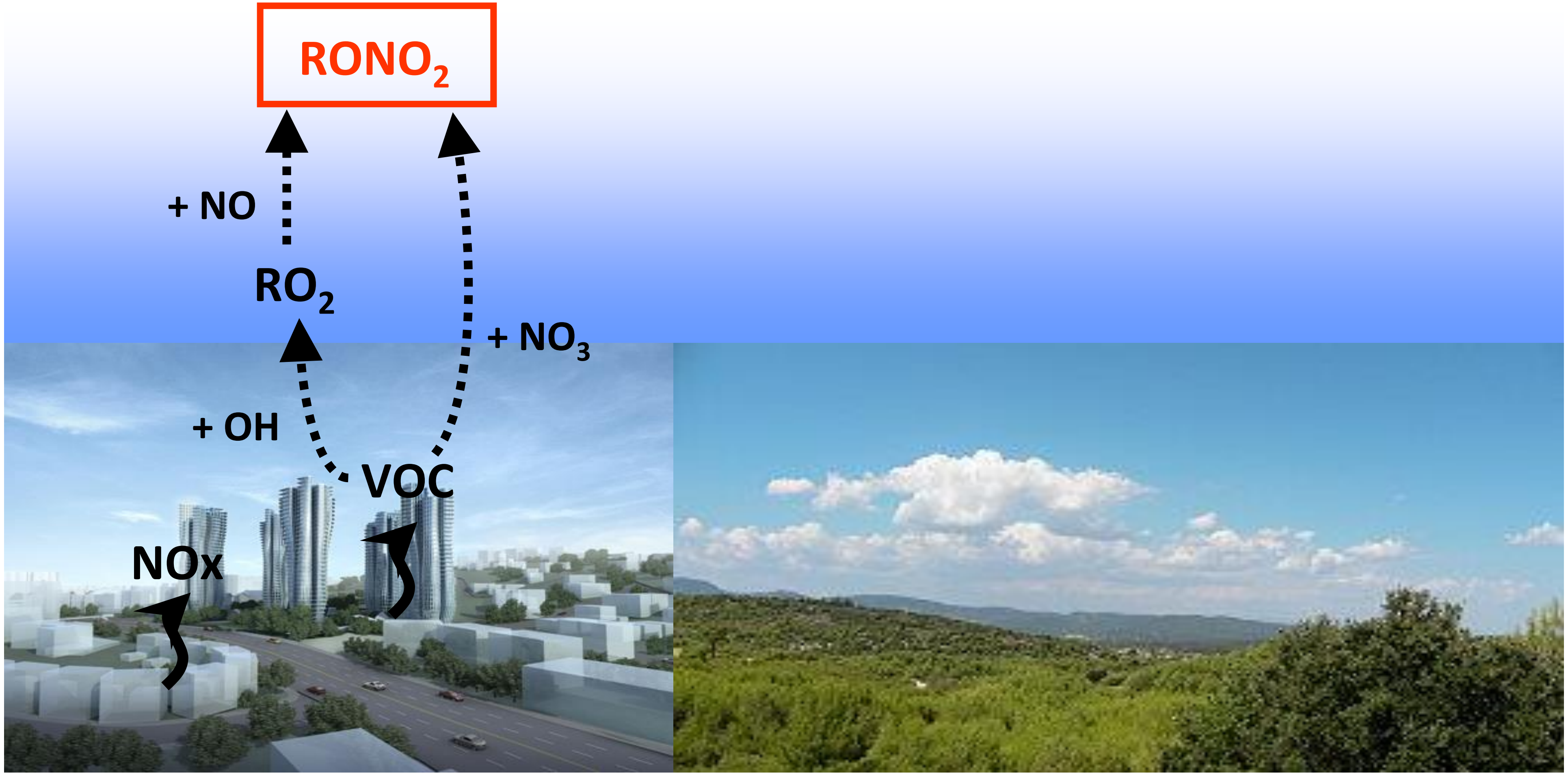
Région PACA ICR Laboratoire Chimie Environnement AirPACA QUALITÉ DE L'AIR DOC2AMU Aix*Marseille université

# Multiphase reactivity of polyfunctional organic nitrates in the atmosphere: MULTI-NITRATES

JUAN MIGUEL GONZÁLEZ SÁNCHEZ

SUPERVISORS: **ANNE MONOD** (LCE), **JEAN-LOUIS CLEMENT** (ICR)

