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Approaches to comprehend and address atmospheric chemical complexity

Max R McGillen

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Habilitation à diriger des recherches

Présentée devant

L'Université d'Orléans



Approaches to comprehend and address atmospheric chemical complexity

Approches pour comprendre et résoudre la complexité chimique atmosphérique

Spécialité :

Chimie et Physique de l'Environnement

Par

MCGILLEN, Max R.

Soutenue le 06/01/2022 devant la Commission d'Examen

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1. Curriculum Vitae:

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10/2020–present	CNRS Chargé de Recherche in the Équipe de Recherche Atmosphérique, ICARE CNRS-Orléans. Group leader: Dr. Wahid Mellouki
09/2018–04/2020	Visiting Research Fellow, Le Studium Institute for Advanced Studies/ ICARE CNRS-Orléans. Group leader: Dr. Wahid Mellouki
05/2018–09/2020	Consultant, University of California/ CRC, Riverside, USA. Group leader: Prof. William Carter
04/2016–04/2018	Marie Skłodowska-Curie Research Fellow, School of Chemistry, University of Bristol, UK. Group leaders: Profs. Dudley Shallcross, Andrew Orr-Ewing and Simon O'Doherty
10/2010–10/2015	Research Scientist, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA. Group leader: Dr. James Burkholder
10/2007–10/2010	Post-Doctoral Research Associate, School of Earth, Atmospheric and Environmental Chemistry, University of Manchester, UK. Group leader: Dr. Carl Percival
10/2004–10/2007	PhD thesis, School of Earth, Atmospheric and Environmental Chemistry, University of Manchester, UK. Thesis advisor: Dr. Carl Percival

Summary of my research activities:

Starting from the commencement of my PhD up until now I have spent over 16 years studying, making progress in, and remaining fascinated by atmospheric chemistry. Over this time, I have become an author of 47 peer-reviewed scientific papers, 15 of which I am first author, and 14 more where I am second author. These statistics speak to the leading role that I play in my many collaborations with scientists from other laboratories, institutions and continents. My overarching aim over this time period has been to obtain a diverse and balanced experience in atmospheric chemistry. An experience that encompasses laboratory, field and modelling work and also one that could bring me into close contact with several leading scientists and the many and varied techniques and analytical instrumentation that they employ to study the atmosphere. I am now in a position where I am skilled in a broad range of instrumentation including chemical ionization mass spectrometers, proton-transfer reaction mass spectrometers, laser-induced fluorescence, UV absorption techniques, gas chromatography and Fourier-transform infrared spectroscopy, and where I am expert enough to share my knowledge of these techniques with students and other trainees. Much of my focus so far has been to apply these techniques to the study of gas kinetics, which (for me), represents the critical process that governs how the emissions from the biosphere and the anthroposphere are transformed in the environment, and how they ultimately affect air pollution and climate. I have recently finished a large and ambitious project in which I, together with my colleagues, compiled and reviewed the gas kinetic literature in its entirety for the reactions of OH, O₃, NO₃ and Cl, a study which is now published in *Earth System Science Data*. (McGillen et al., 2020) Development on this database continues, and we will soon publish our first update since the initial release, together with a new user-friendly website to complement the existing spreadsheet database that is already available. This was a major undertaking, and one that I anticipate will be of much service to the scientific community. An important aspect of this work became an assessment of what the state-of-the-knowledge is regarding atmospheric gas kinetics. It became clear to our group that despite ~50 years of research, our

community's understanding of the vast majority of chemical reactions in the atmosphere is inadequate and that this problem is especially acute for certain important functional groups. It is noted that it is unfeasible to study all of the compounds that are formed and are present in the atmosphere, but it is nevertheless useful to know how fast they react. This is why I am an active participant in an international panel on structure-activity relationships, whose principle aim is to assess and improve our ability to predict unknown reaction rates. With this in mind, it is therefore only appropriate to adopt a strategic and targeted approach to reducing the uncertainties associated with the reactions outlined in this HDR proposal and to find ways to improve our ability to predict the fates of all those chemicals that continue to escape experimental inquiry.

In the following subsections, I present some research highlights from my doctoral thesis/ post-doctoral appointment at The University of Manchester (UK), my time at NOAA (USA), my Marie Skłodowska-Curie fellowship at The University of Bristol (UK), the consultancy work that I provided on behalf of the Coordinating Research Council for Prof. William Carter at The University of California Irvine (USA) and my recent appointment as Le Studium fellow (now CNRS Chargé de Recherche) at ICARE, Orléans.

i. PhD thesis, The School of Earth and Environmental Sciences, The University of Manchester, UK.

Dates: 10/2004–10/2007

I earned my PhD under the tutelage of Dr. Carl Percival. This was a National Environmental Research Council (NERC) appointment culminating in a thesis entitled: "Laboratory and structure-activity relationship (SAR) studies into the oxidation kinetics of non-methane hydrocarbons (NMHCs) in the troposphere". As the title suggests, this work represented a combination of my activities in developing novel, topology-based SARs for the prediction of oxidation reaction kinetics (McGillen et al., 2006a, b, 2007b) together with experimental measurements of OH and ozonolysis kinetics conducted in flow tubes (McGillen et al., 2007a) and chamber systems. (McGillen et al., 2008) My education in atmospheric chemistry was kick-started near the beginning of my PhD when I was awarded an NERC bursary award to attend the European Research Course on Atmospheres (Grenoble), where I took some of my first lectures in atmospheric chemistry from Nobel Laureate, Prof. Paul Crutzen, among several other celebrated scientists.

I was granted a considerable amount of independence as a PhD student, which allowed me to develop my own SAR algorithms for ozonolysis reactions. (McGillen et al., 2008) A major highlight of this work was when I won an INTROP (European Science Foundation) travel grant to visit Prof. John Wenger at University College Cork (Ireland), which exposed me to the science of chamber measurements and allowed me to test SAR predictions against measurements. Back in Manchester, I was also able to learn about the chemical ionization mass spectrometry (CIMS) technique – using what was probably the first CIMS instrument existing in the UK at that time – which was employed to measure absolute reaction rates of OH radicals + alkenes, (McGillen et al., 2007a) as well as peroxy radical cross reactions. (Raventós-Duran et al., 2007a, b) Further experimental studies were also conducted in the bulk solution phase, (Reynolds et al., 2006) where ozonolysis of oleic acid was analysed using ion trap mass spectrometry coupled with electrospray ionization.

ii. Post-doc, The School of Earth and Environmental Sciences, The University of Manchester, UK.

Dates: 10/2007–10/2010

For my first post-doctoral appointment, my main duty was to develop a THS Instruments CIMS for making measurements on the BAe-146 UK research aircraft. This required the construction of a fully airworthy instrument rack, onboard calibration and gas supplies and an automated heated fast-flow

inlet system. An important part of this work was guiding the instrument through the certification process, which is as strict as any commercial aircraft operating in the UK. Another challenge was to develop a working procedure for making measurements in the field, since our research group had no previous experience with measurements outside of the laboratory. In an intermediate step, we began by deploying the instrument to CEH Edinburgh (UK), where we participated in a large-scale intercomparison of ammonia measurements in a rural setting.(von Bobruzki et al., 2010) Following this, the instrument was interfaced to the BAe-146, where it was initially used to make formic acid measurements in-flight around the UK,(Le Breton et al., 2012) but for which it has since been used for many other measurements.

It was important to me that I maintained my laboratory activities during this post-doc, and I drew upon the experience that I had gained at University College Cork, by designing, constructing, using and managing a small chamber system in Manchester. This facility, called the EXTreme RAnge (EXTRA) chamber allowed kinetic measurements over a large range of temperatures and pressures. This was utilized for making several temperature-dependent ozonolysis measurements and also allowed me to test the SAR that I had developed during my PhD, as a function of temperature,(Leather et al., 2010) with different heteroatoms attached to the alkene reactant,(McGillen et al., 2011b; Leather et al., 2011) and with alkenes with large alkyl substitutions.(McGillen et al., 2011a) The chamber was further utilized in determining product yields from ozonolysis.(Leather et al., 2012) I was able to make meaningful contributions to several other publications during this time.(Last et al., 2009; Booth et al., 2009; Ghalaieny et al., 2012; Bacak et al., 2011; Booth et al., 2012) I also had a major role in managing and directing the research of three PhD students.

iii. Research scientist, National Oceanic and Atmospheric Administration, ESRL, Boulder, USA.

Dates: 10/2010–10/2015

My time at NOAA was spent learning about several optical techniques, with which I was not previously familiar. These included laser systems in general, the pulsed-laser photolysis–laser-induced fluorescence (PLP–LIF) technique, UV absorption and Fourier-transform infrared (FTIR) spectroscopy. It was very valuable to my development as a scientist to work in a lab that was very different in terms of instrumentation and also in the method by which research is conducted in a governmental organization. NOAA/ESRL/CSD has an excellent track record with regards to accurate measurements, and I have insisted upon upholding this standard with all of my research as a consequence of this. During this period, I used PLP–LIF, which allowed me to study absolute OH radical kinetics for a series of alcohols(McGillen et al., 2013b) and a fluorocarbon;(McGillen et al., 2015) and O(¹D) kinetics with an emerging CFC compound.(Papadimitriou et al., 2013a) I was also using FTIR and UV spectroscopy to investigate how molecules absorb radiation.(Papadimitriou et al., 2013b; McGillen et al., 2013a; Papadimitriou et al., 2013a; Bernard et al., 2015; McGillen et al., 2015; McGillen and Burkholder, 2015; Jubb et al., 2015; Davis et al., 2016) Based on this information, I was able to arrive at realistic total environmental impacts of several molecules. Analyses of this type are of importance to policy makers and industry, where these metrics are used in the decision-making process of policy and regulation. Another highlight of this appointment was my collaboration with my colleagues John Orlando and Geoff Tyndall at the National Center for Atmospheric Science.(McGillen et al., 2016) Both of whom have had a large influence upon how I think about the organic chemistry that occurs in the atmosphere. During this time, I was responsible for training new post-docs on laboratory procedures and measurement techniques.

iv. Marie Skłodowska-Curie fellow, School of Chemistry, University of Bristol, UK.

Dates: 04/2016–04/2018

In 2016, I was awarded a prestigious Marie Skłodowska-Curie fellowship to conduct EU project HOMER: “*Hydrocarbon Oxidation Mechanisms Elucidated from Radical scavenging*” at the University of Bristol. The initial focus of my time in Bristol was spent in studying the cavity ring-down spectroscopy technique. This was employed to monitor Criegee intermediates in real-time, allowing absolute kinetics to be obtained for the first time for several reactions. (Chhantyal-Pun et al., 2017; McGillen et al., 2017; Chhantyal-Pun et al., 2018, 2019) The study of these chemical systems led me to realize that they represent an important source of functionalized hydroperoxides in the atmosphere (and also in the laboratory). This is an important concept in the attached proposal, which seeks to discover how atmospherically realistic hydroperoxides react in the atmosphere. Further work was conducted on the unique self-scavenging behaviour of vibrationally excited Criegee intermediates. This work was carried out using the world-leading thermal absorption-desorption gas chromatography technologies that have been developed at Bristol. Although this work has not yet been published, it has so far led to face-to-face discussions with the chief scientist at Honeywell Advanced Materials, over concerns about the global warming potential of some commercially important refrigerant gases. During this time, I was also approached to participate as a member of an expert panel on structure-activity relationships, which resulted in a perspective article. (Vereecken et al., 2018) I was also able to contribute to several other papers (Khan et al., 2018; Ashrafuzzaman et al., 2018) and to supervise two undergraduate masters projects.

v. Consultant, University of California Riverside, USA.

Dates: 05/2018–09/2020

Over the time period of 2018 into 2020, I increased my responsibilities in the expert panel on structure-activity relationships, which is a project funded through the Coordinating Research Council. This has allowed our group to pursue more ambitious projects than would otherwise be possible if work was being performed solely on a pro bono basis. Accordingly, during this time I have led a project on a consultancy basis within our group in which we compiled and reviewed the gas kinetic literature in total for the reactions of OH, O₃, NO₃ and Cl, a study which is freely available, online and whose accompanying dataset description paper is published in *Earth System Science Data*. (McGillen et al., 2020) This work has been very educational for me so far, not only from the many exchanges that I have had with my knowledgeable colleagues, but also because it has taught me to be comfortable in a leadership role, even among some of the most senior scientists in my field.

vi. Le Studium research fellow, now CNRS Chargé de Recherche, ICARE, Orléans, France.

Dates: 09/2018–present

Starting in 2018, I was a Le Studium research fellow in the research group of Dr. Wahid Mellouki at ICARE, Orléans. During this time, I became impressed by the facilities, by the quality of the science and by the collegial atmosphere that surrounds ICARE and its neighbouring laboratory, LPC2E. Over this time, I was using and refining my skills in the PLP–LIF technique, and employing it to measure the atmospherically vital, but notoriously challenging third body reaction OH + SO₂ + M, the results of which I have so far presented in the recent International Conference on Chemical Kinetics held in Orléans.

I have also been applying myself to a broad range of other activities. The HELIOS facility at ICARE is an attractive host laboratory, and over this time I have been involved in visits from researchers from Heraklion (Greece), Wuppertal (Germany), Tours (France), Bristol (UK) and Ciudad Real (Spain) as well as from a large intercomparison of PTR-MS instruments from France and several other European countries. I also participated in a field campaign in Morocco, which represents some of the first detailed atmospheric measurements in North Africa. So far, I have co-authored two papers on our chamber activities at ICARE, (Ren et al., 2020a, b) with 5 more papers expected later this year. I have several other projects that I have been supervising that are nearing completion, one regarding the OH + SO₂ reaction, one investigating the atmospheric impact of kerosene emissions upon the environment. These studies have also allowed me to lead in projects involving PhD students, post-doctoral appointees and academics from other institutes. Furthermore, my involvement in the Le Studium Loire Valley Institute for Advanced Studies provided me with several opportunities to explain the important work that we do to non-specialized audiences.

Since starting my role as CNRS Chargé de Recherche at ICARE, I continue my activities in the Équipe de Recherche Atmosphérique. Alongside my research programme, I am now becoming more deeply involved with the management and maintenance of our activities and the attraction of funds and industrial consultancy. Since the beginning of my new position in October 2020, I have successfully applied for funding from CNRS-INSU to build a new reactor in our lab, obtained funds for measuring the reactivity of sulphurous chemicals in the atmosphere (LABEX Voltaire) completed a consultancy project for Air Liquide, and am participating in shared activities with several other French research groups in a large-scale field-based project supported by CNRS-INSU. I have participated in a large consortium bid named HOLICHEM to the EU Green Deal, whose outcome is yet unknown, but which has already increased my network significantly. I have also been playing an active role as co-encadrant for a PhD student who has joined our research group, as well as assisting some of the students in preparing publications as they get ready to submit their PhD theses. (El Othmani et al., 2021a, b)

Summary of my role as a mentor and instructor:

So far, I have enjoyed co-supervising a variety of individuals in their respective research activities, ranging from masters level (×2), PhD students (×5) and also in the training of several post-doctoral appointees (×2). Many of these projects have resulted in peer-reviewed publications in international journals (their respective DOIs are listed directly after each trainee where applicable). My estimated contribution to each trainee's supervision is given in parentheses.

2007-09. Dr. Kimberley Leather, PhD student, University of Manchester, UK. Instructed and supervised and conceived of several major parts of her PhD thesis. **(50%)**

1.) 10.1039/b919731a 2.) 10.1002/kin.20533 3.) 10.5194/acp-12-469-2012

2007-09. Dr. Mohamed Ghalaïeny, PhD student, University of Manchester, UK. Instructed and supervised and conceived of several major parts of his PhD thesis. **(40%)**

1.) 10.5194/amt-3-91-2010 2.) 10.1039/c0cp02643c 3.) 10.1039/c2cp23988d

2008-10. Dr. Michael Le Breton, PhD student, University of Manchester, UK. Instructed and supervised and conceived of several major parts of his PhD thesis. **(30%)**

1.) 10.5194/amt-5-3029-2012

2015. Dr. François Bernard, post-doctoral research assistant, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA. Instructed and supervised in the absolute kinetic measurements using the pulsed-laser photolysis–laser-induced fluorescence technique, as well as several other laboratory techniques such as UV spectroscopic measurements, data analysis. **(30%)**

1.) 10.1002/2015GL064939 2.) 10.1016/j.jphotochem.2015.03.012 3.) 10.5194/acp-16-8043-2016

2016-17. Ms. Laura McMahon, masters student, University of Bristol, UK. Instructed and supervised masters degree project involving the gas-phase reaction between Criegee intermediates and alcohols. **(80%)**

1.) 10.1021/acsearthspacechem.7b00108

2017-18. Ms. Holly Barrett, masters student, University of Bristol, UK. Instructed and supervised masters degree project on the gas-phase kinetics of ozonolysis of various hydrofluoroolefins, and the subsequent products of the excited fluorinated Criegee intermediates. **(80%)**

1.) *manuscript in preparation*

2018-present. Ms. Hajar Elothmani, PhD student, CNRS-Orléans, France. Instructing and supervising major parts of her PhD thesis. **(30%)**

1.) 10.1021/acsearthspacechem.1c00050 2.) *manuscript in preparation*

2019. Dr. Soukaina Foulal, post-doctoral research associate, CNRS-Orléans, France. Designing and supervision on research project associated with aviation fuel. Required new types of data analysis and establishing new collaborations with other French researchers at LISA. **(80%)**

1.) *manuscript in preparation*

2020-present. Ms. Lisa Michelat, PhD student, CNRS-Orléans, France. Instructing and supervising major parts of her PhD thesis. **(50%)**

Past and present research programmes:

Name/ description of programme	Time-period	Institution	Status
Horizon 2020 Marie Skłodowska-Curie Research individual fellowship HOMER	2016–2018	University of Bristol, UK	Complete
Consultancy on kinetic database development CRC contract A-108	2018–2020	University of California at Riverside, USA	Complete
Consultancy for gas-mixture properties for Air Liquide	2020–2021	ICARE-CNRS, France	Complete
INSU-LEFE LARKIN, development of a new reactor for kinetic measurements at ICARE	2021–2023	ICARE-CNRS, France	Funded, on-going
LABEX Voltaire, Measurements of the reaction rate of sulphurous compounds of atmospheric interest	2021–2023	ICARE-CNRS, France	Funded, on-going

2. Scientific context of my research:

In terms of thickness, if the entire Earth was represented by an apple, then the atmosphere would be its skin. In terms of mass, the atmosphere would be an eyelash lying beside that apple. A yet smaller fraction – the trace components of our planetary atmosphere – have a powerful impact on the environment, whether that is the ozone layer that filters out harmful UV radiation, or the >410 ppm of CO₂ that traps heat in the atmosphere and the oceans. Accordingly, my research is dedicated to the atmospheric chemical reactions that control this tiny yet important component of the Earth system.

Atmospheric chemistry defines air quality. Oxidation reactions (including reactions with OH, O₃, NO₃ and Cl) are the dominant factor in destroying most organic and inorganic pollutants that are present in the air. Conversely, these same oxidation reactions also produce secondary pollution. It has been recognized since the early 1950s that the combination of organic molecules, NO_x, sunlight and SO₂ leads to a toxic cocktail of air pollution known as photochemical smog (Haagen-Smit, 1952). The fine particles (e.g. PM_{2.5}) that are present in polluted air masses are generally considered to be the most harmful to human health. As atmospheric models and emission inventories improve, and as epidemiological data and techniques become available, it is becoming apparent that these particles are responsible for millions of deaths globally each year (Lelieveld et al., 2015; Gakidou et al., 2017; WHO, 2018; Vohra et al., 2021). A large fraction of this particulate matter is of an organic composition (Jimenez et al., 2009), and yet some major uncertainties remain in the mechanisms by which organic aerosols nucleate and accumulate, which partly relates to the extraordinary variety and complexity of gas-phase aerosol precursors (Hallquist et al., 2009), and is also a consequence of extremely variable nature of unimolecular processes that lead to functionalization and eventual mass accommodation. And yet, it would be reductive to assume that it is only the aerosols present in the air that are responsible for the deleterious consequences of poor air quality. Toxicological studies suggest, for example, that the effects of environmental exposure are likely to be additive among classes of compound that possess similar toxic modes of action (TMOA) (de Zwart and Posthuma, 2005), or affect the same areas of the body (Vyskocil et al., 2007). The corollary of this being that a vast ensemble of molecules (even if each are present in a small concentration), provided that they share a common toxicological characteristic, could affect human health in a similar way to a toxic concentration of any single component. This may help to explain why exposure to lower, permissible pollution levels still leads to enhanced mortality risk (Yazdi et al., 2021).

