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Getting to know some of the key unknowns in atmospheric chemistry

Max R McGillen

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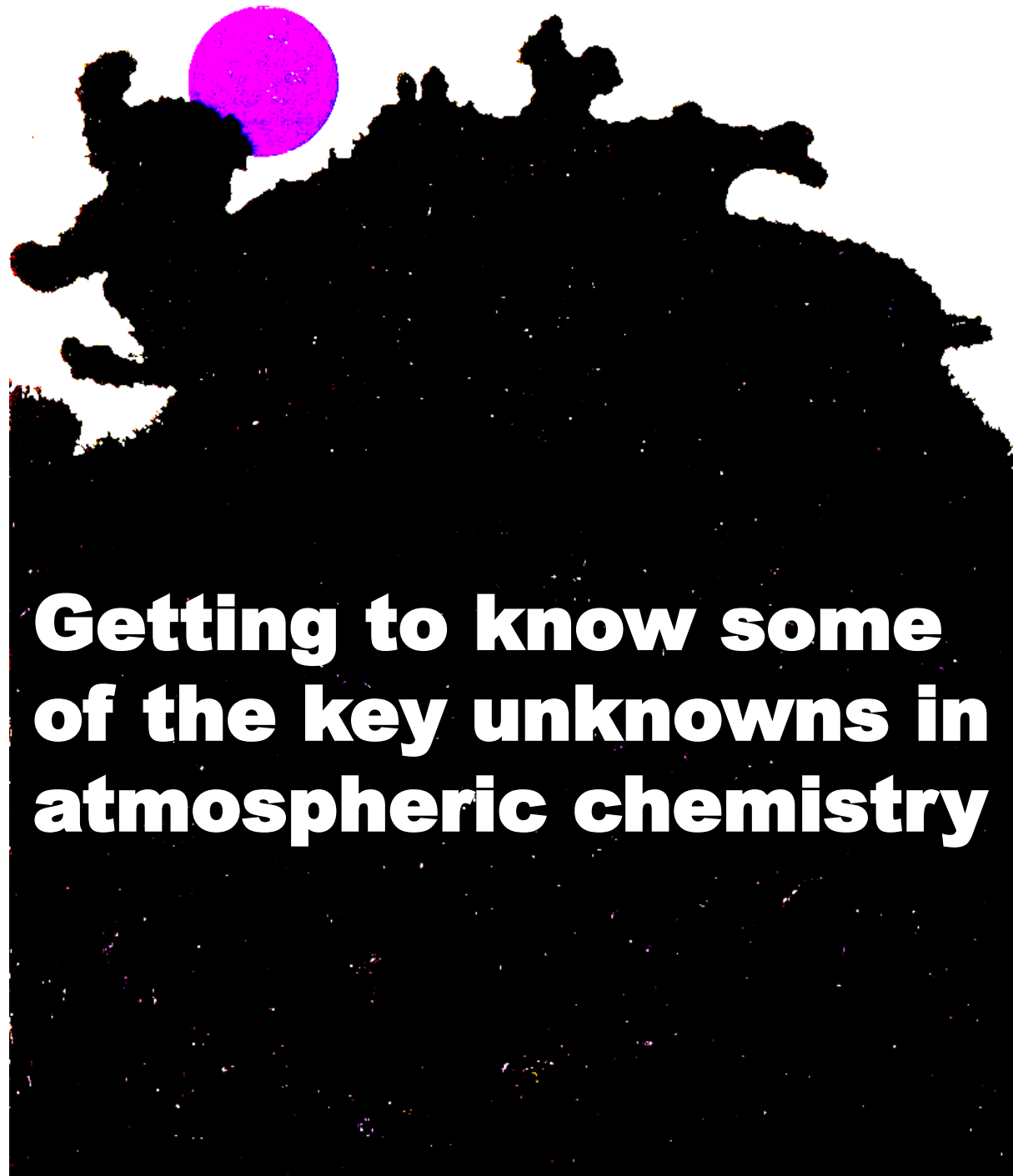
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Getting to know some of the key unknowns in atmospheric chemistry

Dr. Max McGillen

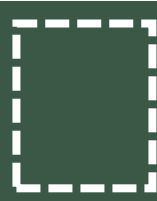
Seminar, Friday 1st November, 2024

IașiCHEM Conference



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Talk outline

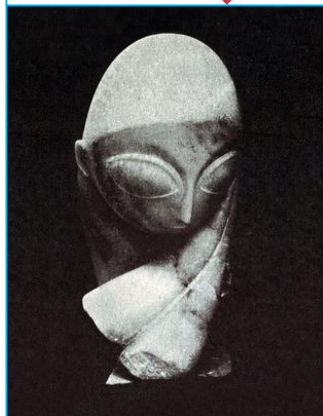


- Introduce myself
- Explain my motivations for studying atmospheric chemistry
- Describe some of the complexity of this subject
- What are the barriers to understanding atmospheric chemistry?
- How can we understand it further?

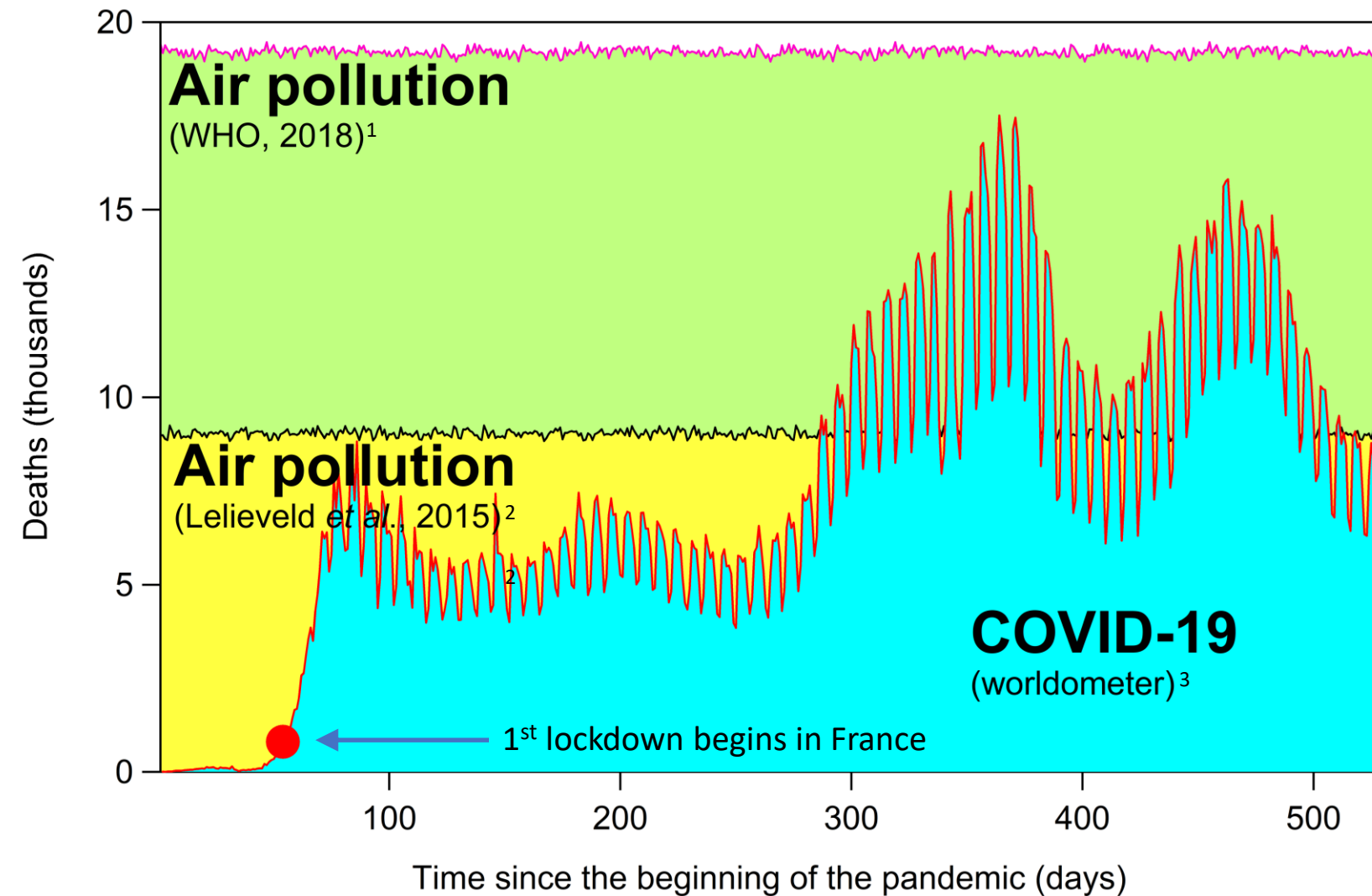
Introducing myself



- I am a researcher at CNRS-Orléans in France
- I have worked in the UK, USA and France
- I focus on atmospheric chemistry
- I am interested in chemical reactivity (experiments/ empirical methods of all types)



Air pollution: an invisible pandemic?



Time-series showing the global daily fatalities due to air pollution/ COVID-19

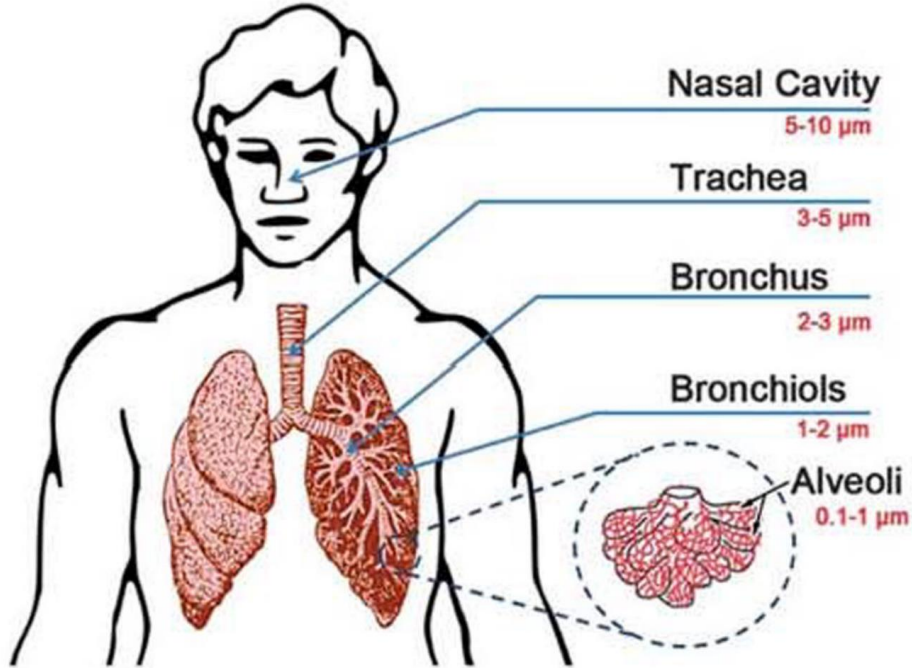
- Impact of our emissions is defined by atmospheric chemistry
- Air pollution is atmospheric chemistry
- Air pollution is an urgent problem
- And it will get worse in the future²
- The only vaccine is to understand it and legislate against it
- **But there is still so much that we don't yet understand**

¹ <https://www.who.int/news-room/detail/02-05-2018-9-out-of-10-people-worldwide-breathe-polluted-air-but-more-countries-are-taking-action>

² Lelieveld, J. *et al.* The Contribution of Outdoor Air Pollution Sources to Premature Mortality on a Global Scale. *Nature* 2015, 525 (7569), 367–371

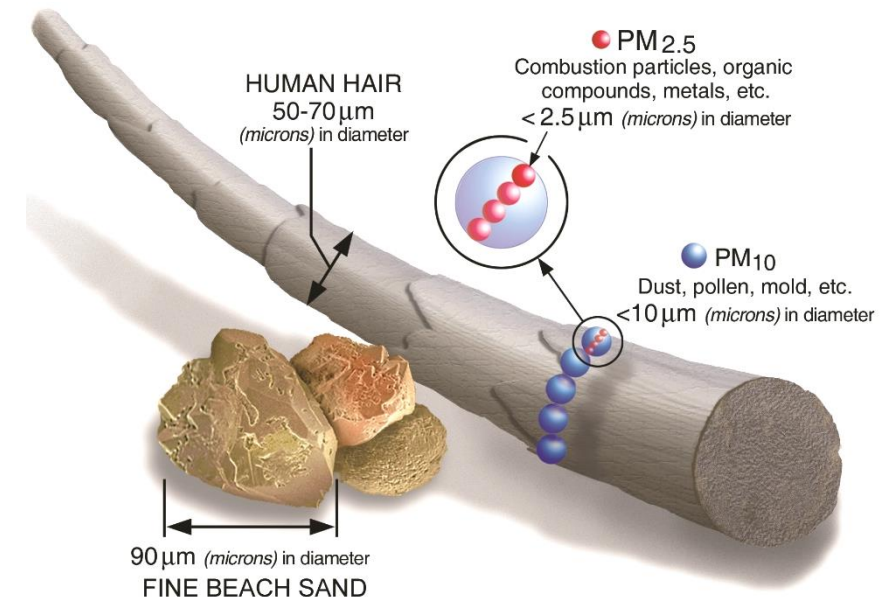
³ <https://www.worldometers.info/coronavirus/coronavirus-death-toll/>

The health effects of air pollution



- Fine particulate matter is considered to be the most dangerous component of air pollution
- These are the most aerodynamic/ mobile particles and they can reach the alveoli
- It is suspected that chemical composition may play a role in toxicity of particulates

- Lung cancer and chronic obstructive pulmonary disease are very bad outcomes
- But many other conditions are correlated with air pollution: asthma, dementia, COVID deaths
- Even behavioural patterns and cognitive ability





Air pollution: then and now



What we knew in the 1950s:

≡ **Hydrocarbons + NO_x** ≡
+ **sunlight + SO₂** ≡

peroxides
aldehydes
acids
???