# Organic Nitrates



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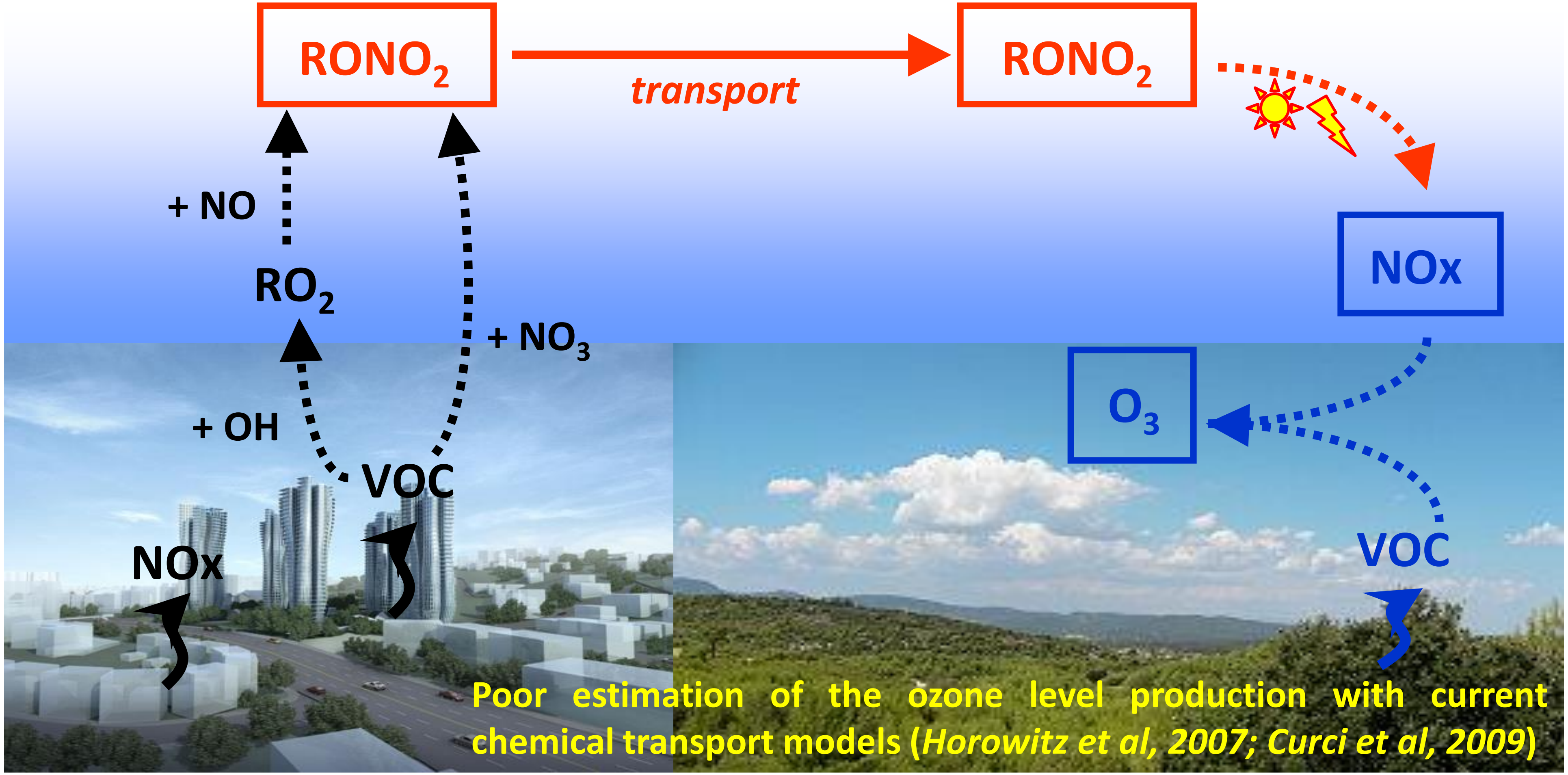