If the effects of atmospheric chemistry on air quality could be summarized as a chemistry that is too rich and too active, the opposite could be said of the effects of atmospheric chemistry upon climate. Some of the gases that possess the highest global warming potentials (GWPs), are those that possess the fewest or slowest atmospheric chemical reactions. One example is the perfluoroalkane CF₄, whose constituent bonds are sufficiently strong (130.5 kcal mol⁻¹), that no atmospheric oxidation reaction is thermodynamically feasible. The loss of CF₄ is therefore governed by rare events, such as a lightning strike or its intake into a high-temperature combustion engine, which results in an extremely long estimated lifetime of 50,000 years and an estimated GWP of 6630 (WMO, 2019).

Understanding the effects of atmospheric chemistry upon climate is of demonstrable importance, but it is likewise relevant to consider how climate may influence atmospheric chemistry, a key example being wildfires. Anthropogenic climate change has already been implicated in the increased size and number of wildfires occurring in the Western United States (Williams et al., 2019) and other regions of the globe (Abatzoglou et al., 2019). Wildfires constitute a large atmospheric source of organic compounds and NO_x and therefore can have a profound effect upon local and regional air quality and human health. As field coverage and instrumentation improve, it is becoming increasingly evident that the composition of wildfire plumes is complex and poorly characterized in a chemical kinetic sense. Wildfires are therefore an emerging topic for laboratory scientists as we attempt to learn more about their effects upon the environment.

Fundamentally, whether the effects of an emitted chemical upon air quality are local, regional or global, whether these effects are toxic or climatic, they are in each case deeply connected with chemical kinetics. Kinetics is what defines how rapidly a reaction proceeds, which reaction channels dominate, which products are formed. It determines how chemical reactions are affected by the wide range of temperatures and pressures experienced in the Earth's atmosphere. It affects a molecule's propensity to nucleate or partition towards aerosol particles. It is what controls whether (and how rapidly) a chemical is transformed by actinic radiation, and how effective it is at absorbing infrared radiation.

Since the beginning of my PhD, and up till now, I have been employing chemical kinetics to understand each of these processes. This represents a diverse range of challenges, both experimentally and also conceptually, and for this purpose I have found it necessary to utilize a large variety of techniques. This includes:

- A large number of analytical chemical techniques (CIMS, PTR-MS, LIF, GC, FTIR, UV-vis).
- A large variety of experimental designs (absolute kinetics, relative rate kinetics, photolysis experiments, product studies, chamber experiments, stopped-flow reactors, flow tubes).
- A range of activities (laboratory observations, field observations, numerical simulations of experiments, the estimation of kinetic parameters using structure-activity relationships (SARs), the collation and assessment of kinetic data).

Having accumulated experience in each of these disciplines, I feel well-prepared to share much of this expertise with students and post-doctoral appointees. Indeed, I have already been enthusiastic in instructing and guiding several students in my position at CNRS-Orléans, as well as at my previous laboratories. Nevertheless, I value the prospect of being responsible in an official capacity for directing the research of the next generation of atmospheric scientists as they enter into what is likely to be a challenging moment for the environment.

3. The chemical complexity of the atmosphere:

There are many lines of evidence to suggest that the atmosphere contains an immensely complex mixture of trace organic molecules. Such evidence can be subdivided into two broad categories:

1. Features that can be observed directly, e.g. a quantitative and speciated field measurement of a given molecule; or knowledge of an anthropogenic or biogenic emission of that molecule into the atmosphere.
2. Features that can be inferred from other observations, e.g. an "OH reactivity" observed in the field, or the knowledge that a substantial fraction of a reactive molecule's flux must be present in any number of its oxidation products.

This represents a good example of the multifaceted challenge faced by atmospheric chemists, and how it is necessary in this case to employ all three legs of the "three-legged stool" of atmospheric chemistry (Abbatt et al., 2014) (see Figure 1) in order to understand a molecule's presence (or indeed absence) in the atmosphere:

1. Field measurements, e.g. field sampling providing direct information about ambient mixing ratios; emission sampling from plants, or industrial effluents.
2. Laboratory measurements, e.g. kinetic measurements leading to estimated atmospheric lifetimes of organic molecules; product studies indicating which molecules are likely to be produced during atmospheric transformation; measurements of fuel compositions.
3. Modelling, e.g. taking information about the sources and sinks of a molecule from field and laboratory measurements, and running a chemistry and transport model to understand how its mixing ratio changes over time; running an automatic mechanism generation software such as GECKO-A in order to understand the multigenerational evolution of carbon in a system.



Figure 1: a schematic of the three central components of atmospheric chemistry adapted from Abbatt *et al.* (2014).

In this section, I will provide an outline of these various concepts, and how, when taken together they present the case for a truly complex challenge that faces atmospheric chemists.

3.1. Emissions, their sources and their sinks:

A logical first approach, when considering the substantial presence of a chemical within the atmosphere, is to view this possibility as a balance between that molecule's sources and sinks. For certain chemicals, such as the perfluoroalkanes mentioned above, this balance is tipped almost entirely towards that of the source terms, with the sinks being so negligible that a time series of the atmospheric mixing ratio of such a molecule would show an inexorable increase until such time as its production and emission ceases entirely. By contrast, some chemicals are consumed so rapidly that despite having large emissions, their mixing ratios often remain small. A good example being isoprene, which represents the largest single non-methane hydrocarbon emission, and yet, as a consequence of its high reactivity toward the OH radical, is often present in the atmosphere at relatively low concentrations in the parts per trillion range.

3.1.1. Sources:

With the notable exception of helium, which possesses a sufficient escape velocity to effuse into space, the Earth system can be considered to be a closed system with respect to any gaseous substance that enters into its atmosphere. Consequently, any substance present in any environment that is sufficiently volatile to be emitted into the gas phase will remain in the atmosphere until it is transformed into a substance that is readily taken up into another phase/ environmental compartment. There are many sources of volatile compounds on Earth, the main ones of which will be described in this subsection.

3.1.1.1. The biosphere

Regarding total mass flux, the biosphere represents the largest overall source of organic compounds into the atmosphere, and is considered to be larger by an order of magnitude than fossil fuel emissions (Guenther et al., 1995). The emission of isoprene alone is estimated to be 500–750 Tg year⁻¹ (Guenther et al., 2006). However, as important as isoprene undoubtedly is, it is only one of an estimated 55,000 terpenoid molecules that have so far been identified (Chen and Baran, 2009). Furthermore, the terpenoids represent only a subset of all the organic molecules that are produced through biosynthetic pathways.

The diversity of compounds produced from the biosphere reflects in part their varying roles within biota and their environments. Many compounds act as signals, semiochemicals, whose purpose is to communicate within and between species. There are many ways in which these communication channels can operate, some examples include:

- Plant-herbivore interactions: triggers the production of chemicals in healthy plant tissues that act as deterrents towards future herbivorous attacks.
- Plant-predator interactions: attracts beneficial arthropods to predate upon herbivorous pests.
- Plant-pollinator interactions: production and dissemination of floral scents for attracting pollinators.
- Plant-plant interactions: in which plants may interfere with other species growth cycles, favouring the emitter in competitions over soil nutrients.

- Mate attraction between animals: pheromones can be an extremely specific calling sign for a mate, and allows for the coverage of a large geographic domain.
- Marker molecules: assisting animals in navigating their surroundings, marking territory, acting as waypoints or warnings.

From a physiological perspective, it is reasonable to expect that the structures of semiochemicals may vary depending on the types of receptors with which the species emitting these substances have evolved to interact. But besides this, in order for these communications to reach their intended recipients, they must survive transit in the atmosphere over an appropriate distance. Furthermore, they should not outlive their useful lifetime, which would only serve to confuse recipients with signals related to a past event.

Still other biological functions include chemicals that exhibit activities that protect against bacterial and fungal infection, ultraviolet radiation or oxidation, each of which could possess a specific chemical structure.

Although emission inventories for the biogenic volatile organic compounds (BVOCs) such as monoterpenes ($C_{10}H_{16}$) are well characterized (Sindelarova et al., 2014), as instrumentation improves, it is becoming apparent that the larger, less volatile phytochemicals such as sesquiterpenes ($C_{15}H_{24}$) and diterpenes ($C_{20}H_{32}$) are also present in the atmosphere (Li et al., 2020). Mixing ratios of these larger terpenoids are found to be considerably less than those of the monoterpenes, nevertheless, these molecules may have a potent effect upon secondary organic aerosol production.

In living systems, emission profiles change over multiple timescales. For example, the diurnal patterns of terpene emissions are well documented. On longer timescales, the life cycle of a plant should be considered, with different types of emissions occurring in developmental, mature, flowering, fruiting and senescent phases, as well as at times of environmental stress. Eventually, plant matter dies and will be incorporated into soil. Emissions from soils, wetlands and peatlands represent a combination of plant, bacterial and fungal metabolism, which leads to a wide variety of emissions including alkanes, cycloalkanes, alkenes, aromatics, oxygenated VOCs, nitrogen-containing compounds and sulphur-containing compounds (Rinnan et al., 2005).

Another potent source of BVOCs comes from wildfires and biomass burning. Complex gas-phase compositions have been observed in wildfire plumes (Decker et al., 2019) as well as in simulated fires in laboratory settings (Gilman et al., 2015; Coggon et al., 2019). Furthermore, when particulate compositions are considered, >10,000 molecular formulas were recently identified in the tar ball component of burning plumes using an orbitrap technique. Compared with other biogenic sources, wildfire emissions are compositionally distinct and have a much higher proportion of aromatics, heteroaromatics and polycyclic aromatic compounds. In addition to pyrolytic emission sources, there is the potential for the locally high temperatures of fires to volatilize chemical species that are not normally emitted during a plant's life cycle, and which can therefore liberate some of the 55,000 terpenoid species that are known, together with the multitudes of non-terpenoid species that are also present in plant tissues.

There is a substantial body of literature that suggests that human-induced climate change is increasing the size, geographical extent and duration of wildfires (Goss et al., 2020), and that many of these fires are caused by human actions, accounting for 84% of all wildfires in the United States (Balch et al., 2017). It is therefore acknowledged that this emission source, despite being a phenomenon of the natural environment, could easily be presented in the following section on the anthroposphere.

3.1.1.2. The anthroposphere

The effects of human emissions on the atmosphere are dominated by major climate-forcing gases such as CO₂, CH₄, fluorine-containing gases (F-gases) and N₂O, that originate from the transport, energy production, agricultural, industrial and domestic sectors. However, like the biosphere, the anthroposphere is also a major atmospheric source of organic chemical complexity.

Transport and energy production are two major sources of VOCs. These sectors rely heavily on fossil fuel combustion. The panoply of molecules that are emitted represent a combination of extremely complex fuel compositions – much of which escapes to the atmosphere in a state of incomplete combustion – and the variety of emissions from the pyrolysis process itself.

A single fuel formulation used in a single application in a single country could represent a forbiddingly complex mixture. Aviation fuel is one such example, which is so complex that it is only with the recent introduction of advanced GC × GC methods and machine learning and other data analysis techniques that the actual number of possible structures is becoming apparent. Recent chemical analyses were performed on a representative jet fuel sample where they were able to identify 55 distinct groupings (Shi et al., 2017). If the number of isomers in each of these groups is enumerated (Benecke et al., 1995), from there it is possible to arrive at a maximum number of possible isomers present in these analyses, which accounts for a total of >800,000 structures. It is logical to suppose that many of these isomers won't be present in any single fuel sample. However, it provides an upper limit for compositional complexity. Furthermore, this represents only one of many different types of fuel formulations, other fuel mixtures are potentially far more complex, including the relatively unrefined residual fuels such as bunker fuel.

Fuel combustion tends to occur under controlled conditions, where combustion efficiency is prioritized, and with end-of-pipe pollution control strategies in place, they are therefore likely to produce a less diverse array of products compared with the wildfires mentioned above. Nevertheless, with a high variety of fuel compositions and combustion conditions, a large number of incomplete combustion products are anticipated.

This combination of complex fuel compositions and incomplete combustion products are likely to be a major contributor to the large collection of organic molecules known as the unresolved complex mixture (UCM) that is encountered ubiquitously in atmospheric samples (Schauer et al., 1999), representing a major analytical challenge for even the most discriminating separation techniques.

As important as transport-derived VOC emissions are, as emission control strategies improve, they are becoming less important in relation to other volatile chemical products (VCPs) (McDonald et al., 2018). These VCPs can be emitted from a variety of sources including the industrial, agricultural and domestic sectors.

Industrial sources of VOCs are numerous. These can come from solvents, refineries, chemical production, manufacturing, coatings, foams, electronics, and many others. Although the emitted volumes of VOCs may be smaller than those emitted from the biosphere, in terms of chemical functionality, industrial chemicals may represent the most diverse subset of VOC sources encountered in the atmosphere. This is a consequence of the range of possible chemical structures that is afforded to chemical synthetic techniques, which are able to produce chemical functionalities that are not known to be formed in natural systems. Although there is no definitive list of chemicals that are entering our environment from industrial sources, from a top-down perspective, it is possible to get a sense of the numbers of these chemicals based on lists of emerging pollutants from environmental laboratory networks such as NORMAN, who document >60,000 chemicals in their databases (Dulio et al., 2018) or the EPA Chemical and Products Database (CPDAT), which documents >75,000 chemicals and >15,000 consumer products (Dionisio et al., 2018). Not all of the chemicals in these databases will have the appropriate physicochemical behaviour to enter into the atmosphere, i.e. they may possess very low vapour pressures or high Henry's law coefficients. However, given the diversity of chemical species contained within these databases, it is probable that a sizeable fraction of these lists of compounds is emitted to the atmosphere.

Agricultural emissions are another large source of organic molecules in the atmosphere. These are dominated by bacterial/ fungal metabolism, which could occur in several environments:

- Animal digestive processes: e.g. methane from cow farming.
- Animal waste: methane, amines, sulphides and carboxylic acids (Liu et al., 2018).
- Soil emissions: methane, alkanes, aromatics, amines.
- Eutrophication from soil run-off of agricultural lands: whereby bodies of water are affected by algal blooms, whose decomposition leads to emissions of sulphides, for example.
- Animal rendering plants: carboxylic acids, other VOCs (Guerra et al., 2017).

Agricultural emissions are therefore intimately connected to bacterial and fungal species, the conditions in which they live, and their respective biochemical cycles.

Another major source of agricultural emissions comes from crop stubble burning activities that occur at the end of the growing season in preparation for the next. These can dramatically reduce air quality in a variety of locations globally (Kumar et al., 2021; Pivello, 2011), and the emission profiles of such sources, although not always well-characterized under field conditions, are likely to have similarities with the wildfire emissions discussed above.

Domestic sources of VOCs are also diverse. Many domestic products are perfumed and emissions can contain substances of a natural origin such as the terpenoids that are found in perfumes, in laundry detergents, air fresheners, and in cleaning products for example. Artificial perfumes such as synthetic musks are also commonplace in domestic settings, and have been linked with several negative health consequences upon environmental exposure (Sealey et al., 2016; Tumová et al., 2019). Many other compounds are not necessarily aroma compounds, but are sufficiently volatile that they enter into the gas phase, examples of which include various siloxanes (Coggon et al., 2018; Gkatzelis et al., 2021) which have been found to account for a significant fraction of total air pollutants in urban settings.

Cooking practices are one of the largest indoor sources of organic pollutants. Typically, these involve the combination of heat, oils, proteins and carbohydrates, and can lead to a variety of gas- and aerosol-phase pollutants, many of which could be toxic and mutagenic (Shields et al., 1995). The emission profile from cooking activity depends upon the raw materials as well as the temperature and the style of cooking (Katragadda et al., 2010). Common emissions include alkanes, alkenes, aromatics, aldehydes and fatty acids. The cooking process can provide a unique environment, leading to phenomena such as the Maillard reaction, which is initiated by the reactions of carbonyl moieties in carbohydrates with the amine groups in amino acids. This chain of reactions leads to the characteristic bouquets of cooked food, such as that of freshly cooked bread, which despite its wholesome aroma, is a complex combination of volatile emissions including furans, pyrroles, oxazoles, thiazoles, imidazoles, pyridines, pyrazines and pyrones (Prost et al., 2020).

Following the useful lifetime of many consumer products, a large volume of waste materials will be formed. Such waste could be disposed of in a managed scenario, such as in landfill sites, incineration or recycling facilities. Landfill sites contain complex mixtures of waste materials. A fraction of these materials will not be transformed in the landfill site, and will simply escape to the atmosphere gradually over time. These emissions would not therefore contribute to the overall organic complexity of the atmosphere, and would reflect the current chemicals in use in various industrial and domestic settings. However, landfill sites may also provide an environment in which chemicals are transformed through bacterial and multiphase reactions (potentially involving a combination of household and industrial wastes) leading to a variety of exotic and hazardous products such as vinyl chloride (Brosseau and Heitz, 1994).

Other types of waste may escape into the environment in an unmanaged way such as the introduction of plastic materials into the oceans, landfills and elsewhere. Indeed, the plastic pollution of marine environments has become so extensive that it is now being considered as a distinct microbiome, referred to as the “plastisphere” (Wright et al., 2021). In such environments, plastic-biodegrading organisms metabolise the polymeric materials (which have a negligibly low volatility) breaking them down into a collection of smaller molecules that possess a higher volatility and could therefore enter into the atmosphere. The variety of molecules that can arise from these processes is highly uncertain, but this is expected to be connected with the specific metabolic pathways that are available in addition to the identity of the monomeric units of which each polymer is composed. Plastics are also

reactive towards aqueous-phase oxidants, and these will also lead to short-chain products some of which will be volatile (Bianco et al., 2020). So far, measurements of gas emissions from a variety of plastics under ambient conditions have been limited to lighter gases, such as methane, ethylene, ethane and propylene (Royer et al., 2018), however, it is probable that many more gases are produced that have yet to be investigated. One recent example being the various metabolic products that have been identified in polyethylene terephthalate (PET) degradation (Wright et al., 2021).

3.1.1.3. The lithosphere.

The solid Earth is more commonly associated with emissions of inorganic gases such as CO₂ and SO₂. However, where biogenic materials have a prolonged exposure to the elevated temperatures and pressures that occur at depth, a sequence of chemical transformations can occur, in a process known as catagenesis, often referred to as “cooking”. Over time, this leads to the highly complex mixture that is crude oil and related fossil hydrocarbon reserves. Whereas many oil and gas reserves are effectively capped by an overlying impermeable layer of sedimentary rock, and are therefore restricted from emitting gases, others are prone to seepage, such as tar pits, leading to atmospheric emissions of the more volatile fractions of these deposits. An interesting historic example of this process has been identified in Greece, whereby the euphoric effects of the high concentrations of light hydrocarbons emitted from a tectonically active bituminous limestone deposit have been attributed to the mythology surrounding the Delphic oracle (de Boer et al., 2001)!

Being composed primarily of hydrocarbons, such emissions will share many characteristics with the various fuel formulations mentioned above. However, there are some important differences. Most notably, crude oil deposits have not undergone the industrial process of cracking and other treatments, and hence will contain a higher fraction of larger, more complex molecules such as kerogens, as well as other molecules that contain sulphur and oxygen (Zhu et al., 2019).

