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A coordinated investigation of the combustion chemistry of diisopropyl ketone, a prototype for biofuels produced by endophytic fungi

Joshua W. Allen [a], Adam M. Scheer [b], Connie W. Gao [a], Shamel S. Merchant [a], Subith S. Vasu [c], Oliver Welz [b], John D. Savee [b], David L. Osborn [b], Changyoul Lee [d], Stijn Vranckx [d], Zhandong Wang [e], Fei Qi [e], Ravi X. Fernandes [d,f], William H. Green [a,*], Masood Z. Hadi [g,1], Craig A. Taatjes [b,*]

[a] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[b] Combustion Research Facility, Sandia National Laboratories Livermore, CA 94551, USA
[c] Mechanical and Aerospace Engineering, University of Central Florida, Orlando, FL 32708, USA
[d] Physico-Chemical Fundamentals of Combustion, RWTH Aachen University, 52056 Aachen, Germany
[e] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China
[f] Physikalisch-Technische Bundesanstalt, Bundesallee 100, D38116 Braunschweig, Germany
[g] Biomass Conversion Technologies, Sandia National Laboratories, Livermore, CA 94551, USA

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ABSTRACT

Several classes of endophytic fungi have been recently identified that convert cellulosic biomass to a range of ketones and other oxygenated molecules, which are potentially viable as biofuels, but whose oxidation chemistry is not yet well understood. In this work, we present a predictive kinetics model describing the pyrolysis and oxidation of diisopropyl ketone (DIPK) that was generated automatically using the Reaction Mechanism Generator (RMG) software package. The model predictions are evaluated against three experiments that cover a range of temperatures, pressures, and oxygen concentrations: (1) Synchrotron photoionization mass spectrometry (PIMS) measurements of pyrolysis in the range 800–1340 K at 30 Torr and 760 Torr; (2) Synchrotron PIMS measurements of laser photolytic Cl-initiated oxidation from 550 K to 700 K at 8 Torr; and (3) Rapid-compression machine measurements of ignition delay between 591 K and 720 K near 10 bar. Improvements made to the model parameters, particularly in the areas of hydrogen abstraction from the initial DIPK molecule and low-temperature peroxy chemistry, are discussed. Our ability to automatically generate this model and systematically improve its parameters without fitting to the experimental results demonstrates the usefulness of the predictive chemical kinetics paradigm.

1. Introduction

Liquid petroleum-based fuels account for more than 30% of world energy consumption, the majority occurring in the transportation sector, where liquid fuels dominate because of their high energy density and ease of storage and distribution [1]. However, insecurity of oil supply and negative impacts of climate change are motivating increased development of alternative liquid fuels [2]. Lignocellulosic biofuels are a promising renewable alternative to conventional petroleum fuels that could lower greenhouse gas emissions. Due to the recalcitrance of lignocellulosic materials, new means for breaking down biomass into fermentable sugars are a central area of biofuels research [3]. However, the products that are most efficiently produced from biomass may not have well-characterized combustion properties. Furthermore, advanced clean, efficient combustion strategies, particularly those that rely on compression ignition, are often very sensitive to fuel chemistry [4,5]. To address these issues comprehensively, coordinated efforts towards biofuel-engine co-development are required.

Figure 1 depicts the Sandia collaborative biofuel development strategy. Synthetic biologists working in close collaboration with combustion researchers develop fundamental mechanisms for the production and combustion of potential biofuels. Ignition and engine trials then provide feasibility tests for fuels and mixtures and yield recommendations for the bioengineering scale-up of specific metabolic pathways. This coupling of fundamental and applied combustion chemistry and synthetic biology is a strategy to identify and investigate the most promising fuel compounds through mutual feedback. Moreover, the development of combustion models will provide the predictive capability needed for eventual efficient utilization of the new biofuel stream. A similar

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* Corresponding authors.

E-mail addresses: whgreen@mit.edu (W.H. Green), cataatj@sandia.gov (C.A. Taatjes).

[1] Present address: NASA Ames Research Center, Moffett Field, CA 94035, USA.

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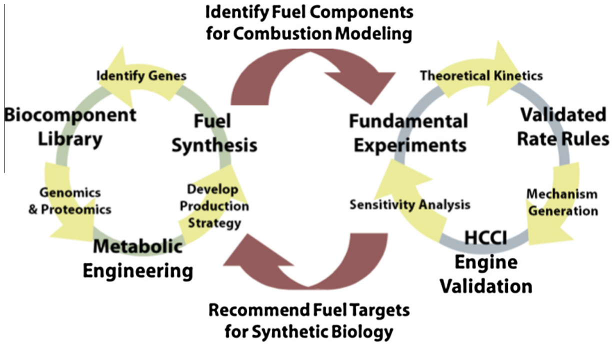
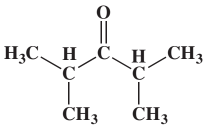


Fig. 1. A framework for collaborative effort toward lignocellulosic biofuel research. The two development cycles inform and adapt to each other's results.

framework involving chemical biomass processing drives the Cluster of Excellence "Tailor-Made Fuels from Biomass" at RWTH Aachen University [6].