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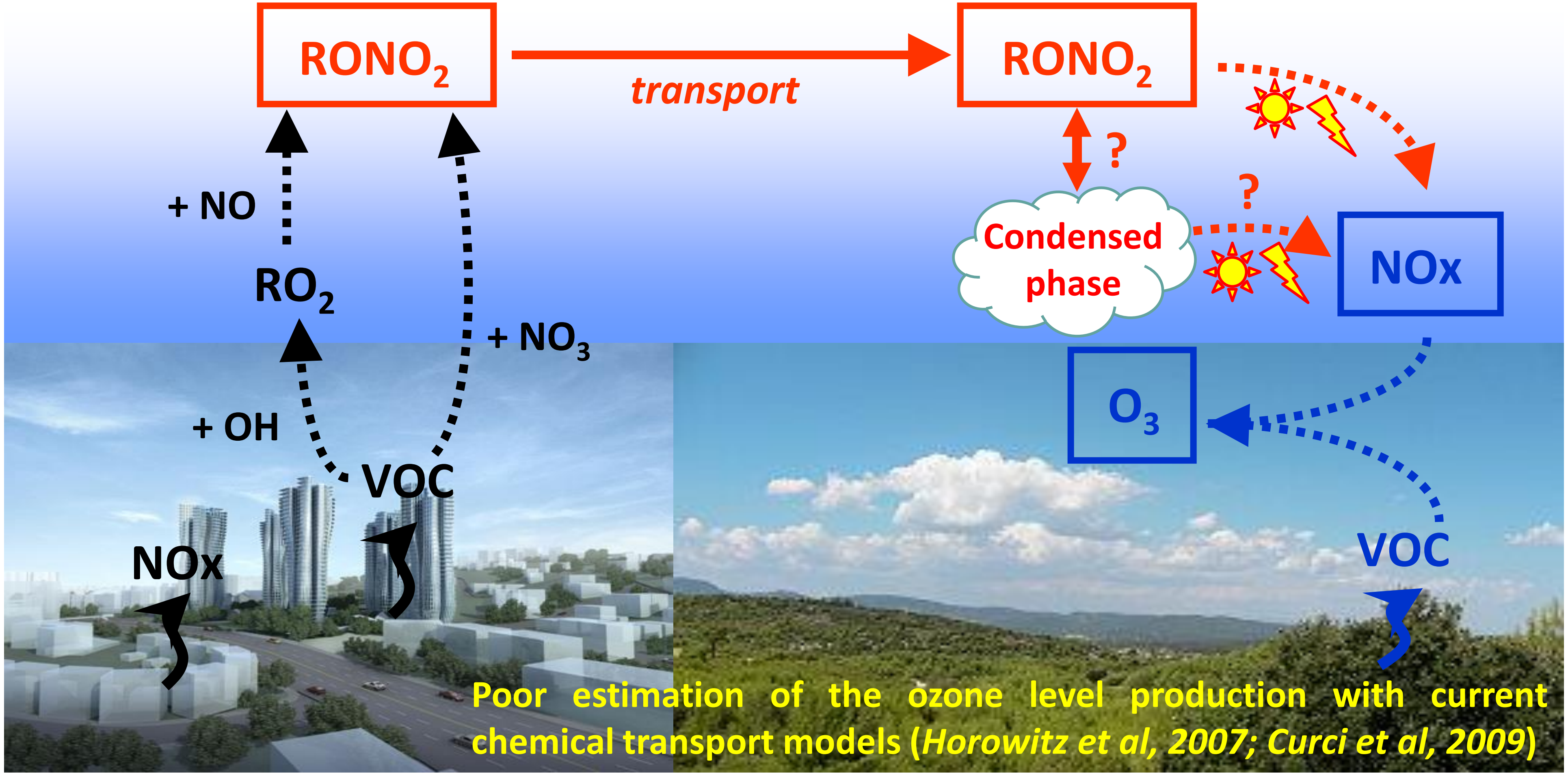
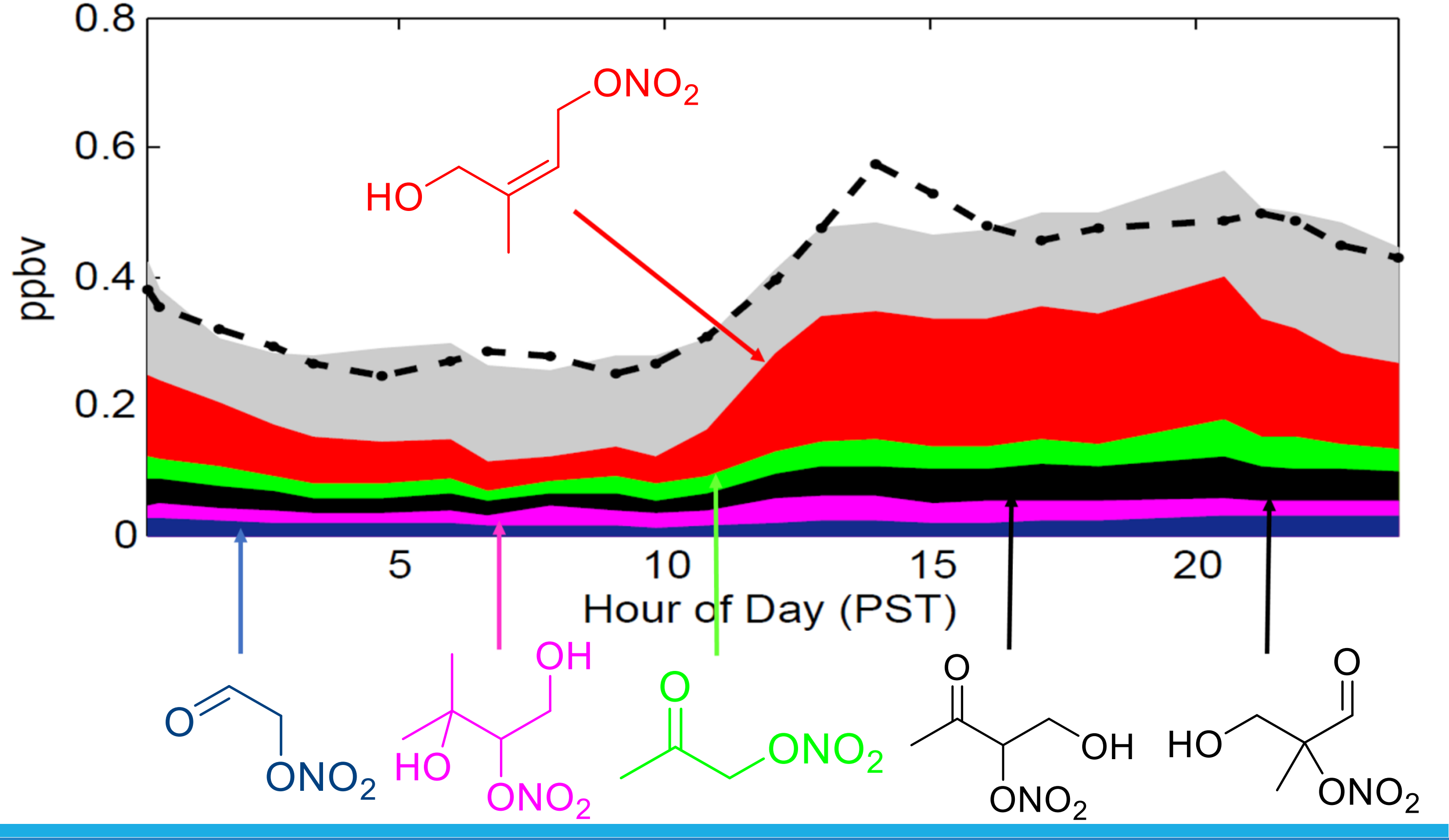