3.1.1.4. The hydrosphere.

Given that the oceans cover approximately 70.8% of the global surface, with additional contributions from fresh surface waters, the possible emission of volatile compounds from these surfaces is of potential importance. Although the oceans are also a sink of many organic molecules (see following section), depending on Henry’s law coefficients and partitioning behaviour, they may also provide a source for gas-phase species (Wurl and Obbard, 2004). An important mechanism by which organic molecules enter the atmosphere from the ocean is in the production of sea spray aerosol (Rasmussen et al., 2017). In this process, aerosol particles are produced from the sea-surface microlayer (SML) through wave action and bubble bursting. The SML is a 1–1000 µm thick layer that rests on the ocean surface and is a highly complex mixture that contains large quantities of organic material, the chemical composition of which remains uncertain and whose characterization has been identified as a priority for future research (Engel et al., 2017). Aerosol production from these marine sources contains a major fraction of organic material (O’Dowd et al., 2004), some of which will then be volatilized (Rasmussen et al., 2017). The composition of evolved gas from

this mechanism is not well characterized, but it can be assumed that it consists of the more volatile components of the SML. Given that the volatilization of sea spray would result in a significant loss of water (Rasmussen et al., 2017), it is possible that molecules with higher Henry's law coefficients could also be emitted from this source.

Another VOC-producing mechanism involves the photosensitization of a selection of surface-bound molecules to their triplet state (Fu et al., 2015; Stirchak et al., 2021). This leads to hydrogen abstraction reactions, and much like gas-phase atmospheric oxidation cycles, can result in more volatile products, that are subsequently emitted to the atmosphere. This is of particular interest, since it provides a mechanism through which ubiquitous extremely low volatility molecules such as the humic-/fulvic-like substances could re-enter the atmospheric gas phase in a fragmented form. Furthermore, the environment in which these reactions take place is distinctly different from the bulk gas phase, and as such may afford different reaction channels than are available to atmospheric chemical mechanisms.

In relation to both of these processes, based on the surface area alone, the ocean surface is likely to be the most significant hydrospheric source of organic molecules into atmosphere. Nonetheless, based on OH reactivity field measurements (see Section 3.3), the VOC emission source strength from the remote ocean environments such as the Pacific are low, although not negligibly so (Mao et al., 2009; Thames et al., 2020).

3.1.2. Sinks:

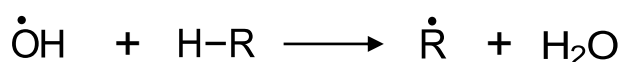
Fundamentally, the atmosphere is an oxidizing environment, and over time, organic molecules will move from a lower carbon oxidation state (OS) to a higher one, eventually terminating in the production of CO₂ (OS = +4). Not all molecules emitted to the atmosphere will reach this stage and many could be metabolized in the biosphere beforehand. For those that do, the path that an organic molecule takes through oxidation space is not necessarily straightforward, and it could go through many intermediate steps such as oligomerization, functionalization and fragmentation before it forms CO₂ (Kroll et al., 2011). This journey is further complicated by the other degradation pathways such as photolysis/ photoisomerization and multiphase processes.

3.1.2.1. Oxidation.

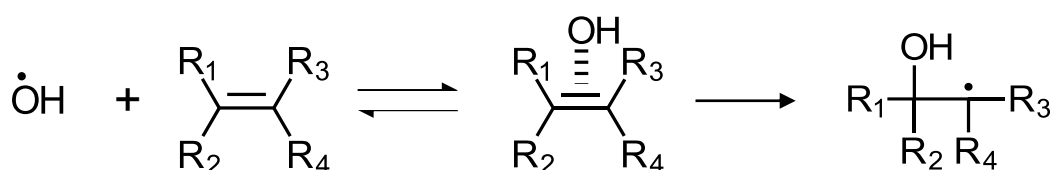
Oxidation begins with an initiation reaction, which involves a strong oxidant such as hydroxyl radical, ozone, nitrate radical, atomic chlorine or Criegee intermediates. The importance of each of these oxidants depends upon the identity of the organic molecules, as well as several environmental factors such as the time of day, distance from the ocean, and the presence (or absence) of natural or anthropogenic co-emissions. The reactivity of a VOC towards each oxidant will determine its potential to accumulate in the atmosphere, and the competition between these oxidants will influence which product molecules are formed in the process.

The hydroxyl radical (OH) is generally considered to be the most important oxidant in the atmosphere, and is mainly present in the day, where it reaches a daytime average of 1×10^6

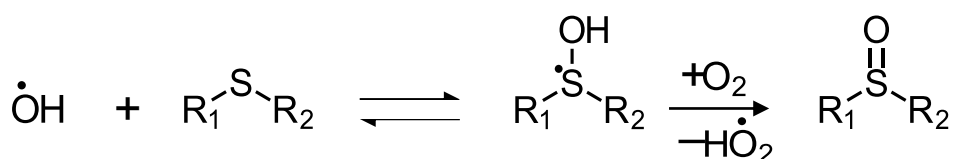
molecules cm^{-3} (Spivakovsky et al., 2000). It engages in two main chemical mechanisms: hydrogen abstraction and electrophilic addition. Hydrogen abstraction reactions are limited by thermodynamics, and in the case of OH, because it forms the highly thermodynamically favourable H_2O as a coproduct, will extract hydrogen from practically any hydrogen environment (with very few exceptions):



OH electrophilic addition occurs in olefinic, furanic and benzenoid reactants, whereby the OH interacts with the π -orbitals, forming a pre-reactive complex before forming a β -hydroxyalkyl radical:

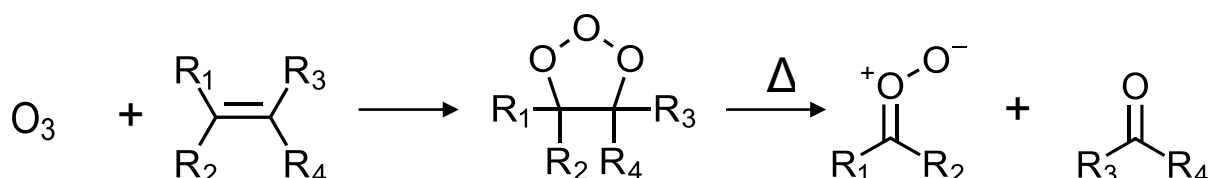


A second type of OH addition can occur in some reagents, especially sulphides, which can represent a major reaction pathway for compounds such as dimethyl sulphide (DMS):

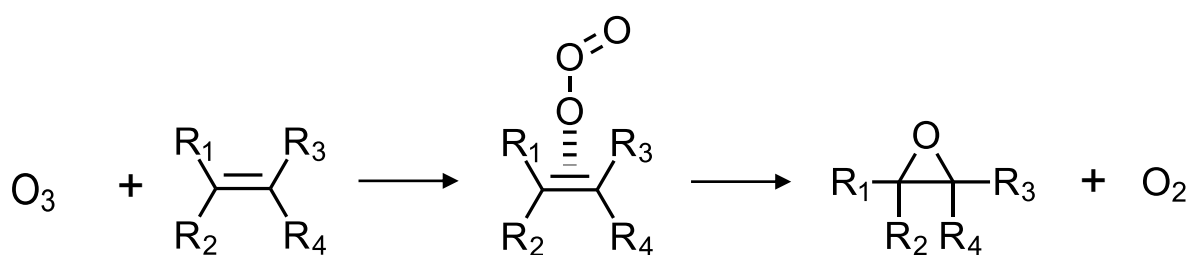


For most alkene reactants, there is competition between hydrogen abstraction and OH addition, and in general, OH addition is more rapid and will dominate. This is not inevitable, however, and for larger/ more reactive saturated substituents, hydrogen abstraction can play an important role (McGillen et al., 2007a).

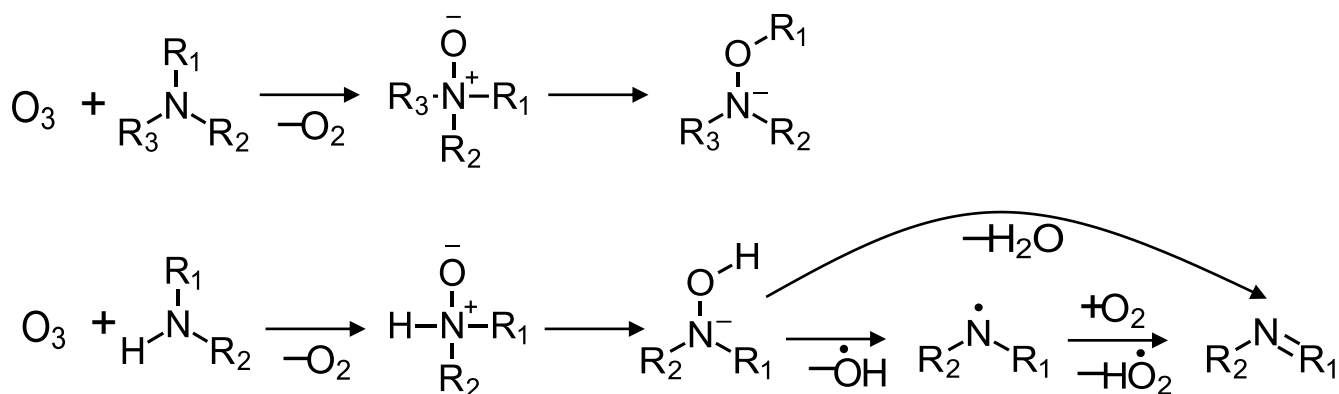
Ozone (O_3) as an oxidant is less reactive and more selective than OH. Partly as a result of this, O_3 mixing ratios can be much higher than those of OH, especially at night, with representative mixing ratios of O_3 being 7×10^{11} molecules cm^{-3} (Monks et al., 2009). Because of higher concentrations, oxidation rates by O_3 can therefore compete with OH under some situations. Unlike OH, O_3 does not react with most saturated species, and reacts primarily through 1,3-cycloaddition to alkenes:



In some situations, O_3 can also react to produce epoxides. This branching ratio between 1,3-cycloaddition and epoxidation remains highly uncertain and is a potential focus of our laboratory in the future:

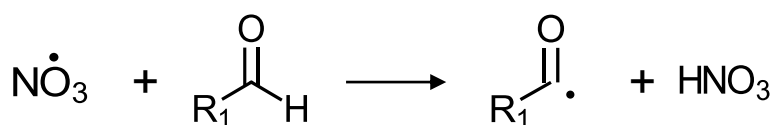


Although most reactions of O₃ involve olefinic bonds, the reactions with amines provide an interesting exception. In this reaction, O₃ adds to the nitrogen atom, forming an *N*-oxide:

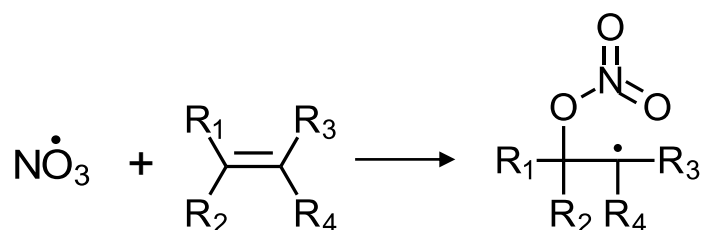


There are not many rate coefficient determinations for the reactions of amines with O₃ in the gas phase, especially for more functionalized amines, and it is unclear whether there are any situations in which these reactions may become competitive in the gas phase. However, in the aqueous phase, it has been noted that the reactivity of amines towards O₃ and the propensity of these reactions to form nitroalkanes is a cause for environmental concern (Lim et al., 2019).

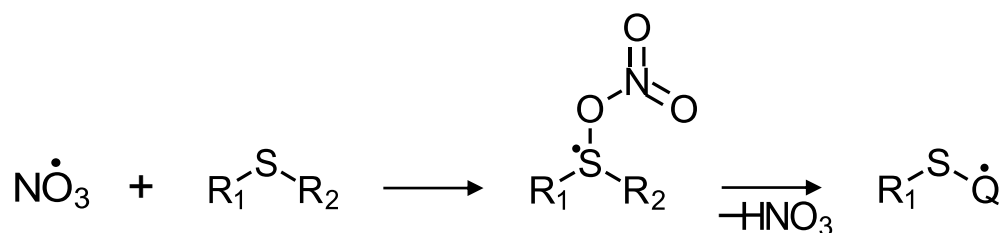
Nitrate radicals (NO₃) are considered to be the principal night-time oxidant and exhibit a high reactivity towards unsaturated species such as alkenes and furans. Nitrate exists in thermal equilibrium with its precursor, N₂O₅, and because of the rapid photolysis of NO₃ (and N₂O₅) during the day, NO₃ will only build up significant concentrations during the hours of darkness (Harwood et al., 1993), with a typical night-time NO₃ mixing ratio of 5 × 10⁸ molecules cm⁻³ (Atkinson, 1991). Similar to OH, NO₃ can engage in hydrogen abstraction and electrophilic addition reactions. Hydrogen abstraction with NO₃ is slow in most cases, compared with OH, but a much higher reactivity is observed for aldehydic C–H bonds:



By contrast, the electrophilic addition of NO_3 to alkenes and furans can be highly efficient, yielding β -nitrooxy alkyl radicals:

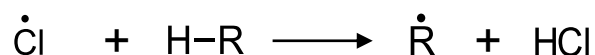


As with OH, NO_3 may also add to sulphur atoms in alkyl sulphides, which explains why the rate coefficient for $\text{NO}_3 + \text{DMS}$ is large in comparison with most reactions with saturated molecules:

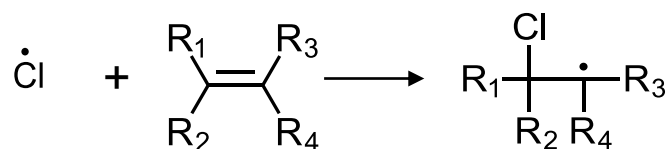


Because of the relative slowness of most NO_3 abstraction reactions, electrophilic addition tends to dominate under most circumstances.

Atomic chlorine (Cl) is a highly reactive radical that was traditionally thought to be of importance only in coastal environments. In recent years, nitryl chloride (ClNO_2) has been identified as an important source of Cl that can act as an effective reservoir species even in inland environments (Thornton et al., 2010). As a consequence of its reactivity, typical daytime concentrations of Cl are very low reaching 1×10^4 atoms cm^{-3} (Wingenter et al., 1996). Similar to OH and NO_3 , mentioned above, Cl reacts through hydrogen abstraction and electrophilic addition mechanisms. Hydrogen abstraction by chlorine atoms is generally highly efficient, leading to HCl as a co-product and the alkyl radical:



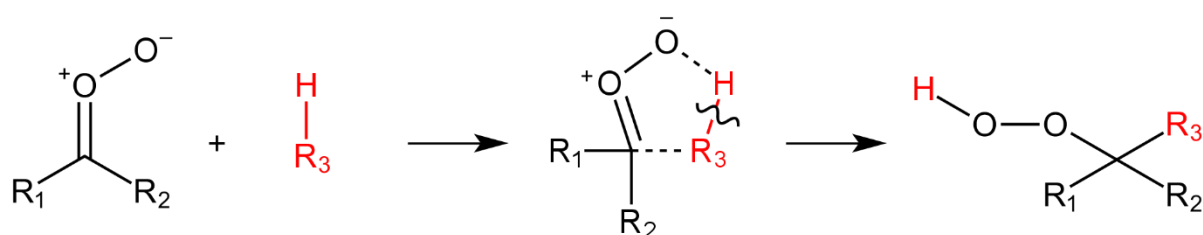
Electrophilic addition is also rapid and results in β -chloro alkyl radicals:



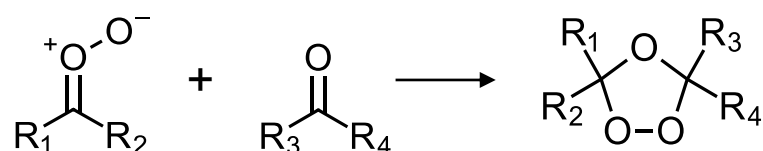
Again, as with OH and NO_3 , Cl is capable of adding to organic sulphur molecules, with a branching ratio of approximately 50% for DMS oxidation (Task Group on Atmospheric Chemical Kinetic Data Evaluation, 2019).

The relative rapidity of Cl abstraction reactions means that it can be competitive with electrophilic addition in many cases, although this reaction may be reversible.

Criegee intermediates (CIs) are a family of oxidants that are produced during the 1,3-cycloaddition of O₃ to olefins. There are no direct measurements of the abundance of CIs in the atmosphere, and model estimates vary broadly. They are a distinctly different oxidant compared with the others mentioned above for several reasons. Firstly, whereas other oxidants relate to a single molecule (OH, O₃, NO₃ or Cl), the identity of CIs depends upon the structure of the olefin from which it is derived. In fact, owing to the zwitterionic structure of CIs and their tendency to be formed in two conformations, the number of possible CIs is potentially larger than the number of alkenes that are present in the atmosphere. As a consequence, CIs exhibit a very broad range of behaviours. Secondly, the mechanisms by which CIs react are different, and tend to involve the insertion of a CI unit into an available hydrogenous bond:



This reaction can be extremely rapid, and may even exceed the collision limit in some cases (Chhantyal-Pun et al., 2018, 2017). Furthermore, species that tend to react very slowly with other oxidants (such as trifluoroacetic acid), can react quickly with CIs (Chhantyal-Pun et al., 2017). There are several other mechanisms by which CIs react with organic molecules, including the formation of secondary ozonides from the reaction with carbonyls:



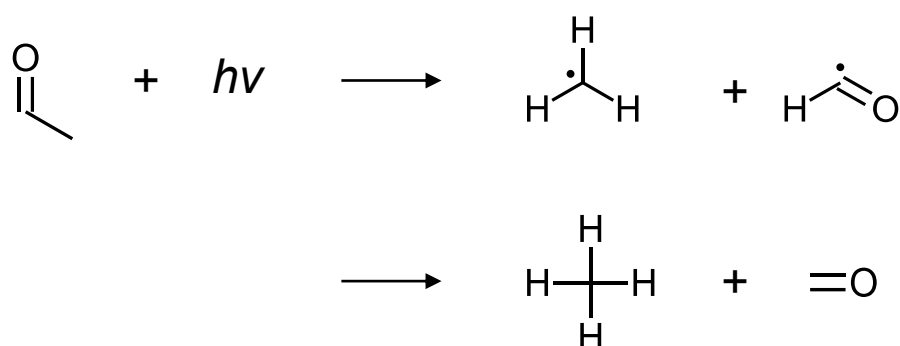
In the gas phase, besides OH, O₃, NO₃, Cl and CIs, there are other potential oxidants in some atmospheric scenarios, for example, the reactions of O(³P), O(¹D) and Br. In the aqueous phase, more possibilities exist, including the role of triplet excited, photosensitized molecules and oxidation by hydroperoxides.

With the variety of mechanisms that are available and the different types of products that are formed, oxidation reactions of organic molecules in the atmosphere have a high capacity for increasing the complexity of atmospheric organic emissions. For hydrogen abstraction reactions, the product will be the same regardless of the oxidant, although the site of the hydrogen that is abstracted will determine the subsequent products, and each oxidant can display different preferences for reactive sites, for example, the enhanced reactivity of Cl towards the primary C–H sites (Jahn et al., 2021). Conversely, for the addition reactions of OH, NO₃ and Cl, these can impart a hydroxyl, nitrate or chloride functionality onto the product molecules. Similarly, the reactions of CIs will insert a given CI's structure inside that of the reactant molecule. The factors that will determine the competition between these mechanisms will depend both on the availability of each oxidant, as well as the preference that each oxidant has for each reactive site in a molecule. These factors are

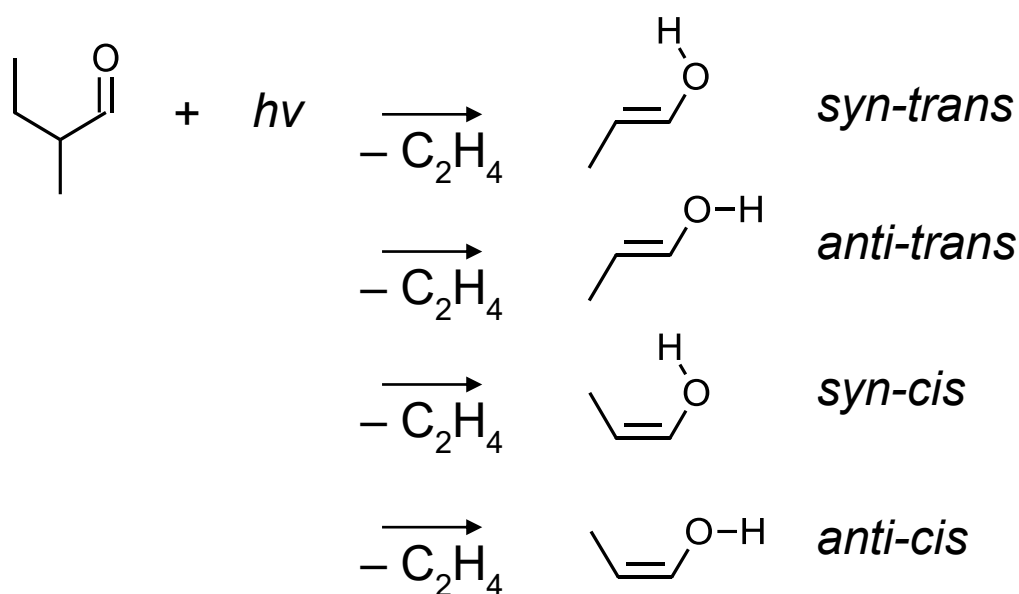
governed by environmental factors such as the time of day, the geographic location, the ambient temperature as well as the organic structure of the molecule itself, and a full realisation of this competition would only be possible with an explicit degradation mechanism in a coupled chemical transport model.