Several endophytic fungi directly convert lignocellulosic material into a variety of volatile organic compounds, and harnessing their metabolic pathways provides a promising platform for cellulosic biofuel generation [7–10]. The natural products of fungal conversion of biomass include a variety of ketones, cyclic ethers and other complex oxygenates. Both fundamental measurements of representative compounds and detailed theoretical kinetics efforts are needed to enable models that can provide feedback on the desirability of specific molecules as fuels.

As part of the collaborative biofuel development effort, this work describes a combined experimental and modeling study of the combustion chemistry of diisopropyl ketone (2,4-dimethylpentan-3-one, denoted DIPK):



DIPK is a representative molecule for branched ketones. Ketones are a class of potential biofuel molecules from endophytic fungal biomass conversion, as well as from other biofuel production methods [11]. Studying the fundamental ignition chemistry of DIPK supports predictive simulation of general ketone combustion.

The central goal of this detailed investigation of DIPK is to derive rules that will enable automatic creation of general, accurate global kinetic models for branched ketone ignition and combustion. The rules will be employed in the Reaction Mechanism Generator (RMG) software developed at the Massachusetts Institute of Technology [12]. Given initial conditions, RMG automatically calculates possible species and reactions from a database of reaction families and libraries, and then uses a flux-based algorithm to select the most important pathways to include in the model. This process is iterated until all important species and reactions are found. Parameters requiring refinement are identified through sensitivity analysis of the RMG prediction and comparison to experiment. These important parameters are not "fitted" to the data; rather the individual reactions are subjected to an increased level of theoretical analysis or direct experimental measurement. The resulting more accurate parameters are then added to the RMG database of chemistry rate rules to improve future model predictions for both the current fuel molecule and similar molecules. The RMG-generated model for DIPK was evaluated and refined based on pyrolysis measurements performed at the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China, oxidation measurements carried out at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, and ignition delay measurements from rapid compression machine (RCM) and shock tube experiments performed at RWTH Aachen University. These experiments span a wide range of oxygen partial pressures, total pressure, and temperature thus probing widely different reaction conditions.

2. Experimental methods

2.1. Pyrolysis

The pyrolysis of DIPK was investigated at the U10 beamline of the National Synchrotron Radiation Laboratory in Hefei, China [13–15]. The experimental setup consists of an alumina flow tube with an inner diameter of 7.0 mm mounted in a furnace such that the heated region of the flow tube is 150 mm and the distance between the outlet of the tube and the sampling nozzle is about 10 mm. An inlet stream of 2 vol% DIPK (purity 98%) in argon (99.99%) was supplied to the pyrolysis tube at a rate of 1.0 SLM. The pyrolytic species were sampled using a molecular beam produced by a quartz cone with a ~500 μm (30 Torr) or ~150 μm (760 Torr) orifice at the tip. The molecular beam was passed through a nickel skimmer to a photoionization chamber, where the products were crossed with the synchrotron beam and analyzed using a reflectron time-of-flight mass spectrometer (RTOF-MS). Seven energies of 16.65 eV, 11.70 eV, 11.00 eV, 10.00 eV, 9.45 eV, 9.10 eV, and 8.80 eV were chosen to obtain near-threshold ionization. Pyrolysis experiments were run at several temperatures over the ranges of 940–1340 K at 30 Torr and 800–1180 K at 760 Torr.

2.2. Chlorine-initiated oxidation

The initial steps in low-temperature DIPK oxidation were probed using pulsed-laser chlorine-initiated oxidation experiments employing time-resolved tunable synchrotron Multiplexed Photoionization Mass Spectrometry (MPIMS) [16,17] with ionizing radiation provided by the Chemical Dynamics Beamline at the Advanced Light Source. The apparatus consists of a heated 1.05 cm inner diameter quartz flow tube with a ~650 μm aperture through which gas escapes. A collimated molecular beam is formed by passing the effluent through a skimmer. Quasi-continuous, tunable ionizing radiation provided by the synchrotron intersects the molecular beam orthogonally and ions are accelerated into a linear time-of-flight mass spectrometer. Products are detected as a function of mass, time, and energy, yielding a 3-dimensional dataset that can be sliced and integrated accordingly to obtain photoionization spectra and temporal profiles for individual species. Photolysis of Cl_2 by a pulsed excimer laser operating at 351 nm and 10 Hz yields an initial Cl atom concentration of approximately 7×10^{12} molecules cm^{-3}. The absorption of DIPK at 351 nm is negligible [18]. Average pre-photolysis background signal is subtracted, resulting in a difference mass spectrum that shows negative signal for the parent compound and its daughter ions. Mass flow controllers are used to introduce reactants and carrier gas into the reactor tube. A bubbler held at 20 °C provides a steady source of DIPK (98%, degassed before use). The DIPK has a vapor pressure of 10.4 Torr at 20 °C and an initial concentration of 5.7×10^{13} molecules cm^{-3} in the reactor is estimated at 550 K. Approximately 13% depletion of the parent is observed within 5 ms of photolysis laser firing, followed by a more gradual depletion for the extent of reaction. Pressure in the tube is maintained at 8.0 Torr by feedback control of a