

Photochemistry of important molecules and radicals in the atmosphere

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The oxidizing capacity of the troposphere is controlled by radical reactions, where the OH radical plays the dominant role. For this reason it is important to know OH sources / sinks. Knowledge on this can be critically assessed from measurement of the OH concentration, [OH], in the atmosphere, where the majority of OH measurements have been made with the low pressure laser induced fluorescence (LIF) FAGE technique (Fluorescence Assay by Gaseous Expansion).¹ Atmospheric chemical models are used to indicate how well these sources / sinks are understood. In general, these models do a reasonable job in predicting the [OH] in remote and urban environments, where the chemistry is simple and NO dominated, respectively.² In pristine, forested, tropical environments, where the chemistry is dominated by isoprene emitted from trees, models do a poor job and under predict the [OH], with differences in the measured and modelled [OH] up to a factor of 10 reported,³ see Figure 1. This dramatic enhancement in the measured [OH] compared to modelled has also been observed in less pristine environments, where there is a wider range of volatile organic hydrocarbons, including isoprene, but low concentrations of nitrogen oxides, [NO_x].⁴

There has been much scientific endeavour into identifying this missing source of OH, where all explanations have revolved around isoprene. In the atmosphere the reaction between OH and isoprene, C₅H₈, is fast and its addition product is rapidly captured by oxygen:



where HO-C₅H₈-O₂ is a peroxy radical, RO₂. The literature has showed that while some RO₂ will react with HO₂ to form OH this is not a significant channel for HO-C₅H₈-O₂. A more promising source of

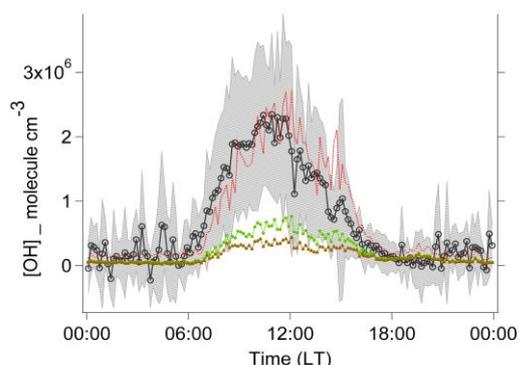


Figure 1. A comparison of the measured mean diurnal [OH] profile (black line, open circles) with modelled [OH] calculated from standard OH chemistry plus OH recycled via the Peeters' mechanism with the rate of RO₂ isomerisation determined by Crouse et al.⁵ (brown ▲) or standard OH chemistry plus OH generated via UV RO₂ photolysis (midday photolysis rate of $2 \times 10^{-3} \text{ s}^{-1}$) (green ●). The grey shading represents the 1σ standard deviation of the mean diurnal OH profile. A total RO₂ photolysis rate of 10^{-2} s^{-1} (broken red line) is required to match measured [OH].

OH from HO-C₅H₈-O₂ has been identified by Peeters and co-workers, where using *ab initio* theoretical calculations an efficient isomerization route from HO-C₅H₈-O₂ to hydroperoxyaldehyde (HPALD) was identified;⁶ HPALD is expected to efficiently photolyse to OH. Experiments have determined the rate of this isomerization, and it was slower than the calculated rate implying that this mechanism cannot explain all the missing [OH],⁵ but it is still a significant minor source, see Figure 1.

More recently we have suggested that HO-C₅H₈-O₂ is a photochemical source of OH:



In funded work we have measured the efficiency of P1, see Figure 2, where two lasers are used to make RO₂ and then photolyse it. The third laser is used to probe OH, 308 nm, blue. The results from our UV measurement on P1 have been put into a chemical model and only small changes in [OH] were observed.