SMOG/Aerosols

Adapted (radically) from: Haagen-Smit (1952)

What we know today:

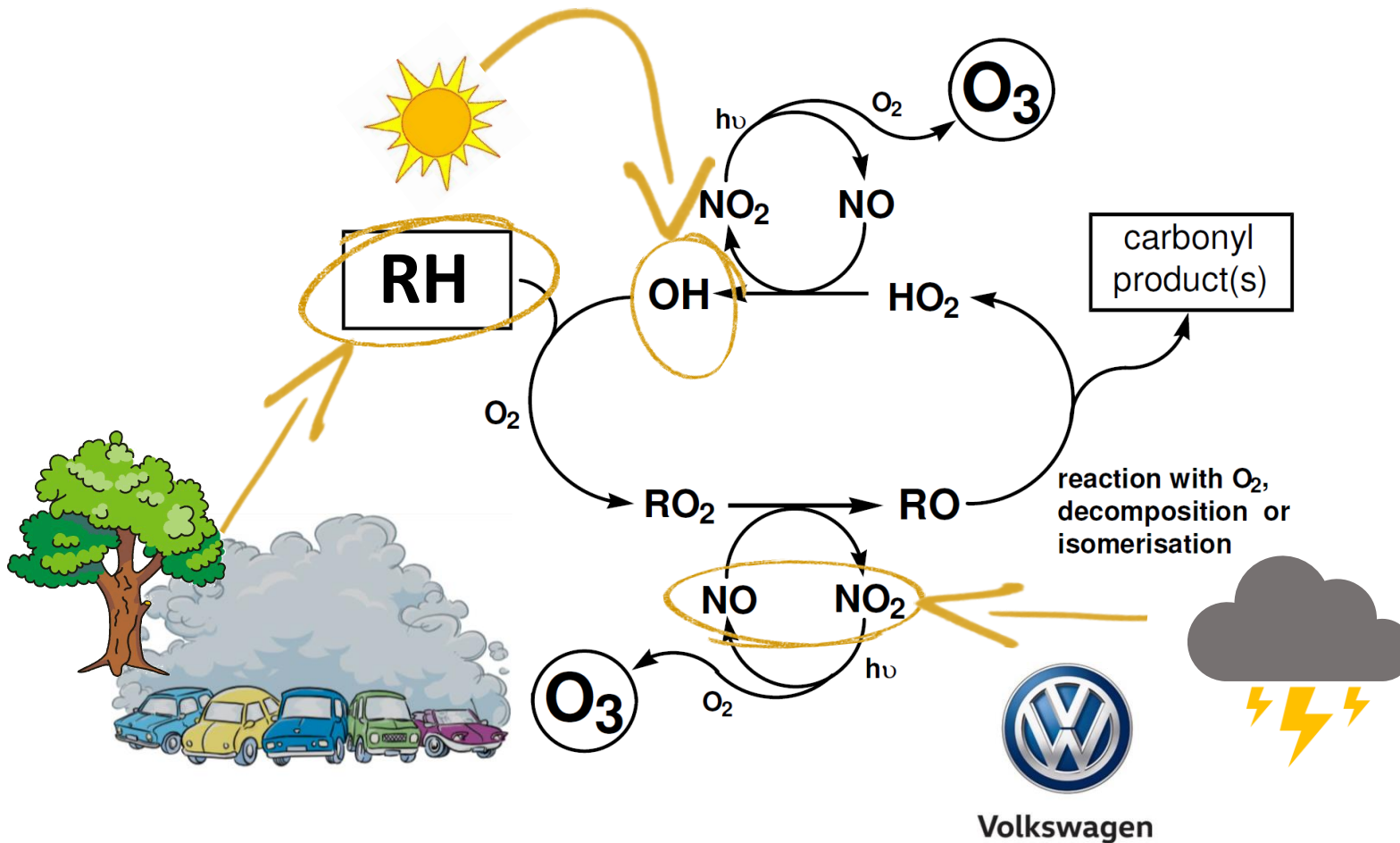
Gases

Gen. 1
Gen. 2
Gen. 3
Gen. 4
Gen. 5
⋮
Gen. n

+ H₂SO₄, + HNO₃, + ... = Aerosols

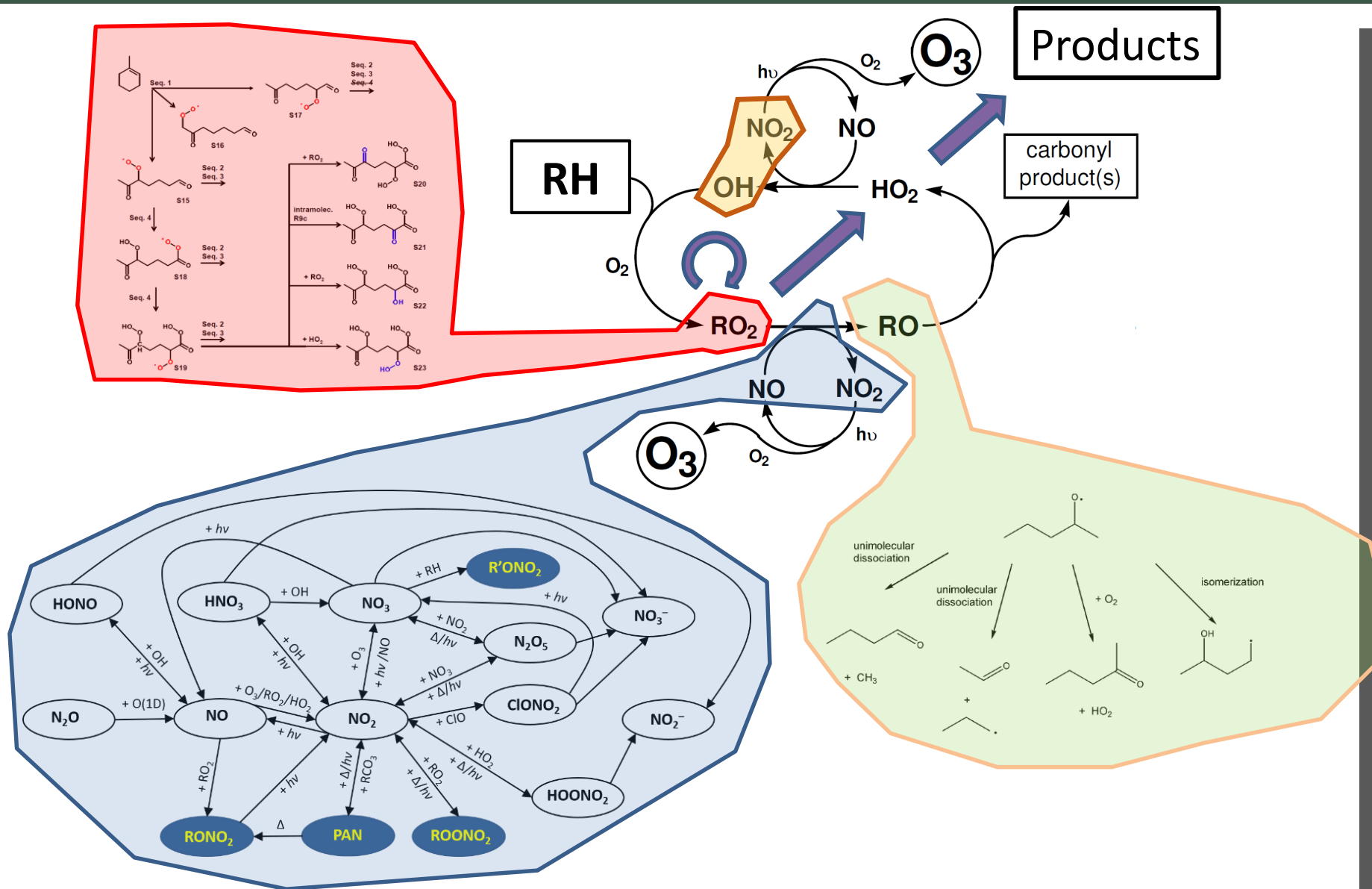
Sources: Valorso et al. (2011), Gao et al. (2004)

Oxidation in the troposphere



- VOCs are emitted from many sources: trees, vehicles, industries, etc.
- They are consumed by OH, but other oxidants are important (NO₃, O₃, Cl)
- **Oxidants are produced in a collectively autocatalytic set**
- Here, VOCs are transformed into a sequence of carbonyls of diminishing size → CO₂
However...

But life is never that easy...



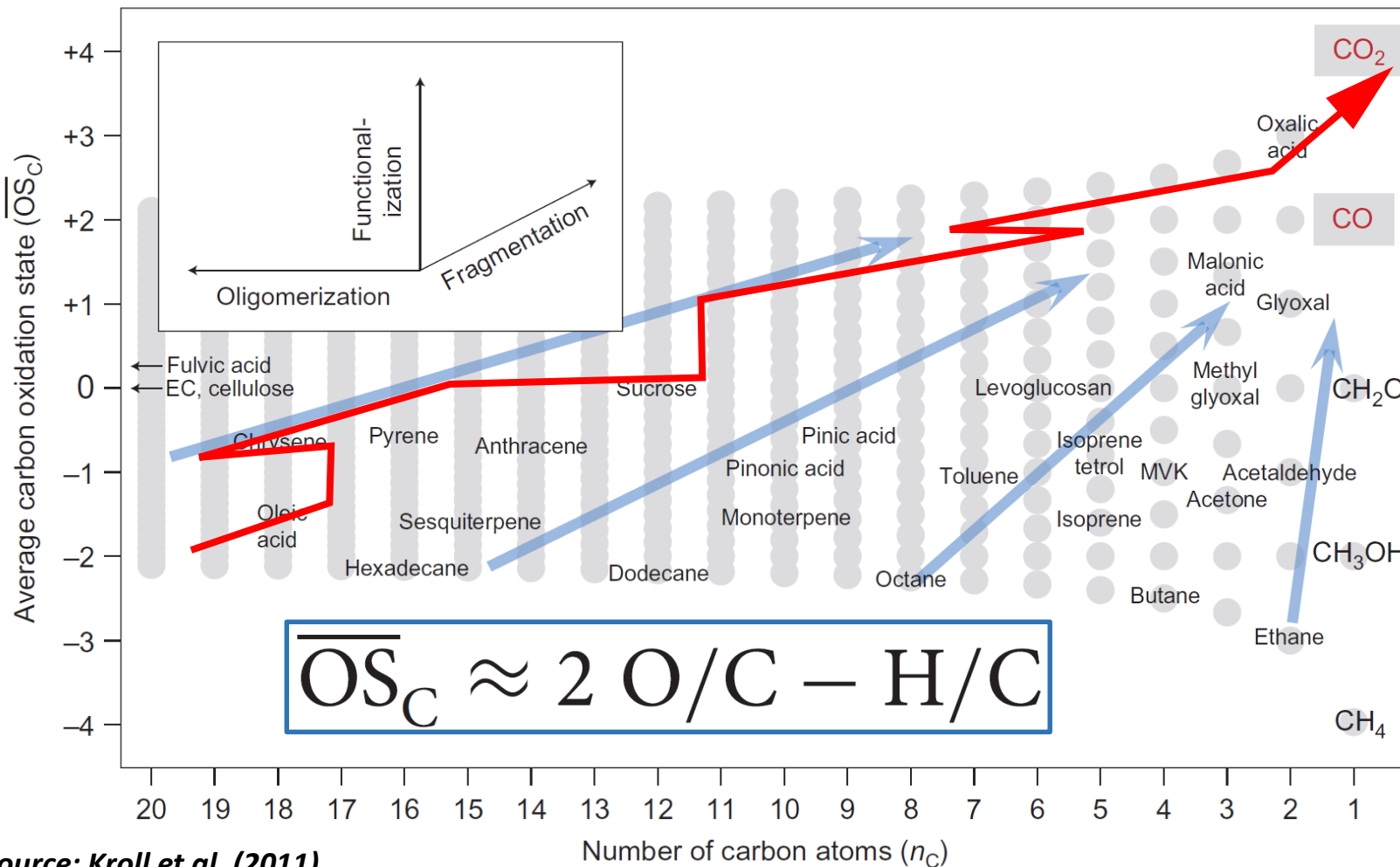
- There are many **branching channels to consider**

- RO₂ and RO have a high capacity for isomerization and fragmentation

- Separate chemical cycles involving nitrogen and sulphur are important

- What if R contains a heteroatom?

