Synthesis, Thermodynamic and Kinetic Studies of Novel Diarylamine Antioxidants

Diarylamine antioxidants are industrially important chain-breaking antioxidants that are used to prevent oxidative degradation of plastics, rubbers, oils and lubricants. However, these compounds are often limited in applicability due to their propensity to undergo one electron oxidation with molecular oxygen – rendering them ineffective. We report here our efforts to synthesize substituted pyridine and pyrimidine-based diarylamine antioxidants having enhanced air stability over equivalent diphenylamines, while maintaining antioxidant efficacy. Kinetic data has been obtained for reactions of these compounds with peroxyl and alkyl radicals using appropriate radical clocks, and the results indicate that these compounds are among the fastest chain-breaking antioxidants known. Standard potentials were obtained for the redox chemistry of these compounds by cyclic voltammetry and BDEs for their N-H bonds were measured using radical equilibration EPR techniques. Correlations between kinetic and thermodynamic data have provided important mechanistic information for reactions between peroxyl radicals and diarylamines, including evidence for a proton-coupled electron transfer (PCET) mechanism.