Kinetics of ARomatics Oxidation with Lasers (KAROL)

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This is a project to study degradation mechanisms of atmospherically important aromatic volatile organic compounds in lab-based experiments at York Department of Chemistry (YDC). Aromatics such as benzene, toluene and the xylenes have long been of interest to atmospheric scientists {1-2}. Key components of both diesel and petroleum, the oxidation of these species in air is associated with production of large quantities of ozone and other harmful pollutants {3}. Scientists at the Wolfson Atmospheric Chemistry Laboratories (WACL) in York have recently observed high levels of alkyl-substituted aromatics (Figure 1) in Beijing air.

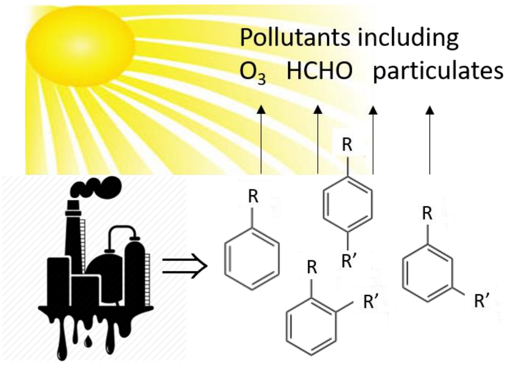

Figure 1– high levels of alkyl-substituted monoaromatics (those with one phenyl group) were observed in Beijing air. Harmful pollutants likely result from as-yet unknown atmospheric photochemistry.

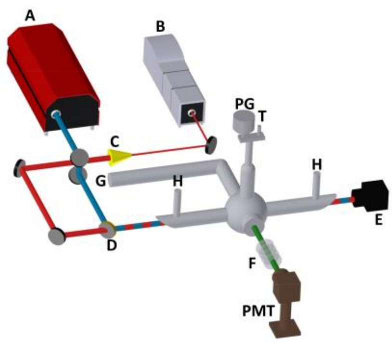

Figure 2 – the new laser apparatus at YDC. Key: UV photolysis laser (B) generates free-radicals for reaction with aromatics; after a suitable delay time OH is detected by laser (A); (C – F) denote optics; (G) is gas-flow in; ((H) gas-flow out.

To date, little is known of the sources of these compounds, nor of their impacts on local and regional air quality {4}. Free radicals such as hydroxyl, OH, initiate breakdown of the majority of organic compounds emitted to the atmosphere. Understanding radical chemistry is crucial therefore to calculate organic lifetimes, assess impacts of their degradation chemistry on air quality, composition and climate, and confidently predict the impact of future emission scenarios. Based upon what we know of the smaller aromatics, we anticipate rapid radical initiated breakdown in air (R1) and consequent production of high levels of harmful atmospheric pollutants.

$$\cdot OH + C_6H_5R \rightarrow C_6H_5R'\cdot + H_2O \qquad (1a)$$
$$\rightarrow HOC_6H_5R\cdot \qquad (1b)$$

The details of these oxidation mechanisms are important, as production of the most harmful products (eg. ozone, particulate matter) depend crucially upon the rates and relative yields of initiation processes such as (R1a) and (R1b), together with the subsequent reactions of radical fragments with other reactive atmospheric species such as O_2, NO and NO_2.

Science outcomes of this project will be key to answering big atmospheric questions such as "are large aromatics important for ozone production?", "what is the impact of large aromatics on air in megacities?", and "what level of detail do atmospheric chemical model mechanisms such as the Master Chemical Mechanism [3] actually need?"

Objectives

You will work with leading atmospheric, laser kinetics and free-radical scientists in York. Expert supervision will ensure appropriate support and guidance. As the project progresses you will:

1) use new laser-based chemistry developed in York to accurately determine rate coefficients for the crucial aromatic + radical processes that initiate breakdown of aromatics in air
2) explore aromatic oxidation mechanisms via isotopic labelling experiments and in short chamber studies at EU partner laboratories www.eurochamp.org/
3) incorporate results into the Master Chemical Mechanism mcm.leeds.ac.uk/MCM/ and quantify atmospheric impacts using photochemical box models.

Potential for high impact outcome

Radicals control the removal and transformation processes for most pollutants in our atmosphere; radical chemistry impacts on important subjects such as air quality, composition and climate. Previous work on these issues resulted in multiple high-impact publications [1,5], presentations to international conferences and stimulated new collaborative research worldwide [2,6].

Training

You will work under the supervision of Dr. Terry Dillon, Dr Andrew Rickard and Dr. Pete Edwards at University of York Department of Chemistry (YDC). You will be based in the Wolfson Atmospheric Chemistry Laboratories (WACL), a new facility bringing together experts in atmospheric measurements, Earth system models and lab-studies to form the largest integrated UK atmospheric science research team. This project provides a high level of specialist scientific training in: experimental kinetics and photochemistry, notably use of lasers and laser safety; data analysis; mass-spectrometry; computational methods (GAUSSIAN, MCM & AtChem online box modelling). Dr Dillon and Dr Edwards have a wealth of experience studying radical reactions, mechanisms and products, and together with the WACL team will provide comprehensive training in all laser techniques and instrumentation required. Dr Rickard has research interests that span mechanistic chemistry of complex gas- and condensed- phase systems, kinetic modelling of complex processes and the chemistry of reactive radical intermediates. He currently curates the internationally renowned Master Chemical Mechanism.

This studentship is offered as part of the Leeds/York Chemistry PANORAMA Doctoral Training Programme that will provide training in addition to that offered by YDC. Courses specifically aid your development throughout the PhD, improving transferable skills, putting research into a wider scientific context and preparing for thesis presentations and viva. The University of York and the wider NERC PANORAMA DTP provide comprehensive training programmes for students throughout their PhD studies, with a range of courses on both hard and soft skills (e.g. improving transferable skills, putting research into a wider scientific context and preparing for thesis presentations and viva). Dr Rickard also works for and with the National Centre for Atmospheric Science (NCAS), and thus the student will have access to the wider resources that NCAS provides. You will also have access to training provided by NCAS such as the Arran instrumental Summer School, the Earth System Science Summer School (ES4), and future further developments in computations and data analysis.

Student profile:

You will have a strong background in the physical sciences (good degree in chemistry, physics or similar science), a keen interest in environmental issues, and an aptitude and enthusiasm for experimental work. We appreciate that this project encompasses several different science and technology areas, however the York team is well supported with experienced scientists. Training is part of the PhD, and no previous experience with specific techniques or instruments is necessary.

References

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{2} Hamilton, J.F. and Lewis, A.C.: Monoaromatic complexity in urban air and gasoline assessed using comprehensive GC and fast GC-TOF/MS, Atmospheric Environment, 37, 5, 589-602, 2003

{3} Molteni, U., Bianchi, F., Klein, F., El Haddad, I., Frege, C., Rossi, M. J., Dommen, J., and Baltensperger, U.: Formation of highly oxygenated organic molecules from aromatic compounds, Atmos. Chem. Phys., 18, 1909-1921, https://doi.org/10.5194/acp-18-1909-2018, 2018

{4} Yan, Y., Cabrera-Perez, D., Lin, J., Pozzer, A., Hu, L., Millet, D. B., Porter, W. C., and Lelieveld, J.: Global tropospheric effects of aromatic chemistry with the SAPRC-11 mechanism implemented in GEOS-Chem, Geosci. Model Dev. Discuss., doi.org/10.5194/gmd-2018-196, in review, 2018.