, B., S. Joniec, R. Winterhalter and G. K. Moortgat
Mass spectrometric characterisation of 4-oxocarboxylic acid and gas phase fragmentation mechanisms studied by Electrospray Triple Quadrupole-MS/MS-TOF system and DFT theory, J. Mass Spectrom., submitted, 2007.

Related work :

J.-F. Müller, T. Stavrou, S. Wallens, A. Guenther, M. Potosnak, J. Rinne, B. Munger, A. Goldstein
Global isoprene emissions estimated using MEGAN and a detailed canopy environment model
Atmos. Chem. Phys., submitted, 2007.

I. Hermans, P.A. Jacobs, J. Peeters
To the Core of Autocatalysis in Cyclohexane Autoxidation
Chem. Eur. J., 16, 4229-4240, 2007 (VIP paper and cover)

I. Hermans, J. Peeters, P.A. Jacobs,
Autoxidation of ethylbenzene: The mechanism elucidated
J. Org. Chem., 72, 3057-3064, 2007.

I. Hermans, P.A. Jacobs, J. Peeters
The formation of byproducts in the autoxidation of cyclohexane
Chem. Eur. J., 13, 754-761, 2007.

8.1.2. Others

M. Capouet
Modeling the oxidation of alpha-pinene and the related aerosol formation in laboratory and atmospheric conditions
PhD Thesis, Université Libre de Bruxelles, 2006.

F. Herrmann
Produkte und Reaktionsmechanismen des Sesquiterpeneozonolyse
Diplom Thesis (Master) at Johannes-Gutenberg University Mainz, December 2006.

8.2. Co-publications

8.2.1. Peer review

L. Vereecken, J.-F. Müller, J. Peeters
Low-volatility poly-oxygenates in the OH-initiated atmospheric oxidation of α -pinene: Impact of non-traditional peroxy radical chemistry
Phys. Chem. Chem. Phys., in press, 2007.

submitted :

M. Capouet, J.-F. Müller, K. Ceulemans, S. Compernelle, L. Vereecken, J. Peeters
Modeling Aerosol Formation in Alpha-pinene Photooxidation Experiments
submitted to J. Geophys. Res., 2007