# Polyfunctional Organic Nitrates

The **majority of the found ON are highly functionalized**. However, the **studied compounds are usually alkyl nitrates**, because there are not commercial polyfunctional ON

**Therefore we will focused on the study oh these polyfunctional compounds**

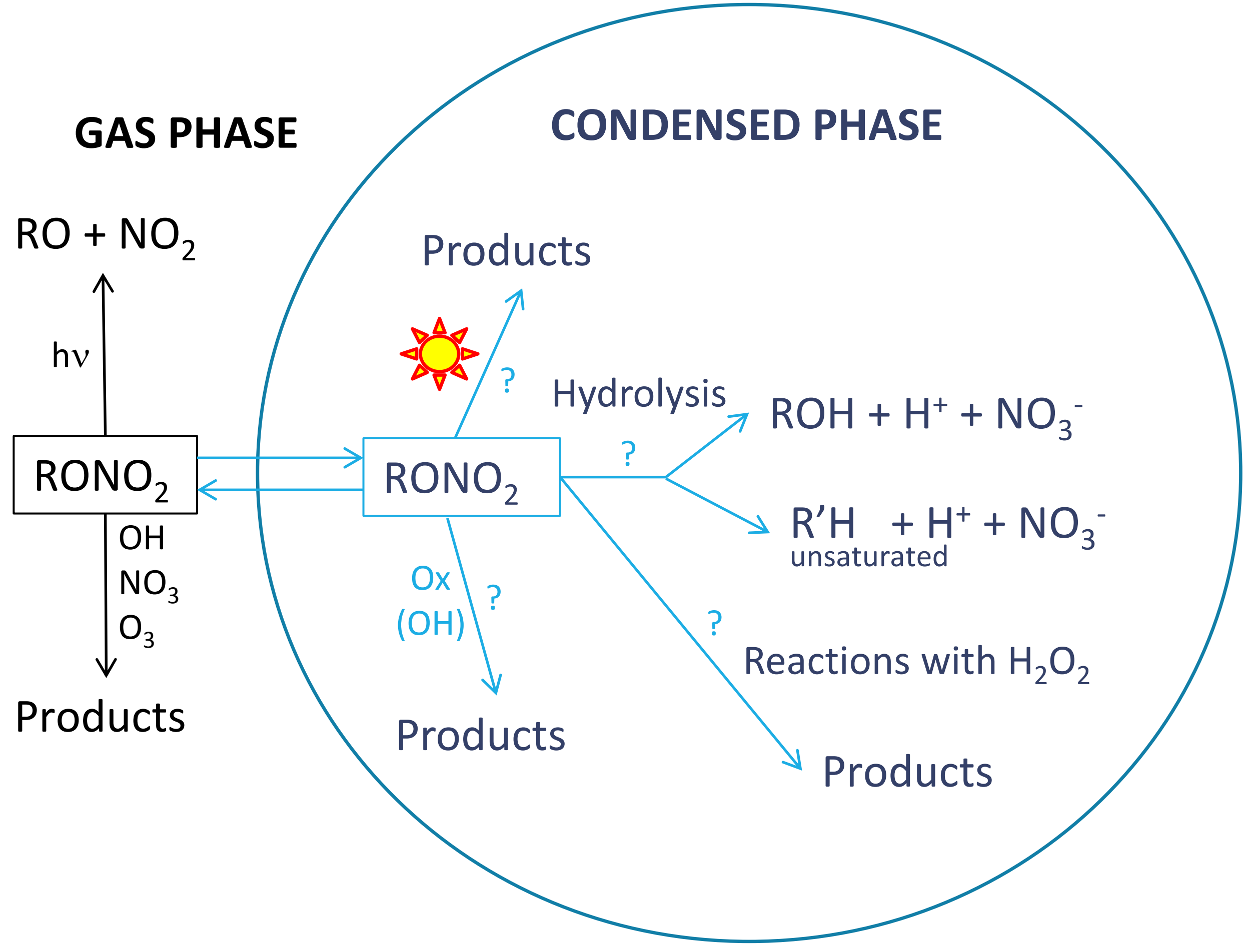
**Observations of multifunctional ON during BEARPEX 2009 in California (Beaver et al. 2012)**



# PhD Objectives

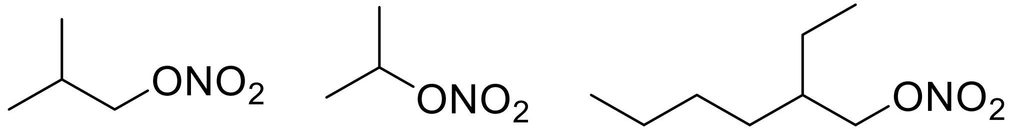
- **Study the fate, mechanisms, kinetics and lifetimes** of atmospherically relevant organic nitrates in the condensed phase **under atmospheric conditions**.

- **Implement the obtained data** in a box multiphase model and a chemical transport model **to evaluate the impact** of these multiphase processes to organic nitrates on ozone and other pollutants in the atmosphere.



