

FINAL REPORT PROGRAM LEFE

Program LEFE/CHAT	Project Title Atmospheric multiphase reactivity of multifunctional organic nitrates (MULTI-NITRATES)	Years 2016 – 2018
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<p>Context: Organic Nitrates (ONs) are formed in rich NO_x air by the degradation of VOCs. Due to their rather long lifetimes, they act as reservoirs for reactive nitrogen and contribute to the “export” of NO_x in remote regions. They, therefore, play a key role in the budget of ozone and other secondary pollutants at the regional scale. Among the ONs, a variety of multifunctional species is formed and significantly contributes to the reactive Nitrogen budget. These multifunctional ONs being low-volatile and highly soluble, they also partition into the atmospheric condensed phases and can thus affect chemistry in both aqueous and aerosol phases. A good understanding of their reactivity is therefore necessary.</p> <p>Objectives / scientific questions: MULTI-NITRATE aimed at studying the photo-chemical reactivity of multifunctional ONs in both gaseous and condensed phases. Initially, it was intended to be organized in five tasks: 1) organic syntheses of multifunctional organic nitrates (LISA), 2) experimental study of the gas-phase reactivity of ONs (LISA, ICARE), 3) experimental study of the aqueous-phase reactivity of ONs (LCE), 4) experimental study of the multiphase reactivity of ONs (LISA, LCE) and 5) modelling study of the multiphase reactivity of ONs. However, due to significant reduction of the requested funding, only tasks 1 to 3 could be carried out.</p> <p>Main results</p> <p>1) Organic syntheses of multifunctional organic nitrates (LISA) Because multifunctional organic nitrates are not commercially available, they have to be synthesized. However, these syntheses are tricky because of the explosive property of such compounds. Several protocols have been successfully tested at LISA leading to the syntheses of five ONs: two keto-nitrates (3-nitrooxy-2-propanone, 3-methyl-3-nitrooxy-2-butanone), two aldehyde-nitrates (3-nitrooxy-2-propanal and 4-nitrooxy-2-butanal) and one hydroxy-nitrate (1-nitrooxy-2-propanol). Once the protocols have been optimized at LISA, they were duplicated at LCE and ICARE.</p> <p>2) Study of the gas-phase reactivity of ONs (LISA, ICARE) At LISA, the photolysis and the reaction with OH radicals of two aldehyde-nitrates (3-nitrooxy-2-propanal and 4-nitrooxy-2-butanal) were investigated for the first time. Experiments were performed in simulation chambers using the same experimental protocols as those previously used for keto-nitrates (<i>Suarez-Bertoa et al., 2012; Picquet-Varrault et al., 2020</i>). The results indicate that photolysis is a very efficient sink for these compounds with atmospheric lifetimes of few hours. They also confirm that, similarly to keto-nitrates, these aldehyde-nitrates have enhanced UV absorption cross sections, i.e. higher than the sum of the mono-functional species cross sections. This may be explained by electronic interactions between the two chromophore groups. Rate constants for the reaction with OH radicals were also measured and shown to be quite high. Comparison with photolysis rates suggests that OH-initiated oxidation of aldehyde nitrates is competitive with their photolysis. Products study is still under progress and will allow us to propose mechanisms (see Figure 1). At ICARE, the temperature dependence of the OH oxidation rate constant was investigated for two keto-nitrates: 3-nitrooxy-2-propanone and 3-methyl-3-nitrooxy-2-butanone. Experiments were performed over the temperature range 285-350 K. For 3-nitrooxy-2-propanone, the temperature dependence was found to be very small and a temperature independent value was proposed. However, this value is significantly lower than the value measured at room temperature at LISA (<i>Suarez-Bertoa et al., 2012</i>) and it is suspected that the presence of impurities may affect the absolute rate determination performed at ICARE. For the reaction of OH radical with 3-methyl-3-nitrooxy-2-butanone, a temperature independent value was also proposed and is in good agreement with the previous determination from <i>Suarez-Bertoa et al., 2012</i>.</p> <p>3) Study of the aqueous-phase reactivity of ONs (LCE) The aqueous phase reactivity (hydrolysis, photolysis and oxidation by OH radicals) of several ONs was investigated</p>		

for the first time. Photolysis frequencies and mechanisms were provided for isobutyl nitrate, isopropyl nitrate, 3-nitrooxy-2-propanone and 3-nitrooxy-2-propanol. It was observed that photolysis rates are quite similar whatever the ON considered. This result is very interesting as it differs from what has been observed in the gas-phase, i.e. that the presence of the two chromophore groups significantly enhances the absorption cross sections. Among the photolysis products, a majority of ONs were detected. Rate constants for the oxidation by OH radicals were determined for the same ONs as in the gas-phase study (see Figure 2). These first kinetic data were used to develop a parametrization for ONs in the structure-activity relationship developed by *Doussin and Monod 2013* which was then used to estimate the aqueous phase reactivity of various isoprene and terpene nitrates. Estimated lifetimes suggest that aqueous phase chemistry may be a significant sink of these compounds in the atmosphere.