Meandering through oxidation space

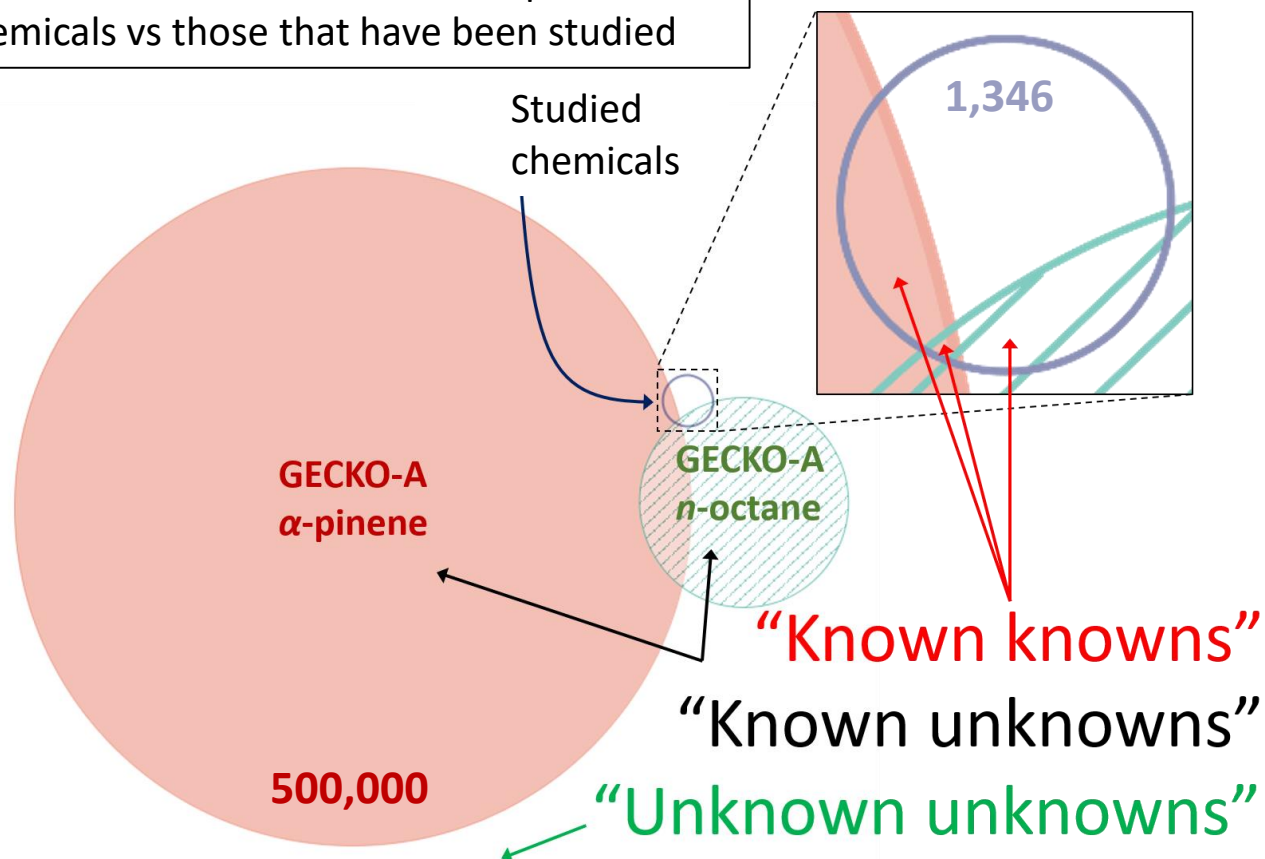


Source: Kroll et al. (2011)

- Atmospheric chemistry is a very cold, very slow combustion
- Eventually, a “fuel” may be converted to CO₂ and H₂O
- **But the path through this space is not simple or direct**
- At what point is atmospheric chemistry unknowable/unpredictable?

The many unknowns of atmospheric chemistry

Area-proportional Venn diagram: number of products formed from two atmospheric chemicals vs those that have been studied



Source: McGillen et al. (2020)

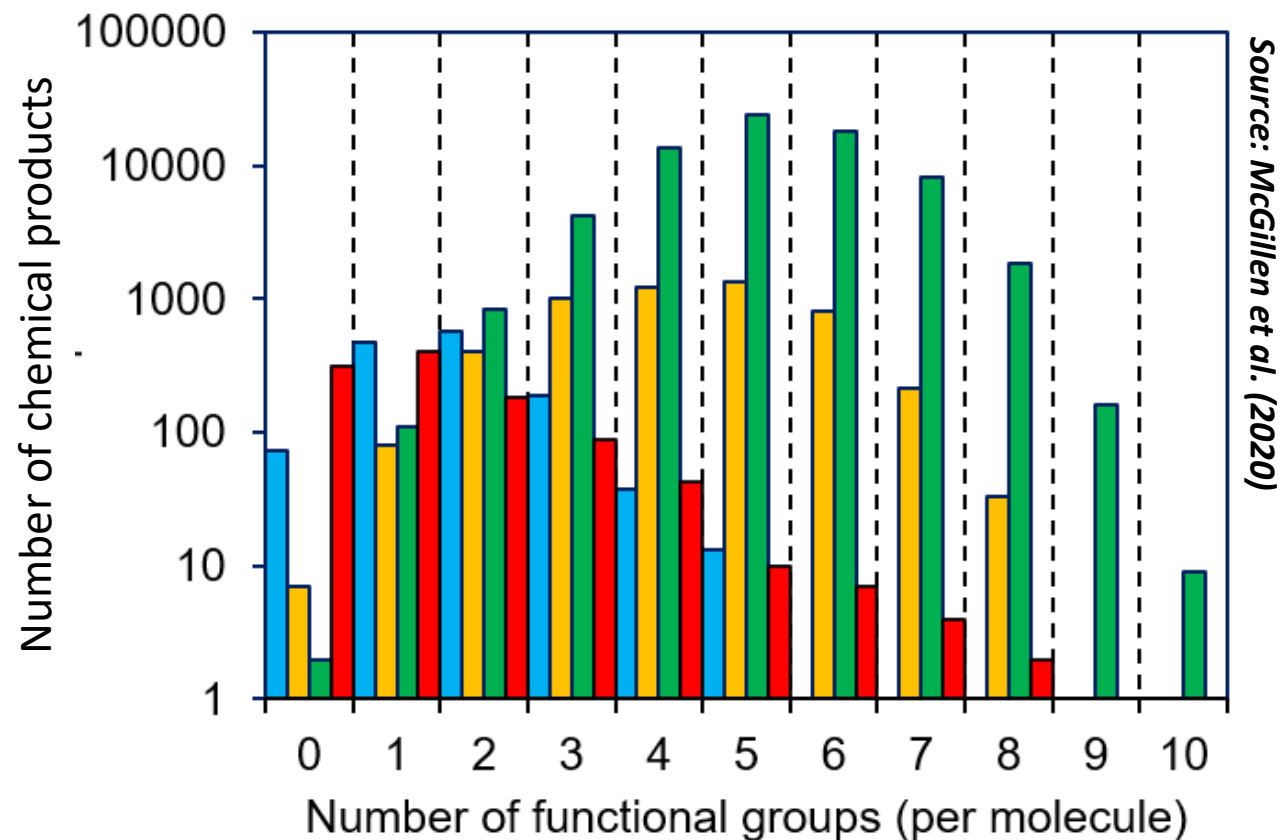
- Far more chemicals expected to form in the atmosphere¹ than have been studied²
- Remember: these are just two primary emissions, what about the 1000s of others?³
- **It is surprising how much we don't know yet (reactivity, products, multiphase)**
- Why? Partly because of the huge numbers, partly because of the types of chemicals formed...

¹ Aumont, B. et al. Modelling the Evolution of Organic Carbon during Its Gas-Phase Tropospheric Oxidation: Development of an Explicit Model Based on a Self-Generating Approach. *Atmospheric Chem. Phys.* 2005, 5 (9), 2497–2517.

² McGillen, M. R. et al. Database for the Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds. *Earth Syst. Sci. Data*, 2020, 12, 1203–1216.

³ Goldstein, A. H.; Galbally, I. E. Known and Unexplored Organic Constituents in the Earth's Atmosphere. *Environ. Sci. Technol.* 2007, 41 (5), 1514–1521.

A closer look at these unknowns

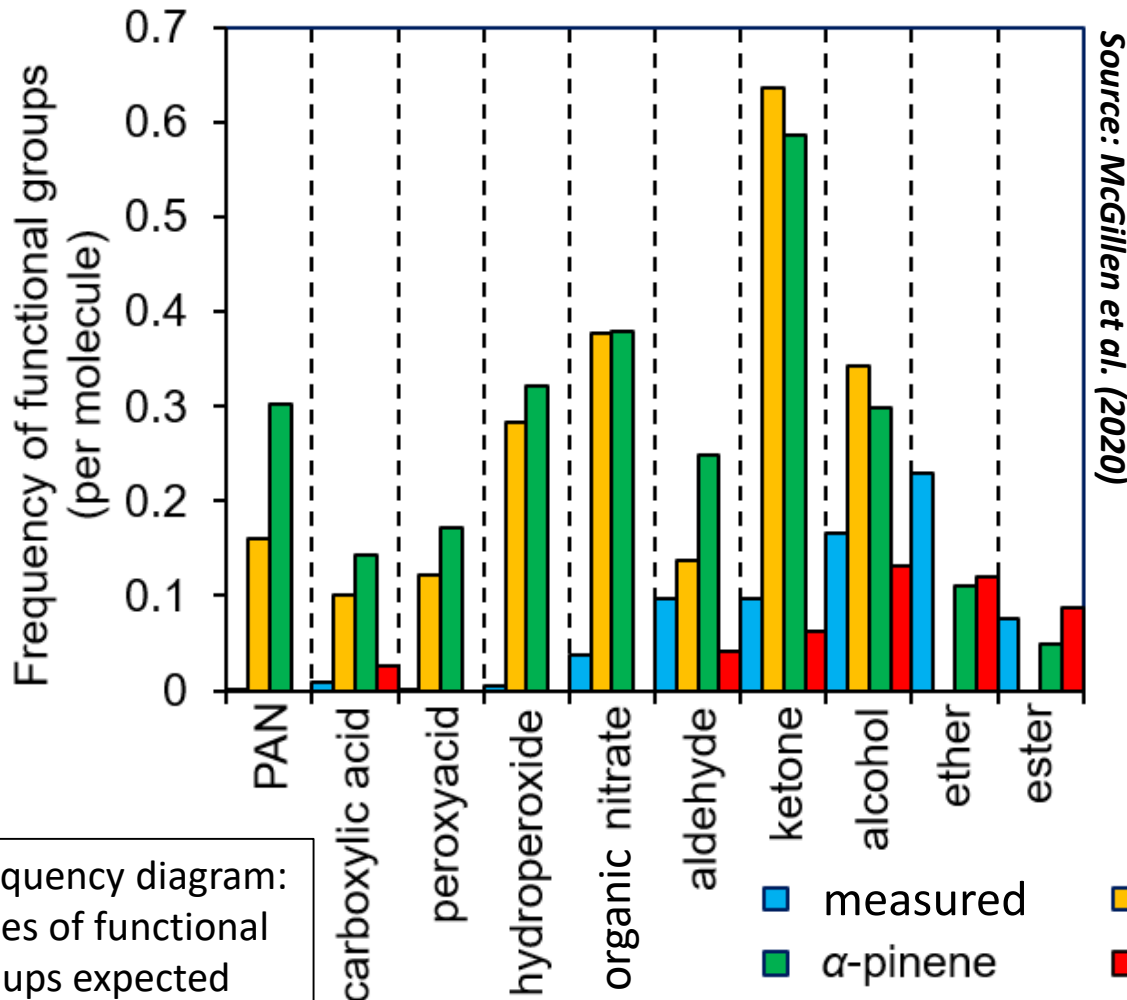


Frequency diagram: number of functional groups found in realistic atmospheric chemicals

