4.010 Development of Portable Chemosensors for Atmospheric Radicals.

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Abstract:

The complex chemical photo-oxidation cycles involved in the degradative removal of anthropogenic and biogenic hydrocarbons from the atmosphere are mediated by radical intermediates. Peroxy radicals (HO_2 and RO_2) are key reactive intermediates/chain propagators directly involved in the formation of ground-level ozone, photochemical smog and in the production of secondary organic aerosols. Thus they can significantly impact upon air quality and human health.

Speciated measurements of atmospheric radicals pose considerable challenges to analytical chemistry. Owing to their low concentrations, high reactivity, and short lifetimes, free radicals cannot be easily sampled and hence direct offline analysis is extremely difficult. Although a number of highly sensitive sophisticated techniques have been developed, *selectivity, full structure determination, portability* and *cost* remain challenging obstacles to atmospheric radical analysis.

We present the synthesis and development of a series of novel chemosensors, organic trapping compounds that are stable and can efficiently and selectively react with a range of important atmospheric radical species. The reaction products conserve the radical structure and are stable enough for off-line analysis using a range of EPR and mass spectrometric techniques. This approach allows accurate determination of the radical structures.

Modification of sample supports has also been investigated, leading to a greater reactive surface area, giving a better sampling efficiency and increasing the temporal resolution of measurement.

The developed chemosensors have been tested and evaluated in laboratory and chamber experiments using a range of atmospherically relevant systems (e.g. ozonolysis of small alkenes and monoterpenes, reactions of OH with alkanes), giving key insights into radical selectivity and reaction mechanisms.