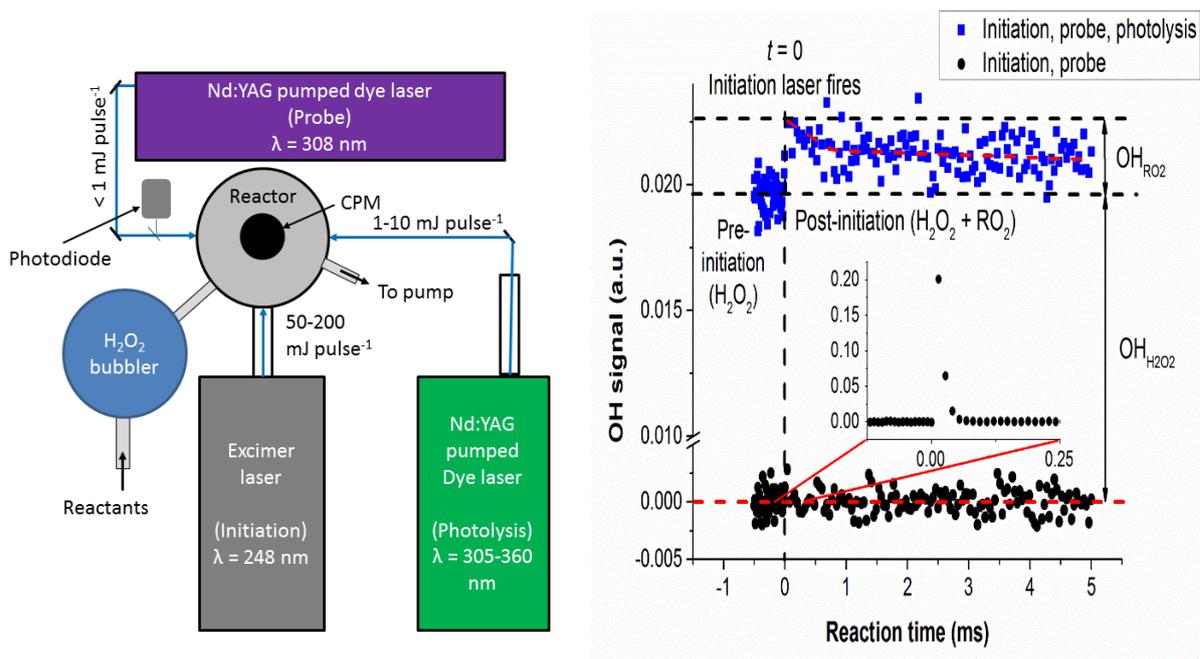


Figure 2: Left: Apparatus to determine the OH yield from RO₂ photolysis, where RO₂ is generated by the photolysis of H₂O₂ in the presence of C₅H₈/O₂ using the excimer laser. RO₂ is photolysed over a range of the wavelengths using the high energy dye laser and the resultant OH is detected using the probe laser, 308 nm; Right: the three laser experiment yields the blue trace, the signal before t=0 is equal to H₂O₂ photolysis, which allows the RO₂ signal, after t=0, to be quantified.

This high observed [OH] in isoprene rich environments still remains unexplained and the search continues.

In this project you will work extensively in the Dainton laboratory where there is a large suite of independent laser based experiments that can study kinetics and photochemistry over a wide range of temperatures, $T = 40 - 1000 \text{ K}$, and pressures, $p = 0.001 - 10 \text{ Bar}$. In the laboratory you will be working with students, Mchem / PhD, Post-Doctoral research fellows and Research Scientists. In addition there is technical (mechanical and electrical) help in the maintenance of the experiments and instrumental control via LabVIEW.

In addition, within the group reaction rate theory has been developed (Mesmer <http://www.chem.leeds.ac.uk/mesmer.html>) that calculates rate constants from theoretical reactions (e.g. Gaussian) and thus allows direct comparison between theory and experimental data. This comparison tests the reaction mechanism and the fine details on the reaction surface.

In addition, the expectation is that you would also use the HIRAC simulation chamber (<http://www.chem.leeds.ac.uk/hirac-group/hirac-group.html>). The individual reaction / photochemical processes from the Dainton laboratory experiments can be further tested in HIRAC where processes occur on a much longer timescale and hence provides a more rigorous test of how well an overall system is known.

The atmospheric impact from a chemical perspective can be assessed with using photochemical box models, containing a very detailed chemical oxidation scheme based on the detailed Master Chemical Mechanism (MCM). The photochemical / kinetics data from the laboratory can readily be incorporated in these models to assess the maximum environmental impact of the chemistry, where emissions are constrained to measurements.

