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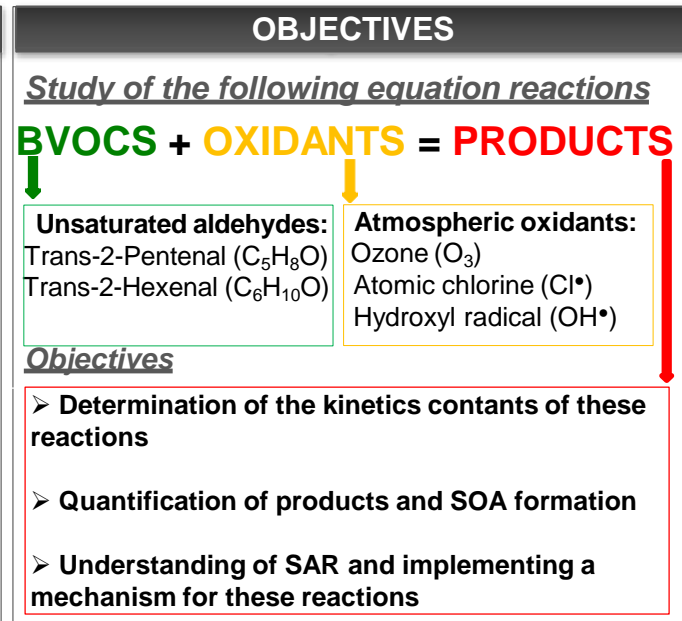
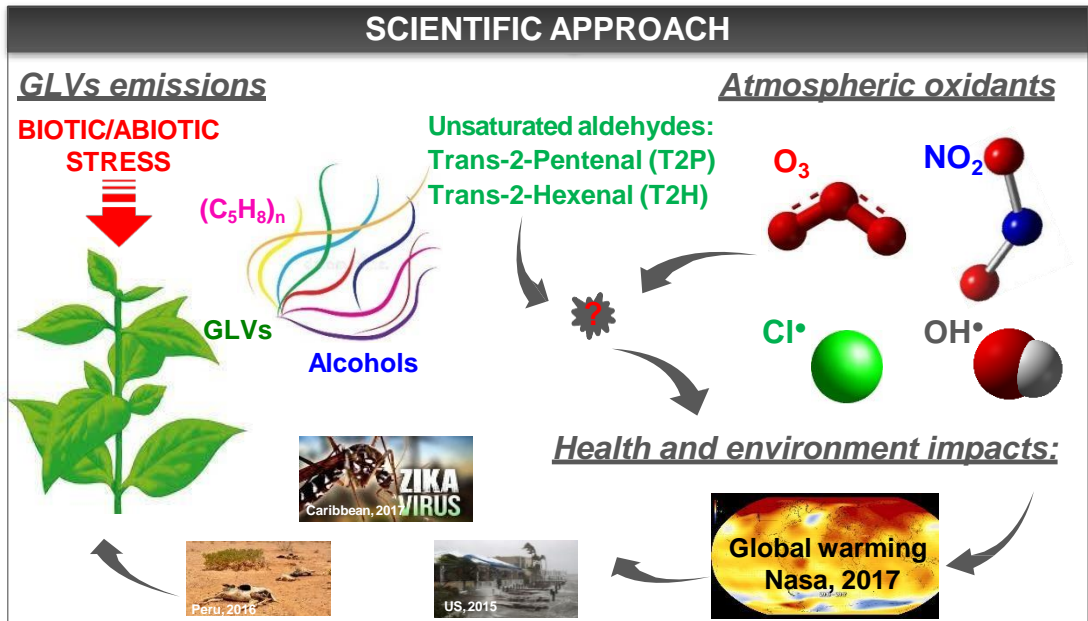
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Reactivity of Green Leaf Volatiles (GLVs) in the atmosphere : Kinetics, Products and Secondary Organic Aerosol (SOA) formation

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EXPERIMENTAL SETUPS

Atmospheric Simulation Chambers & Laminar Flow Reactor (LFR)

Teflon 0.3 m³, Douai (CSA)

Stainless steel 9 m³, Dunkerque (CHARME)

Quartz 1 m³, Wuppertal (QUAREC)

Pyrex 7 L, Douai (LFR)

Reactants analysis

- Analysis of T2P and T2H by FTIR spectroscopy (CSA / QUAREC), PTR-ToF-MS IONICON 1000 (CHARME), PTR-ToF-MS Kore (CSA), GC-FID/MS (LFR)
- Analysis of ozone by UV absorption spectroscopy (Environmental SA 49C)

SOA and products analysis

- SOA size distribution analysis by SMPS-TSI (DMA, model 3080 ; UCPC, model 3788) in CSA and (DMA, model 3071A ; UCPC, model 3025A) in QUAREC
- Product analysis by FTIR spectroscopy and by Carbotrap-202 cartridges further analyzed by GC-FID/MS