■ measured ■ *n*-octane
■ α -pinene ■ US emissions

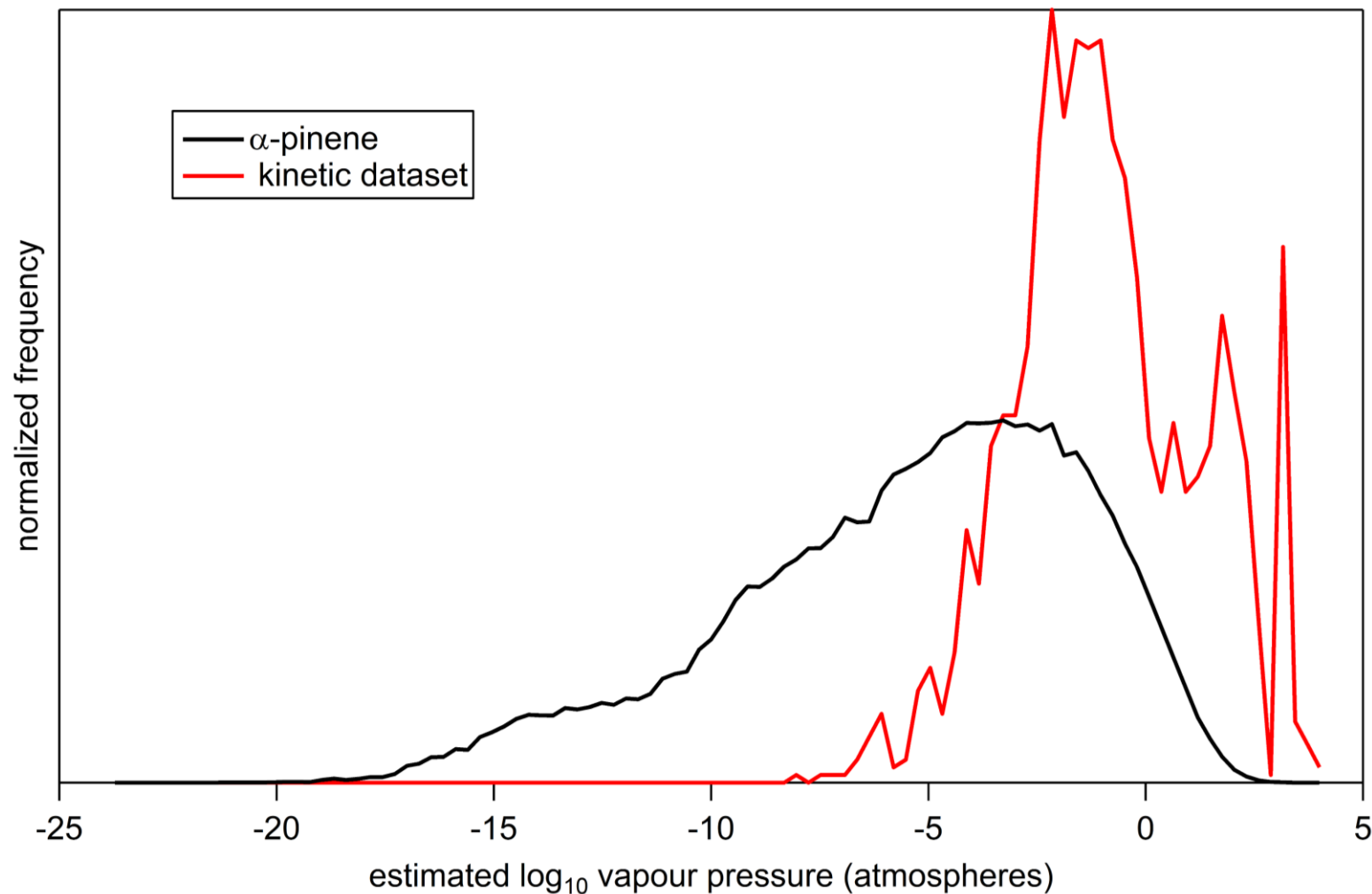
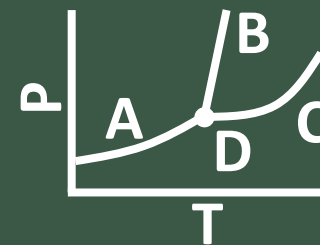
- The types of molecules formed in the atmosphere are messy and complicated
- Measured molecules tend to have 0–3 functional groups, realistic molecules have 4–6
- Why? Very functionalized species tend to be difficult to work with and impossible to purchase
- **On-line instrumentation that measure species at low concentrations only available last ~5 years**

An even closer look at these unknowns



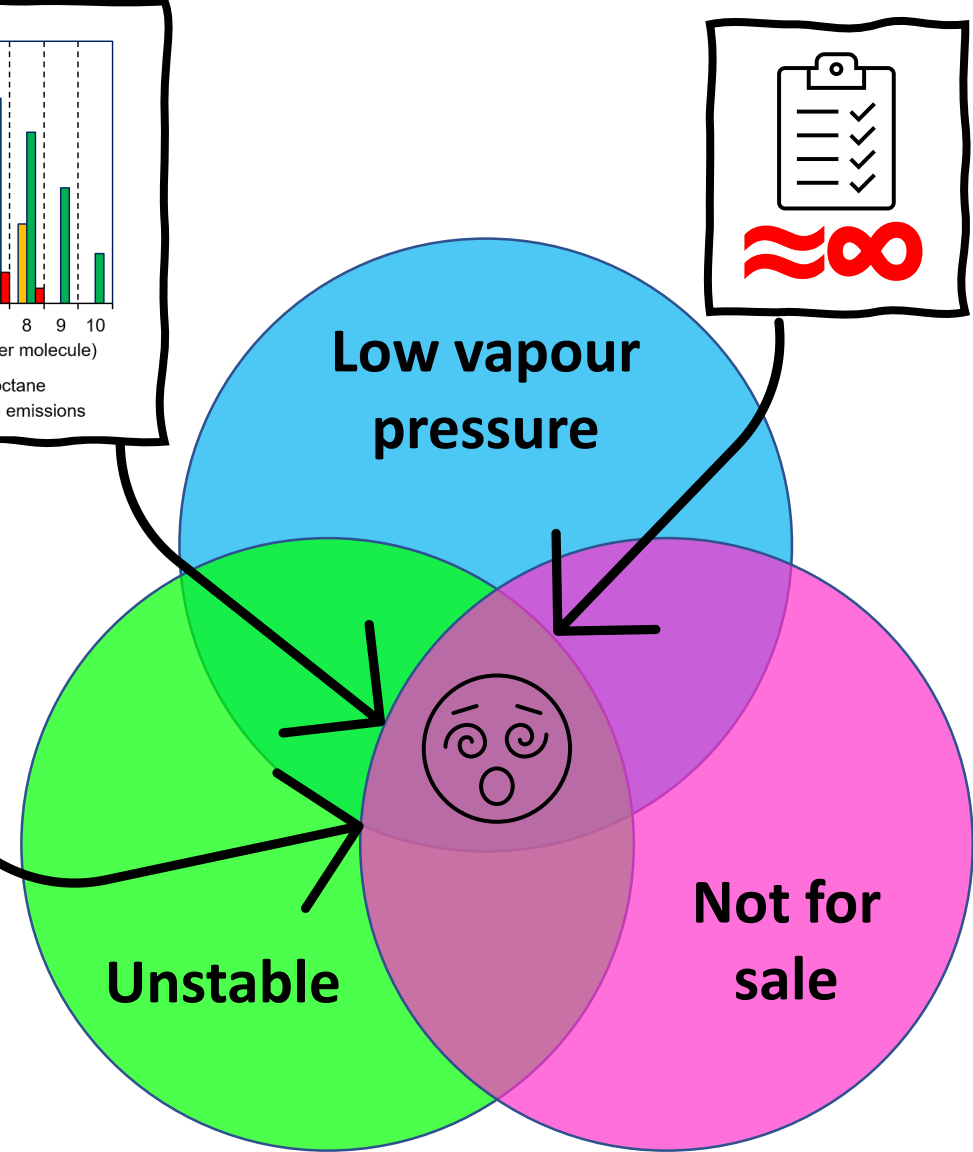
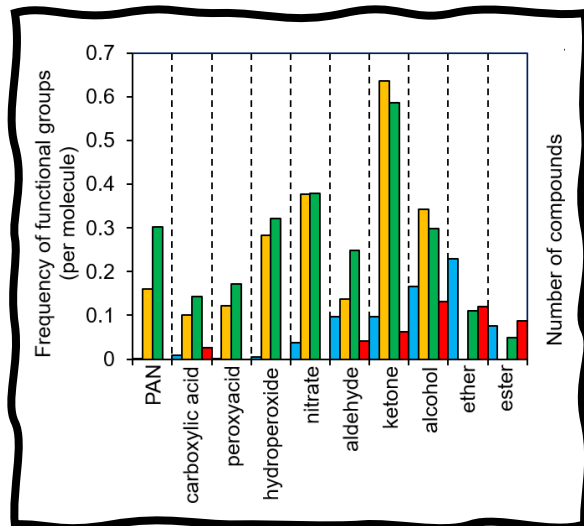
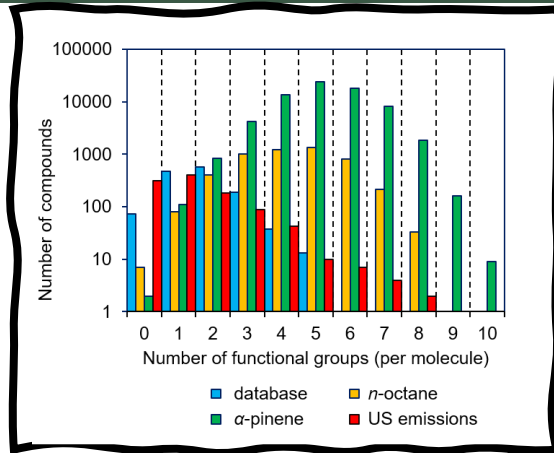
- Furthermore, the types of chemicals that are well represented are very different
- Almost no data is available for nitrates, hydroperoxides, peroxyacids, carboxylic acids and PANs
- **Despite their importance in NO_x -partitioning, new particle formation, secondary organic aerosol formation and oxidizing capacity**
- Why? Because they are difficult to handle, purchase and analyze

Phase-space of the unknowns



- Atmospheric chemistry has a tendency to form oxygenated functional groups
- Carbonyls, carboxylic acids, hydroperoxides, peroxyacids, multi-functional compounds, which tend to form H-bonds easily
- **Real atmospheric molecules are low volatility and are difficult to handle**

How do we solve these problems?

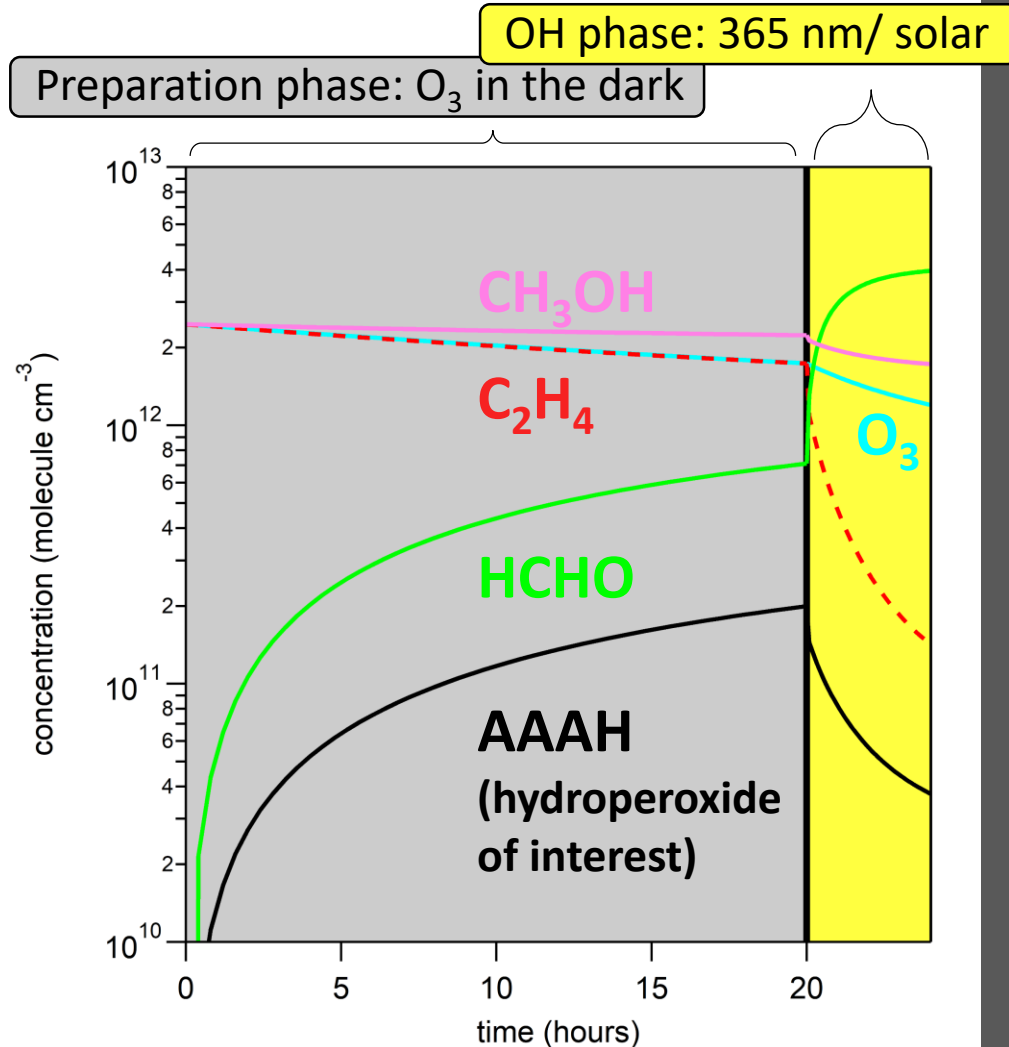


- Recap: real atmospheric molecules are very numerous, difficult to purchase and experiment upon
- The goal: study the atmospheric chemistry of representative species for the first time (reactivity, products, presence in ambient air)
- The plan: exploit very recent advances in analytical chemistry and kinetics (and the extensive infrastructure in CNRS-Orléans)

