

Investigating the Oxidation Chemistry of Ketones and Cyclic Ethers

Adam M. Scheer,¹ Subith S. Vasu,^{1,2} Oliver Welz,¹ Haifeng Huang,¹ John D. Savee,¹ David L. Osborn,¹ Connie W. Gao,³ Joshua W. Allen,³ William H. Green,³ and Craig A. Taatjes^{1*}

¹Combustion Research Facility, Sandia National Laboratories, MS 9055, Livermore, CA 94551 USA

²Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, P.O. Box 162450, Orlando, FL 32816 USA

³Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139 USA

* Corresponding author: cataatj@sandia.gov

Several classes of endophytic fungi convert cellulose directly into a range of molecules that are potentially useful for combustion fuels. Among the native products of these fungi are significant amounts of ketones and other oxygenates for which the ignition chemistry is not well understood. In this study, the oxidation chemistry of several ketones (diisopropyl ketone, $[(CH_3)_2CH]_2C=O$; isopropyl-*tert*-butyl ketone, $(CH_3)_2CHC=OC(CH_3)_3$; di-*tert*-butyl ketone, $[(CH_3)_3C]_2C=O$; cyclopentanone, $c-C_5H_8=O$; and 2-methylcyclopentanone, $CH_3-c-C_5H_7=O$) and cyclic ethers (tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, and 1,8-cineole) has been studied, employing the technique of chlorine-initiated oxidation to examine the initial reactions that are important in autoignition of these fuels. Products of pulsed-laser initiated oxidation are monitored as a function of reaction time, mass, and photoionization energy by using Multiplexed Photoionization Mass Spectrometry (MPIMS) with tunable ionizing radiation provided by the Chemical Dynamics Beamline at the Advanced Light Source. Complementing the MPIMS experiments, direct, time-resolved detection of OH and HO₂ radicals from the Cl-initiated oxidation is performed in a slow-flow Herriott reactor cell. Quantitative OH and HO₂ species profiles provide an important monitor of the overall balance between chain-propagating and chain-branching channels, represented by OH formation, and the effectively chain-terminating formation of HO₂. The observed differences in the initial oxidation reactions displayed by these ketones and cyclic ethers will affect their autoignition properties.

The correlation of initial oxidation behavior with molecular structures is being employed to validate more general rate rules for oxidation of ketones and cyclic ethers, in the context of the Reaction Mechanism Generation program developed by the Green group at MIT. The MIT Reaction Mechanism Generator provides an important bridge between the direct observation of individual reactions in a limited temperature and pressure range and the extensive chemistry of an engine. This collaboration is aimed at developing full models to predict the potential of fungi-generated renewable fuels.

This work is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy (USDOE)'s National Nuclear Security Administration under contract DEAC04-94AL85000. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the USDOE, under contract DE-AC02-05CH11231 between Lawrence Berkeley National Laboratory and the USDOE.