3.1.2.2. Photolysis and phototautomerization.

As a general rule, photolysis will lead to the fragmentation of molecules, and as a consequence, will ultimately simplify the atmospheric organic burden. The extent to which photolysis occurs is largely controlled by the availability of an ultraviolet- or visible-active chromophore in the actinic range. Atmospheric chemistry has a propensity for forming carbonyl products, whose $n \rightarrow \pi^*$ transitions are often shifted into the actinic range ($\lambda \geq 300$ nm). Carbonyls typically display branching photolysis channels, with both radical and molecular product channels:



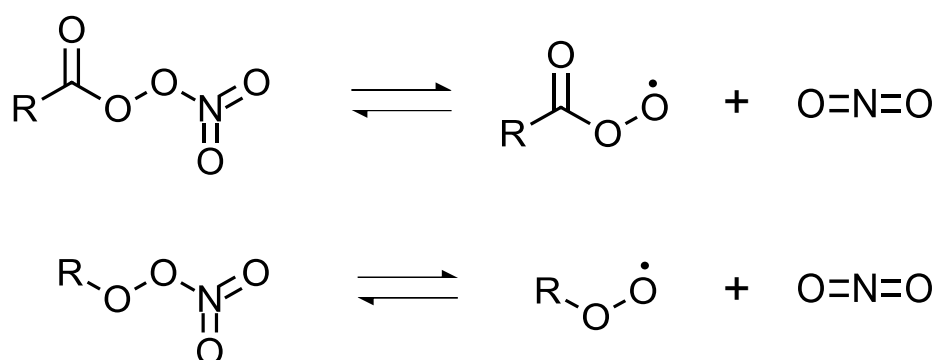
The products of these reactions are generally commonplace and are produced or emitted from various other sources. However, carbonyls are also shown to phototautomerize towards enols, which, unlike photolysis, does not lead directly to fragmentation, and given that it can yield several stereoisomers in various conformeric populations (Shaw et al., 2017), would serve to increase the overall complexity of the carbonylic VOCs:



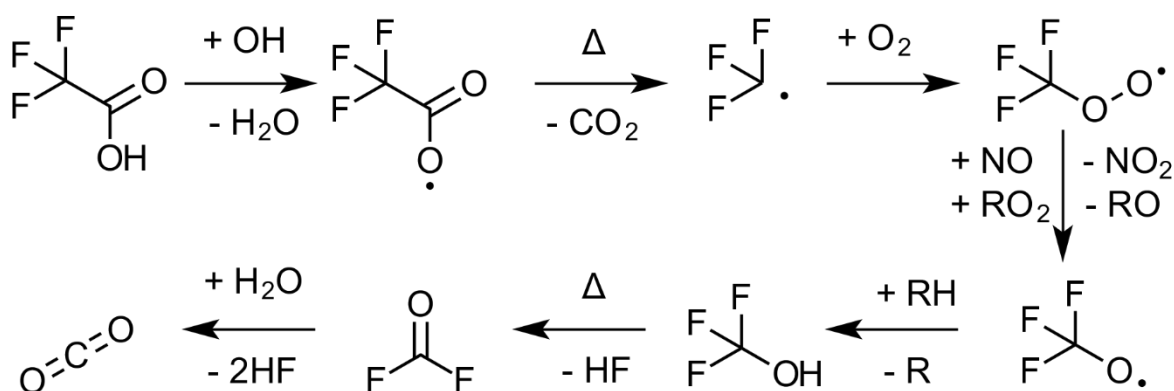
Another aspect of phototautomerization is that it accesses a relatively uncommon functionality in atmospheric chemistry, the vinyl alcohol substitution, which has the potential to form 1,1-*gem*-diol functionality in the gas phase and participate in several unusual reaction channels, which may lead to high O:C ratio (So et al., 2014) as well as cyclic products (Newland et al., 2019).

3.1.2.3. Thermal decomposition.

Similar to photolysis, thermal decomposition is not likely to lead to an overall simplification of the organic chemistry. In terms of mass-flux, some of the most important compounds affected by thermal decomposition are the peroxy nitrates and the peroxy acyl nitrates, both of which have the potential to act as NO_x reservoirs in the following thermal equilibrium with the peroxy radical and NO₂:



Interestingly, thermal instability results in one of the only known decomposition pathways for TFA in the environment, in which the OH radical-initiated reaction sequence leads to the thermally unstable alkoxy acyl radical, leading to trifluoromethanol, which may then eliminate CF₂O:



3.1.2.4. Wet deposition and hydrolysis.

Wet deposition is an effective loss process for gas-phase molecules that possess higher Henry's law coefficients. In principle, this applies to a large range of oxygenated products that are generally formed in the atmosphere, whose polar, oxygen-containing functional groups will enhance the Henry's law coefficient. Deposition onto cloud droplets represents the largest wet-depositional sink, and for molecules of a high Henry's law coefficient, they

have an approximate atmospheric lifetime of ~ 10 days, similar to the atmospheric lifetime of a water molecule (Brasseur et al., 1999). If particles subsequently evaporate, then absorbed species can re-enter the gas phase, and so, this is not necessarily a permanent sink.

Upon dissolution, an organic molecule can be transformed in a hydrolysis reaction, which can also be reversible, but which often leads to a permanent chemical change. A good example of this is the production of tetrols in isoprene oxidation (Hu et al., 2011), which may be formed from the aqueous uptake and transformation of hydroxy- and nitrooxy-substituted parent molecules and represents a permanent sink for these species.

Other nucleophilic substitution reactions can also occur in the aqueous phase, including the reactions of sulphate ions, which impart organosulphate functionality. The competition between hydrolysis and these other nucleophilic substitutions depends on pH and the availability of sulphate and other ions, and therefore depends on many factors relating to the aqueous microenvironment.

3.1.2.5. SOA uptake.

Although organic molecules that are formed in the atmosphere can have high Henry's law coefficients, and therefore a high affinity for the aqueous phase, they may also partition readily into an organic condensed phase, even if they are present at partial pressures that are lower than their saturation vapour pressure (Pankow, 1994). This means that even though absorption of a gas-phase organic molecule is an equilibrium process, equilibrium favours the condensed phase, and therefore represents an effective sink for organic gases.

However, there are several factors that could modify this behaviour. This includes the general rule that the mixture of chemicals found within SOA will depart to some extent from ideality, especially in mixtures of organic and inorganic components (Zuend et al., 2011). This could affect the tendency of molecule to partition into the condensed phase directly. Furthermore, this non-ideal behaviour can produce inhomogeneities within a particle, such as a mixture of phases (solid and liquid), heterogeneities within the liquid phase and the presence of surface layers. Because of the high mixing ratios of water in the atmosphere, the surface of aerosols is often coated with water, and the probability of aerosol uptake will therefore be affected by the affinity of a gas-phase VOC with the aqueous interface.

Aerosols also provide environments in which permanent chemical changes occur. One of the most important reactions in the aerosol phase is that of oligomerization, which occurs when a carbonyl reactant becomes either protonated or hydrated, leading to condensation reactions with other available carbonyls. This can result in a rapid increase in carbon number and a corresponding decrease in volatility, thus forming product molecules that are unlikely to evaporate back into the gas phase.

3.1.2.6. Other depositional processes.

Other depositional processes exist, many of which fall under the umbrella term "dry deposition". An important contributor to dry depositional loss is the uptake of VOCs onto plant surfaces. This process can, through enzymatic action, transform molecules to a less

cytotoxic form (Canaval et al., 2020; Karl et al., 2010). There is also some evidence to suggest that many organic molecules are taken up, and subsequently re-emitted in a bidirectional flux with the biosphere (Park et al., 2013). It is therefore difficult to gauge the role of these processes with respect to atmospheric organic complexity, which would appear to hinge on the variety of metabolic products of these processes.

3.2. Atmospheric degradation schemes:

In the previous sub-sections, two major features of atmospheric composition were outlined:

1. The large variety of VOCs emitted to the atmosphere
2. The large number of possible initiation reactions that elicit chemical change

Depending on the structure of the VOC that is emitted, and the precise route that it takes through oxidation space, different product molecules will be formed along the way. In fact, for a single molecule of only an intermediate complexity such as α -pinene, the array of molecules that are formed after several generations of oxidative reactions can be forbiddingly complex, and is estimated to account for nearly 500,000 separate structures (Valorso et al., 2011). This phenomenon, known as the “combinatorial explosion”, is a consequence of the sequence of multifurcating paths that a molecule must encounter before it is eventually removed from the atmosphere. This is partly a result of the number of potential oxidative sinks, but is also strongly dependent upon the multifarious fates of key radical species, especially the alkoxy radicals and the peroxy radicals. Among other possibilities, alkoxy radicals are able to form carbonyls upon reaction with O₂; perform hydrogen shifts that form hydroxyalkyl radicals; and fragment across potentially several C–C bonds (Orlando et al., 2003). Recently, it is becoming increasingly apparent that peroxy radicals are similarly complicated, being able to perform several hydrogen shift reactions; engage in ring-closure reactions; and condensation reactions that are likely to be instrumental in the formation of highly oxidized molecules (HOMs) (Bianchi et al., 2019).

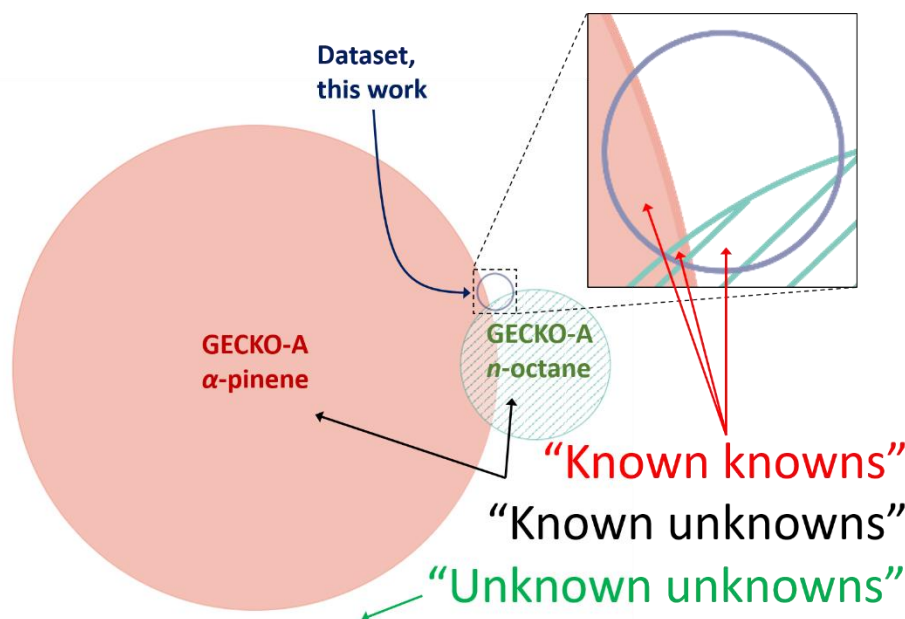


Figure 2: Area-proportional Venn diagram showing the overlap between species formed in GECKO-A for *n*-octane and α -pinene oxidation, and species present in our database. Here, “known knows” reflect compounds that are formed in GECKO-A for which measurements are available. “Known unknowns” represent chemicals that are formed in GECKO-A for which no measurements are available. “Unknown unknowns” represent species that could be formed from the oxidation of other primary emissions besides *n*-octane and α -pinene that are not considered in this diagram, and may also represent compounds that are formed through mechanisms that are currently unknown to/ not considered in GECKO-A.

The combinatorial explosion is a phenomenon that occurs in the atmosphere as well as other oxidative environments, such as combustion systems, and explicit chemical mechanisms that describe these systems are so large that they transcend human capabilities to construct and maintain them (Vereecken et al., 2018). Consequently, automated mechanism generation (AMG) software has been developed for this purpose (Aumont et al., 2005; Gao et al., 2016; Carter, 2019; Battin-Leclerc et al., 2011). Modelling of combustion systems generally involves the oxidation of a select few compounds, conversely, an accurate representation of the atmospheric environment would necessitate the oxidation of many 1000s of different chemicals. An example of the combinatorial explosion is the atmospheric oxidation of α -pinene in GECKO-A (Figure 2). If α -pinene is indeed representative in its number of products, and if the overlap between various oxidation schemes is not so high, as is suggested when α -pinene is compared with *n*-octane, then the true number of species that are capable of forming in the atmosphere is in the billions, and is likely to be a far greater number still. However, α -pinene cannot be classed as a comparatively complex VOC emission when it can be shown that much larger molecules can be measured in the gas phase, such as the diterpenes (C_{20}) (Li et al., 2020) and compounds as large as C_{26} (Lyu et al., 2019). Bearing in mind that the mechanism size reported by the AMG approach of GECKO-A is shown to be a strong function of carbon number (Aumont et

al., 2005, 2013), it can therefore be recognized that these observations serve to compound the problem of the combinatorial explosion still further.

The sheer number of species is only a single dimension in which atmospheric compositional complexity arises. The complexity of a single species and the interplay between its various functional groups could present its own set of challenges. In the oxidation of α -pinene, a distribution of chemical functionality is observed (see Figure 3), with a modal value of 5 functional groups. These 5 functional groups could represent any combination of the functional groups available to atmospheric chemical mechanisms, and the many inter- and intramolecular interactions that are possible under these circumstances could have a profound effect upon the ability of a molecule to oxidize further, to partition to the aqueous or condensed phases, or to act as a nucleating agent for new particle formation.

3.3. Observations:

In the previous sections, a bottom-up perspective was employed to argue the case for a large number of emitted and partially oxidized molecules being present in the atmosphere. This is a direct outcome of the large variety of emitted species that possess several branching degradation pathways. However, merely listing the total number of species that are outputted by AMG software such as GECKO-A does not convey the probability of forming any single compound. Indeed, many of these molecules will be formed in possible, yet rare events. In such a situation, atmospheric mixing ratios could remain immeasurably low. It appears to be most probable that field instrumentation may never possess sufficient sensitivity or speciation to resolve every trace component of the atmosphere, however, as the community's analytical capabilities continue to improve, the top-down view of atmospheric trace organic complexity becomes more complete.

Considering the large number of compounds that are simultaneously present in atmospheric samples, any mass-based unidimensional analytical method, regardless of its resolving power, will encounter the problem of isobaric structures, that is, multiple structures that possess an identical molecular mass. Therefore, of all current techniques, the separation techniques possess the highest potential for resolving complex mixtures, and among these, the GC \times GC (2D-GC) method has been deployed most successfully in this regard. This technique exploits the concept of double-column chromatography in which an analyte can be separated according to its volatility and its polarity, for example. This method was first applied to atmospheric samples in the year 2000 (Lewis et al., 2000), when it was able to speciate >500 chemical components. This represented major progress, and highlighted the presence of many semi-volatile species that were hitherto considered to exist primarily in the condensed phase.

In their concise overview of known and unexplored constituents of Earth's atmosphere, Goldstein and Galbally (2007) noted that the total number of organic compounds that are identified in atmospheric samples increases rapidly over time, and in lieu of a comprehensive list of measurements, guessed that the overall number could be in the range 10^4 – 10^5 molecules. The use of the word "guess" is instructive in itself, and highlights the challenges that remain. One such challenge is the size of GC \times GC datasets, which in many

cases precludes manual data treatment. As a result, data analysis is becoming increasingly dependent upon advanced statistical and chemometric methods, and it has been suggested that this ability to interpret these datasets is becoming the rate-determining step in GC × GC chemical analysis (Hamilton, 2010). Another fundamental challenge is the phenomenon of the unresolved complex mixture (UCM) (Schauer et al., 1999), which is comprised of a large number of non-polar organic compounds that cannot be separated with current chromatographic methods. This remains true of current GC × GC methodologies, which report a large unresolved “hump” in their chromatograms (Chan et al., 2013). To resolve samples further, additional dimensionality can be introduced after chromatographic separation, one example of which is the use of tuneable vacuum ultraviolet light to distinguish between aromatic and aliphatic components in crude oil samples (Nowak et al., 2018).

Although the GC × GC approach has been highly instructive in atmospheric chemical speciation, there are several reasons why this approach may only capture a fraction of the total organic trace composition of the atmosphere. Principal among these is the combined requirement of thermal desorption, cryofocusing and column separation, which, without a specific countermeasure, could prohibit the transmission of entire families of organic constituents that are thermally labile. In some cases, this can be circumvented using derivatization, such as in the detection of hydroperoxidic species, but these approaches are laborious and are not necessarily universal, demonstrating a limitation in producing stable trimethylsilyl derivatives of certain hydroxy functionalized hydroperoxides, for example (Docherty et al., 2004).

In contrast to the GC methods, are the soft-ionization techniques. These methods minimize analyte fragmentation and decomposition using a combination of direct sampling, chemical ionization (CIMS) and ion optics, affording pptv-sensitivity without the requirement of a pre-concentration stage. By reducing fragmentation, these methods can be used to determine the parent molecular mass, but do not generally provide structural information, and hence cannot distinguish between the potentially many compounds that could be present at the same m/z . However, the high selectivity of the various CIMS techniques can provide definitive information on the chemical functionality of molecules, for example, the acetate reagent ion is found to react almost exclusively with acidic compounds (Veres et al., 2008). This principle has been employed recently to explore the organic chemical space of α -pinene oxidation using a multi-instrumental approach including proton-transfer, iodide ion and electron impact techniques, with a view to understanding the coverage, overlap and analytical gaps in an ensemble of organic molecules (Isaacman-VanWertz et al., 2017). CIMS techniques are progressing rapidly, and ionization schemes continue to be developed. For example, recent developments in proton-transfer reaction mass spectrometry have found that the ammonium ionization scheme (NH_4^+) has a high affinity for oxygenated moieties, with minimal fragmentation as a result of the lower drift-tube voltages that are employed. Such a configuration would therefore significantly alter the chemical space that is available even when compared with the relatively recent study of Isaacman-VanWertz et al. (2017).

Whether it is a GC × GC or an ensemble of CIMS techniques, each analytical approach will have blind spots in coverage and speciation. Therefore, it is useful to consider the carbon that can be accounted for with that that cannot. Central to this idea are the concepts of total organic carbon (TOC) and total observed organic carbon (TOOC) (Heald et al., 2008). TOOC is a subset of TOC and represents the mass of organic carbon that has been speciated and quantified. Closing the TOC–TOOC gap represents an important goal for characterizing atmospheric composition, however, reliable measurements of TOC remain elusive, and quantitative knowledge of this gap is therefore missing. Nevertheless, as atmospheric trace organic measurements continue to improve, it is probable that the TOC–TOOC gap is shrinking in general.

