

Time-Resolved Kinetic Experiments Utilizing Photo-Ionization Mass-Spectrometers

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A pulsed laser initiation of a reaction combined with time-resolved photo-ionization mass-spectrometry detection of reactants and/or products is a versatile method to investigate combustion chemistry. Excimer laser photolysis is often used for radical production, either directly by breaking, for example, the -C-Br bond of a bromide precursor, or indirectly by producing Cl-atoms that subsequently react with a hydrocarbon. For mass-separation and detection of ionized species both quadrupole mass-spectrometer (QMS) and time-of-flight mass-spectrometer (ToF-MS) have their advantages; QMS is probably more sensitive which is important when no synchrotron radiation is available while a great advantage of ToF-MS is its ability to detect all masses of interest practically simultaneously. Combining ToF-MS with a tunable synchrotron radiation is brilliant method to investigate fuel-molecule oxidation under low-temperature-combustion conditions where multiple reaction channels are important. Scanning kinetic time, mass, and photon energy provides quantitative information on branching ratios of products, which can be directly compared with kinetic models of combustion. However, synchrotrons are very expensive facilities and not many have VUV-beamlines with energy range ($\sim 7 - 15$ eV), resolution, and intensity (preferably an undulator beamline) suitable for time-resolved kinetic experiments, where efficient ionization of a sample beam taken from a reaction mixture is required. Due to these reasons, in experiments employing synchrotron radiation one needs to concentrate on the most important research topics, leaving much space for experiments which can be performed in a normal university laboratories. For this and also other reasons QMS with an intense ionization radiation provided by a gas-discharge (plasma) resonance radiation source is an attractive method for time-resolved kinetic experiments. In this presentation these methods are introduced and their capabilities and differences are discussed with example reactions.

Reactions which will be discussed range from alkyl-radical oxidation reactions central in autoignition of fuel – air mixture to reactions of resonantly-stabilized radicals with O_2 and NO_2 . Alkyl radical R reactions with O_2 , formation of RO_2 and bimolecular products, as well as formation of ketohydroperoxides in chain-branching reaction channel will be discussed. Very recently kinetics of these reactions have been measured for *n*-butane using the above instruments. Resonantly-stabilized radicals have low reactivity toward O_2 and high barrier for decomposition and, consequently, they play a central role in formation of aromatic ring-structures, which under favorable, fuel-rich conditions fuse together and initiate soot formation, for example in diesel engines. NO_x (= $NO + NO_2$) formation is also a significant problem in diesel engines and their reactions with resonantly-stabilized and other radicals is also discussed.