

FINAL REPORT PROGRAM LEFE

Program LEFE - CHAT	Project Title <i>Dégradation atmosphérique des Produits d'Oxydation de première génération des Monoterpènes (DPOM)</i>	Years 2019 – 2021
PI : Adelhaleq CHAKIR, GSMA UMR 7331 abdel.chakir@univ-reims.fr Participating Laboratories : -Institut Mines-Télécom Lille Douai, -Institut de Physique de Rennes, UMR 6251 CNRS, Rennes	Other funding sources: - PhD (M. Fakhri 2020-2023) grant from Reims University Champagne Ardennes. - M2 internship (M. Fakhri, 2020, 5 months) - M2 internship (A. El-DIB 2019, 5 months) - M2 internships SAGE (N. Aloui 2020, 4 months, F. Saafet 2021, 6 months) - TNA Eurochamp2020 in 2021 & TNA Atmo-Access (SAGE) at Cernesim lab (Romania), 4 weeks	
<p>Context: Monoterpenes play an important role in tropospheric chemistry. Atmospheric degradation of these compounds leads to the production of first-generation mono and dicarbonyl compounds with significant yields such as keto-aldehydes and cyclic ketones. Thus, more information regarding the atmospheric reactivity of these compounds toward atmospheric oxidants is needed.</p> <p>Objectives: The objectives announced in the project were: (i) the determination of rate constants, at different temperatures, of reactions between selected compounds and atmospheric oxidants (OH radicals, ozone); (ii) the development of reaction schemes for the photo-oxidation of these compounds by OH radicals and by ozone; (iii) the determination of SOA formation potential, nucleation thresholds, and aerosol yields; (iv) the determination of the UV absorption spectra of the selected compounds and the evaluation of the importance of the photolysis pathway of the studied compounds.</p> <p>Main results: The objectives fixed by this project have been achieved except for mechanistic studies of the reactions between the targeted compounds and OH-radicals; instead, kinetic oxidation of the investigated compound by Cl-atoms at different temperatures has been investigated. In addition, since some compounds were not available at the start of the project (synthesis needed), the OH and O₃ kinetics of two other oxygenated terpenes (verbenone and 4-terpineol) were also investigated.</p> <p>A) Photolysis studies The UV absorption spectra of nopinone, myrtenal, ketolimonene, caronaldehyde and limononaldehyde were investigated in the spectral range 210-370 nm at 353 K. All the spectra show an important absorption band beyond 290 nm (Figure 1), meaning that these species absorb solar radiation reaching the troposphere and could be photolyzed in the atmosphere. The natural lifetimes estimated using cross-sections were within a few hours during the daytime. Thus, photolysis could be an important loss process of these compounds in the troposphere inducing a relatively low atmospheric persistence considering a quantum yield of one for the calculation of the photolysis rate. Photolysis experiments were carried out on limononaldehyde, showing that this compound might be photolyzed in the atmosphere, with an estimated photolysis lifetime of about 10 days.</p> <p>B) Kinetic Studies</p> <p>Ozonolysis – Experimental kinetic studies as a function of temperature were carried out to investigate the ozonolysis of myrtenal, ketolimonene, and limononaldehyde, over the temperature range 298-353 K. These species are highly reactive towards ozone. At room temperature, rate coefficients vary between (1 to 10) × 10⁻¹⁷ molecule⁻¹ cm³ s⁻¹. The rate coefficient for limononaldehyde ozonolysis is approximately 10 times lower than ketolimonene ozonolysis; this shows that the degree of substitution of the olefinic bond impacts the reactivity of this process. Conversely, 4-terpineol shows a much higher rate constant of 3×10⁻¹⁶ molecule⁻¹ cm³ s⁻¹ while verbenone is almost unreactive towards ozone (although verbenone is unsaturated) with a rate constant < 4×10⁻²⁰ molecule⁻¹ cm³ s⁻¹. Thus, the kinetics seems sensitive to the investigated compounds' chemical structure. Concerning the T dependence of the rate constant, as expected, a significant temperature effect on this process is observed with an activation energy of 16 to 25 kJ mol⁻¹.</p> <p>Several experiments were performed to identify and quantify the ozonolysis products of ketolimonene and myrtenal. The analyzes were performed by PTR-MS-TOF, in situ FTIR, and GC/MS/SPME. Secondary organic aerosol (SOA) formation was also observed for ketolimonene, limononaldehyde, and 4-terpineol. A CHARON inlet coupled to PTR-MS was used for SOA analyses (ketolimonene only). The main products are formaldehyde, glycoaldehyde, glyoxal, methylglyoxal, these species are formed with yields of 20 to 80%. Other products have been identified and quantified, more than twenty multifunctional compounds in C₄ to C₈; their yields of formation vary from 1 to 10%. C₉ compounds bearing up to 6 oxygen atoms were detected in the condensed</p>		

phase (ketolimone). Using these results, the reaction mechanisms of the studied reactions were elaborated.