Can we use chambers to build molecules



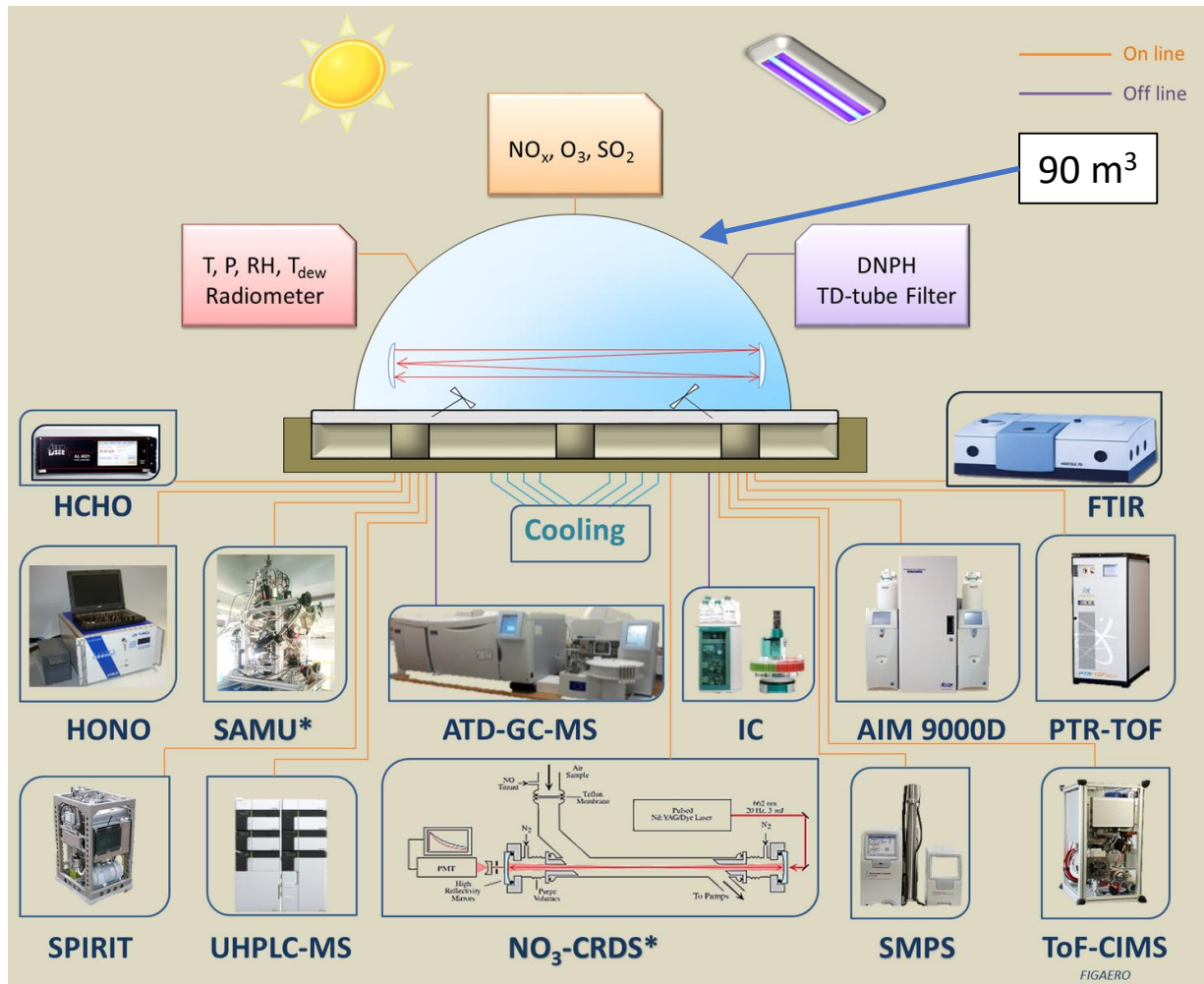
Above: HELIOS platform
Right: numerical simulation of hydroperoxide experiment



- Objective: use chamber facilities to build molecules of interest
- Challenging experiments, requires careful planning
- Begin with model simulations
- Next: consider real-world requirements: chamber, instruments, reagents

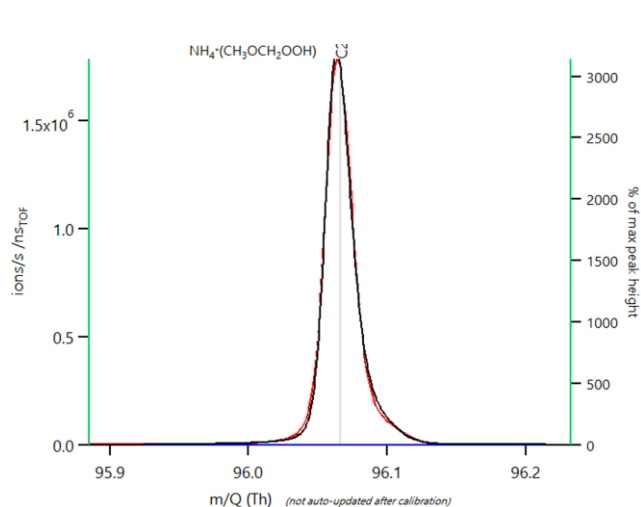
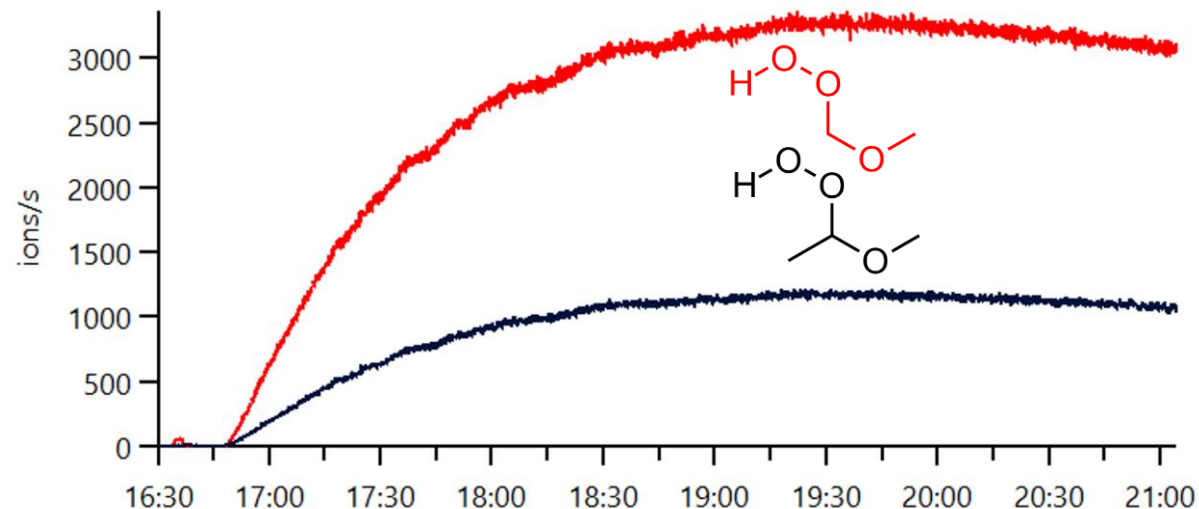
The HELIOS platform

The HELIOS infrastructure



- We have many on-line and off-line capabilities
- With all this analytical capability, it is an opportunity to really characterize these molecules
- HELIOS facilities are already good (but we keep upgrading)
- Instruments operate in field conditions, we can observe at realistic [x]

For simpler ROOH

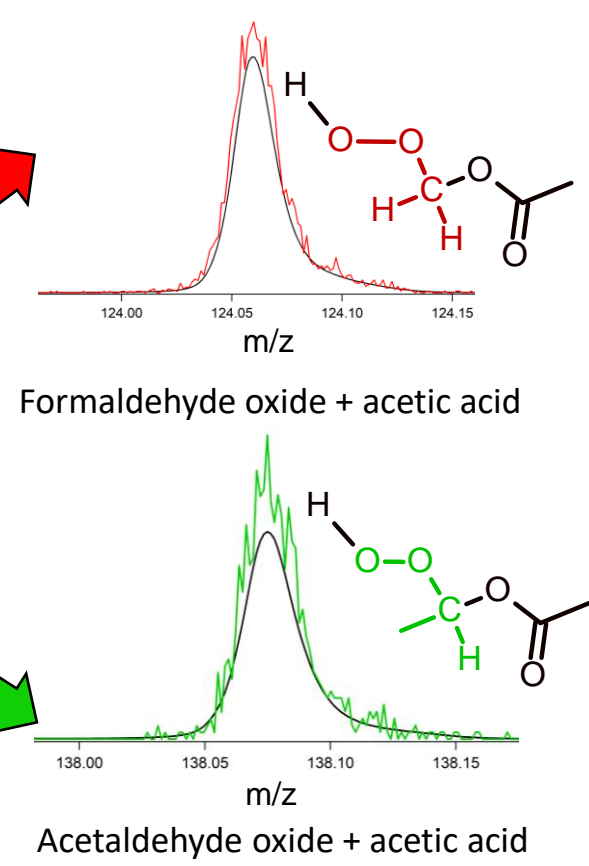
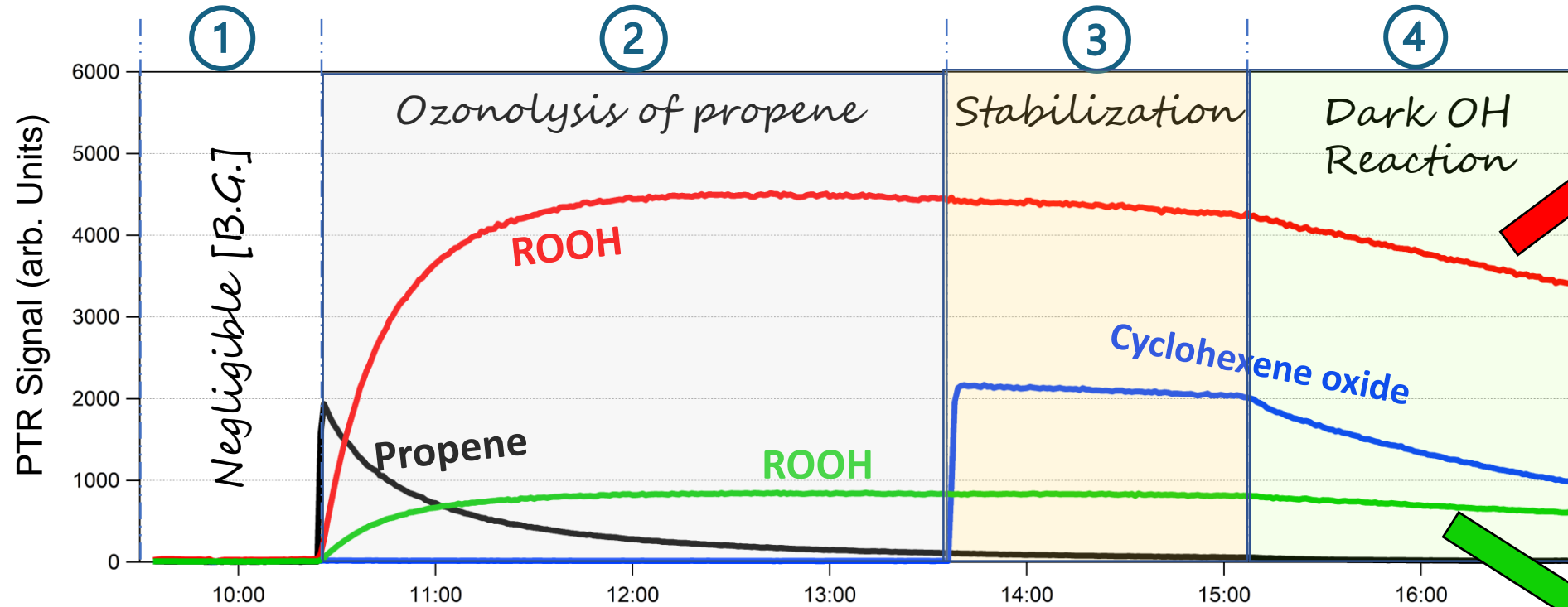


Above: time-series of two hydroperoxides formed under chamber conditions

Left: mass peak demonstrating the application of NH_4^+ ion chemistry to hydroperoxide detection

- **This is good!**
- Chamber-based sample preparation is effective
- Upgrade of PTR-ToF-MS to NH_4^+ demonstrates reliable, sensitive peroxide detection
- Further upgrades to ion drift tube and inlet materials improve transmission/sensitivity
- Many different peroxides tested so far, many more possible

Also for more complicated ROOH

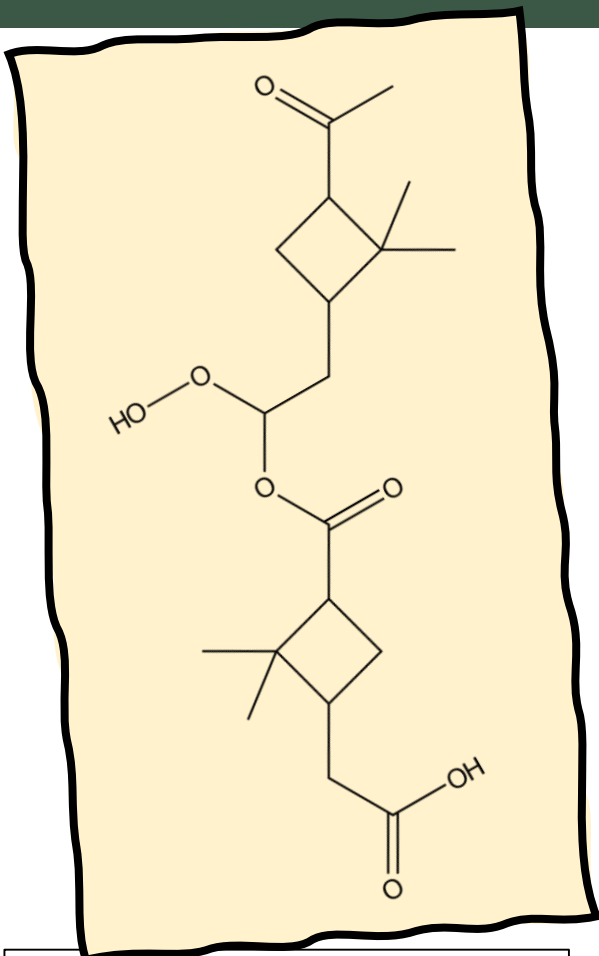


- In the chamber we can build some quite sophisticated molecules
- This was achieved with ozonolysis, whereby the Criegee intermediates sequentially insert into labile O-H bonds.

