

REACTIVE INTERMEDIATES OF CHEMICAL REACTIONS BY MASS SPECTROMETRY: FROM IONS TO RADICALS

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Mass spectrometry provides a unique tool for the generation and study of highly reactive neutral species, molecules, carbenes, radicals, biradicals, etc. In particular, intermediates of chemical reactions thought to occur in the interstellar space, stratosphere, troposphere, as well as in processes as diverse as combustion, radiolysis, and oxidative stress can be generated and studied as isolated species in the mass spectrometer to determine their intrinsic properties in the absence of solvent, walls, and reactive gases.

Studies of reactive intermediates use neutralization-reionization tandem mass spectrometry. Stable ions of known structure are generated first and investigated by the methods of gas-phase ion chemistry combined with quantum chemical calculations. The ions are converted to neutral intermediates by femtosecond electron transfer occurring during a glancing collision with a gas molecule. New methods have been developed recently to study the kinetics of unimolecular dissociations of transient species in fast beams and to probe electronic states by laser photoexcitation and photoionization. The unimolecular chemistry of transient species can thus be studied on the microsecond time scale followed by complete analysis of reaction products by mass spectrometry.

In the lecture, recently developed methods for the study of transient radicals will be described and illustrated with examples from the chemistry of nucleobase radicals and their analogues, peptide radical analogues, Wheland radical intermediates, and other systems.