Related to this idea is the concept of OH reactivity, which represents a highly informative way of comparing the VOCs that are quantifiable in the field with those VOCs that are not. The total reactivity of OH can be described as follows:

$$k_{\text{OH}} = \sum_i^n k_{\text{VOC}_i} [\text{VOC}]_i + \sum_i^n k_{\text{inorganic}_i} [\text{inorganic}]_i - k_{\text{regenerated}}$$

EQN. 1

where k_{OH} is the first-order decay rate of OH, k_{VOC} , $k_{\text{inorganic}}$, [VOC] and [inorganic] represent the OH rate coefficients and concentrations of all organic and inorganic components in the system, and $k_{\text{regenerated}}$ is the amount of OH that that is produced secondarily from sources such as $\text{HO}_2 + \text{NO}$. Theoretically, if all VOCs and inorganic components were quantified in the field and all rate coefficients were known accurately, then the measured decay rate of OH radicals would equal that of EQN. 1. In reality, although inorganic species such as CO, NO, NO₂, SO₂ and O₃ are generally well-characterized, there are many unquantified organic species, that result in measured OH decay rates being faster than what is calculated, this shortfall in the calculation is referred to as the “missing OH reactivity”. OH reactivity measurements have been performed in many different locations globally, in urban, suburban, rural and remote environments (Yang et al., 2016), and regardless of where the measurement is taking place, there is a substantial component of missing reactivity, which ranges from ~20–80% depending on the location and the time of year. Typically wintertime urban measurements and remote forested environments present the largest missing reactivities (Yang et al., 2016). The highest missing OH reactivity recorded so far, both as a fraction of the total reactivity measured at that site and also in an absolute sense, occurred in the Amazon in the dry season of 2013 (Nölscher et al., 2016). One of the potential explanations of this large fraction is the influence of biomass burning on the loading of a large variety of unresolved VOCs, the possibilities of which have been highlighted in section 3.1.1.1. The measurements with the lowest missing reactivity are from urban and suburban sites in the summertime, typically with a higher petrochemical contribution, and where VOC processing is relatively rapid, such that the less constrained multigenerational oxidation products have a lower probability of building up to appreciable concentrations.

Although missing OH reactivity measurements can be very insightful, they have no inherent capability for specificity. That is, as an ensemble, the missing components could have a

comparatively high concentration and a low reactivity or a low concentration and a high reactivity, furthermore, it could represent a smaller number of molecules, or a vast array of different molecules and in each case, they would potentially yield the same result. Knowledge of the dominant emissions in a region would help to constrain this missing compositional data. For example, an emission of a highly reactive molecule such as isoprene is likely to evolve towards less reactive species over time as a result of losing its olefinic functionality, in contrast, a larger saturated molecule such as *n*-decane may yield more reactive products as molecules acquire more reactive functionality (Peng et al., 2021).

Another potential problem with any instrument that requires a sampling inlet (and this would apply to any of the analytical methods mentioned in this section) is that many compounds are anticipated to engage in absorptive partitioning towards surfaces (Deming et al., 2019), and depending on the functionality, have a high decomposition rate on many surface materials. Therefore, even when concerted efforts are made to reduce these effects, such as inert inlet materials, rapid sample flows and heated walls, transmission through the inlet is likely to be significantly less than 100%, especially for some of the more heavily functionalized structures that are anticipated in the GECKO-A mechanisms, which are calculated to possess much lower saturation vapour pressures than molecules that are normally encountered in the laboratory (see Figures 3 and 4). As a consequence, even though missing reactivity represents a major insight into the atmospheric unknowns, it is potentially more correctly termed the “total observed reactivity”.

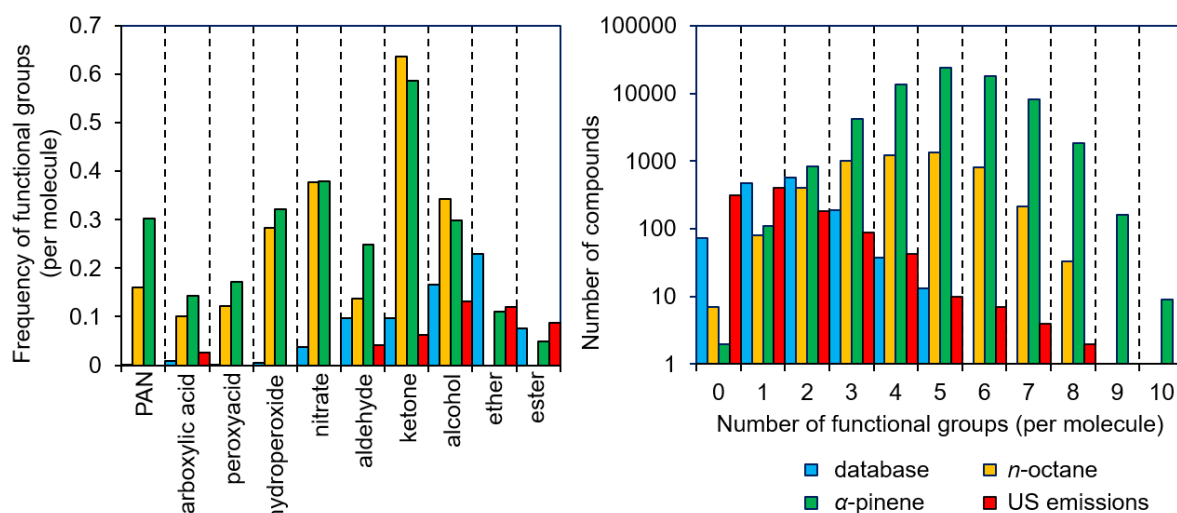


Figure 3: Frequency plots comparing the functionalization of compounds within the GECKO-A mechanism of *n*-octane and α -pinene oxidation; a database of anthropogenic emissions (Carter, 2015); and the compounds present in our kinetic database. (Left) Functional groups such as ethers and esters are overrepresented within this database compared with GECKO-A, whereas other functional groups (e.g. nitrates, peroxy acyl nitrates and hydroperoxides) are very poorly represented. (Right) a mismatch is demonstrated between the number of functional groups per molecule in GECKO-A and that of the compounds found in this database. Better agreement is observed in both cases compared with primary emissions profiles.

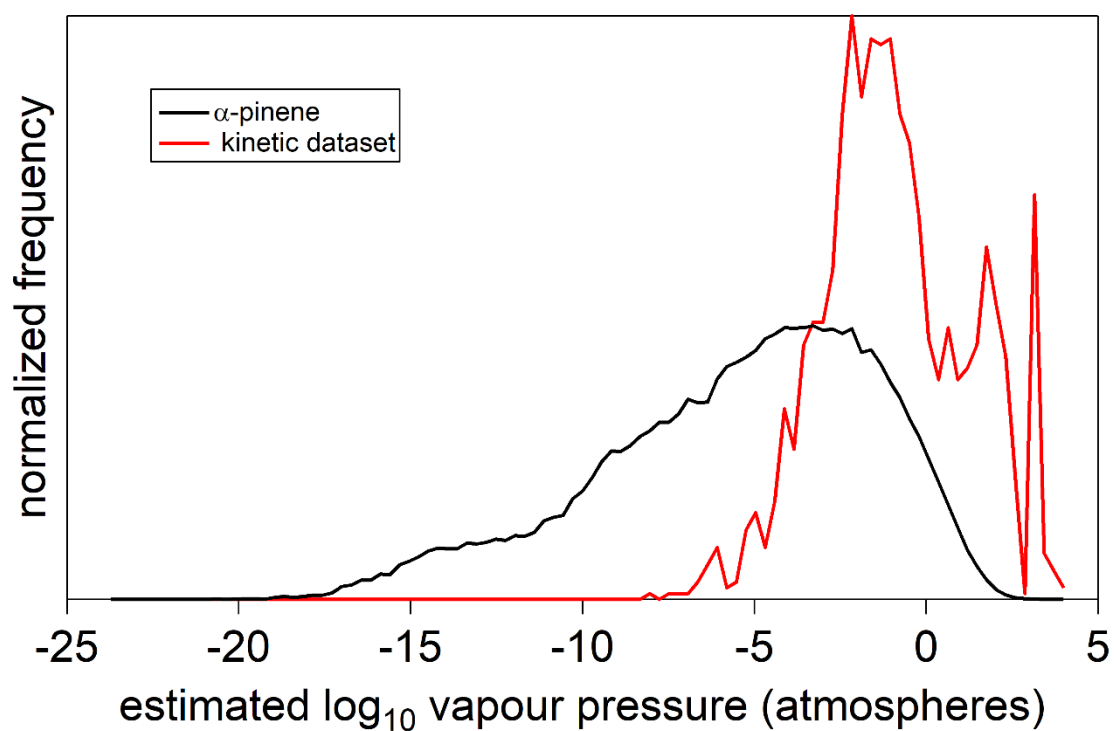


Figure 4: Distributions of the estimated vapour pressures of the compounds contained within experimental kinetic dataset (McGillen et al., 2020), compared with that of the collection of compounds predicted to form in α -pinene oxidation (Valorso et al., 2011). Vapour pressures are estimated using UManSysProp (Topping et al., 2016).

4. Approaches to address the chemical complexity of the atmosphere:

Through the combination of a high diversity of emissions and a cascade of secondary chemistry, a large number of organic compounds are present in the atmosphere, which has now been demonstrated from both the top-down as well as bottom-up perspectives. For the vast majority of these compounds, almost nothing is known experimentally, and given the time and expense that would be necessary to build a comprehensive experimental database, methods for calculating their physical behaviours are essential. In fact, the list of possible compounds is so long that with the available computational resources, any such calculation ought to be computationally trivial. Structure-activity relationships (SARs) are the standard approach for tackling such a problem, where input can be generated in an automated way in the form of unique textual identifiers (e.g. SMILES, InChI), which are ultimately rendered into chemical graphs, upon which simple algorithms can be applied. Such calculations are highly efficient and can be performed in large batches to provide estimates of important physical properties such as gas-phase reaction rates, vapour pressures and Henry's law coefficients, among other characteristics. There are many principles upon which SARs can be derived, with some providing more reliable and complete estimates than others, however, even in the best cases, these calculations remain a crude parameterization of the processes to which they are applied. It is therefore necessary to assess and benchmark SAR performance against experimental data wherever possible.

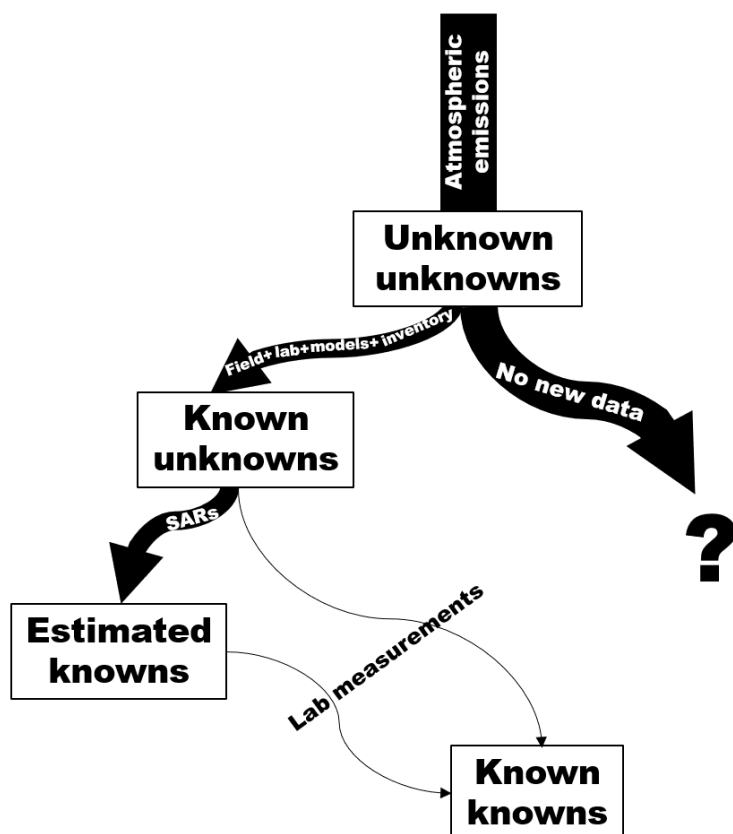


Figure 5: A visualization of how information moves through atmospheric chemistry, and the constrictions that are encountered along the way. The importance of “estimated knowns” is a vital placeholder, with the rate-limiting step being the laboratory measurements.

A schematic diagram of the flow of data and the bottlenecks encountered in furthering the knowledge in atmospheric chemistry is shown in Figure 5. SARs represent an effective stopgap in producing estimated data where no measurements are available.

4.1. Assessing the known knowns

Before the performance of SAR approaches can be assessed, compendia of high-quality experimental observational data must first be compiled. Within the present context, a “known known” is considered to be a datum that has been experimentally observed and quantified. There are several collections of experimental data that are available for gas-phase rate coefficients, vapour pressures, Henry’s law coefficients, absorption cross sections and solution-phase kinetics. Whereas some of these databases have a strict focus on the most atmospherically important reactions, others take a more comprehensive approach. From the perspective of measuring SAR performance, the comprehensive databases are much preferred, since larger amounts of data could result in a larger amount of reliable information contained within a training set. However, in order for the foundations of an SAR parameterization to be reliable, database contents must be vetted and reviewed such that unreliable data can be removed or at least minimized. The database of McGillen et al. (2020) is the largest reviewed database of gas-phase oxidation reactions that is currently available, and documents the reactivity of 1667 different molecules. Figure 6 is a set of area-proportional Venn diagrams that shows the size of this database compared with other databases, and also the relative amount of data for each of the four oxidants (OH, Cl, NO₃ and O₃) that are considered.

The aims of this database project are to compile as much experimental data as possible, to make it freely available and easily searchable, and to provide an indication of the reliability of the data contained within it. Furthermore, it is desirable that database updates are frequent enough that it can take advantage of any recent progress in laboratory measurements. One update has already been implemented, and a second is underway, with the overall update cycle being maintained at roughly once a year.

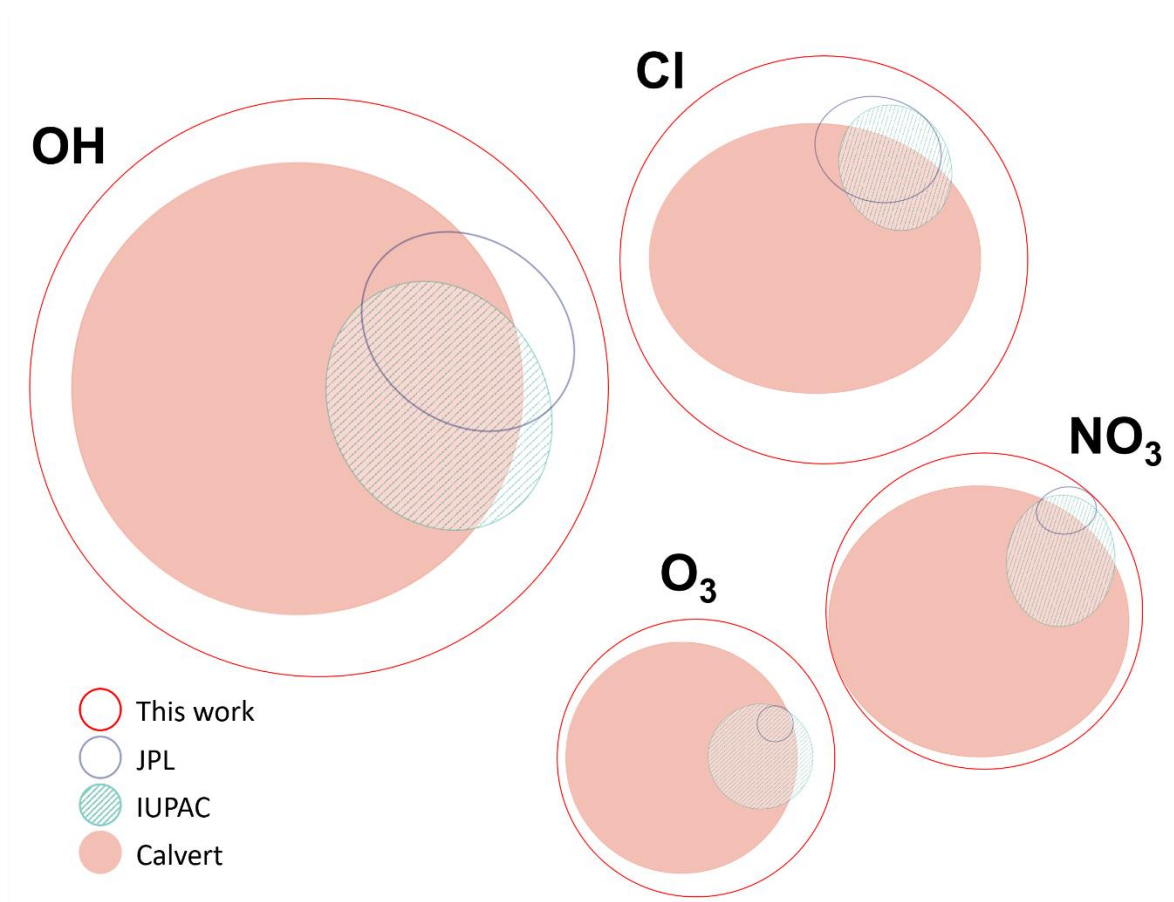


Figure 6: Area-proportional Venn diagrams constructed using the eulerAPE software (Micallef and Rodgers, 2014). The size and position of each curve is proportional to the number of species studied with respect to each oxidant, the number of compounds available in each review, and the overlap between these reviews.

The process of data evaluation is something that is done on the basis of consensus of a panel of experts on experimental data. Reported kinetic data is fundamentally simple, and can be reduced to a single number, that is, the size of the rate coefficient. Encoded within this number are all of the factors that can contribute to a molecule's reactivity, but also any artefacts or systematic errors that were introduced in the measurement and interpretation. As a consequence, a diverse range of factors are considered during the evaluation including:

- Is the measurement technically difficult?
- How well was the measurement performed?
- Were appropriate tests made?
- Is the apparatus suited to measuring this reaction?
- Is the measurement generally consistent with analogous reactions?

To maintain quality, and to remove as much arbitrariness as possible from the decision-making process, a protocol for the review process has been constructed:

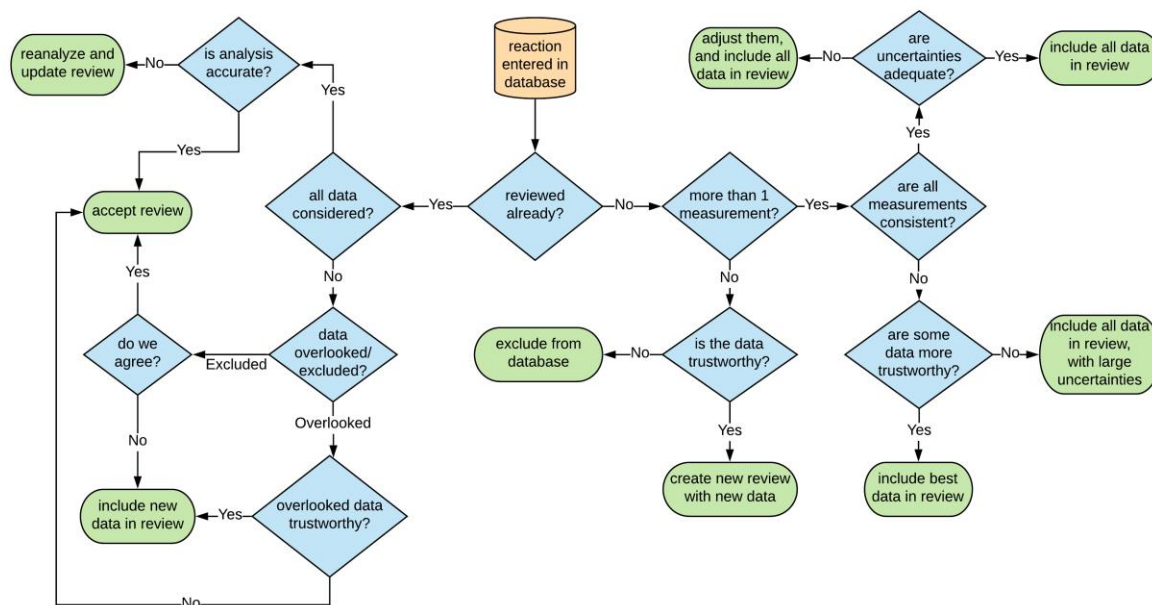


Figure 7: Decision tree describing the data review process for our database.