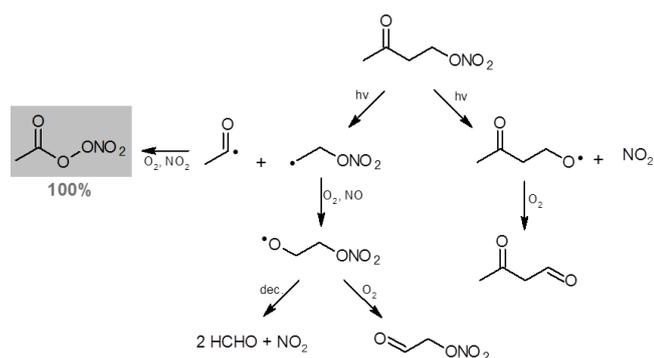


Figure 1: Example of mechanism proposed for the photolysis of 4-nitrooxy-2-butanone in gas phase. Detected products are indicated with a grey background and their formation yield is given in percentage (*Picquet-Varrault et al., 2020*).

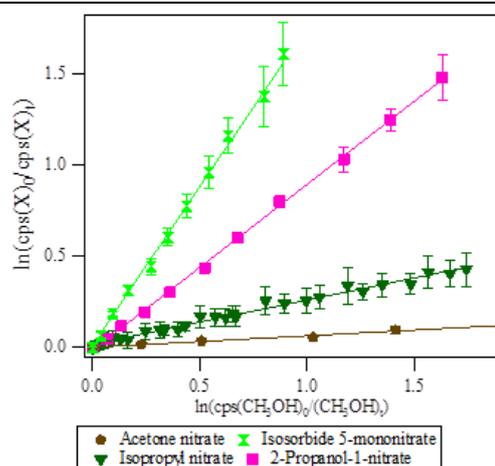


Figure 2: Relative kinetic plots for the OH oxidation of a selection of organic nitrates (ONs) in aqueous phase.

Future of the project: An ANR project (MONET) has been submitted in order to continue the work initiated within MULTI-NITRATES but has not been funded yet. Other funding channels are being investigated.

Publications related to the project:

Fouqueau A., Duncianu M., Cazaunau M., Pangui E., David M., Doussin J-F., Picquet-Varrault B., *Photolysis and oxidation by OH radicals of aldehyde-nitrates: 3-nitrooxy-2-propanal and 4-nitrooxy-2-butanal*. To be submitted in ACPD.

González-Sánchez J. M., Brun N., Morin J., Temime-Roussel B., Wu J., Clément J.-L., Monod A., *A new approach for studying aqueous-phase kinetics of low reactive compounds using PTR-MS: application to organic nitrates*. To be submitted to ACPD.

PhD thesis:

González-Sánchez J. M. Multiphase reactivity of polyfunctional organic nitrates in the atmosphere: MULTI-NITRATES. In progress (started in October 2017)

Oral communications:

Picquet-Varrault B., Duncianu M., David M., Suarez-Bertoa R., Le Quilleuc M., Fouqueau A., Pangui E., Cazaunau M., and Doussin J-F., *Atmospheric reactivity of organic nitrates: impact on the long-range transport of NOx*, 24th International Symposium on Gas Kinetics, July 2016, York, UK.

González Sánchez J.M., Khemiri S., Ravier S., Durand A., Clément J.L., Monod A. *Study of the reactivity of the isobutyl nitrate in the aqueous phase of the atmosphere: Development of a methodology for studying the fate of polyfunctional organic nitrates*. European Geosciences Union General Assembly 2018. Vienna, Austria, April 2018.

Gonzalez-Sanchez J. M., Morin J., Temime-Roussel B., Ravier S., Durand A., Clément. J.-L., Monod A., *Aqueous phase reactivity of polyfunctional organic nitrates under atmospheric conditions*. American Chemical Society, National meeting, San Diego (California, USA), August 2019.

Posters: 4 posters in national and international conferences.