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1 Introduction

Limonene is widely employed in scented products used in indoor environments such as fresheners and household cleaners (Nazaroff 2004). It also displays one of the highest potential for the formation of Secondary Organic Aerosols (SOAs) following ozonolysis (Jaoui 2006; Chen 2010).

Besides, indoor ozone concentration, influenced by outdoor concentration and indoor sources, can be quite important to initiate gas phase chemistry (Weschler 2000) and possibly lead to secondary products formation.

This work investigates SOAs formation from the ozonolysis of limonene as emitted from a detergent, in order to gather information on aerosols that are an important source of exposure for people using household products.

2 Materials/Methods

This work combines simulation chamber ozonolysis experiments in the EUphorePHOtoREactor (EUPHORE) facility (Valencia) to specifically study limonene ozonolysis and field studies in an experimental house (CSTB MARIA) to reproduce real household products use conditions. To describe multiphase chemistry involved in SOAs formation and to take into account gas/particles partitioning phenomena, a new analytical approach is employed. Both gas and particulate phases have been simultaneously collected, respectively on sorbent tubes and filters, and molecular composition is investigated using PFBHA and MTBSTFA derivatisation prior to thermal-desorption coupled with gas chromatography and mass spectrometry (TD-GC-MS) analysis (Rossignol et al, in press). For each experiment, chemical data are coupled with physics characterization of formed particles: mass evolution and size and number distribution evolution. VOC have been sampled on Tenax tubes and analyzed by GC/MS. A pseudo-continuous analyzer (15 min time resolution) has been used to monitor limonene concentrations.

Finally, in order to overcome the difficulties related to the achievement of airways exposure experiments, a toxicological profiling of the chemicals was carried out by means of experimental data retrieved from the literature and structure-toxicity analogies based on a series of chemicals that are structurally related to the analyzed ozonolysis products.

3 Results and Discussion

As soon as the household product is used, limonene concentration increases, going from the background level of 6 $\mu g\,m^{-3}$ to a maximum of 70 $\mu g\,m^{-3}$.

Limonene increase is followed a few minutes later by a $PM_{2.5}$ particle number concentration increase going from 2800 particles cm^{-3} to a maximum value of about 70 000 particles cm^{-3}.

The so formed particles are small, displaying a mode at 25 nm whereas the background mode is about 100 nm.

These small particles can be suspected to be secondary organic aerosols formed from limonene ozonolysis. To confirm that hypothesis two experiments have been performed: The same household product use in the MARIA kitchen but without any ozone generation (it has resulted in no particle formation), simultaneous

study of the gaseous and particulate phase to search for limonene ozonolysis formation products.

23 carbonyle compounds and 13 hydroxyle and acid carboxylic compounds have been positively or tentatively identified in the gaseous and/or the particulate phases. Most compounds display a concentration increase consequently to the use of the household product. Chemical analysis results from the MARIA experiment have been compared to results obtained in the EUPHORE simulation chamber to ease limonene ozonolysis compounds identification.

Some compounds are common to EUPHORE and MARIA experiment revealing the products formed from limonene ozonolysis consequently to the use of the housecleaning product.

Among these compounds, the three most abundant have been quantified in both gaseous and particulate phases. The concentration increase of methyl-glyoxal, 4-oxopental and Limononaldehyde are significant ranging from 6 to 200 % for gaseous phase and 8 to 150 % for the particulate phase.

Among these three compounds, limononaldehyde is the only limonene ozonolysis specific product. Its identification in both phases confirms SOA formation from limonene ozonolysis consequently to the use of the detergent.

Methylglyoxal and 4-oxopental can be formed from the oxidation of other precursors. And indeed, citronelal, myrcene and terpineol have been identified in the gas phase

Table 1: Experimental and predicted toxicological hazards:

	4-oxo-pentanal	**Methyl-glyoxal**	**Limon-aldehyde**
Skin irritation	PositiveST	Structural Alert + msds	PositiveST
Skin sensiti-zation	Positive^{EXP}	Positive^{EXP}	PositiveST
Eye irritation/ corrosion	PositiveST	Positive^{EXP}	PositiveST
Muta-genesis	NegativeST	Positive^{EXP}	NegativeST
Carcino-genicity	Structural Alert	Positive^{EXP}	Structural Alert
Inhalation toxicity	Positive^{EXP}	Positive^{EXP}	PositiveST

PositiveEXP experimental evidence exist; PositiveST Structure-Toxicity analogies among similar chemicals exist to substantiate toxicological hazard , NegativeST Structure-Toxicity analogies among similar chemicals exist to substantiate the absence of toxicological hazard, msds indicates that data from material safety data sheets exist to substantiate toxicological hazard, n.d. (no data).

One issue that can be addressed regarding indoor people exposure to these pollutants is the role of each individual volatile or semi-volatile compound on health effect. Experimental toxicological findings and toxicological predictions obtained by means of structure-toxicity analysis (read-across and QSAR modelling) for the selected VOC chemicals are described in the table 1 and display a large spectrum of toxicological hazards

4 Conclusions

The formation of secondary organic aerosols from the ozonolysis of limonene emitted consequently to the use of a house cleaning product has been observed and demonstrated by physical (size distribution) and chemical (specific limonene oxidation product quantification in gaseous and particulate phases) particle characterization.

Toxicological profiling of the so analysed chemicals indicated a large spectrum of probable toxicological hazards (skin/eye irritation, skin sensitization, mutagenicity carcinogenicity, inhalation toxicity).

5 References

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