# ABSTRACT

The composition of the troposphere is strongly affected by biogenic and anthropogenic emissions of chemical compounds, including hydrocarbons, carbon monoxide, and the nitrogen oxides. The emissions of non-methane hydrocarbons, in particular, have a large impact on the oxidizing capacity of the atmosphere (which determines the fate and lifetime of a large number of pollutants and greenhouse gases) and on the budget and distribution of tropospheric ozone and aerosols. These compounds are therefore key actors in both air quality and climate change issues. The terrestrial vegetation represents by far their largest source on the global scale. Foliar emissions include isoprene ($C_5H_8$), monoterpenes ($C_{10}H_{16}$) and other compounds.

Whereas the chemistry of isoprene is relatively well established and realistic mechanisms for its atmospheric oxidation are included in many chemistry-transport models, the degradation of monoterpenes remains speculative at this stage. Due to the low volatility of a number of their oxidation products, monoterpenes are considered as important precursors of organic aerosols in the atmosphere. In addition, acetone, a known oxidation product of several monoterpenes, is believed to be an important source of radicals in the region of the tropopause, and to influence the budget of ozone and hydroxy radicals. Due to the cold temperatures and low pressures prevailing in this region, however, the precise influence of acetone and other oxygenated organic compounds is uncertain, due to the possibility of unexpected behaviour of key reactions in the conditions typical of the tropopause.

In this project, the impact of monoterpenes and other key organic compounds on the formation of oxidants and aerosols has been investigated through a combination of laboratory, theoretical and modelling studies.

Experimental techniques developed in Leuven in a previous project (under the PODO 1 programme) have been further elaborated in both Leuven (C.V.) and Brussels (E.A.) to study the reaction of important monoterpenes (α- and β-pinene, $\Delta^3$-carene and limonene) with hydroxyl radicals (OH) in presence of oxygen (20%) and under reaction pressures of 50-200 Torr. These reactions have been studied in fast flow reactors equipped with a microwave discharge as clean OH radical source. In order to clarify the role of the terpene chemistry a major challenge is the identification and quantification of the semi-volatile compounds formed as oxidation products.

In the study conducted in Leuven (C.V.), these products are collected on a liquid nitrogen trap and "derivatized" prior to analysis. Reaction products are identified and quantified using two complementary techniques, HPLC-MS and HPLC-DAD. New ionization techniques have been explored (for HPLC-MS), and appropriate analytical methods have been developed. The following products are found in the reaction of β-pinene with OH: formaldehyde, acetaldehyde, acetone, trans-3-hydroxynopinone, nopinone, perilla alcohol, perillaldehyde and myrtanal, with formaldehyde and nopinone the most important ones. Caronaldehyde is identified as the most important reaction product in the $\Delta^3$-carene+OH reaction, together with formaldehyde and acetone. For limonene, endolim is identified as the dominant product together with 4-AMCH, formaldehyde and acetone. The relative yields have been determined under a variety of experimental conditions. The impact of variations in the reaction time, reaction pressure, nitric oxide concentration, initial hydrogen concentration and OH/terpene concentration ratio on the product yields has been investigated. Finally, a kinetic reaction study of the α-pinene+OH reaction has been carried out. It suggests that a large number of polyfunctional products (such as hydroxyperoxides) could not be detected, possibly representing as much as 50% of the total on a molar basis. This problem should be solved in future studies by using our newly developed HPLC-$MS^n$ technique coupled with a suitable ionisation source (ESI or APCI).

