

Development of Portable Chemosensors for Atmospheric Radicals

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The complex photochemical oxidation cycles involved in the degradative removal of anthropogenic and biogenic hydrocarbons from the atmosphere are mediated by a range of radical intermediates. For example, peroxy radicals ($\text{HO}_2\cdot$ and $\text{RO}_2\cdot$) are key reactive intermediates/chain propagators directly involved in the formation of ground level ozone, photochemical smog and in the production of secondary organic aerosols¹. Thus they are of particular interest in relation to air quality and thus human health.

Speciated measurements of atmospheric radicals pose considerable challenges to analytical chemists. Owing to their low concentrations, high reactivity, and short lifetimes, free radicals species cannot be easily sampled; therefore direct offline analysis is extremely difficult. Although a number of highly sensitive and sophisticated techniques have been developed², issues such as *selectivity, full structure determination, portability* and *cost (logistics, electricity provision, expertise)* remain challenging obstacles to atmospheric radical analysis³.

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 chemosensor is designed with the aim of radical addition to a double bond, resulting in the loss of a stable radical leaving group (Fig. 1). The trapped radical structure is maintained in the reaction products, which are sufficiently stable for off-line analysis using a range of HPLC and mass spectrometric techniques. This approach allows for accurate determination of the radical structures, and is different to traditional spin trapping, with the captured radical now converted to a stable non radical form.

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

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 $\cdot\text{OH}$ with alkanes), giving key insights into radical selectivity and reaction mechanisms.

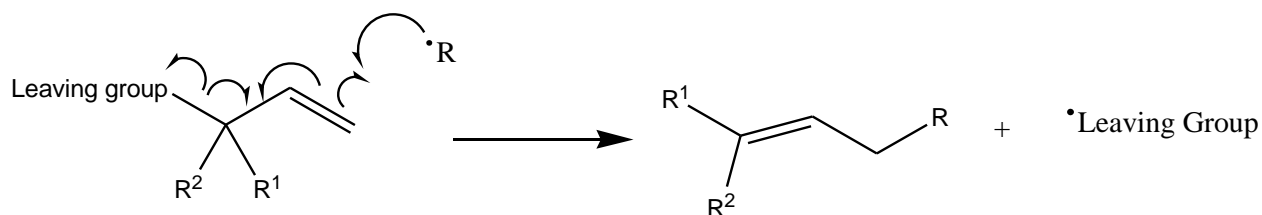


Figure 1: Target reaction for the trapping of an atmospheric radical, R

References

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