Other databases are available for other experimental properties, such as:

- Vapour pressure, e.g. (Yaws, 2015; Dortmund Data Bank, 2021)
- Henry's law coefficients, e.g. (Sander, 2015)
- UV-vis absorption cross sections, e.g. (Noelle et al., 2020; Keller-Rudek et al., 2013)
- FTIR absorption cross sections, e.g. (Pacific Northwest National Laboratory (PNNL) Infrared Database)
- Solution-phase kinetics, e.g. (Herrmann et al., 2015; NIST Standard Reference Database 40, 2020)
- Thermochemical information, e.g. (Ruscic et al., 2005)

Although many of these resources are extremely useful, not all of them are comprehensive, reviewed, up-to-date, easily searchable or freely available; and improvements can and should be performed if SARs for these other properties are to be developed or improved further.

4.2. Predicting the known knowns

The performance of estimation techniques of gas-phase VOC + OH rate coefficients will be described in this subsection. Techniques exist for many of the other experimental properties listed above, but the SAR methodologies and free-energy relationships of this quantity in particular have reached a level of variety and maturity that affords a more detailed discussion.

Regularities and patterns in the rate coefficients of VOC + OH reactions were first identified near the time that the first reliable gas-phase measurements became available, and indeed, such behavioural trends were a motivating factor in early measurements (Greiner, 1970). The principle behind this early work was based upon the concept of group-additivity in

which a total rate coefficient is considered as the sum of separate contributions from each of its constituent reactive sites (or hydrogen environments):

$$k_i = C_i N_i \exp(E_i/RT)$$

EQN. 2

where k_i is the bimolecular rate coefficient of the i^{th} reactive site, and C_i , N_i and E_i are its A-factor, number of hydrogen atoms and activation energy respectively.

Since different sites exhibit a varying degree of reactivity as a function of temperature, a partial activation energy and pre-exponential factor for each type of hydrogen environment encountered in the alkanes was ascribed, the sum of which yields the total phenomenological rate coefficient (k_{total}):

$$k_{\text{total}} = \sum_i C_i N_i \exp(E_i/RT) = \sum k(T)_{\text{prim}}^{\circ} + \sum k(T)_{\text{sec}}^{\circ} + \sum k(T)_{\text{tert}}^{\circ}$$

EQN. 3

where $k(T)_{\text{prim}}$, $k(T)_{\text{sec}}$ and $k(T)_{\text{tert}}$ represent the temperature-dependent rate coefficients of the primary, secondary and tertiary sites that are present in aliphatic alkanes.

This approach was found to be adequate for the collection of alkanes for which it was originally intended. However, within the VOCs there exist many more atom types and substitution types besides the carbon and hydrogen that is found in the alkanes, and the ability of these functional groups to modify the hydrogen abstraction rate coefficient presents a greater challenge. For this purpose, Atkinson (1987) developed a structure-activity relationship that included substituent-factors (F -factors) that accounted for the electron-withdrawing, electron-supplying and other effects that are encountered within the whole gamut of substituents of the larger substituted alkyl dataset. Atkinson's approach is described as follows:

$$k_{\text{total}} = \sum k(T)_{\text{prim}}^{\circ} F(X) + \sum k(T)_{\text{sec}}^{\circ} F(X)F(Y) + \sum k(T)_{\text{tert}}^{\circ} F(X)F(Y)F(Z)$$

EQN. 4

which is of a very similar functional form to the work of Greiner (1970) – and which is itself based upon the earlier work of Benson (1968), and where $F(X)$, $F(Y)$ and $F(Z)$ represent multiplicative correction terms for the positive ($F > 1$) or negative effect ($F < 1$) of a substitution type upon each partial rate coefficient.

Hydrogen abstraction is not the only mechanism of importance in the VOC + OH reactions, and the electrophilic addition of OH towards olefinic sites can dominate the overall rate coefficient in many cases. The factors that govern the reactivity of these unsaturated sites are different from the C–H bonds in hydrogen abstraction reactions, and centre around the electron density of the π -orbitals of the olefinic bond. Accordingly, a separate algorithm is used to describe this reactivity:

$$k_{\text{total}}(\text{CH}_2=\text{CHX}) = k(\text{CH}_2=\text{CH-})C(X) + k_{\text{abstraction}}$$

EQN. 5

where the rate coefficient of a monosubstituted alkene $\text{CH}_2=\text{CHX}$ is constructed from the base rate coefficient of the monosubstituted olefinic bond, $k(\text{CH}_2=\text{CH-})$, multiplied by a substituent factor, $C(X)$. Finally, the contribution of abstraction reactions, $k_{\text{abstraction}}$, from substituent (X) are accounted for using k_{total} from EQN. 4 above. Analogous calculations are performed on alkenes with any possible substitutions and their substituent factors, with separate factors being used to describe 1,1-di-substitution, *cis*-1,2-di-substitution, *trans*-1,2-di-substitution, tri-substitution, tetra-substitution as well as the various condensed and conjugated systems that are members of the polyene family.

This approach has been found to be reliable in most cases, and as a result it has found widespread adoption in the atmospheric community, and despite several major updates it remains mostly unchanged up until the time of writing. As AMG software matures, automated SAR calculations are becoming available for the structure contained within mechanisms (Jenkin et al., 2018a, b; Carter, 2021). These calculations are performed by updated SARs which, despite showing significant improvements in estimation accuracy, represent only an iteration upon the original concept of Atkinson (1987) and the work of Greiner (1970) and Benson (1968) that preceded it.

However, the bases upon which various prediction methods rely is potentially far more diverse (Vereecken et al., 2018), a non-exhaustive list of which includes:

- Alternative formulations of the group-additivity concept, e.g. (DeMore, 1996).
- Mixtures of group-additivity and theoretical calculations, e.g. (Paraskevas et al., 2015).
- Geometric topological calculations, e.g. (McGillen et al., 2008; Leather et al., 2011; McGillen et al., 2011).
- Topological indices, e.g. (McGillen et al., 2006a, b, 2007b; Pompe et al., 2004; Markelj and Pompe, 2016).
- Linear free-energy relationships (LFERs) with ionization potentials, e.g. (Percival et al., 1995; McGillen et al., 2006a, b, 2007b; Pfrang et al., 2006; King et al., 1999).
- LFERs between rate coefficients of different oxidants, e.g. (Sulbæk Andersen et al., 2005).
- LFERs between the gas and aqueous phases, e.g. (Klöpffer et al., 1985; Wallington et al., 1988).
- LFERs with infrared C–H stretching frequencies, e.g. (Nip et al., 1979).

In general, these methods are not as widely used as the Atkinson approach, and this is likely to relate to a combination of visibility, reliability, ease-of-calculation and availability of correlated parameters. Notwithstanding, the Atkinson approach has some known weaknesses, for example, poor estimations were observed for some relatively simple multifunctional compounds (Bethel et al., 2001), which appeared to be a limitation of the

algorithm itself, and not something that could be remedied by re-fitting SAR parameters. Given that the predicted mechanisms of AMG software yields molecules of a high degree of multifunctionality (see Figure 3), these problems are unlikely to disappear and have the potential to remain a limiting factor in forecasts that use these approaches.

4.3. Predicting the known unknowns

Answers to the question of how well conventional SAR methodologies handle a molecule of representative atmospheric complexity are not forthcoming, since very few experimental measurements are available for highly functionalized species (see Figure 3). And so, the status of predicting the “known unknowns” of atmospheric chemistry remains one of extreme uncertainty. In light of this, in a scenario where the community remains unsure about how well any single approach can describe the physical behaviour of a molecule, and where extrapolating any such approach far beyond its training set is routine, it appears to be justifiable to be sceptical about the monoculture described in Section 4.2 that is encountered in atmospheric chemical prediction-space.

One potential solution to this problem is to consider an ensemble of estimation methods. Within the field of atmospheric science, ensemble approaches have so far been applied to large, macroscopic systems, such as global climate models and meteorological models, where greater consistency and reliability has been demonstrated (Hagedorn et al., 2005). In such systems, it has been recognized that:

“Every attempt to represent nature in a set of equations, resolvable on a digital computer, inevitably introduces inaccuracy.” (Hagedorn et al., 2005)

Such inaccuracies will then propagate throughout the prediction-space, leading to an amplification of error over time. The rationalization of why the ensemble succeeds in these applications is largely based on the idea that, with a variety of independent and skilful models, a better overall coverage of the prediction-space is obtained, and inaccuracies would have a tendency towards error cancelation.

Can it be assumed that applying a similar methodology towards the microscopic scales of molecules would yield similar benefits to SAR predictions? This is not necessarily guaranteed, however, it is nevertheless true that whether it is the meteorological conditions of the atmosphere, or the interactions of functional groups within a molecule, the overall state of the system will be determined by contributions from many non-linear processes, and the accuracy with which each of these processes is described will be less than perfect.

As mentioned above, of the variety of prediction methods that are available, some are inherently more reliable than others. It is therefore preferable that the contribution of a given method can be weighted by its estimated uncertainty. For this purpose, a weighted average can be calculated:

$$k_{\text{ensemble}} = \frac{\sum_{i=1}^N w_i k_i}{\sum_{i=1}^N w_i}$$

EQN. 5

where k_i is the i^{th} prediction of k , N is the number of estimation methods, and w_i is a weighting function of the i^{th} prediction, which is defined by:

$$w_i = 1/\sigma_i^2$$

EQN. 6

where σ_i represents the uncertainty of the i^{th} prediction.

Finally, the ensemble uncertainty, σ_{ensemble} , can be expressed as:

$$\sigma_{\text{ensemble}} = 1 / \sqrt{\sum_{i=1}^N w_i}$$

EQN. 7

To trial this idea, a limited subset of the 1667 molecules found in the database of McGillen et al. (2020) was necessary. This subset should be manageable in size, should express a range of reactivities, and should fall within the domain of applicability of a large variety of estimation methods. The subset that was considered most appropriate included alkanes and haloalkanes, a selection which fulfils each of these criteria.

In total 11 different techniques were employed for making estimates. These are described as follows:

1. EPI Suite AOPWin G-A method, based on the conventional approach of Kwok and Atkinson (1995).
2. Calvert G-A method, a modified version of Kwok and Atkinson (1995), further modified by this study to impose limits on combined F -factors.
3. DeMore G-A method, unmodified, but refitted with new data (DeMore, 1996).
4. Poutsma hybrid Evans-Polanyi method (Poutsma, 2013).
5. Cohen and Benson empirical thermokinetic method (Cohen and Benson, 1987).
6. Ionization potential LFER, e.g. (Percival et al., 1995).
7. Log-log OH-Cl rate coefficient LFER, e.g. (Sulbæk Andersen et al., 2005).
8. Log-log OH-O(³P) rate coefficient LFER.
9. Log-log OH-F rate coefficient LFER.
10. Log-log OH-OH gas-aqueous rate coefficient LFER, e.g. (Wallington et al., 1988; Klöpffer et al., 1985).
11. Electrotopological state, a fundamentally new SAR concept of the present work based upon the Kier-Hall index (Hall et al., 1991).

A truly detailed analysis of the performance of each one of these rate coefficient estimation techniques is beyond the scope of the present document. The estimates of the ensemble approach are shown in Figure 8. As a general summary, these methods demonstrate a variety of coverage and model skill. Furthermore, the strengths and weaknesses of these techniques are generally dissimilar, which is to be expected given the broad variety of input data, algorithms and underlying principles upon which each depends. A final analysis of this

complex prediction-space is still in progress, but one of the most interesting outcomes so far is that the performance of the ensemble is potentially inferior to some of the single methods such as DeMore (1996). This would not be anticipated if the findings of Hagedorn (2005) also apply to microscopic scales of chemical kinetics.

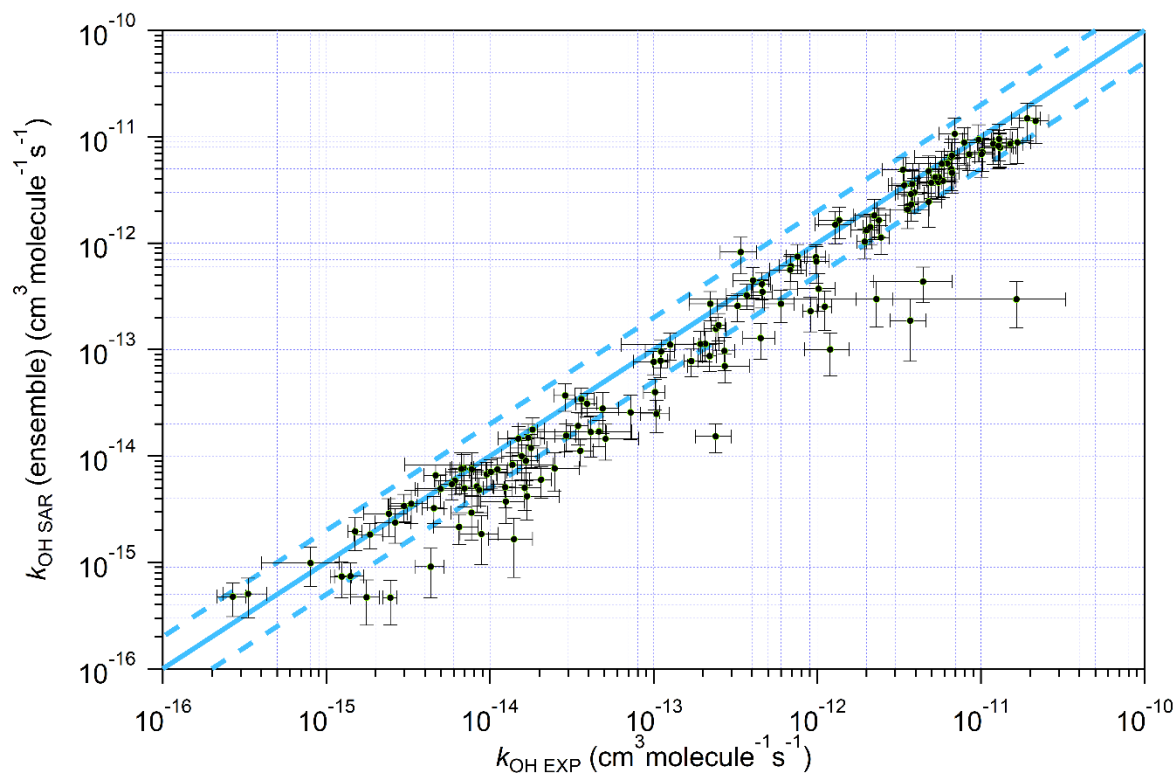


Figure 8: Estimations of halocarbon and hydrocarbon rate coefficients using a large ensemble of estimation methods. A notable asymmetry in the prediction-space is observed, which could indicate that some measurement biases are present in the kinetic database.

This outcome could be interpreted in several ways. One hypothesis is that some of these methods possess correlating errors, in which certain datapoints are consistently underpredicted or overpredicted between methods, and instead of error cancellation, error reinforcement would result. This is unexpected, in view of the variety of methods that are present in this ensemble. Another notable feature of the ensemble output is that there appears to be an asymmetry in estimation error, with a general bias towards underprediction. This would only be expected if the individual estimation techniques possessed a notable asymmetry in their correlations, which is not the case. If the hypothesis of correlating errors can be discounted, then this leads to a potentially provocative alternative hypothesis: that the dataset itself contains measurement biases. Although considerable efforts were spared in selecting reliable kinetic data (McGillen et al., 2020), and there is no obvious reason to suspect any individual experiments were of low quality, it is nevertheless true that no measurement is perfect and some experimental error is to be expected. Furthermore, as a general rule, systematic errors towards rate coefficient measurements that are too large is a concern in the haloalkane dataset, where rate coefficients can be small and where contributions from minor chemical impurities and secondary chemistry could have a proportionally large effect. If this second hypothesis is

valid, then the corollary is that current assessments of the climatic impacts of some of the most environmentally damaging anthropogenic compounds could actually be underestimated (WMO, 2019). A result such as this could drive future work in our lab to re-evaluate some of these consistently underestimated halocarbon rate coefficients to check whether current assessments of the climate forcing of these compounds are accurate.

4.4. Measuring the known unknowns

From a gas kinetic perspective, the earliest reliable oxidation rate coefficients were made in the 1970s. Since that time, 1667 individual compounds have been added to the kinetic database (McGillen et al., 2020). At a first approximation, the rate at which new measurements enter the database is ~33 measurements per year. If the number of unknown rate coefficients in the atmosphere was in the 10^6 range (and this could be a substantial underestimate), then, assuming a business-as-usual approach, it could take 10,000s of years to gain a comprehensive atmospheric kinetic dataset. In the short-term, the case for estimating rate coefficients and other properties is abundantly clear, after all, new measurements are time-consuming and expensive. Despite this, there are several reasons why laboratory measurements should continue. Firstly, all commonly used estimation methods are empirical and are ultimately based upon laboratory data. There are many configurations of molecules anticipated by both AMG software and a mechanistic knowledge of tropospheric chemistry, which are very poorly represented in SAR training sets. It is therefore necessary for laboratory scientists to work towards augmenting this data, such that predictions can be tested against observations. Secondly, under current conditions, estimation methods will remain generally inferior to direct observations. Consequently, for reactions of critical importance, experimentation remains the preferred choice. This is the reason why some of our recent laboratory activities have centred upon a reaction that is pivotal for aerosol production ($\text{OH} + \text{SO}_2 + \text{M}$) (see Figure 9), as well as the secondary chemistry of a molecule with an enormous atmospheric emission (isoprene) (see Figure 10). Thirdly, when considering the difficulties with which important atmospheric processes such as aerosol formation are modelled, it must be contended that our knowledge of atmospheric chemistry is incomplete. This implies that, as a community, we don't yet know all of the rules that govern atmospheric chemical mechanisms. It appears that it is through various new observations that a more complete knowledge of atmospheric chemistry will emerge.

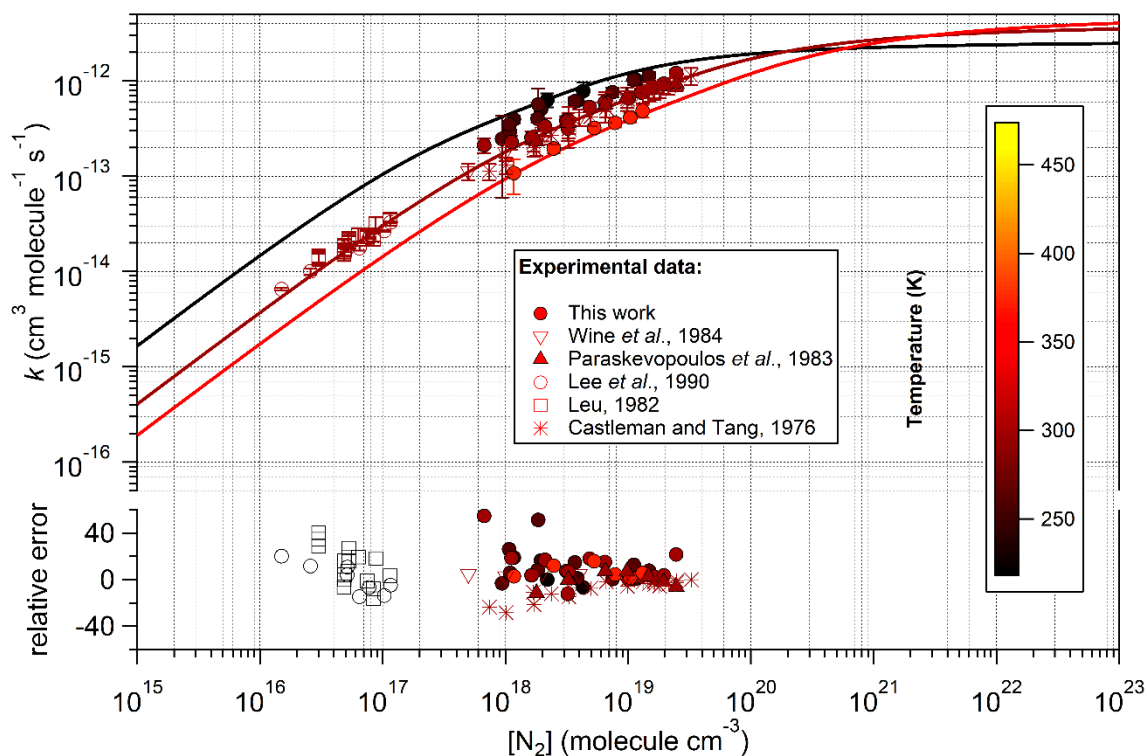


Figure 9: The reaction of $\text{OH} + \text{SO}_2 + \text{M}$ is of critical importance to atmospheric chemistry, but very few measurements are available under atmospherically relevant conditions.