# Methodology I

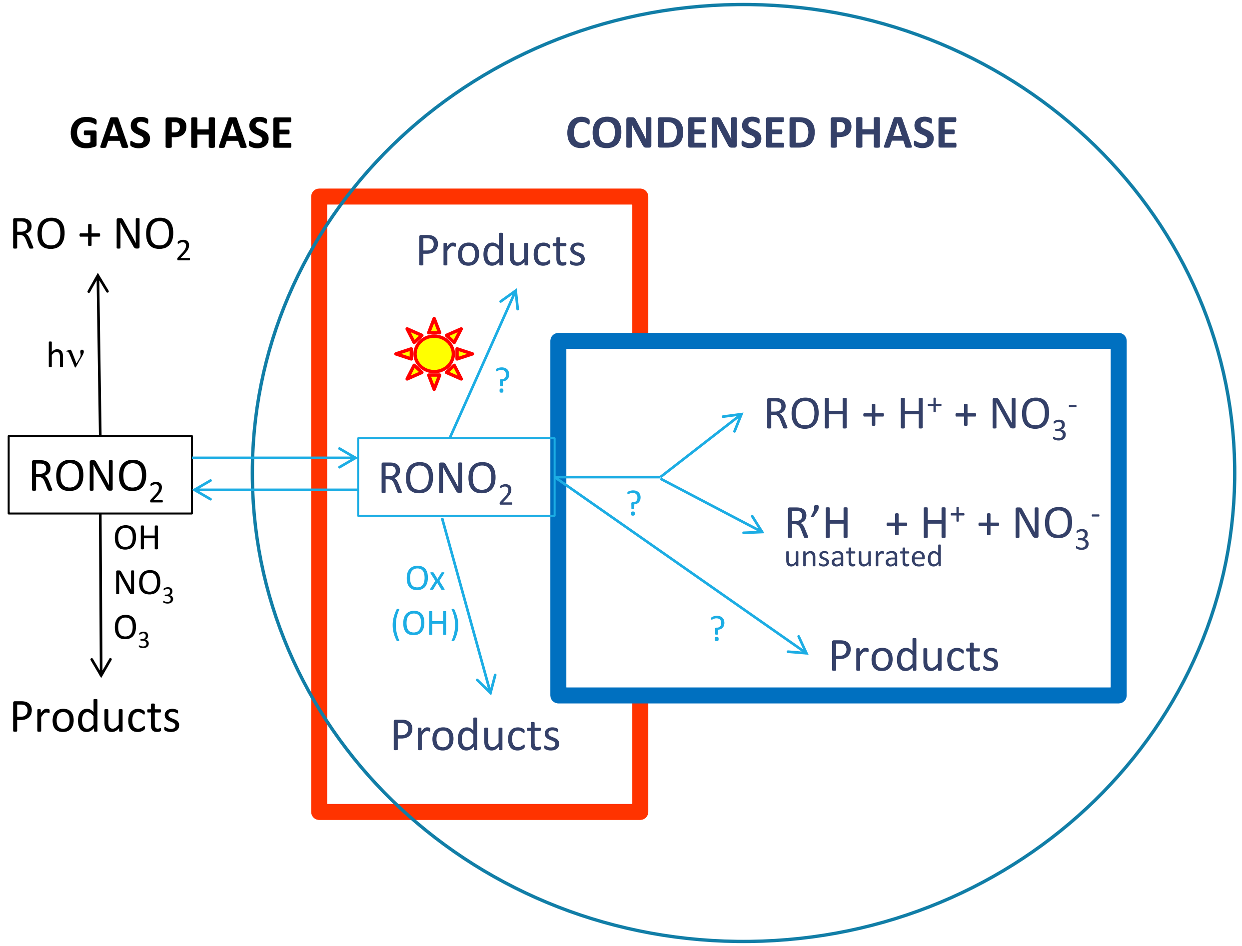
1. Study of the fate of commercial organic nitrates (**ON**) in the condensed phase




**Isobutyl nitrate** **Isopropyl nitrate** **2-ethylhexyl nitrate**

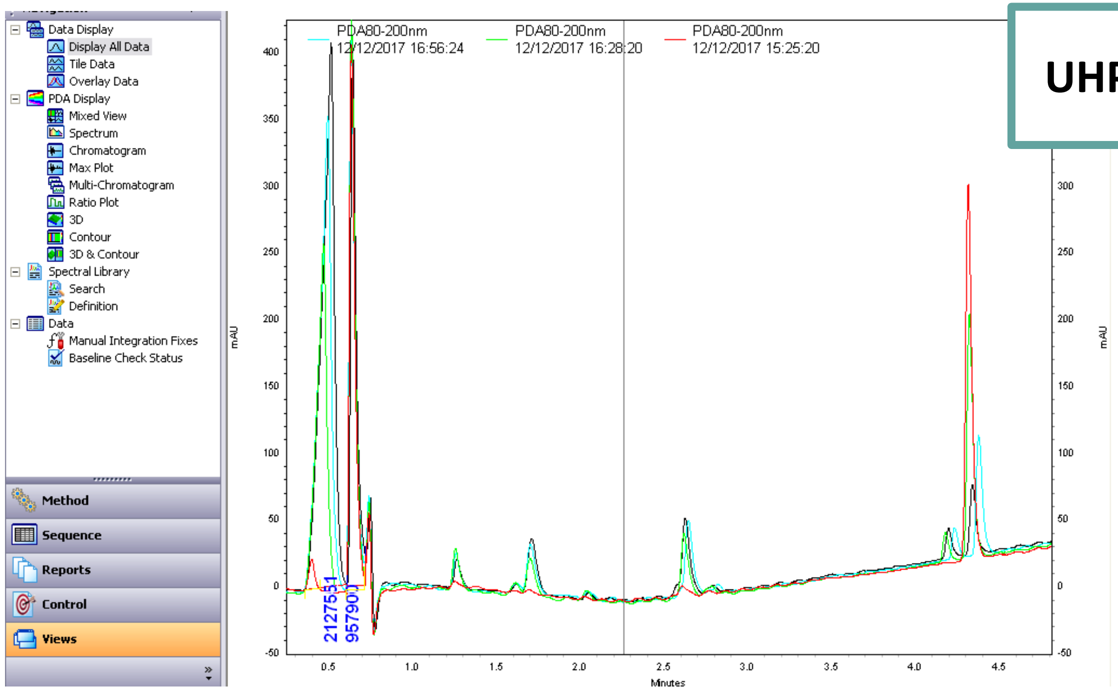
**I) Hydrolysis kinetics and other reactions without without light).**

