CHEM M901 Project Synopsis 2014

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Radicals and biradicals in atmospheric chemistry

Natural oxidation of hydrocarbons in the atmosphere is essential for the control of their abundance and consequently their effect on environmental processes such as global warming. The removal of the principal hydrocarbon, methane, which is emitted to the air from both natural and anthropogenic studies, is controlled by hydrogen abstraction and subsequent formation of the methylperoxy, CH_3O_2, radical. Reactions of CH_3O_2 thereafter go on to define the atmospheric impact of methane oxidation. Unsaturated hydrocarbons are oxidised differently in the air, and recent work has shown that reaction of naturally occurring ozone with alkenes may result in the formation of exotic biradical species – known as Criegee radicals – whose reactivity is very poorly characterised. Again the fate and reactivity of such species defines the environmental impact of hydrocarbon oxidation.

The aim of this project is to first investigate the reactions of methylperoxy radicals using well-established techniques, but also to investigate the *possibility* of generating and monitoring Criegee biradicals, of which the first gas phase UV absorption spectrum was reported in late 2013. It is not known how transient the Criegee species are in the gas phase, so this part of the project is entirely speculative. Laser flash photolysis of methyl di-iodide has been shown to produce the biradical species, and this would be attempted to produce and follow such species using UV absorption. If is possible to generate a detectable amount of biradicals on the timescale of their subsequent decay, then the nature and kinetics of their loss will be investigated. This would represent one of the first investigations into atmospheric Criegee radical reactivity.

References:

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