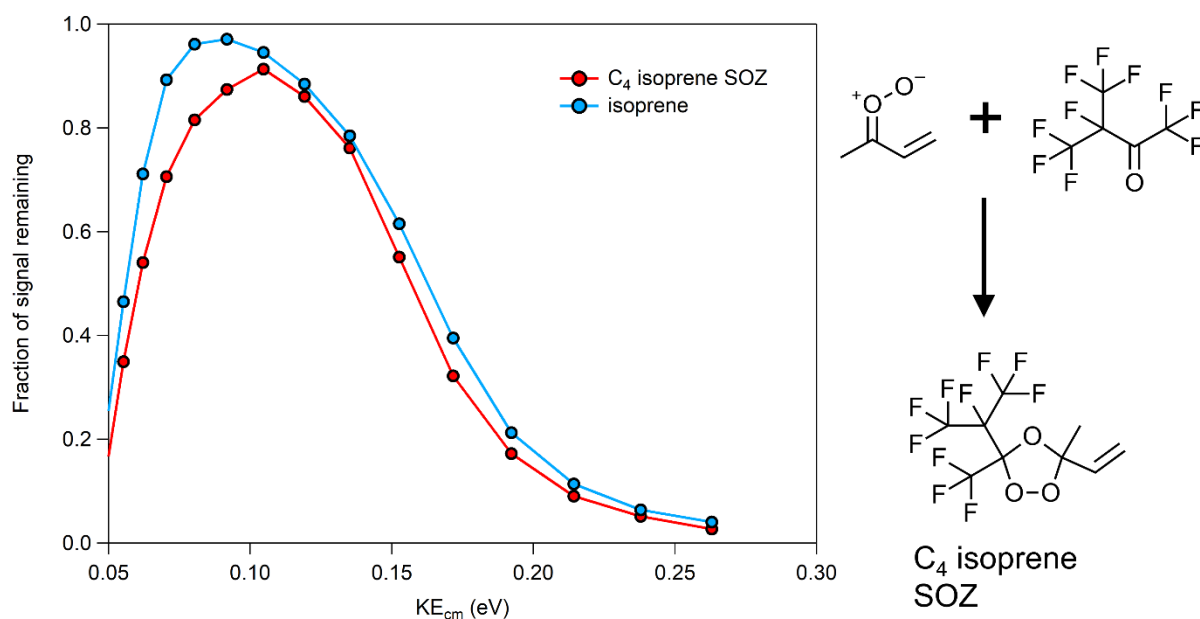


Figure 10: The reaction of isoprene + O_3 has been found to yield a C_4 isoprene stabilized Criegee intermediate, in contrast to the recent findings of (Nguyen *et al.*, 2016).

4.5. Identifying the unknown unknowns

The “unknown unknowns” of atmospheric chemistry can be viewed as anything that has yet to be discovered. By this definition, it would be impossible to gauge directly how complete

our knowledge of the atmosphere has become at any given moment. Indirectly, as models absorb larger quantities of reliable information, they should become more physically realistic, at which point their predictions will become more reliable. Although it will remain possible that a model provides an accurate forecast for the wrong reason(s).

Given that we can't anticipate what has yet to be discovered, progress in the "unknown unknowns" is set to occur by random chance. This is more likely to happen in exploratory work, which could involve laboratory measurements, field measurements or *in silico* experiments. This could become more likely as new analytical or computational techniques are applied to atmospheric processes, even to familiar systems. For example, our laboratory recently determined that epoxide formation is non-negligible in the well-studied tetramethylethylene ozonolysis system (see Figure 11). This was unexpected, and resulted from our recent adaptation of the PTR-MS instrument towards NH_4^+ ionization. This observation alone could guide several of our future investigations, each of which could yield unexpected outcomes *ad infinitum*, we cannot know until we try.

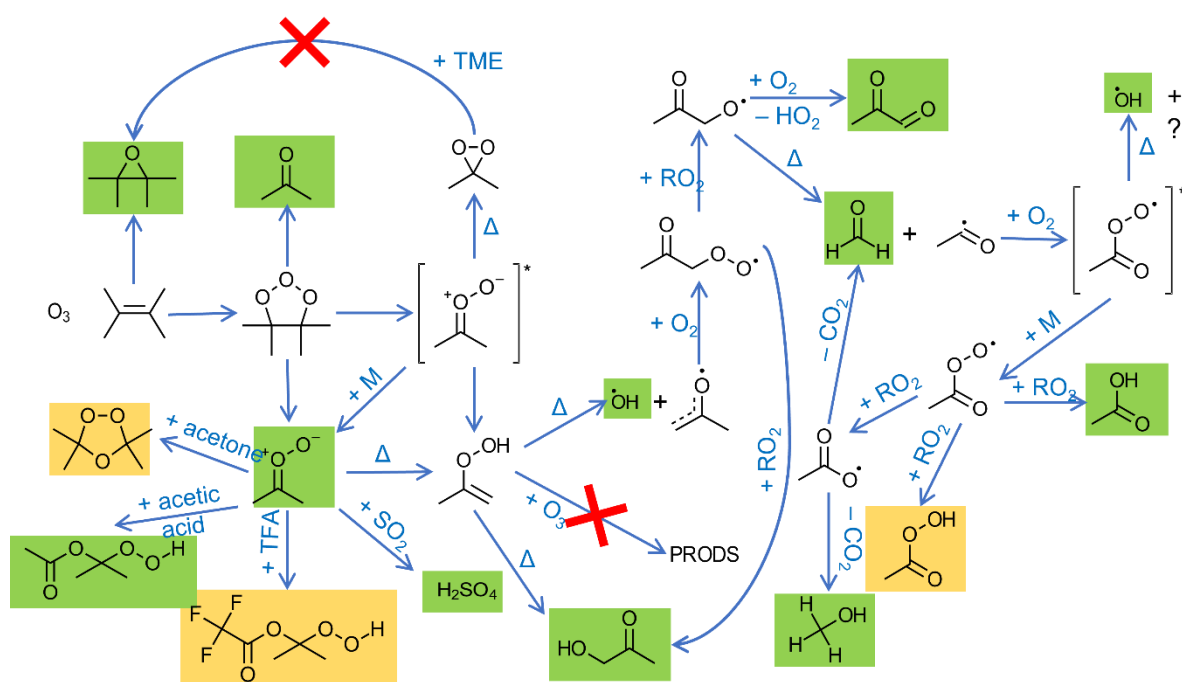


Figure 11: The reaction of tetramethylethylene + O_3 . A classic, well-studied ozonolysis system of a simple symmetrical alkene, but some surprises remain.

4.6. Too much information

The combinatorial explosion generates chemical schemes that are far too large and unwieldy. To run a truly realistic atmospheric chemical simulation in a box model would be difficult. To couple this with real-world physics, meteorology and emission fields could draw parallels with the early days of numerical weather simulation, where, to predict the weather 6 hours in the future demanded a calculation of at least 6 weeks to perform (Lynch, 2006). It is therefore necessary to carry out mechanism reduction. There is no standard mechanism reduction protocol, and the choices made in this regard are defined by the goals of the forecast. Predictions of ozone, for example, may be amenable to relatively simple schemes,

whereas for SOA production, more detailed mechanisms are likely to be necessary (Vereecken et al., 2018).

The main concern of mechanism reduction is that by losing chemical detail, model skill is also lost. A practical method to probe this possibility is to produce a benchmark mechanism. Keeping in mind the complexity that has been described in the chapters above, it would appear to be most probable that even the best benchmarks of tropospheric chemistry are incomplete mechanistically and underinformed kinetically. Therefore, to an unknown extent, the skill demonstrated by these benchmarks is also a consequence of lumping and parameterization.

Improving the knowledge of how emissions perturb the climate, the environment and the human exposome will be achieved by informing and improving these benchmarks and their subsequent reduced schemes.

I will try to bare this in mind as I continue (and guide) work in the laboratory, the field and in SAR development.

5. Teaching, mentoring and dissemination of scientific culture:

Summary table:

Level (Diploma)	Student	Period	Institution
Masters	Laura McMahon	2017	University of Bristol, UK
Masters	Holly Barrett	2018	University of Bristol, UK
PhD	Kimberley Leather	2007-2009	University of Manchester, UK
PhD	Mohamed Ghalaieny	2007-2010	University of Manchester, UK
PhD	Michael Le Breton	2008-2010	University of Manchester, UK
PhD	Hajar El Othmani	2018-present	ICARE-CNRS, France
PhD	Lisa Michelat	2020-present	ICARE-CNRS, France
Post-doc	François Bernard	2015	NOAA-Boulder, USA
Post-doc	Soukaina Foulal	2019	ICARE-CNRS, France

University of Manchester (2007–2010):

It was recognized at an early stage by the line-manager (Dr. Carl Percival) in my first post-doctoral appointment, that I was able to manage and direct research projects with minimal oversight. During my three year appointment as post-doctoral research associate at the university of Manchester, I was able to provide extensive training and leadership for the following three PhD students:

Kimberley Leather (PhD): I worked with Kim between 2007 and 2009. Together, we developed, tested and used a new reaction chamber at the University of Manchester. This chamber was called the EXTreme RAnge chamber (EXTRA) and was capable of measuring ozonolysis kinetics and products between 218 and 336 K, over a pressure range of ~1 to 3750 Torr. Kim was a talented student, was quick to understand and refine experimental protocols, was a careful laboratory worker, and we were able to write three research papers together:

1.) 10.1039/b919731a 2.) 10.1002/kin.20533 3.) 10.5194/acp-12-469-2012

I estimate that my supervision contributed approximately 50% of Kim's training.

Mohamed Ghalaieny (PhD): I worked closely with Mohamed between 2007 and 2010. Mohamed's thesis began on the subject of developing a new chemical ionization mass spectrometer for measuring atmospheric chemicals onboard the UK BAe 146 research aircraft. This was a new mode of working for me and Mohamed, where we were to encounter the tight and inflexible deadlines of field projects. It became apparent over this period that Mohamed did not always respond well to external pressure of this type, and following our first campaign in Edinburgh, we made the unanimous decision for Mohamed to work primarily on lab-based projects. This time was very education for me as an instructor, since it showed that sometimes it is best to adapt to the strengths of a student, rather than trying to persevere on a project that they are not well-suited. I co-wrote three research papers with Mohamed:

1.) 10.5194/amt-3-91-2010 2.) 10.1039/c0cp02643c 3.) 10.1039/c2cp23988d

I estimate that my supervision contributed to approximately 40% of Mohamed's training.

Michael Le Breton (PhD): I worked with Mike from 2008 to 2010. Mike's thesis was focused on the interfacing and operation of chemical ionization mass spectrometer for measuring atmospheric chemicals onboard the UK BAe 146 research aircraft. Mike was very well suited to fieldwork and

coped well with deadlines and pressure. I trained Mike in the methods of maintaining and using equipment in field conditions, which were often highly regimented to make certain that we had the resources to deploy our instrument even where unexpected situations arose. Mike had a talent for scientific programming allowing us to process data soon after measurements were made. I co-wrote one paper with Mike:

1.) 10.5194/amt-5-3029-2012

I estimate that my supervision contributed to approximately 30% of Mike's training.

National Atmospheric and Atmospheric Administration (2010–2015):

Unlike the University of Manchester, our laboratory at NOAA did not have an influx of PhD students, and the focus was mainly on my personal research activities. I was, however, able to provide training to post-doctoral appointees that entered the lab. Notable among these was Dr. François Bernard.

François Bernard (Post-Doc): Upon appointment, François had not yet received training in several areas in which I was specialized. This included the measurement of absolute rate coefficients using pulsed-laser photolysis–laser-induced fluorescence, and the measurement of UV and FTIR cross sections. François was already trained in several other techniques, and was quick to pick up these new techniques. He was very patient in the laboratory, and together I co-wrote three papers with François:

1.) 10.1002/2015GL064939 2.) 10.1016/j.jphotochem.2015.03.012 3.) 10.5194/acp-16-8043-2016

I estimate that my supervision contributed to approximately 30% of François' training.

The University of Bristol (2016–2018):

I spent only two years at the University of Bristol, and therefore, it was difficult to participate in a major way to the theses of PhD students. I did, however, find the time to supervise two masters students:

Laura McMahon (Masters student, 2017): Laura worked with me on the measurement of Criegee intermediate reaction kinetics using a cavity ring-down spectrometer system. Although she was an able student, it was clear from the outset that Laura did not wish to pursue a scientific career, and so, rather than training her in the more challenging aspects of laboratory work, such as realignment of ring-down mirrors and gas-mixture preparation, we set out to produce a series of routine and thorough laboratory measurements. This was very productive, and together we co-wrote a research paper:

1.) 10.1021/acsearthspacechem.7b00108

I estimate that my supervision contributed to approximately 80% of Laura's training.

Holly Barrett (Masters student, 2018): Holly worked with me on the use of the EXTRA chamber (imported to Bristol from Manchester) to measure the long-lived product yields of fluorinated alkene ozonolysis. Holly was a genuinely talented student, who was very capable in the laboratory and also in data analysis. The measurements that Holly made with me were scientifically interesting, so much so, that they prompted a visit from a chief scientist at Honeywell Corporation (Rajiv Singh). The detailed interpretation of our data became dependent upon external researchers for quantum chemical calculations, which has led to a delay in a publication from this work. However, I hope to submit a paper on this subject later on this year.

I estimate that my supervision contributed to approximately 80% of Holly's training.

Institut de Combustion, Aérodynamique, Réactivité et Environnement, CNRS-Orléans (2018–present):

Since joining ICARE, I have had the chance to work closely with PhD and post-doctoral trainees in the Équipe de recherche atmosphérique. The group-leader, Dr. Wahid Mellouki, is supportive of my role as mentor, and gives me a lot of freedom to decide how I would like to direct a trainee's efforts. Although I have been working with several students and post-docs, I will limit this section to the three that I have worked most closely with.

Hajar El Othmani (PhD, 2018–present): I have been training Hajar on the use of pulsed-laser photolysis–laser-induced fluorescence for making absolute kinetic measurements, as well as chamber systems, for measuring relative kinetic measurements. Hajar is an able student, and her strength is her ability to make consistent, careful measurements, which is an asset in kinetics. Although she has not expressed an interest in continuing her scientific studies, by the end of her thesis, she will have made some good contributions to gas kinetics. So far, I have co-written a paper with Hajar, with another expected to follow soon:

1.) 10.1021/acsearthspacechem.1c00050 2.) 10.1016/j.cplett.2021.139056

I estimate that my supervision contributed to approximately 30% of Hajar's training.

Soukaina Foulal (Post-doc, 2019): Soukaina joined our team at ICARE for less than a year. I designed Soukaina's project, which focussed on the environmental consequences of aircraft jettisoning kerosene fuel in the atmosphere. This project evolved over time, and I recognized that Soukaina had a talent for data analysis, which is where I decided to channel her efforts. Over this time we were able to collaborate with Prof. Bernard Aumont (Paris-LISA). Although Soukaina's funding ran out before we were able to complete this project, I am confident that we be able to complete a paper based on her work soon.

I estimate that my supervision contributed to approximately 80% of Soukaina's training.

Lisa Michelat (PhD, 2020–present): I am an official co-supervisor for Lisa, who joined our group at the same time that I joined as CNRS chargé de recherche. Although Lisa has not been with the group very long, it is clear that she has a lot of potential as a scientist, and I look forward to helping shape her thesis, which will be on the subject of the atmospheric chemistry of biomass burning processes.

I estimate that my supervision contributed so far to approximately 50% of Lisa's training.

Besides the training that I provide to PhD students and post-doctoral appointees, I consider that communicating with the broader scientific community in meetings and workshops is essential. I am therefore committed to presenting my research in a clear and interesting way to a variety of specialist and non-specialist audiences.

6. Research projects and perspectives:

My current research has a main focus on laboratory work. It centres on types of molecules that are formed in atmospheric chemistry after several oxidation steps. As is detailed throughout this document, the types and numbers of these molecules are too numerous to count, and so, this research must be conducted in a targeted way. My current research goals are therefore to further the understanding of chemical functionality that is particularly poorly characterized. These goals are inherently multifaceted. It requires work in experimental design and chemical analytical methods. It requires the use of chemical mechanisms and numerical simulations for planning and interpreting experiments. Finally, there is a need to parameterize these data into a form that can be integrated into a modelling framework.

The types of molecules that are of most interest to me are: hydroperoxides, peroxy-carboxylic acids, carboxylic acids, peroxyacyl nitrates, peroxy nitrates and nitrates. How fast do they react with the atmospheric oxidants? What governs their reactivity? What products do they make? Many of these compounds are formed easily in atmospheric chemical mechanisms (see Figure 3), but they are very difficult to produce in their pure form, often because of their explosive or unstable nature. An important aspect of my work is to build these molecules *in situ* in the chamber facilities of ICARE (see Figure 12).

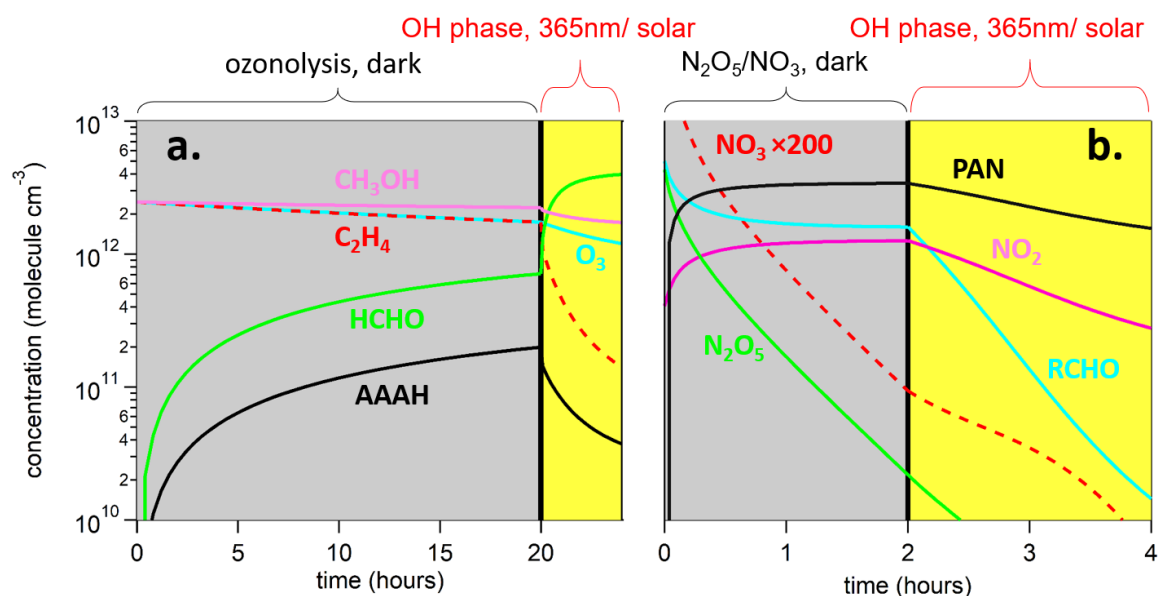


Figure 12: Numerical simulations of experiments that are designed to form a suite of elusive compounds that are subsequently studied using the relative rate method. Panel a. shows the progress of a dark ozonolysis experiment which is conducted overnight, followed by injection of methylnitrite during a photolysis phase that is initiated after 20 hours. Here, Criegee intermediates formed from the ozonolysis of ethene are subsequently reacted with methanol to form the α -alkoxyalkyl hydroperoxide (AAAH). Panel b. shows a simulated experiment in which a peroxyacyl nitrate (PAN) is formed from an aldehyde precursor through oxidation by the NO₃ radical. After 2 hours, an injection of methylnitrite and exposure to 365 nm light generates OH radicals leading to the decay of the PAN.