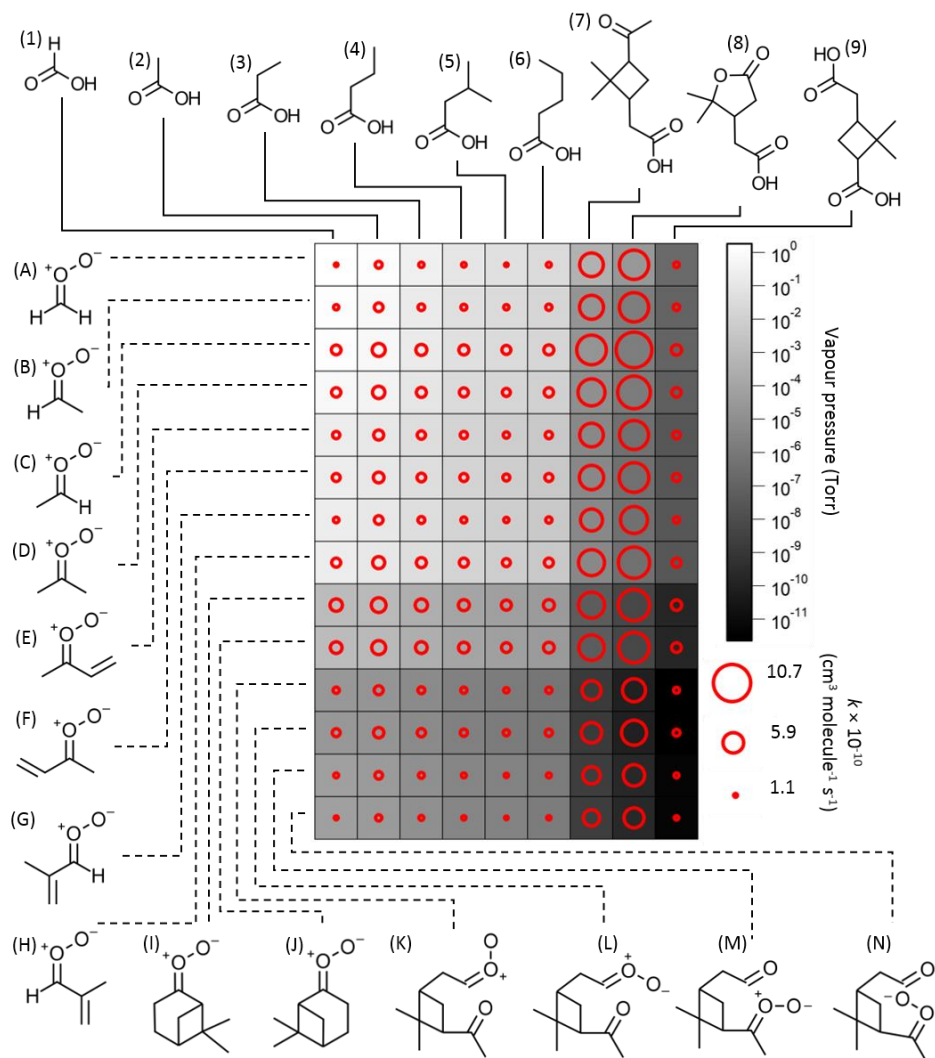
• **These chemicals are happy in our chamber, but imagine trying to isolate them...**



Why are ROOH interesting?



Above: A low-vapour pressure hydroperoxide
Right: A matrix of different Cl and acid combinations

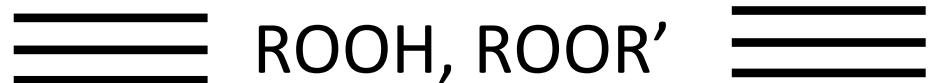


Source: Chhantyal-Pun et al. (2018)

- There are potentially lots of different Criegee intermediates and R(O)OH in the atmosphere
- These rate constants are really big
- It's a way of adding carbon and oxygen in one step
- **This could be a source of particles in the atmosphere**

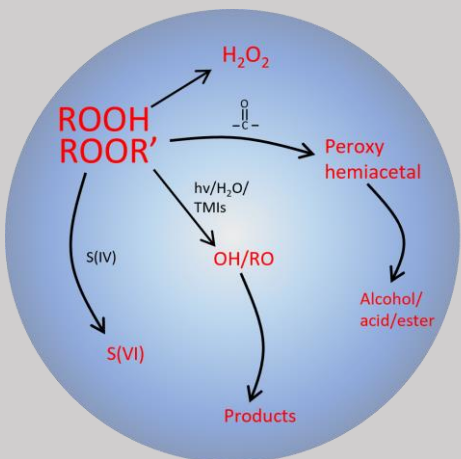
Many types of peroxides...

- What is their overall effect on the atmosphere?
- Which reactions dominate?



Particles ←

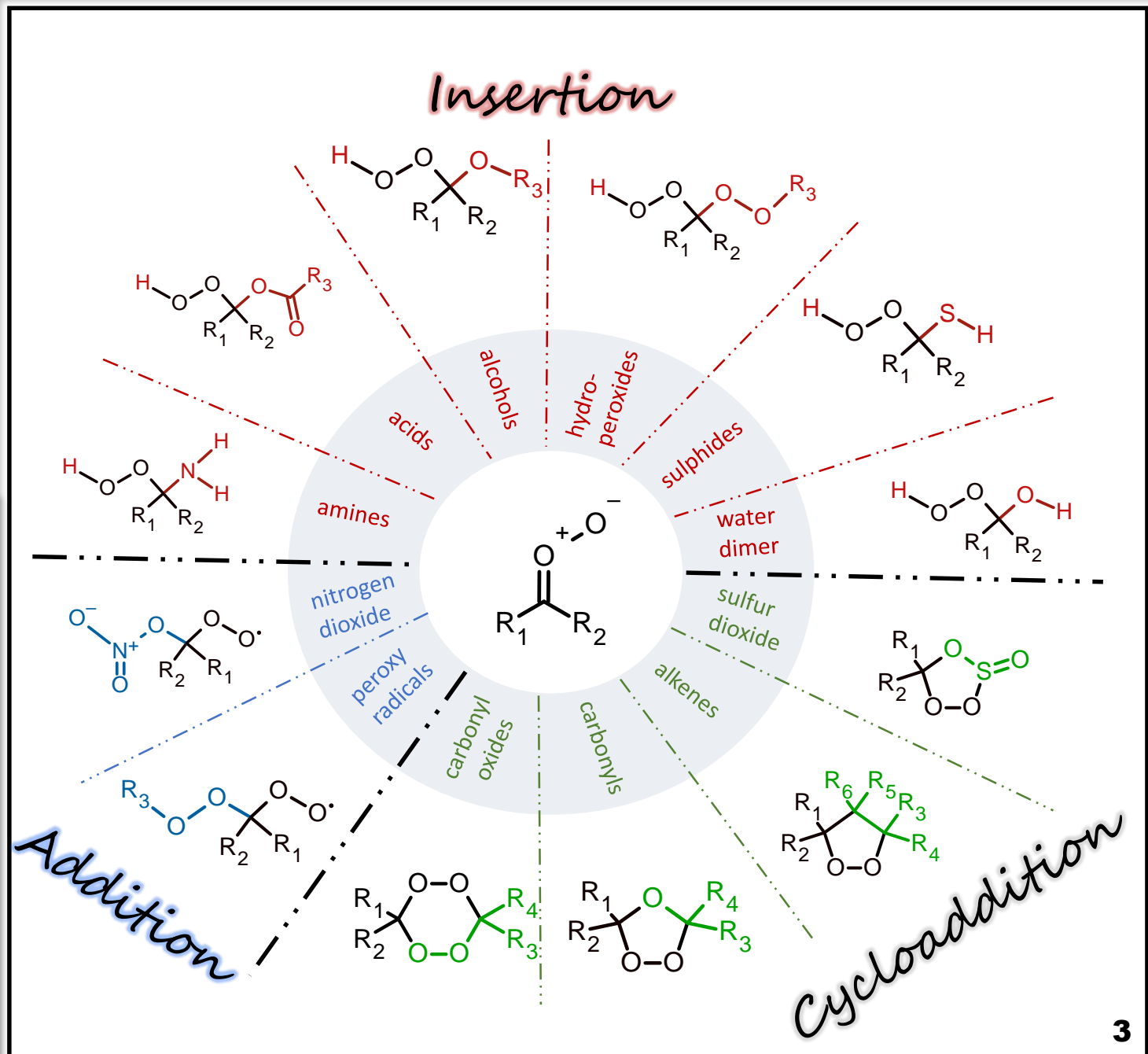
Gas



Oxidation?

Photolysis?

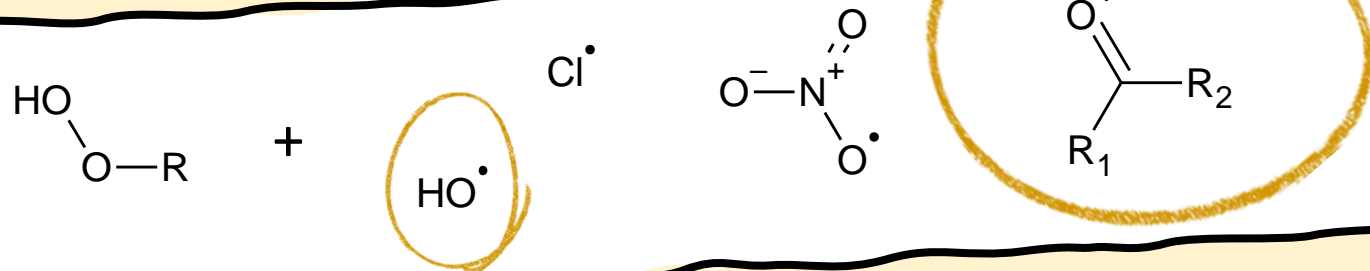
Thermal decomposition?



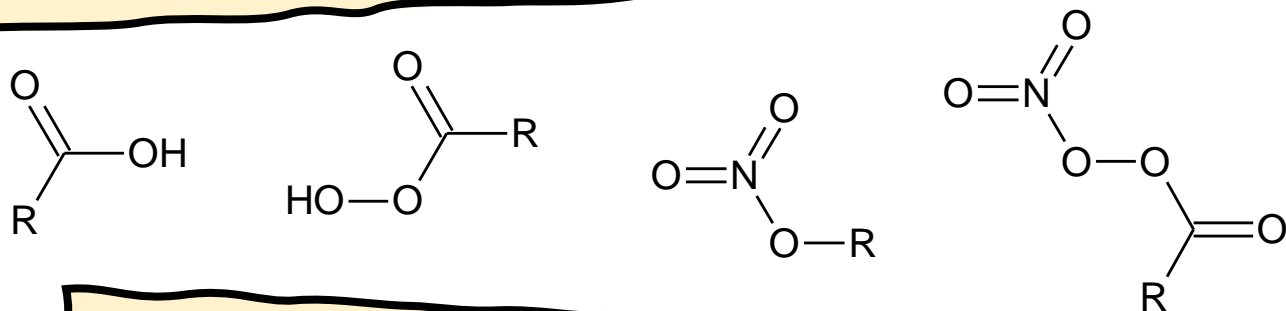
Where next?



Kinetic studies of ROOH



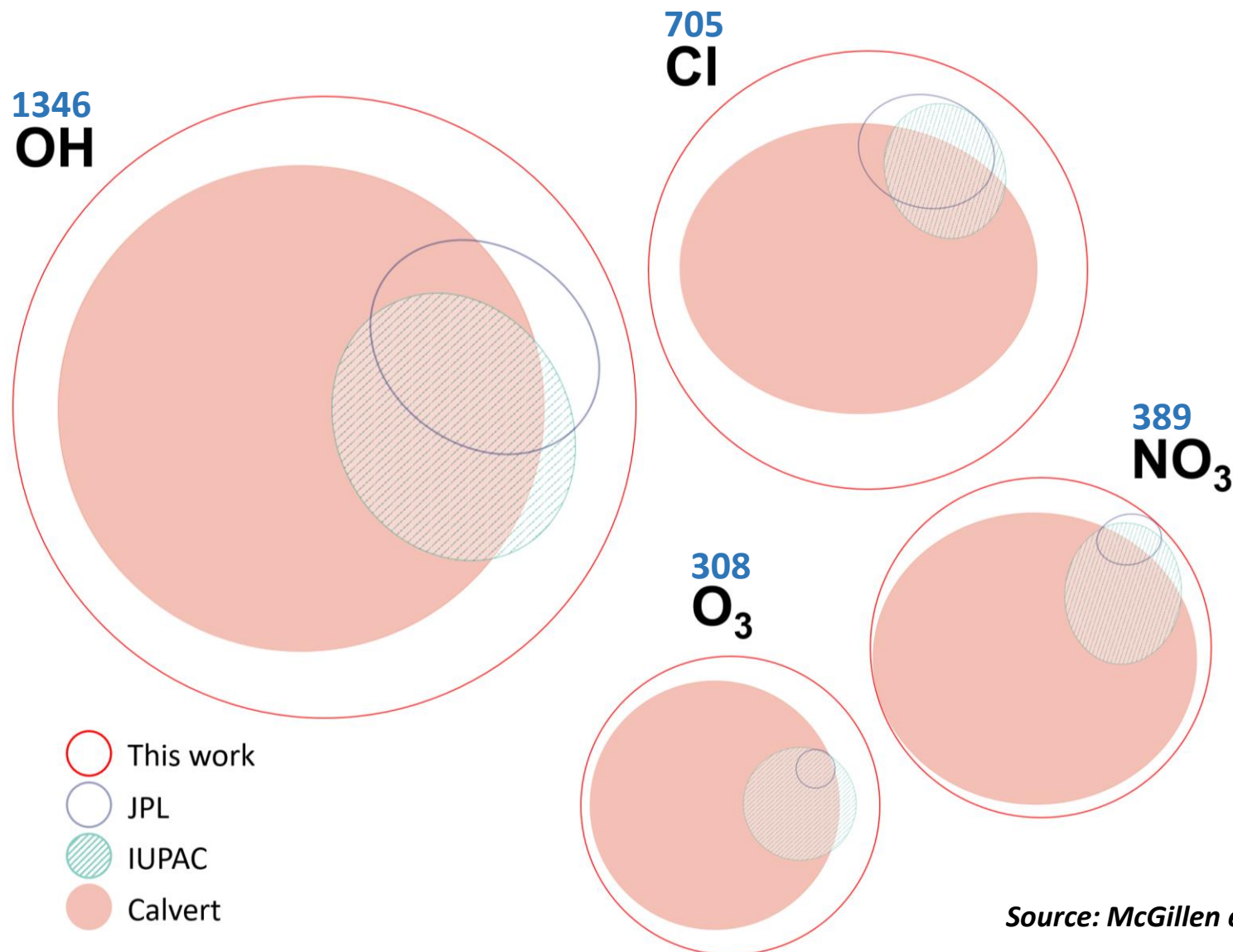
Kinetic studies of other underrepresented functionalities



