

Endoperoxides as Probes into Electron Transfer Kinetics: A mechanistic investigation of the electron transfer reduction of 3,3,6,6-tetraaryl-1,2-dioxanes

One focus of our groups' research has been the study of electron transfer (ET) to endoperoxides. Many of our early studies involved aliphatic endoperoxides as models for biologically relevant endoperoxides and were found to undergo a 2 electron reduction, generating the corresponding diol. These results produced valuable thermochemical information but little mechanistic insight into the processes that follow ET. The objective of the study 3,3,6,6-tetraaryl-1,2-dioxanes (**1**) was to introduce aromatic moieties into a endoperoxide and determine the effects on the initial ET process, as well as any following processes. ET to endoperoxides has previously been found to be a non-adiabatic concerted dissociative process, however the introduction of aryl rings has allowed a stepwise dissociative process to become energetically feasible. As well, alkoxy radical reactivity stemming from the distonic radical anion, the species generated from a single ET and O-O bond fragmentation, has been observed and is responsible for a dramatic variation in product ratio dependent upon the means of reduction. A mechanistic rationale accounting for all observations from the voltammetry and product studies will be presented.