From these numerical simulations, it appears to be practical to have a synthesis stage in the experiment, followed by an oxidation stage. Recent work in our laboratory shows that this is indeed possible:

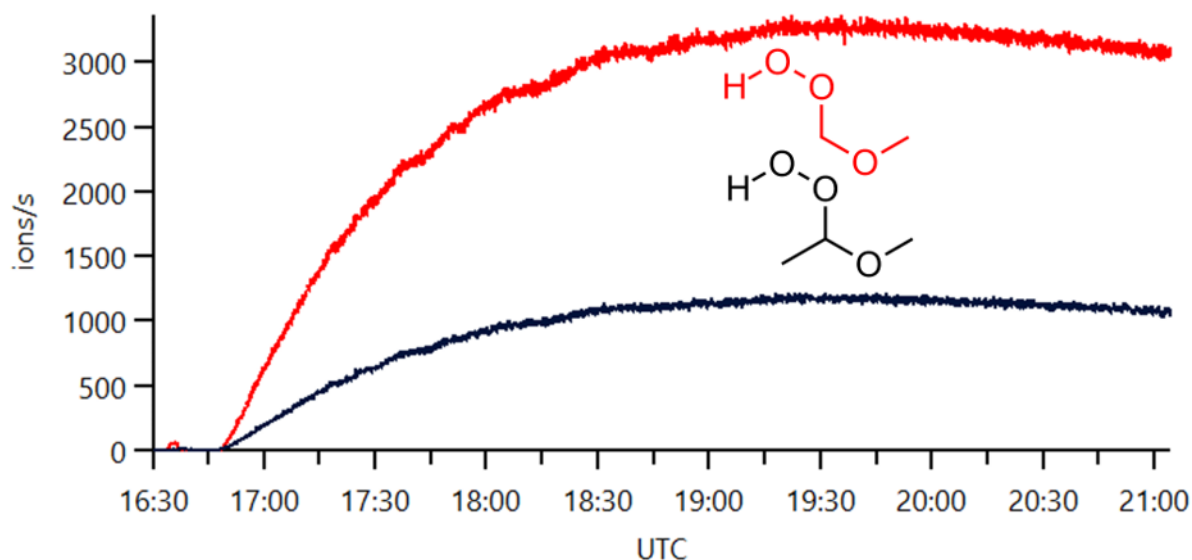


Figure 13: Formation and subsequent decay of the two AAHs that are formed when propene reacts with ozone in the presence of an excess of methanol. These species can be speciated and monitored sensitively with our upgraded PTR-ToF-MS using NH_4^+ ionization.

In fact, far more complex molecules can be built and studied using this methodology, here is another example:

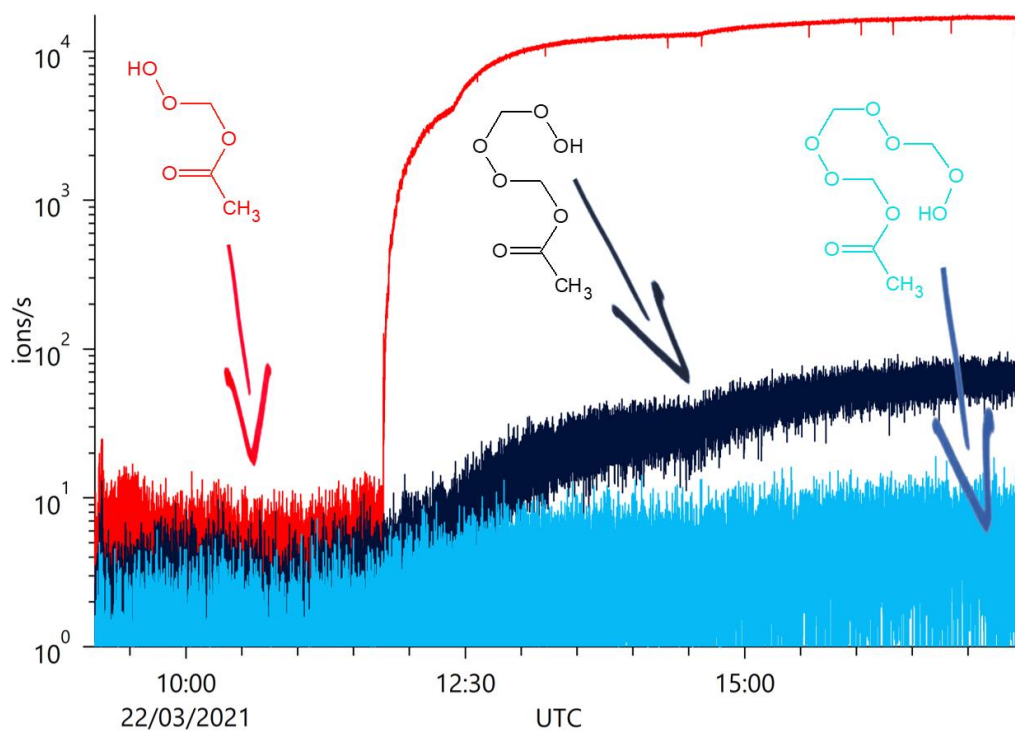


Figure 14: Multigenerational peroxide production in the reaction of formaldehyde oxide with acetic acid in the HELIOS reactor.

Accessing and detecting such exotic, and yet, potentially ubiquitous atmospheric molecules is therefore a practical consideration for our facilities at ICARE. The next step is to try to understand more about their atmospheric chemical behaviours.

Following this, finding the patterns of these behaviours and developing SARs is also a priority for my research. This is something that is needed increasingly, as AMG software improves and as mechanisms become more explicit – accurately parameterized kinetic data will become a limiting factor. Improving these SAR parameterizations is of continued interest to our group, for these exotic compounds, but also for more familiar compounds such as alkenes:

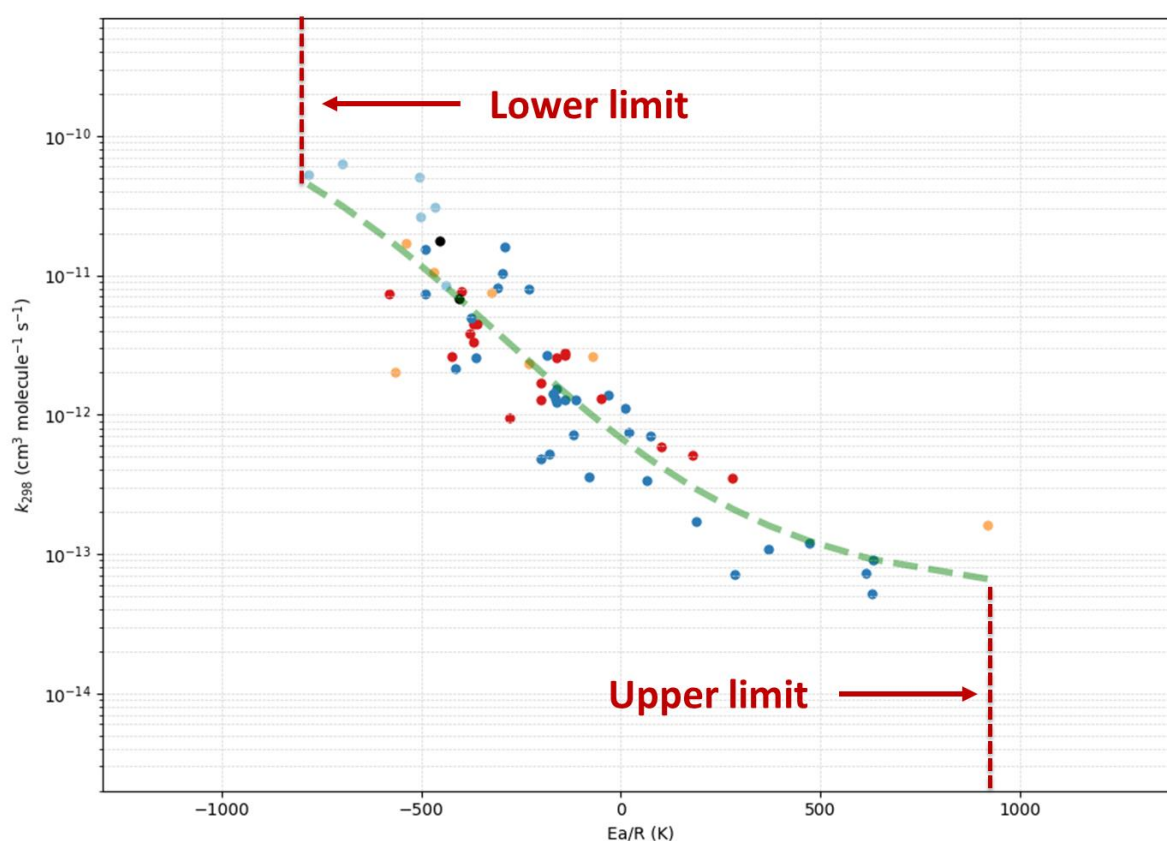


Figure 15: An observed trend in the temperature dependence of alkene oxidation that is being studied by doctorante Lisa Michelat, under my supervision. This may lead to a better representation of alkene lifetimes under real atmospheric conditions.

Although there are many possibilities for experimentation in the chamber facilities of ICARE, these facilities are tied to standard pressures and temperatures. This is true of many facilities worldwide, which place an emphasis on room temperature and atmospheric pressure which stems from the preference of constructing large chambers out of Teflon foil. The HELIOS platform is somewhere intermediate, in that, as an outdoor chamber it can potentially be used to probe some of the boundary layer conditions available in Orléans, France. However, this is very much dependent upon the meteorological conditions and it is difficult to plan experiments systematically in this regard. Since tropospheric conditions can range from -50 – 50°C and 100 – 760 Torr, and many chemical reactions exhibit a sensitive

dependence upon these parameters, an important part of my work involves developing a new system for measuring kinetics under a range of conditions, and for that, I will use the Long-Axis Reactor for KINetic measurements (LARKIN). This system will be interfaced with various artificial light sources and analytical techniques as necessary, with the overall aim to improve the kinetic knowledge outside of 298 K and 760 Torr:

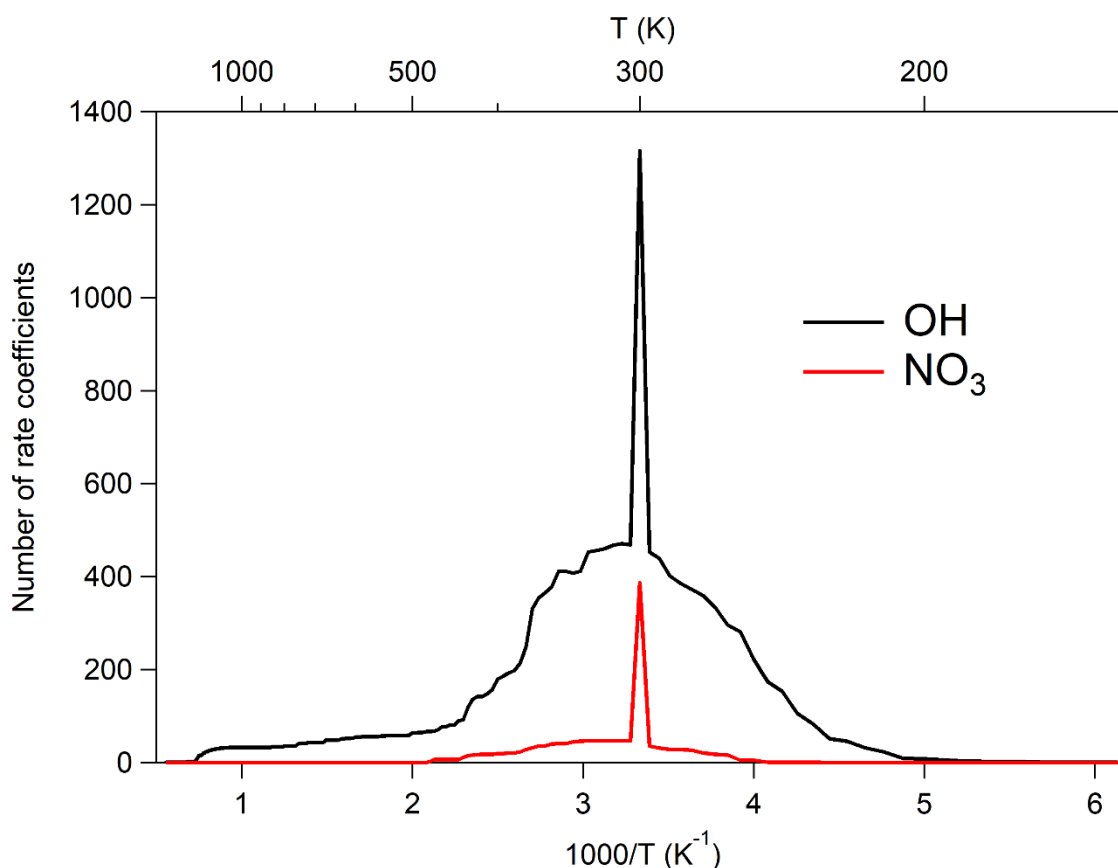


Figure 16: Histograms showing the frequencies of kinetic measurements as a function of temperature for OH and NO₃ rate coefficient measurements. It is clear that much more is known at room temperature, than at temperatures either side.

LARKIN is a tubular, jacketed Pyrex reactor, with quartz window assemblies on each end (see Figure 17). Temperature is regulated using a cryostat. To avoid condensation on atmospheric moisture on the window assemblies, these have been designed to be evacuable. Photolysis can be performed using laser light (355 nm), Nd:YAG (tripled), or a tuneable lamp light source, that can access a range of actinic wavelengths. This reactor is designed to be slow flow/ stopped flow, with the gaseous contents being circulated using an all-Teflon diaphragm pump. The reactor is designed for both oxidation and photolysis experiments, and can be interfaced to a variety of analytical instruments including, for example, FTIR, GC-MS and other mass spectrometry methods.

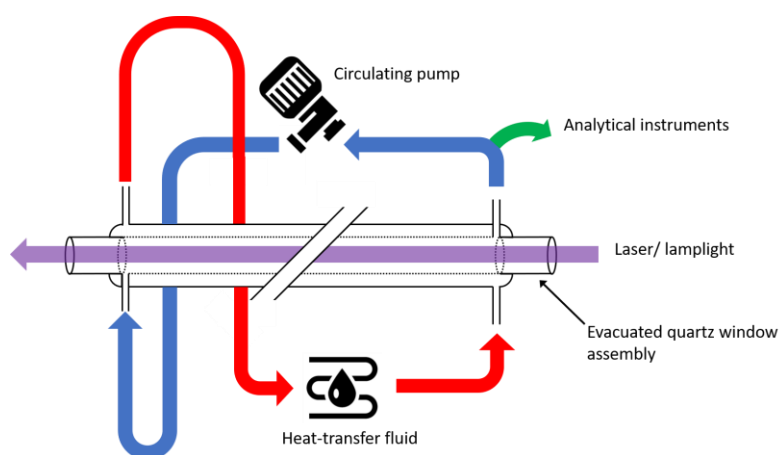


Figure 17: A schematic of the LARKIN experimental apparatus.

A further advantage of this apparatus is that it can allow reactions to be performed under anoxic conditions, and can also allow for photolysis rates that are far higher than those that are available through natural solar photolysis or black lamp light. This further expands the experimental range of LARKIN and will allow us to study many more experimental systems.

When all of these activities are considered, there are many possible research directions that we can pursue in the group, and these possibilities continue to expand as we upgrade our facilities. Amongst these activities, of course, I will aim to follow my interests, and those of my research group. Besides this, I believe that we should try to remain agile, and to respond to the needs and interests of the wider atmospheric community. This is something that can be fostered within the ATMO ACCESS programme of the ACTRIS network, which will allow people to visit our chamber platforms for expanding their research capabilities. I am already an active member of this programme and its precursor, the EUROCHAMP trans-national access programme, and I look forward to the various surprising new projects that will come my way in the future.

7. My publication record:

- (1) **McGillen, M. R.**; Fairchild, I. J. An Experimental Study of Incongruent Dissolution of CaCO_3 under Analogue Glacial Conditions. *J. Glaciol.* 2005, 51 (174), 383–390. <https://doi.org/10.3189/172756505781829223>.
- (2) **McGillen, M. R.**; Percival, C. J.; Raventos-Duran, T.; Sanchez-Reyna, G.; Shallcross, D. E. Can Topological Indices Be Used to Predict Gas-Phase Rate Coefficients of Importance to Tropospheric Chemistry? Free Radical Abstraction Reactions of Alkanes. *Atmos. Environ.* 2006, 40 (14), 2488–2500. <https://doi.org/10.1016/j.atmosenv.2005.12.053>.
- (3) **McGillen, M. R.**; Crosier, J.; Percival, C. J.; Sanchez-Reyna, G.; Shallcross, D. E. Can Topological Indices Be Used to Predict Gas-Phase Rate Coefficients of Importance to Tropospheric Chemistry? Reactions of Alkenes with OH, NO_3 and O_3 . *Chemosphere* 2006, 65 (11), 2035–2044. <https://doi.org/10.1016/j.chemosphere.2006.06.062>.
- (4) Reynolds, J. C.; Last, D. J.; **McGillen, M. R.**; Nijs, A.; Horn, A. B.; Percival, C.; Carpenter, L. J.; Lewis, A. C. Structural Analysis of Oligomeric Molecules Formed from the Reaction Products of Oleic Acid Ozonolysis. *Environ. Sci. Technol.* 2006, 40 (21), 6674–6681. <https://doi.org/10.1021/es060942p>.
- (5) **McGillen, M. R.**; Percival, C. J.; Pieterse, G.; Watson, L. A.; Shallcross, D. E. Predicting Arene Rate Coefficients with Respect to Hydroxyl and Other Free Radicals in the Gas-Phase: A Simple and Effective Method Using a Single Topological Descriptor. *Atmospheric Chem. Phys.* 2007, 7 (13), 3559–3569. <https://doi.org/10.5194/acp-7-3559-2007>.
- (6) **McGillen, M. R.**; Percival, C. J.; Shallcross, D. E.; Harvey, J. N. Is Hydrogen Abstraction an Important Pathway in the Reaction of Alkenes with the OH Radical? *Phys. Chem. Chem. Phys.* 2007, 9 (31), 4349–4356. <https://doi.org/10.1039/b703035e>.
- (7) Raventós-Duran, M. T.; **McGillen, M. R.**; Percival, C. J.; Hamer, P. D.; Shallcross, D. E. Kinetics of the $\text{CH}_3\text{O}_2 + \text{HO}_2$ Reaction: A Temperature and Pressure Dependence Study Using Chemical Ionization Mass Spectrometry. *Int. J. Chem. Kinet.* 2007, 39 (10), 571–579. <https://doi.org/10.1002/kin.20269>.
- (8) Raventós-Duran, M. T.; Percival, C. J.; **McGillen, M. R.**; Hamer, P. D.; Shallcross, D. E. Kinetics and branching ratio studies of the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2$ using chemical ionisation mass spectrometry. *Phys. Chem. Chem. Phys.* 2007, 9 (31), 4338–4348. <https://doi.org/10.1039/B703038J>.
- (9) Archibald, A. T.; **McGillen, M. R.**; Taatjes, C. A.; Percival, C. J.; Shallcross, D. E. Atmospheric Transformation of Enols: A Potential Secondary Source of Carboxylic Acids in the Urban Troposphere. *Geophys. Res. Lett.* 2007, 34 (21), L21801. <https://doi.org/10.1029/2007GL031032>.
- (10) **McGillen, M. R.**; Carey, T. J.; Archibald, A. T.; Wenger, J. C.; Shallcross, D. E.; Percival, C. J. Structure–Activity Relationship (SAR) for the Gas-Phase Ozonolysis of Aliphatic Alkenes and Dialkenes. *Phys. Chem. Chem. Phys.* 2008, 10 (13), 1757–1768. <https://doi.org/10.1039/b715394e>.
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