Product studies

- Now that we have successfully made some “representative” compounds, we need to quantify their effect
- There are several other chemical functionalities of interest, and combinations thereof
- We also need to start thinking about what products are being formed

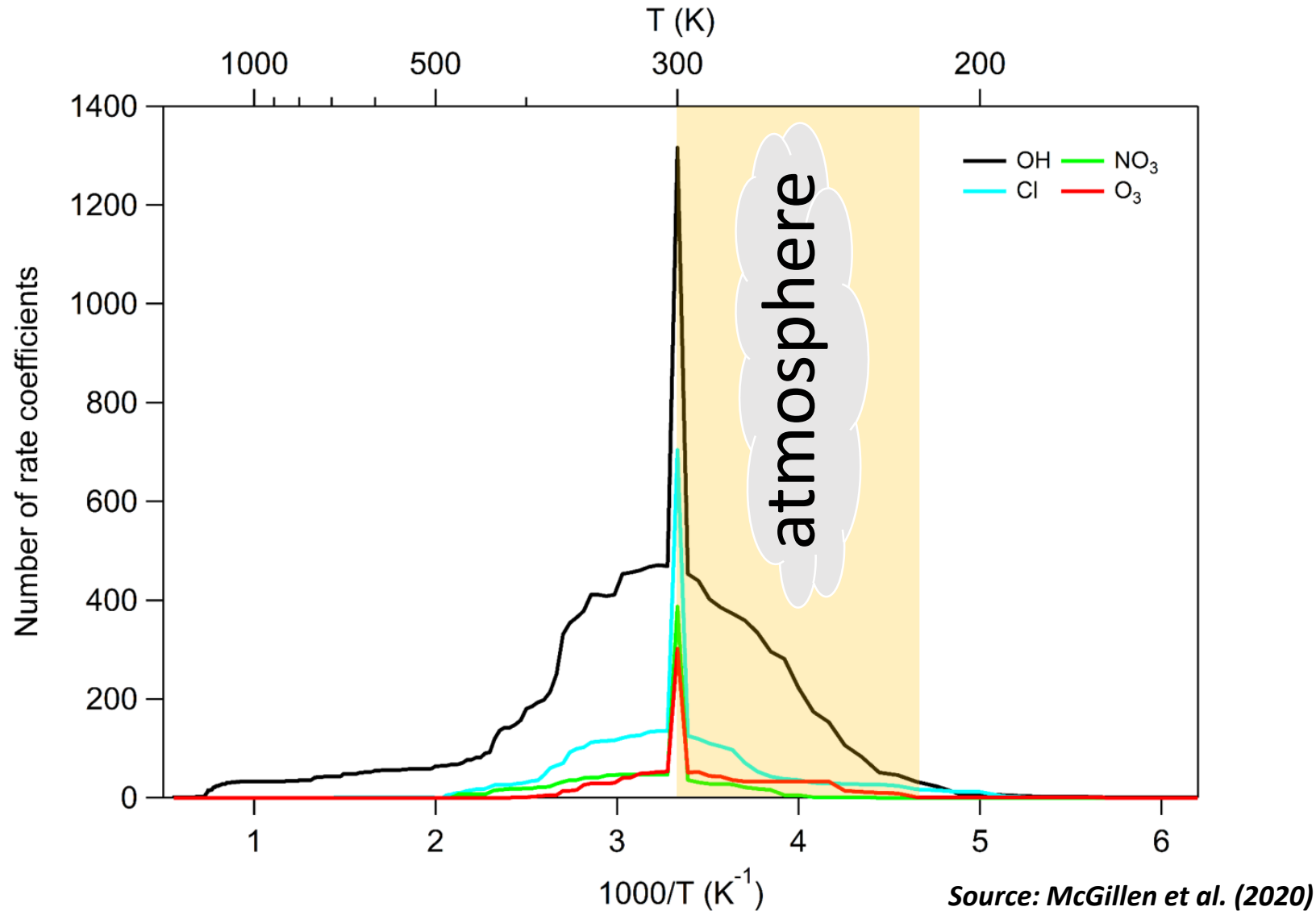
Improving the kinetic database



- All of this new data will contribute to our kinetic database
- **This is the biggest database of its type for atmospheric reactions**
- This should be useful to chemical modellers and laboratory scientists

Source: McGillen et al. (2020)

Improving the kinetic database



- This is OK, but most of the data is at room temperature

- **Our labs are room temperature, but our atmosphere is not:**

$$\overline{T_{\text{trop}}} = 274^{+30}_{-60} \text{K}$$

- That's not too bad for OH, but it's really bad for other important reactions NO₃, O₃, Cl

<https://data.eurochamp.org/data-access/kin/#/data>


LOGIN HOME SEARCH DATABASE DOWNLOAD DATABASE DOWNLOAD & SEARCH STATISTICS

RESET SEARCH

VIEW BY COMPOUND VIEW BY RECOMMENDED RATE CONSTANTS

← methoxymethane

Compound



Names: dimethyl ether; methoxymethane; methoxy-methane
Molecular formula: C2H6O
Smiles: COC
CAS number: 115-10-6
InChI: InChI=1S/C2H6O/c1-3-2/h1-2H3
InChIKey: LCGLNKUTAGEVQW-UHFFFAOYSA-N
MG ID: CH3-O-CH3
Type: Ether

Rate constants: $k(T)=A*\exp(-B/T)*(T/300)^n$

Recommended	Oxidant	k298 (cm ³ molec ⁻¹ s ⁻¹)	Δk (%)	A (cm ³ molec ⁻¹ s ⁻¹)	B (K)	n	T (K)	SHOW MORE
✓	OH	2.83 × 10 ⁻¹²	10	1.02 × 10 ⁻¹²	-308	2.0	195 - 1470	SHOW MORE
✗	OH	2.7 × 10 ⁻¹²	15	5.7 × 10 ⁻¹²	222	-		SHOW MORE
✗	OH	2.8 × 10 ⁻¹²	20	5.7 × 10 ⁻¹²	215	-	230 - 300	SHOW MORE
✗	OH	2.7 × 10 ⁻¹²	10	9.7 × 10 ⁻¹²	380	-	256 - 333	SHOW MORE
✓	NO3	1.87 × 10 ⁻¹⁶	60	8.99 × 10 ⁻¹³	2526	-	273 - 373	SHOW MORE
✗	NO3	2.55 × 10 ⁻¹⁶	50	2.3 × 10 ⁻¹²	2714	-	273 - 373	SHOW MORE
✗	NO3	1.07 × 10 ⁻¹⁶	10	-	-	-	-	SHOW MORE
✗	NO3	2.6 × 10 ⁻¹⁶	40	1.36 × 10 ⁻¹²	2526	-	273 - 373	SHOW MORE
✗	NO3	1.95 × 10 ⁻¹⁶	40	-	-	-	-	SHOW MORE
✓	Cl	1.8 × 10 ⁻¹⁰	15	1.8 × 10 ⁻¹⁰	-	-	200 - 500	SHOW MORE

Rows per page: 10 1-10 of 10

- Please take a look at our website!
- It is free, easy to search and you can download the whole thing
- It is evaluated
- **Although my focus is the atmosphere, I have included combustion temperature and other data wherever possible**

But our to-do list is very long...



- We need kinetics and products of reactions, $k(T)$
- $>10^4$ compounds observed in atmosphere^a
- $>10^4$ compounds observed in plants^b
- $>10^5$ industrial chemicals^c
- $\sim 10^5$ isomers within fuel formulations(?)^d
- In total we might have emissions of $\sim 10^6$ species, if each of these makes $\sim 10^5$ products
- Then we could have $\sim 10^{11}$ different reactions
- After 50 years of research, we managed 10^3
- **We need to estimate the kinetics (efficiently)**

^a Goldstein and Galbally (2007)

^b USDA, Dr. Duke's Database (1992)

^c US EPA,

https://comptox.epa.gov/dashboard/chemical_lists

^d From enumerating isomers of a detailed chemical analysis [Shi et al. (2017)]

Estimating reactivity



Pergamon

Atmospheric Environment Vol. 29, No. 14, pp. 1685-1695, 1995
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1352-2310(95)00069-0

ESTIMATION OF HYDROXYL RADICAL REACTION RATE CONSTANTS FOR GAS-PHASE ORGANIC COMPOUNDS USING A STRUCTURE-REACTIVITY RELATIONSHIP: AN UPDATE

ERIC S. C. KWOK and ROGER ATKINSON*†

Statewide Air Pollution Research Center, University of California, Riverside, CA 92521, U.S.A.

1275 citations!

$$k(\text{CH}_3\text{-X}) = k_{\text{prim}}F(\text{X})$$

$$k(\text{X-CH}_2\text{-Y}) = k_{\text{sec}}F(\text{X})F(\text{Y})$$

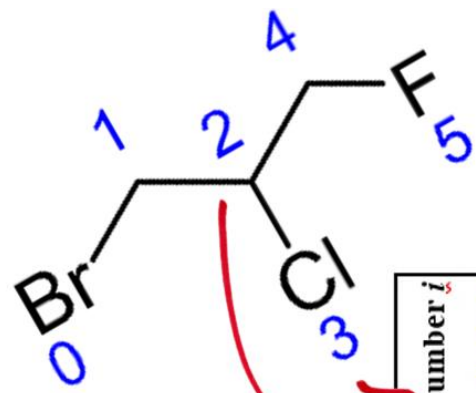
$$k[\text{X-CH}(\text{-Y})\text{-Z}] = k_{\text{tert}}F(\text{X})F(\text{Y})F(\text{Z})$$

- There are too many reactions to study experimentally
- Models with lots of reactions are pointless without reasonable kinetic parameters
- Therefore structure-activity relationships are necessary
- The normal way to approach this is to simplify and assume that many substitutions are the same (lumping)
- **Maybe this isn't good enough**

Estimating reactivity



Simple graph-theoretical algorithm

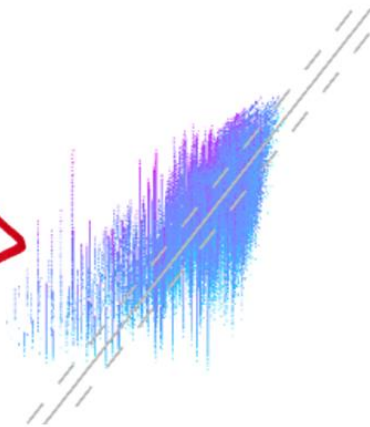


Atom number i	Atom number j	0	1	2	3	4	5
0	0	0	1	2	3	3	4
1	1	1	0	1	2	2	3
2	2	2	1	0	1	1	2
3	3	3	2	1	0	2	3
4	4	3	2	1	2	0	1
5	4	4	3	2	3	1	0

