Direct observations of Criegee intermediates and reaction products in atmospheric chemistry

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The chemistry of trace species in the atmosphere is central to air quality and climate change, with policies designed to address such issues reliant on a fundamental understanding of the chemistry controlling atmospheric composition.

Volatile organic compounds (VOCs), emitted from both anthropogenic and biogenic sources, undergo oxidation in the atmosphere, leading to complex reaction cascades and production of highly reactive trace species (Johnson & Marston, 2008). One of the major atmospheric degradation pathways of unsaturated VOCs, including alkenes emitted in vehicle exhausts and isoprene and monoterpenes emitted from biogenic sources, is oxidation by ozone, which has long been proposed to produce Criegee intermediates (R_2COO) (Johnson & Marston, 2008). However, owing to their high reactivity and transient nature, Criegee intermediates have proven difficult to measure directly, leading to large uncertainties in their chemistry and their impacts on atmospheric composition (Johnson & Marston, 2008; Donahue et al., 2011).

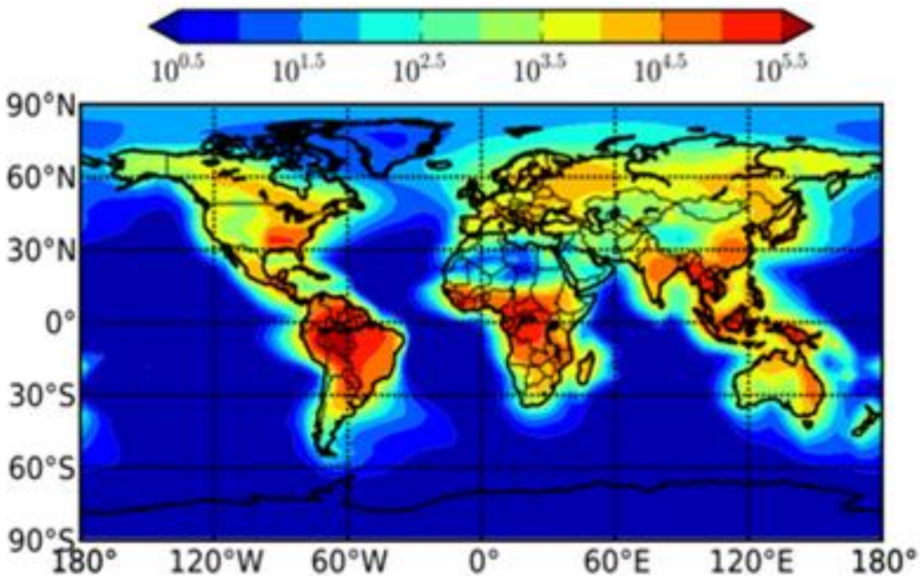

Figure 1: Global annual average production rates ($cm^3\ s^{-1}$) of Criegee intermediates in the surface layer in the GEOS-Chem model (Pierce et al., 2013).

Recent experiments have led to the first direct observations of Criegee intermediates, showing them to be much more reactive than previously anticipated (Welz et al., 2012; Taatjes et al., 2013). The reaction products of Criegee intermediates and the effects of temperature on the reaction kinetics of Criegee intermediates, however, are largely unknown.

Work in the Leeds group has shown that several reactions of the simplest Criegee intermediate (CH_2OO) produce formaldehyde (HCHO) (Stone et al., 2013; Stone et al., 2014). However, there is still much uncertainty regarding the yields and nature of co-products, and the reaction products of larger Criegee intermediates have yet to be fully investigated.

Objectives:

In this project you will take advantage of new opportunities to investigate the chemistry and impacts of Criegee intermediates in the atmosphere. You will use laser flash photolysis combined with novel time-resolved multipass broadband UV spectroscopy techniques recently developed in Leeds (Lewis et al., 2015) to monitor Criegee intermediates directly, in real-time, to determine their reaction kinetics. You will also be involved in the development of novel instrumentation using quantum cascade lasers (QCLs) to make direct observations of Criegee intermediates and reaction products by time-resolved infrared spectroscopy in order to determine product yields at temperatures and pressures relevant to the atmosphere. According to your particular research interests, the studentship could involve:

- Laser flash photolysis coupled with time-resolved broadband UV spectroscopy to monitor Criegee intermediates in real-time throughout their reactions to determine reaction kinetics.
- Development of novel instrumentation using quantum cascade lasers to monitor Criegee intermediates and reaction products *via* infrared spectroscopy in real-time throughout a reaction.
- Further instrument development to enable monitoring of Criegee intermediates in complex reaction systems in an atmospheric chamber.
- Modelling of experimental results to assess atmospheric impacts.
- Application of experimental techniques to combustion chemistry and other areas of atmospheric relevance.