**II) Photochemical and radical reactivity** of the organic nitrates in the condensed phase.



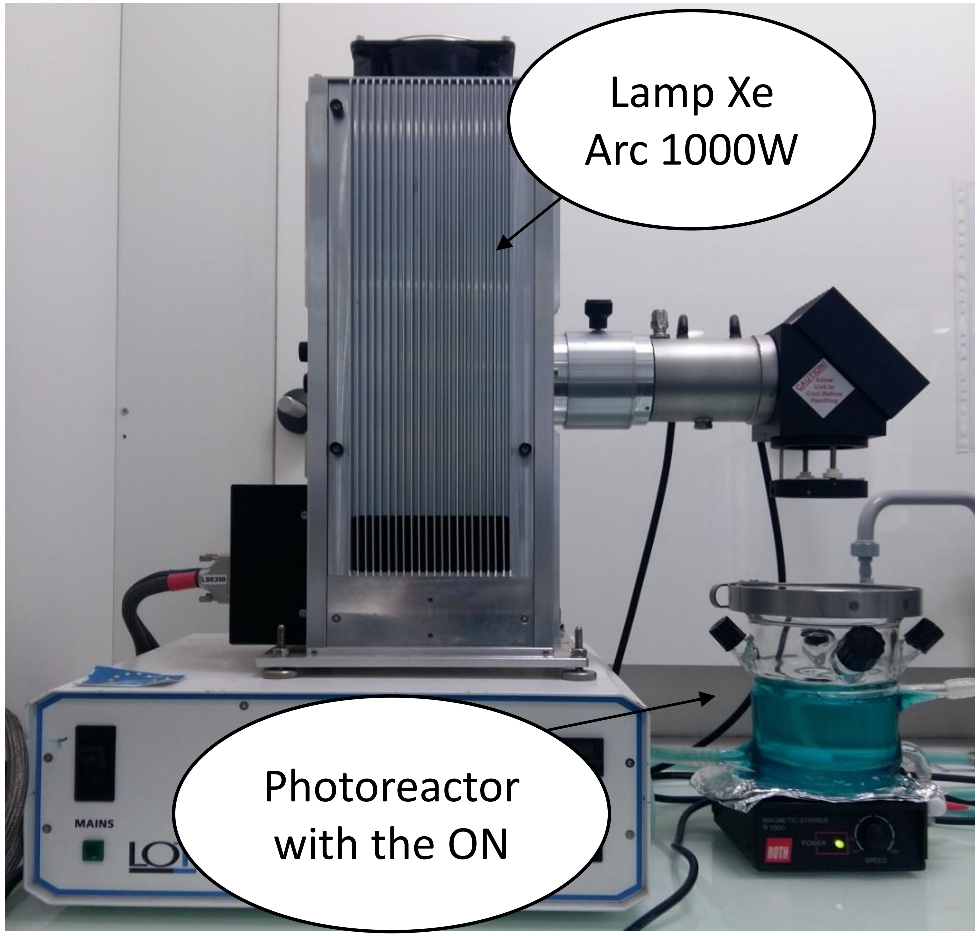
# Methodology I – Development of a detection method

Development of a detection method which could detect the different ON in order to study the decay of the compounds and therefore calculate their kinetics constants




UHPLC-UV

# Methodology I – Kinetics Studies




**Photolysis kinetic studies**

$$RONO_2 + h\nu \rightarrow Products$$

$$\frac{-d[RONO_2]}{dt} = J[RONO_2]$$

**OH oxidation kinetic studies**

$$RONO_2 + OH \rightarrow Products$$

$$\frac{-d[RONO_2]}{dt} = k_{OH}[OH][RONO_2]$$

# Methodology I – Products and Mechanisms Studies

**EPR (Electronic Paramagnetic Resonance)** is a technique which can detect radicals. The signal depends on the chemical surrounding of the radical. We will use this technique **for elucidating the mechanisms** of the degradation of the ON.