In the study conducted in Brussels (E.A.), the organic reactant and its products are led into a chemical ionization mass spectrometer (CIMS) where they react with appropriate precursor ions (e.g. $H_3O^+$, $NO^+$, $CH_3O^-$ or $SF_6^-$). The ion/molecule reactions result in specific product ions which are the "fingerprints" of the molecules to be detected. A low pressure fast-flow reactor has been used in the first stage of the project. It has been replaced later on by a high pressure turbulent flow reactor, which combines the advantage of efficient mixing with the possibility to perform experiments at higher pressures (200 Torr). Since absolute and accurate CIMS-based quantification requires the knowledge of the rate constants and product ion distributions of the relevant ion/molecule reactions, these parameters have been measured in a selected ion flow tube instrument (SIFT), and confirmed by theoretical calculations in collaboration with Leuven (J.P.). The characterization of ion/molecule reactions for the monoterpenes, for their oxidation products and for a large number of other oxygenated organics constituted an important part of the work in this project. The absolute yields of the main oxidation products (acetone, formaldehyde, pinonaldehyde and nopinone) in the reactions of α-pinene (at 2 and 50 Torr) and β-pinene (at 200 Torr) with OH have been determined in varied conditions.

An extensive theoretical and mechanistic study of the OH-initiated oxidation of α-pinene, pinonaldehyde and β-pinene has been conducted in Leuven (J.P.). On objective theoretical grounds, the fate of the many oxy radicals involved in these mechanisms has been predicted. This work is based on objective chemical kinetics knowledge, or quantitative structure-activity relationships (SARs)—some of which were further developed in this project—and *ab initio* or density functional theory (DFT) barrier heights and rotation/vibration parameters, in combination with statistical rate theories. Based on these studies, we have developed detailed mechanisms for the OH-initiated oxidation of α-pinene, pinonaldehyde and β-pinene. Our mechanisms describe the chemistry of all existing OH addition and H abstraction pathways. This work led us to discover novel reaction pathways, which were entirely overlooked so far. These non-traditional "ring closure" reactions of oxy and peroxy radicals were never reported in laboratory conditions, but are nonetheless important or even crucial in the oxidation of isoprene and many monoterpenes in the real atmosphere, due to the lower concentrations of radicals in the atmosphere compared to the laboratory. In typical experimental setups, the ring closure reactions are usually outrun by other reactions.

The total product yields (obtained by propagating the product fractions in each step of the mechanism) are in good general agreement with experimental values, with the exception of the formaldehyde yield in the oxidation of pinonaldehyde, which is about one order of magnitude lower than the only reported experimental result (very high value that remains unconfirmed). We have performed a critical evaluation of the few mechanisms available in the literature, especially concerning the steps leading to the main products. The same methods have been also applied, to a more limited extent, to the ozonolysis of α-pinene.

The α-pinene mechanism described above has been generalized and implemented in a chemical "box" model (J-F.M., J.P.). We have estimated the rates of the photolysis processes and of the peroxy radical reactions involved in this mechanism on the basis of a detailed literature survey. The impact of the numerous permutation reactions of peroxy radicals is accounted for by including the reactions of each individual radical with pseudo-species representing radical classes. We have validated the mechanism and the model against the series of ~40 photooxidation experiments performed by Nozière *et al*. (1999). The model performs well for all species, except acetone in the absence of NO. This is a probable consequence of the non-explicit treatment of the chemistry following specific reactions in the mechanism (ring closure, oxidation of primary products). Based on the explicit mechanism (2000 reactions), a reduced mechanism of only ~100 reactions has been designed, suitable for use in 3-dimensional models.

We have developed a model for calculating the partitioning between the gas and particulate phases of the monoterpene degradation products (J-F.M.). It relies on the estimation of the vapor pressures of organic compounds according to group contribution principles. The method has been adjusted by using a large set of vapor pressure measurements. It is found to be of comparable or better performance than a widely used prediction method, UNIFAC. Since pinic acid can be expected to be mostly present as dimer in laboratory conditions, we suggest that the partial vapor pressure of this dimer should be close to the experimental subcooled vapor pressure for pinic acid. Results from ozonolysis experiments have been used to test both the mechanism and the gas-particle partitioning model. The total aerosol concentration observed by one group is fairly well reproduced by the model, in contrast with the yields observed by another group at higher temperatures.

