Multiplexed Detection of Reaction Products: Probing radical reactions with synchrotron photoionzation mass spectrometry.

Adam J Trevitt
School of Chemistry, The University of Wollongong

The reactions of small, carbon-bearing radicals with unsaturated hydrocarbons dictate combustion processes, exhaust composition and soot formation as well as being integral to the chemical composition of interstellar clouds, comets and extraterrestrial atmospheres. Although the kinetics of many radical-neutral reactions have been well studied, experimental undertakings examining the reaction products and product-branching fractions of these systems are relatively scarce. Detailed, isomer-specific product data are vital, however, in order to gain a comprehensive understanding of the intriguing radical-mediated molecular weight growth chemistry ocurring in systems such as soot formation on Earth, haze evolution on Titan (Saturn's largest moon) and PAH formation in the interstellar medium.

In this undertaking we probe the products of reactions of various radicals (eg CH, CN) with unsaturated hydrocarbons using time-resolved, multiplexed mass spectrometry coupled with tunable VUV synchrotron photoionization (Advanced Light Source, Berkeley, USA). For a radical-neutral reaction, this experimental configuration (depicted below) produces a three-dimensional data matrix consisting of ion intensity as a function of mass-to-charge, photoionization energy and reaction time. Reaction products are then identifiable by mass and corresponding kinetic profile. In addition, their photoionization efficiency (PIE) curves provide the valuable isomer-specific detail.

Recently, have focused our attention on the reactions of larger radicals with O_2 and recently gathered a PIE spectrum consistent with that of the elusive gas-phase Criegee intermediate (CH_2OO). The phenyl radical (C_6H_5) reaction with with O_2 has also been probed, in this case over a large temperature range (300 – 1000 K). Altogether, these results provide for interesting comparison with, and vital validation of, computationally derived potential energy surfaces and kinetic simulations.