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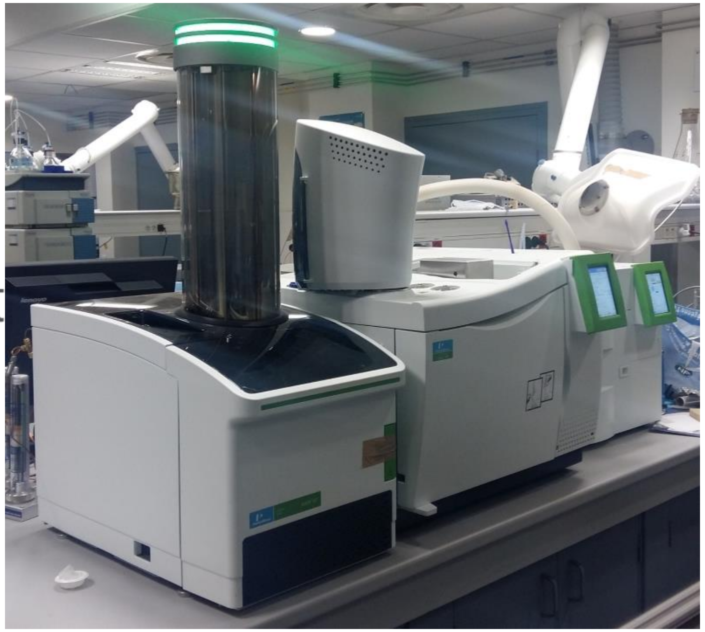
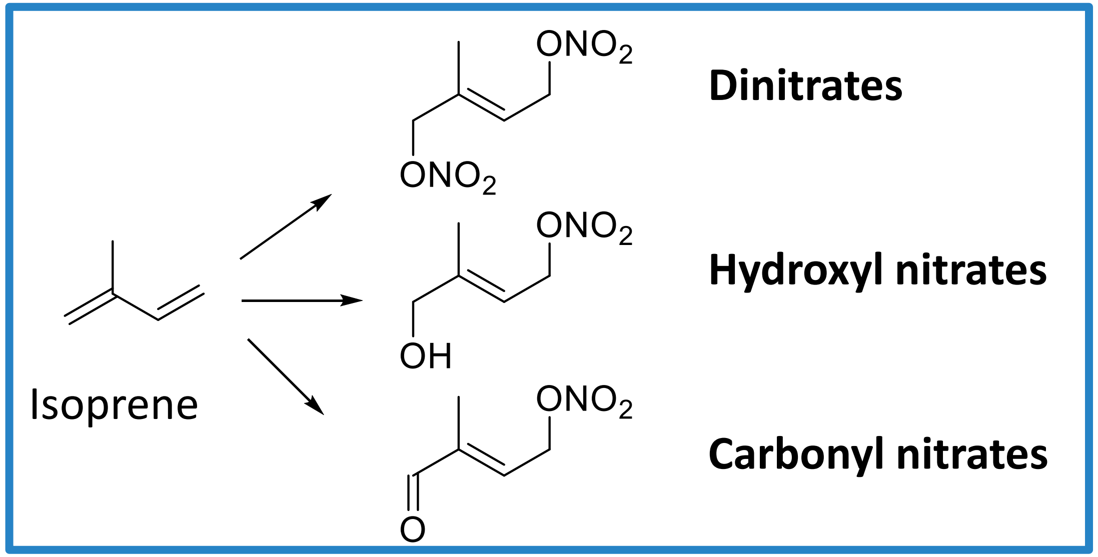


**Cold EI GC-QTOF** can give us information about the structure of the reaction products. We could see the **molecular peak** and also some fragmentation of the molecules so we could deduct which are them.

