Observation of Transient Ions in Radiolysis*

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Abstract: Pagodane radical cation and its transformation into pagodiene radical cation was observed by time-resolved FDMR. Other highly unstable radical cations will be discussed as well.

Keywords: Unstable radical cations, pagodanes, cubane, quadricyclane.

Introduction: The high energy radiation from electron beam accelerators and intense UV lasers induces ionization when it interacts with matter. The nature of the energy deposition process, the transient species produced and the ultimate stable products define the chemistry of ionizing radiation. The study of radiation chemistry has a long history and many successes which led to many beneficial and useful applications. However, the intimate details of the earliest time events is in many instances still obscure because of the considerable experimental challenges encountered in studying very fast phenomena. While the modern lasers have made tremendous inroads into the study of ultrafast processes like electron solvation, there are many advances in the study of other transient species. Utilizing magnetic resonance methods in the time domain experiments one can obtain very detailed information about the transient paramagnetic species which are important intermediates in many chemical processes. We illustrate here our recent efforts to study transient radical cations. Specifically we focus on the observation of very unstable radical cations many of which were predicted to exist based on theoretical calculations only. Many highly strained radical cations are involved in novel synthetic approaches. Several types of strained molecules will be illustrated. Observations of pagodane, cubane and quadricyclane radical cations will be discussed.

Experimental: The technique used to study transient radical cations is the Time-resolved Fluorescence Detected Magnetic Resonance (FDMR) [1]. The technique utilizes X-band pulsed EPR to observe radiolytically produced radical ions. The short pulse of electrons (~5 nsec or longer) initiates radiolysis in a sample which is placed inside of the cavity of a pulsed EPR spectrometer. One observes the fluorescence from radical ion recombination. The microwave induced fluorescence decrease at resonance represents an optically detected EPR spectrum of two geminate ions which have recombined to give the fluorescence. The scheme below summarizes the pertinent steps of ion creation, scavenging and recombination.
where RH is a hydrocarbon solvent which can be both liquid or solid. A is a scintillator. Many common scintillators can be used. Often we use a deuterated aromatic compound e.g. deuterated anthracene in order to reduce the EPR spectral overlap. The solvent radical cation RH⁺ can be observed, under certain conditions, or we scavenge it by the appropriate substrate to give another radical cation S⁺. In the studies to be discussed S will be pagodane, cubane or quadricyclane molecule. Charge scavaging occurs fast and spin coherence is preserved. Recombination of S and A can be observed on the submicrosecond time scale and thus an optically detected EPR spectrum of S⁺ and A⁻⁻ is obtained. Since different hydrocarbon solvents can be used one can create S⁺ radical cation with very little excess energy.

Results and Discussion: So far unseen radical cation of the pagodane molecule was observed (Fig. 1). By changing the temperature and the time window of observation (microwave pulse) we could observe the transformation into pagodiene radical cation and determine the activation energy for that transformation. The observed structure i.e., the hyperfine coupling constants are in a remarkable agreement with the theoretical predictions [2]. Several other pagodane radical cations were also observed. Other hard to see radical cations include cubane⁺ which was observed by us previously and quadricyclane⁺ which was previously studied by us in zeolite matrices and was recently observed by time resolved EPR [3,4,5]. FDMR observations are in a close agreement with the time-resolved EPR studies.
References

Figure 1: Isomerization of the [1.1.1.1] pagodane radical cation.