RESULTS

Kinetic constants of the reactions BVOC + O₃

CSA: $\ln \left(\frac{[O_3]}{[O_3]_0} \right) = -k' \times t_{mes}$ with $k' = k \times [BVOC]_0 + k_{wall\ loss}$

LFR: $T_{cal} = \frac{V}{Q}$ with $T_{mes} = \frac{T_{cal}}{0.97 + 0.18 \times \exp \left[-\frac{Re}{H} - 0.38 \right]}$ (4)

$\ln \left(\frac{[O_3]}{[O_3]_0} \right) = -k' \times t_{mes}$ with $k' = k \times [BVOC]_0 + k_{wall\ loss}$

T2P + O₃

$k_{CSA} = 1.28 \times 10^{-18} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (1)
 $k_{Bille} = 1.59 \times 10^{-18} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (2)
 $k_{Bille} = 1.28 \times 10^{-18} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (3)

T2H + O₃

$k_{CSA} = 2.03 \times 10^{-18} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (1)
 $k_{Bille} = 2.01 \times 10^{-18} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (2)
 $k_{Bille} = 1.28 \times 10^{-18} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (3)

Hypothesis: Transformation of trans to cis for both compounds; the cis isomer would be more stable at high temperature and more responsive with O₃

Comparison of the SOA formation from the ozonolysis of T2P and T2H

CSA:

- The ozonolysis of trans-2-hexenal forms a number of particles 4 times bigger than the trans-2-pental.
- At the end of the experiment, the diameters of the particles formed from the T2H are 2 times larger than those formed from the T2P.

Evaluation of the products of the ozonolysis of T2P and T2H

Products formation:

The calculation of the formation yield of a product is done by the following formula:

$$Yields_{product}(\%) = \frac{[Product]}{[BVOC]_{cons}} \times 100$$

FTIR spectroscopy analyzes:

T2P (1.7 ppm) + O₃ (3 ppm):

CCCC=CC + O=O=O >> C=O + CCCC=O
 Glyoxal (20%) Propanal (70%)

T2H (1.3 ppm) + O₃ (3.8 ppm):

CCCCC=CC + O=O=O >> C=O + CCCCC=O
 Glyoxal (14%) Butanal (87%)

CSA & QUAREC:

- The maximum SOA yield for trans-2-hexenal is much higher (~12%) than for trans-2-pental (~1-2%).
- The formation of particles for these two compounds seems very high compared to the length of their carbon chains (max 6 C atoms).
- The experiments done at QUAREC have confirmed that of the CSA, that shows that the geometry and the material of two reactors did not affect the formation of the particles.
- New experiments are underway in the CHARME reactor in Dunkerque to verify these previous results.

Kinetic constants of the reactions BVOC + Cl*

CSA: $\ln \left(\frac{[BVOC]}{[BVOC]_0} \right) = \ln \left(\frac{[Ref]}{[Ref]_0} \right) \times k'$ with $k' = \frac{k_{BVOC/Cl}}{k_{Ref/Cl}}$

Two references are used isoprene (C_5H_8) hexanal ($C_6H_{12}O$):

$k_{isoprene/Cl^*} = (4.45 \pm 0.7) \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (5, 6)
 $k_{hexanal/Cl^*} = (2.72 \pm 0.2) \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (7, 8)

T2P + Cl*

$k_{CSA} = 2.8 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (8)
 $k_{Bille} = 1.31 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (8)

T2H + Cl*

$k_{CSA} = 3.28 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (8)
 $k_{Bille} = 1.92 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (8)

CONCLUSIONS

- The values of the kinetic constants of the BVOC/O₃ reactions are in good agreement with the literature whereas those for the BVOC/Cl* reactions are high by a factor of 2 (a single value found in the literature).
- The SOA formation is more important for T2H than for T2P and in both cases it depends on the initial concentrations of the reactants but especially on that of O₃. The particle size of the particles and their yields are influenced by the structure of the BVOC.
- The products mainly formed by the ozonolysis of T2P are glyoxal, propanal but other products appear in GC-FID/MS analyzes such as: propanoic and 2-pentanoic acid. Similarly, the products of the degradation of T2H with ozone were mostly glyoxal and butanal. Additional analyzes by gc showed the presence of butanoic and 2-hexenoic acid.

FUTURE WORK

- Quantification of products by the TD-GC-FID / MS system.
- Other T2P/Cl* experiments in CSA are planned to ensure the results found for the kinetic constants.
- A series of experiments will be carried out at University Castilla La Mancha (Spain) in order to determine the products of the reaction of the selected BVOC with atomic chlorine (Cl*).
- The different programs / organisms whose logos on the right are deeply thanked for their financial support.

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