Objectives

- Determination of the photochemical parameters of a range of radicals (RO_2) and molecules (HPALD) that are implicated in OH formation. The experiments will be carried out over the wavelength region where the solar flux is active in the troposphere: $\lambda > 300 \text{ nm}$. Where appropriate temperature and pressure will be varied, e.g. glyoxal and acetone are molecules that show dependences on p and T .
- Absorption spectra of a range of peroxy radicals and molecules such as HPALD that are not known, plus known molecules to wavelengths beyond currently known in the literature. The absorption spectrum is equal to the maximum photochemical impact of a given species. A recently constructed multipass absorption spectrometer simultaneously measures many wavelengths as a function of times. This can measure radicals and molecules an order of magnitude better than previous designs.
- A newly acquired proton transfer reaction (PTR) time-of-flight mass spectrometer (ToFMS), which offers the high sensitivity required to detect products under the experimental conditions used, can be used to unravel the photochemical products. The laser based experiments are setup mainly to measure the OH channel and the absorption experiments yield the sum of all channels. The PTR mass spectrometer can be used to investigate the non-OH channels, or OH co-product.
- HIRAC will be used to assess chemistry/photochemistry over a longer timescale. In particular, HPALD is formed slowly over 100 seconds at room temperature. However, if the temperature is increased to 340 K it will be formed much faster. HPALD can be detected with the PTR ToFMS therefore its kinetics can be followed. This information should allow HIRAC to positively identify HPALD from its FTIR spectrum, and hopefully its UV spectrum.
- There are a number of photochemical box models with most the detailed chemistry already setup for a number of scenarios. The results from the laboratory can be inputted into these photochemical box models, with particular attention to the pristine, forested, tropical scenario in order to assess its impact with respect to [OH].

Potential for high impact outcome

Isoprene related chemistry in remote and tropical environments remains a 'hot topic'. Isoprene related chemistry helps control HOx concentrations and as $\text{OH} + \text{CH}_4$ is the main route for removing methane, an important greenhouse gas, the work links directly to the climate change agenda. Related work has led to several publications and we therefore anticipate the project generating several papers with at least one being suitable for submission to a high impact journal such as the Nature series.

Training

The successful PhD student will be exposed to a whole range of experimental and computational techniques for which training will be provided, either in situ from experienced PhD students or post-doctoral workers or through the DTP (e.g. computing languages). The programme will equip the successful student with a wide range of skills suitable for a career in research (industrial or academic) or in other areas. Supervision takes place a number of levels – all important in different ways. Day-to-day informal chats with more experienced staff and colleagues builds your skills and expertise; more formal monthly meetings give you and the supervision team an opportunity to review progress, plan future activities and ensure that your training and career planning needs are being met.

You will be expected and encouraged (and financed!) to attend and present your work at national and international conferences and training in presentation skills is provided as part of your DTP training. The DTP also looks after various other aspects of generic skills training such as project management, scientific writing and viva preparation (<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

1. Heard, D. E.; Pilling, M. J., Measurement of OH and HO₂ in the Troposphere. *Chem. Rev.* **2003**, *103* (12), 5163-5198.
2. (a) Ehhalt, D. H., Radical ideas. *Science* **1998**, *279* (5353), 1002-1003; (b) Ren, X.; Harder, H.; Martinez, M.; Leshner, R. L.; Oliger, A.; Simpas, J. B.; Brune, W. H.; Schwab, J. J.; Demerjian, K. L.; He, Y.; Zhou, X.; Gao, H., OH and HO₂ chemistry in the urban atmosphere of New York City. *Atmos. Environ.* **2003**, *37* (26), 3639-3651.
3. Lelieveld, J.; Butler, T. M.; Crowley, J. N.; Dillon, T. J.; Fischer, H.; Ganzeveld, L.; Harder, H.; Lawrence, M. G.; Martinez, M.; Taraborrelli, D.; Williams, J., Atmospheric oxidation capacity sustained by a tropical forest. *Nature* **2008**, *452* (7188), 737-740.
4. Hofzumahaus, A.; Rohrer, F.; Lu, K.; Bohn, B.; Brauers, T.; Chang, C.-C.; Fuchs, H.; Holland, F.; Kita, K.; Kondo, Y.; Li, X.; Lou, S.; Shao, M.; Zeng, L.; Wahner, A.; Zhang, Y., Amplified Trace Gas Removal in the Troposphere. *Science* **2009**, *324* (5935), 1702-1704.
5. Crouse, J. D.; Paulot, F.; Kjaergaard, H. G.; Wennberg, P. O., Peroxy radical isomerization in the oxidation of isoprene. *Phys. Chem. Chem. Phys.* **2011**, *13* (30), 13607-13613.
6. Peeters, J.; Nguyen, T. L.; Vereecken, L., HOx radical regeneration in the oxidation of isoprene. *Phys. Chem. Chem. Phys.* **2009**, *11* (28), 5935-5939.