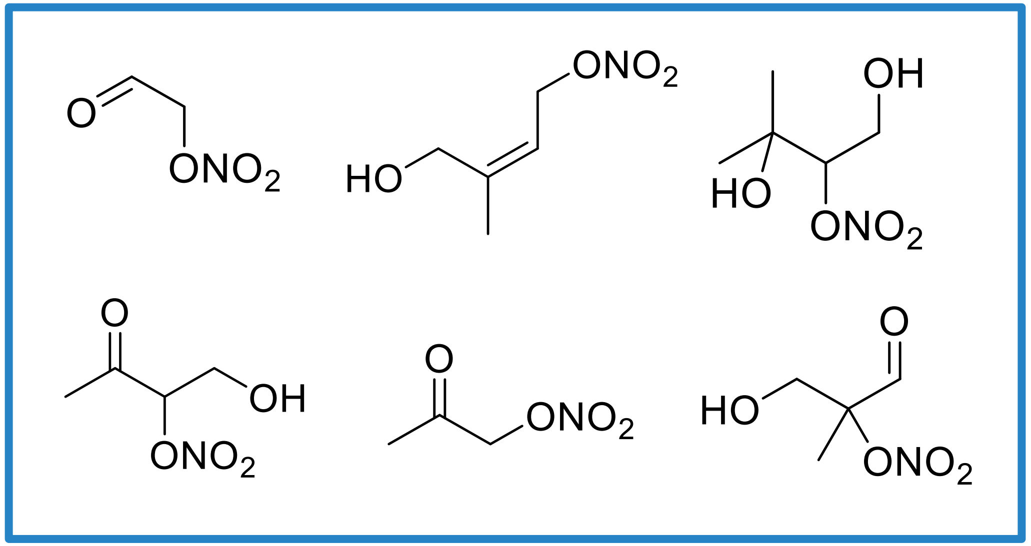
# Methodology II

2. Polyfunctional **organic nitrate syntheses,** most of the compounds are not commercial.

Isoprene derivatized organic nitrates

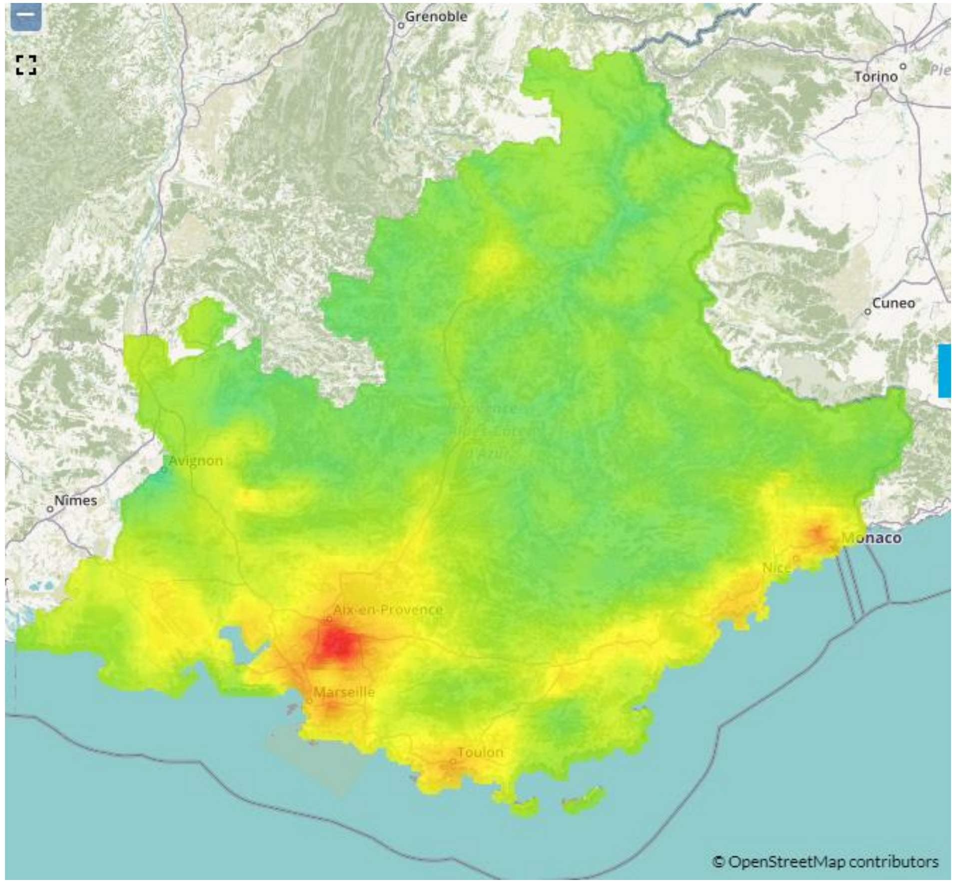



Polyfunctional ON found in California




3. **Study of the fate** (kinetics and mechanisms) of these synthesized compounds.

# Methodology III – Sharing the data with AirPACA




- **Sharing the data with AirPACA and implement the obtained results** in a box multiphase model and a chemical transport model **to evaluate the impact** of these multiphase processes to organic nitrates on ozone and other pollutants in the atmosphere

AirPACA
QUALITÉ DE L'AIR

# Conclusions

- **ON spread $NO_x$ to remote areas**. Thus, not taking into account its reactivity in models could lead to a overprediction of ozone in urban areas and underprediction in rural areas.
- Most ON are present in condensed phases so their **chemistry in this phase has an important role**.
- There is a **lack of information** of the reactivity of polyfunctional ON, overall in the condensed phase.
- The objectives of this PhD will be to **study the fate of polyfunctional ON in the aqueous phase**
- Finally, we will try to implement data in existent box multiphase models

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# Annexe I – Competitive technique

$$RONO_2 + OH \rightarrow Products$$

$$\frac{-d[RONO_2]}{dt} = k_{OH}[OH][RONO_2]$$

$$\frac{d[RONO_2]}{[RONO_2]} = -k_{OH}[OH]dt$$

$$R + OH \rightarrow Products$$

$$R \equiv Reference\ compound$$

(we know its constant)

$$\frac{-d[R]}{dt} = k_R[OH][R]$$

$$[OH] = -\frac{d[R]}{[R]}\frac{1}{k_R dt}$$

$$\frac{d[RONO_2]}{[RONO_2]} = \frac{k_{OH}}{k_R}\frac{d[R]}{[R]}$$

$$\int_0^t \frac{d[RONO_2]}{[RONO_2]} = \frac{k_{OH}}{k_R}\int_0^t \frac{d[R]}{[R]} \xrightarrow{\text{Integrating}} \frac{\ln[RONO_2]_t}{\ln[RONO_2]_0} = \frac{k_{OH}}{k_R}\frac{\ln[R]_t}{\ln[R]_0}$$

**Plotting $\frac{ln[RONO_2]_t}{ln[RONO_2]_0}$ vs $\frac{ln[R]_t}{ln[R]_0}$ we can easily calculate $k_{OH}$**