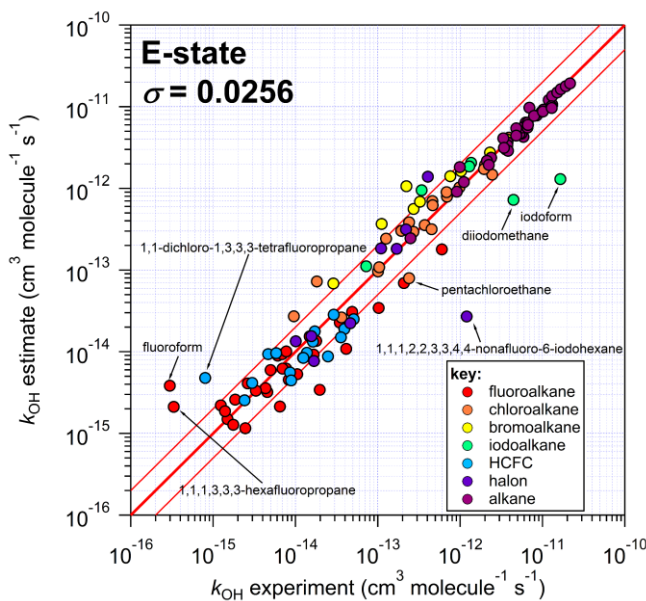
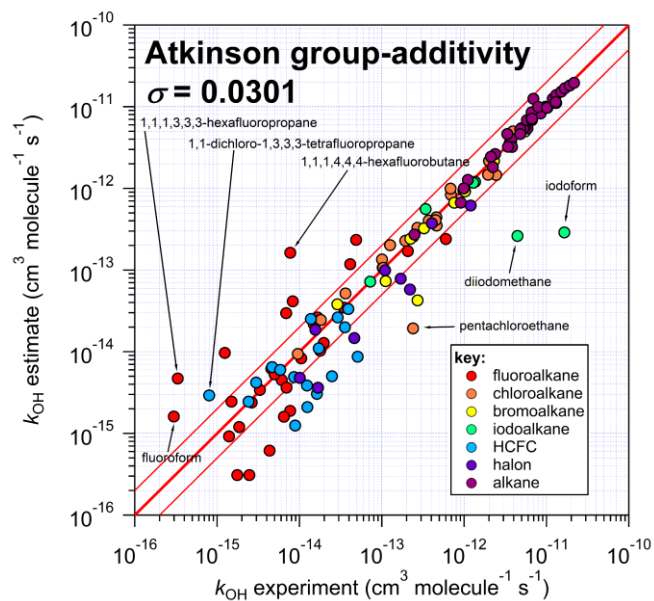


Automated Python code

Rapid rate coefficient estimates

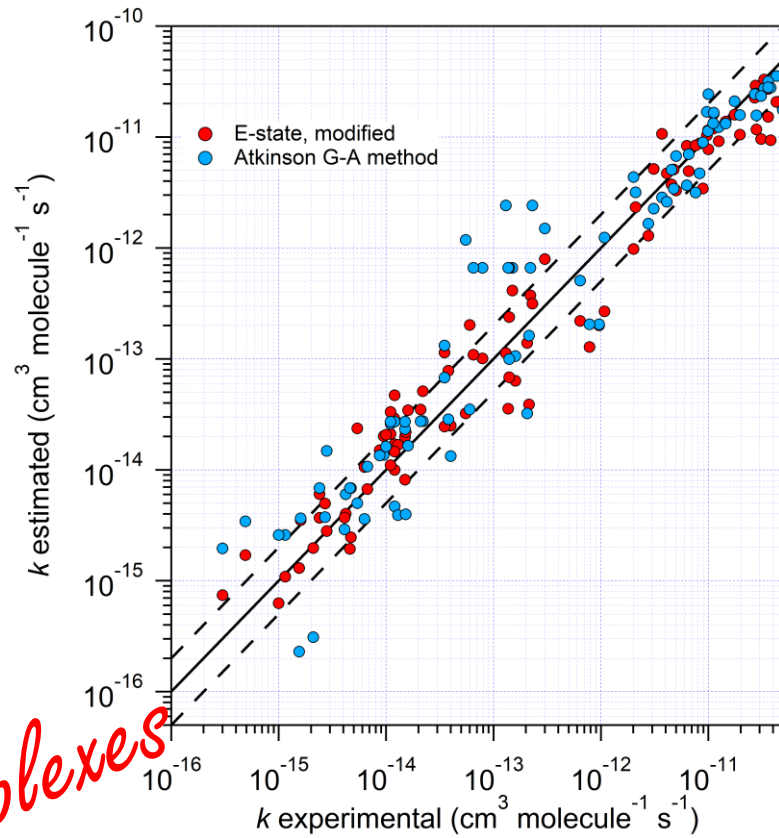
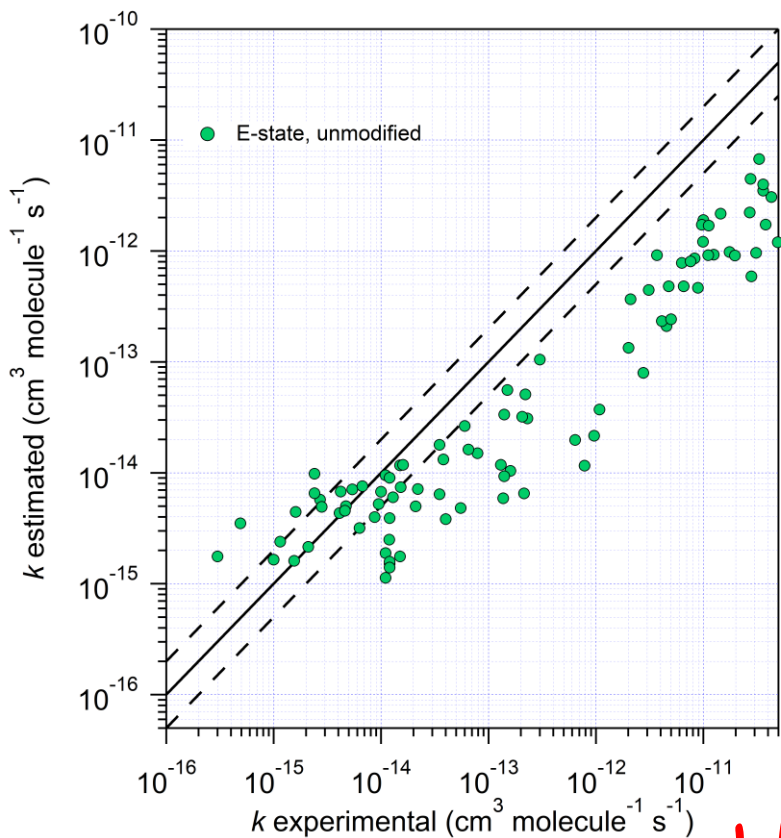


- Is there another way?
- New idea: use the electrotopological state to calculate *a priori* information about substitution

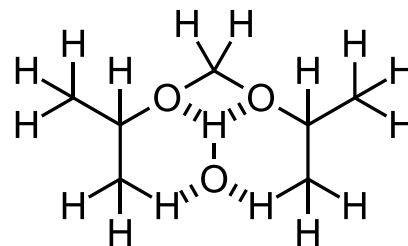
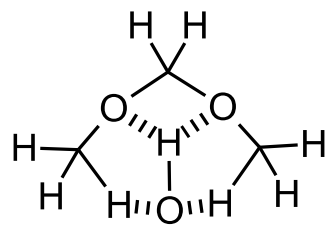
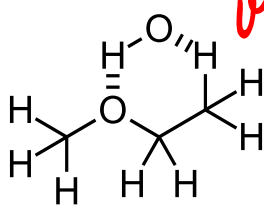
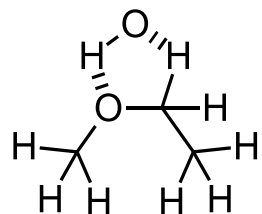


- So far, this appears effective for alkanes and haloalkanes
- **Can it work for other substitution types?**

Estimating reactivity

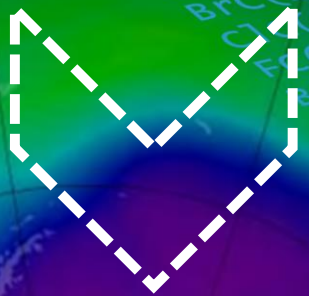


vdW complexes



- **Yes, we can!**
- It works for ethers, but with modification
- It is necessary to parameterize the pre-reactive complex formation
- So it works for alkanes, haloalkanes, ethers and haloethers. What else can it work for?

Check it out!



```
import numpy as np
import pandas as pd
from rdkit import Chem
pd.options.mode.chained_assignment=None
from rdkit.Chem import rdDistGeom

#####
#-----#
#-----# Functions -----#
#-----#
def Wiener_index(mol):
    """Calculate the Wiener index (topological index of a molecule).
    Input: molecule Mol format; If not, use: mol=Chem.MolFromSmiles(m)
    Return: value of Wiener index"""
    res=0
    global amat
    amat=Chem.GetDistanceMatrix(mol)
    num_atoms=mol.GetNumAtoms()
    for i in range(num_atoms):
        for j in range(i+1,num_atoms):
            res += amat[i][j]
    return res

def sum_Hs(x):
    """Calculate the sum of hydrogens in the molecule.
    Input: List of elements to sum (list).
    Returns: sum of the element of a list."""
    for i in range(len(Hs)):
        return sum(x)

def mol2radical(smiles, idx):
    """Converts a molecule SMILES that undergo H-abstraction on an atom to the resulting radical SMILES.
    Input: SMILES of the molecule (str), idx: index of the atom to which H to abstract is attached to (int).
    Return: SMILES of the resulting radical (str)."""
    mol=Chem.MolFromSmiles(smiles)
    mol.Chem.AddHs(mol)
    edit=Chem.RdMol(mol) # editable Mol
    edit.Chem.AddHs(edit)
    rdDistGeom.EmbedMolecule(edit)
    for atom in edit.GetAtoms():
        if atom.GetIdx() == idx: # Carbon where abstraction occurs
            idx_nbr=[]
            for nbr in atom.GetNeighbors():
                if nbr.GetAtomicNum() == 1:
                    idx_nbr.append(nbr.GetIdx())
            if len(idx_nbr) != 0:
                edit.GetAtomWithIdx(idx_nbr[0]).SetAtomWithIdx(idx_nbr[0])
            else:
                pass
    edit.Chem.DeleteSubstructs(edit, Chem.MolFromSmarts('[C]1C1'))
    try:
        Chem.SanitizeMol(edit)
    except:
        edit.GetAtomWithIdx(4).SetNumExplicitHs(1) # if len
    edit.Chem.RemoveHs(edit) # standard Mol
    smiles_rad=Chem.MolToSmiles(edit)
    return smiles_rad
```

atoms_indexed	iist	9	['atom_1', 'atom_2', 'ato
bond_type	list	1	['SINGLE']
check	int	1	1
col	list	2	['knot', 'Wiener_index']
columns	iist	38	['knot', 'Wiener_index',
count	dict	2	{ '[CH2]':1, 'CF':1}
count_add	dict	2	{ '[CH2]':1, 'CF':0}
counter	int	1	1

Console I/A X

STRUCTURE: FCF

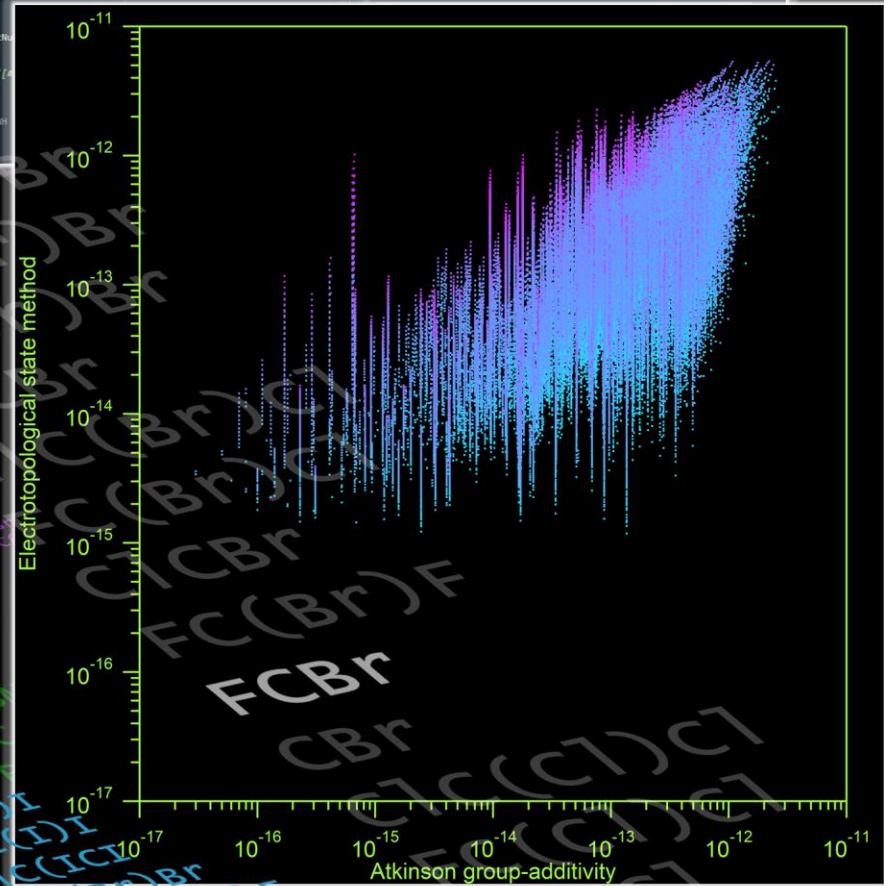
Atom idx: 0
Neighbors idx: [1]
Bond types: ['SINGLE']

Atom idx: 1
Neighbors idx: [0, 2]
Bond types: ['SINGLE', 'SINGLE']

Atom idx: 2
Neighbors idx: [1]
Bond types: ['SINGLE']

Atom	Idx	I_val	SI	Valence	Hs	kpred	Radical_product
0	F	0	8.0	9.625	1	0	0.000000e+00
1	C	1	1.5	-1.750	2	2	5.311505e-15
2	F	2	8.0	9.625	1	0	0.000000e+00

knot 5.311505150262281e-15



Some closing remarks



- Introduce myself

Done ✓

- Explain my motivations for studying atmospheric chemistry

It is killing us!

- Describe some of the complexity of this subject

There are too many unknowns!

- How can we understand it further?

By using all of the analytical tools, reactors and kinetic data

By learning how to predict missing data

Merci de votre attention !