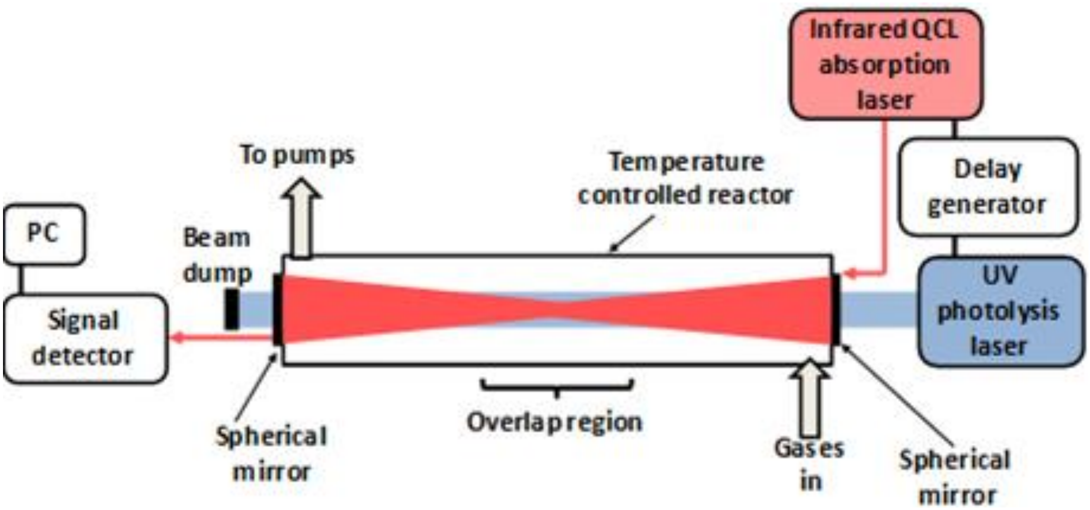

Figure 2: Schematic of experimental apparatus for infrared absorption measurements of Criegee intermediates and reaction products.

Potential for high impact outcome

The role of chemistry in controlling atmospheric composition is of fundamental importance to our understanding of air quality and climate change. This work will lead to improved understanding of the chemistry and impacts of Criegee intermediates in the atmosphere, providing greater constraints on model calculations of global oxidising capacity and production of sulfate aerosol. Criegee chemistry has been the subject of a number of high impact papers in *Science* and *Nature* in recent years (Welz et al., 2012; Mauldin et al., 2012; Taatjes et al., 2013; Su et al., 2013). It is anticipated that this project will generate several papers, with potential for publication in high impact journals.

Training

The student will work under the supervision of Dr Daniel Stone and Prof Paul Seakins within the atmospheric and physical chemistry group. You will be supported by a range of supervisions from monthly meetings and group presentations, through to daily informal chats with supervisors. You will work in well-equipped laboratories and be part of an active, thriving and well-funded atmospheric chemistry community. The Leeds and York groups receive funding from the National Centre for Atmospheric Science (NCAS) and are part of the Atmospheric Measurement Facility, and have an internationally leading reputation in atmospheric chemistry for field measurements of atmospheric composition, laboratory studies of chemical kinetics and photochemistry, and the development of numerical models and chemical mechanisms, including the *Master Chemical Mechanism* (MCM). Activities in these three areas are intimately linked and interdependent, providing a significant advantage. You will be supported to attend both national and international conferences, and will receive a wide range of training, for example in communication skills, project management, and with other technical aspects (for example Labview and computing). The PhD will provide a broad spectrum of experience in the use of high power lasers, vacuum systems, optics, computer controlled data acquisition systems and methods in numerical calculations. The successful PhD student will have access to a broad spectrum of training workshops that include an extensive range of training workshops in numerical modelling, through to managing your degree, to preparing for your viva (http://www.emeskillstraining.leeds.ac.uk/).

Student profile:

The student should have an interest in atmospheric chemistry, air quality and global environmental problems, with a strong background in experimental physical chemistry or similar (e.g. physics, engineering, environmental science).

References

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