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Preface

The chemistry of radical ions

The impact that adding or removing an electron from a molecule can have on accessible reaction pathways is genuinely remarkable. Stable bonds fragment. Electron-rich alkenes and arenes react with nucleophiles. Electron-poor alkenes react with electrophiles. Super acids and potent bases are formed. Highly reactive intermediates are formed in downstream processes. The abundance of unusual pathways is perhaps the reason that radical ion chemistry is often viewed as being somewhat esoteric. Of course, this wealth of reactivity creates ample opportunities for new reaction development, provided that a particular pathway can be predictably accessed. Indeed biological systems make extensive use of radical ion intermediates to lower activation energies for a range of processes. Substantial progress toward understanding the reactivity patterns of radical ions has been reported over the years, leading to a level of predictive capacity that allows for efficient new processes to be developed on complex substrates that yield integral components of important materials.

The purpose of the *Symposium-in-Print* is to highlight advances in design and theory for processes that proceed through radical ion intermediates. Several elements of the manuscripts should be noted. The structural features that make a molecule susceptible to single electron oxidation or reduction are often unique relative to those that lead to reactivity through other manifolds such as acid/base association. For example, alkenes, arenes, strained rings, and sulfides are common precursors to electrophiles, and ethers can be used as precursors to nucleophiles. Methods of accessing radical ions are also diverse. Radical cations can be formed through oxidation under electrochemical conditions, electron transfer to ground state or photoexcited oxidants, or radical solvolysis. Radical anions can be generated by electron transfer from other radical anions or photoexcited neutral molecules, or by electrochemical reduction. Substrates that contain an electron donor and an electron acceptor can undergo intramolecular electron transfer to yield a radical cation and a radical anion in the same molecule, creating the potential for truly unique transformations. Reaction pathways can be controlled through rational substitution. Fragmentation processes can be promoted by installing a group that either stabilizes a reactive intermediate or releases strain adjacent to the radical ion. Otherwise electrophilic character will dominate for radical cations and nucleophilic/basic character will dominate for radical anions.

As editor of this *Symposium-in-Print*, I owe a debt of gratitude to those who contributed to this endeavor. They have done an outstanding job of illustrating the versatility and power of radical ion intermediates at a level that is enjoyable for both those who work with these species routinely and those who are looking to develop a greater understanding of this chemistry. My underlying personal objective is for this issue to stimulate new creative applications for radical ion intermediates, allowing electron transfer reactions to be considered as attractive options for routine applications in synthesis design.

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