OH and Cl-atoms oxidation – The reaction of OH radicals and Cl atoms with nopinone, myrtenal, ketolimone and limononaldehyde have been investigated experimentally, over the temperature range 298-353 K. Verbenone and 4-terpineol OH kinetics at room temperature were also determined. These processes' rate constants exhibited no or low temperature dependence under our experimental conditions (Figure 2). The kinetics of the reaction of OH-radical with the investigated compounds was found to be sensitive to their structures whereas, rate coefficients of the reaction of Cl atoms with these species are of the same order of magnitude, showing that chemical structure weakly impacts the reactivity of these compounds toward chlorine atoms. The reactions of OH radicals with nopinone and myrtenal have also been investigated theoretically using the Density Functional Theory (DFT) method, M06-2X/6-311++G(d,p) basis set. The rate coefficient of the reaction is calculated using canonical variational transition state theory (CVT) with a small curvature tunneling method. These calculations allowed us to establish the energy diagram (Figure 3) of the studied reactions. By analyzing this diagram, the branching ratios of the different reaction pathways were determined.

In terms of atmospheric implications, this project shows that the contribution of the different processes in the elimination of the investigated compounds is of the same order of magnitude. The tropospheric lifetimes of these species are estimated of about a few hours. Mechanism reaction studies show that the atmospheric degradation of these compounds leads to the formation of numerous oxygenated multifunctional compounds, which results in the formation of SOA and an increase in the oxidizing capacity of the troposphere.

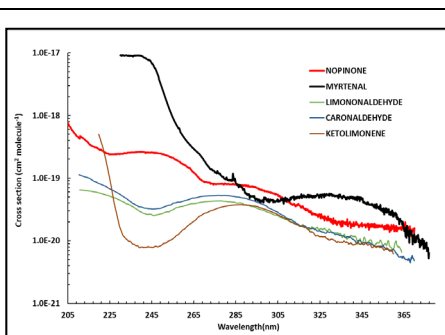


Figure 1

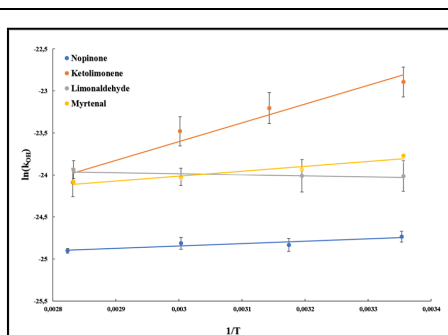


Figure 2

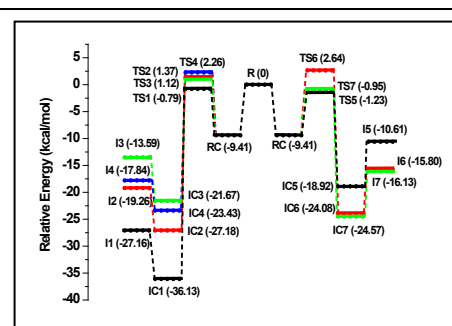


Figure 3

Figure 1: UV absorption spectra of Nopinone, Myrtenal, Limononaldehyde, Caronaldehyde and Ketolimone in the spectral range 205-370 nm.

Figure 2: Arrhenius plot of rate constants for the reaction of OH radicals with Nopinone, Myrtenal, Limononaldehyde, and Ketolimone.

Figure 3: Relative Energy Profile of Initial H-atom abstraction of the reaction of nopinone with OH.

Future of the project:

These studies will be continued within the framework of an ANR (AF2OM) project, since January 2023, and whose objective is to study the atmospheric fate of the oxygenated biogenic organic compounds and their implication on ozone budget and aerosol properties. In addition, another LEFE-Chat project is in progress implying three labs (IMT, IPR, GSMA); it concerns the atmospheric reactivity of other oxygenated biogenic compounds such as unsaturated monoterpene alcohols.

These studies will also be continued in the frame of the current post-doctoral research project at IPR-Rennes under the MOPGA 2022-2023 Visiting Fellowship Program (laureate Dr. Mano Priya Angappan).

Nombre de publications, de communications et de thèses

Publications: 2 in press and 7 publications in preparation; Communications: 7 ; 1 PhD thesis ; 4 M2 internships.

1- Gas-phase UV absorption spectra of a series of of terpenic oxygenated VOC: Nopinone, Myrtenal, Ketolimone, Limononaldehyde and Caronaldehyde. M. Fakhir, E. Roth, S. Gatard, R. Plantier-Royon, A. Chakir. Chemical Physics Letters, Volume 803, 16 September 2022, 139832, <https://doi.org/10.1016/j.cplett.2022.139832>.

2- Investigation of the Gas-Phase Reaction of Nopinone with OH Radicals: Experimental and Theoretical Study. G. El Dib, M. P. Angappan, S. Lakshminpathi, Atmosphere, 2022, 13 (8), pp.1247. (10.3390/atmos13081247).

PhD thesis: Mariam Fakhir, Titre : 'Réactivité Atmosphérique des principaux produits d'oxydation de première génération des monoterpènes'.