We have determined the product distribution of the controversial elementary reaction of acetone with OH radicals in flow reactors by molecular beam sampling mass spectrometry in Leuven (J.P.) and by the CIMS technique in Brussels (E.A.; see above). Recent reports had indicated that this reaction proceeds for ~50% by a mechanism leading to acetic acid, with potentially significant implications for the chemistry of the upper troposphere. However, our direct measurements of the acetic acid yield show unequivocally that this reaction path is minor (<5%) and that the H-abstraction path is the only route of importance. We have also performed theoretical calculations (J.P.) which confirm this result and explain the negative temperature dependence of the reaction rate at low temperatures.

Similarly, we have shown (J.P.) by direct measurements that the elementary reactions of OH with acetaldehyde and propionaldehyde proceed for >90% by H-abstraction and, again contrary to earlier reports, do not yield acids in any significant amount; this finding is of key importance for the budget of peroxyacylnitrates (PAN) in the atmosphere. The elementary reaction of OH with acetic acid was found to yield directly 65% $CH_3$ + $CO_2$, consistent with our theoretical predictions; in addition, we confirmed the strongly negative temperature dependence of the total rate coefficient, of importance for Upper Troposphere chemistry models.

Carbonyls are usually assumed to either photodissociate or react with OH radicals in the atmosphere. In this project, we have shown by state-of-the-art theoretical calculations that their reactions with $HO_2$ radicals might play a significant role in the vicinity of the tropopause (J.P.; J-F.M.). The peroxy radicals formed by these reactions can either decompose back to the original reactants or undergo other reactions leading for the largest part to the formation of carboxylic acids. The strong temperature dependence of the decomposition rates explains the negligible impact of the overall reaction sequence throughout most of the troposphere (at T>~220 K). We have assessed the potential significance of these reactions for formaldehyde and acetone by three-dimensional model calculations. Their contribution to the overall sink of these compounds is calculated to reach ~30% or more in the tropical tropopause region, with significant effects on the levels of OH and $HO_2$ radicals.

We have developed a detailed vegetation canopy model for estimating the temperature and radiative fluxes at the leaf level (J-F.M.). By this way, the widely used algorithms of Guenther *et al*. (1995) for the calculation of biogenic emissions could be evaluated against flux measurements from selected campaigns, and alternative algorithms have been tested. A good model performance is noted, except at an Amazonian site and at a mid-latitude site in spring and autumn, where the model largely overestimates the fluxes. Based on the canopy model and on available climatologies for meteorological and vegetation parameters, the global emissions of isoprene and monoterpenes have been estimated at a resolution of 0.5°. The calculations show that the leaf/air temperature difference might enhance the emissions by 30% or more in subtropical areas during the dry season.

An alternative approach for estimating the emissions of reactive compounds has been developed, using a global chemistry-transport model (J-F.M.). The emissions in the model are optimized by minimizing the bias between the model predictions and a set of atmospheric observations. The innovative aspect of our study lies in the use of the adjoint model technique. This method has been successfully applied to the optimization of the carbon monoxide and nitrogen oxides emissions. The method is also appropriate for estimating the emissions of biogenic volatile organic compounds based on satellite observations of their oxidation by-products formaldehyde and carbon monoxide.

Finally, the global model IMAGES has been used (J-F.M.) to predict the composition of the troposphere for present-day as well as for future conditions, in the framework of model intercomparisons supervised by IPCC. These simulations are based on different anthropogenic emission scenarios. These scenarios reflect possible future population, economic and technological changes, including the effect of regulations aimed at mitigating the adverse effects of these emissions. The results of these studies are part of the latest IPCC-TAR report.

**Keywords**: troposphere, ozone, secondary organic aerosols, biogenic emissions, volatile organic compounds, oxidation mechanisms, oxidizing capacity of the atmosphere