Laser Flash Photolysis Studies of Hydrogen Abstraction Reactions of Phenoxyl Radicals

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Aryloxy radicals are important intermediates in the thermal decomposition of lignin and low rank coals. Their rates of formation, termination, hydrogen abstraction, and addition (i.e. crosslinking) have a significant impact on the product yields and distributions. Numerous examples of hydrogen abstraction reactions of phenoxyl radicals with substituted phenols and hydroperoxides have been reported.' However, only a few reports of Arrhenius parameters for hydrogen abstraction from hydrocarbons by phenoxyl radicals are available. This is mainly due to the experimental challenges associated with the slow relative rates of hydrogen abstraction by phenoxyl radical from hydrocarbons and the very rapid recombination rates of phenoxyl radicals. In previous studies reported by Britt et al. z the Arrhenius parameters for hydrogen abstraction by phenoxy radicals have been assumed to be similar to those of benzyl radicals. This assumption, however, does not take into account the well-known polar effects in free radical reactions. 3 Since hydrogen abstraction reactions of aryloxy radicals plays an important role in the processing of energy resources (e.g. lignin, low rank coal, and in the chemistry of antioxidants), we have undertaken this study to investigate the kinetics of hydrogen abstraction from hydrocarbons by phenoxyl and substituted phenoxyl radicals. The data obtained from such studies will serve as a benchmark for thermochemical kinetic estimates on related systems.

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Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.