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Preface

Organic reactions initiated by single electron transfer have a long history in chemistry. The field has its foundation in the 1834 publication of Faraday in which he noted the formation of gas at the anode upon electrolysis of acetate. This process, now known as the Kolbe reaction, was studied extensively in the early to mid-20th century and was used to produce hydrocarbons, ethers and esters. It is now understood that the reaction proceeds through oxidation of a carboxylate leading to loss of CO_2 and production of an intermediate radical. Once formed, the radical can either dimerise or be oxidised further to a cation, which can be trapped by nucleophiles to produce a range of products. Though this process showed the potential power of single electron transfer in synthesis, a lack of understanding of the reactive intermediates formed in such processes slowed the development of other reactions. Although the chemistry of cations and anions was becoming well-understood by the mid-20th century, radicals were thought to be too reactive and unpredictable to be useful in synthesis. With the growing recognition that radicals and related radical ions could be tamed and exploited in selective reactions, it was only a short period of time before electron transfer became an essential tool for synthetic chemists.

Today, the high degree of sophistication possible in electron transfer-initiated organic reactions is a result of our understanding of mechanisms involving cations, anions, radicals and related radical ions. The ability of chemists to interconvert these species at will through the use of electron transfer reagents or electrochemistry has led to the development of cascade reactions that use one or more reactive intermediates in bond-forming events to produce complex molecules of great societal importance.

The aim of this Tetrahedron Symposium-in-Print is to set out the state of the art in the use of electron transfer in organic synthesis and highlight some of the most important recent advances in the field. The contributions cover a range of topics including reviews on the chemistry of electron transfer reagents, mechanistic studies on synthetically important reagents and intermediates, electrochemical approaches to redox-initiated reactions, tandem and cascade reactions and radical ion chemistry. It is our hope that this collection will stimulate further study and inspire additional work in this important area of organic synthesis. We thank the authors and reviewers for their contributions to this issue and Professor Richard Taylor, Professor Harry Wasserman and Ms. Jane Quinn for their help in putting together this important collection of work.

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