

# High-NO<sub>x</sub> photooxidation of n-dodecane: Influence of temperature and relative humidity on secondary organic aerosol formation.

Houssni Lamkaddam<sup>1</sup>, Aline Gratien<sup>1</sup>, Edouard Pangui<sup>1</sup>, Mathieu Cazaunau<sup>1</sup>, Marc David<sup>1</sup>, Jean-Michel Polienor<sup>1</sup>, Murielle Jerome<sup>1</sup>, Cécile Gaimoz<sup>1</sup>, Bénédicte Picquet-Varault<sup>1</sup> and Jean-François Doussin<sup>1</sup>

<sup>1</sup>Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR-CNRS 7583, Université Paris-Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, 94010 Créteil, France

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Presenting author email: houssni.lamkaddam@lisa.u-pec.fr

Our current knowledge of oxidation pathways and chemical composition of the secondary organic aerosol (SOA) is limited and poorly understood considering the difficulty of the chemical transport model (CTM) to predict the organic aerosol mass in the atmosphere (Heald et al., 2011). It leads to a lack of precision in the estimation of the impact on climate and air quality of the atmospheric aerosols.

In this context, the aim of this work is to study SOA formation from oxidation of precursors such as long chain alkanes which represent a substantial fraction of the unresolved complex mixture in diesel fuel (Gentner et al., 2012). Beside the fact that it represents a relevant class of compound for the urban atmosphere, simple alkanes are also very interesting model-molecule to investigate the sensitivity to different reaction pathways of the organic matter, i.e. fragmentation, functionalization or oligomerization, during its atmospheric oxidation. The project aims hence at building parameterization that represents physical-chemical processes controlling SOA formation from supposedly well-known precursor. Doing so it will allow the testing of the hypothesis that fund explicit models before their reduction in view of their insertion in CTM models. In particular, the present work assesses the effect of temperature (from 10 to 30°C) and relative humidity (from <1 to 70%) on the high-NO<sub>x</sub> photooxidation of n-dodecane.

The experiments were carried out in the CESAM chamber (<http://cesam.cnrs.fr>) (Wang et al., 2011). It is a 4,2 m<sup>3</sup> stainless steel chamber which permit to conduct experiments at different temperature and relative humidity, constant pressure and under a very realistic actinic flux.

In each experiment, seed particles of ammonium sulfate and n-dodecane were injected in the chamber together with isopropyl nitrite (IPN) as OH source and allowed to stabilize before irradiation. The gaseous phase was analysed by a Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-ToF-MS), an in situ Fourier Transform Infrared Spectrometer (FTIR), NO<sub>x</sub> and O<sub>3</sub> analysers. SOA formation was measured with a Scanning Mobility Particle Sizer (SMPS). Figure 1 shows a typical example of SOA formation during an OH initiated oxidation experiment. The role of temperature and relative humidity on SOA yields and products distribution will be presented. Aside aerosol mass production, the mechanism was also investigated by measuring SOA

composition after sampling on filter with a supercritical fluid extraction technique coupled to gas chromatography and mass spectrum (SFE-GC-MS). Mechanistic pathways of the gaseous and particulate products will be proposed.

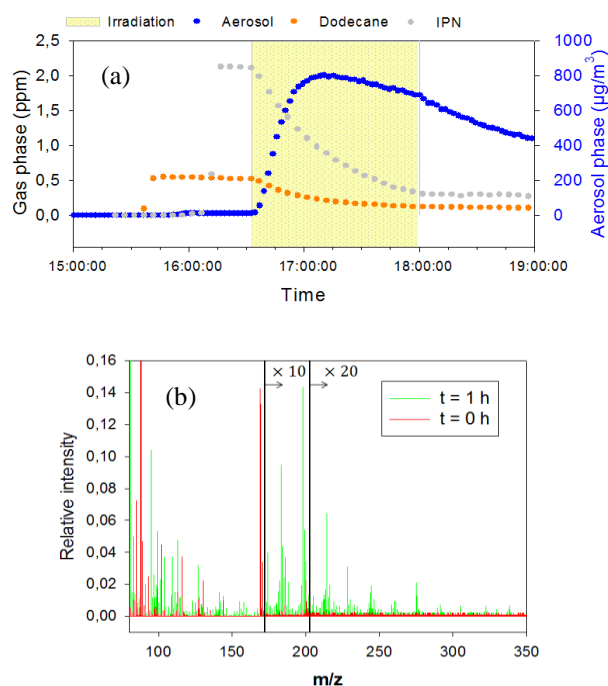


Figure 1. Typical experiment of OH oxidation of dodecane at 30°C and <1% RH: (a) Time dependent concentrations and aerosol mass, (b) comparison of PTR-ToF-MS mass spectra before irradiation (t=0h) and after 1 hour (t=1h).

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