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Elucidation of the Reaction Mechanisms of Autooxidative Processes in Complex Condensed-Phase Mixtures

November 2020

J. Timothy Bays, Amity Andersen, Jon D. Egbert, John C. Linehan, Richard E. Overstreet

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Abstract

In this report, we discuss the oxidative processes of gasoline surrogate fuels comprised of a neat olefin, such as 1-hexene. Oxidative reactions are thought to involve the peroxyl radical and peroxide chemistry with initial hydrogen abstraction by O_2, followed by addition of O_2 or HOO· to the hydrocarbon to form unstable peroxy radicals and peroxides that result in a chain reaction. In the condensed phase environment (liquid), we also consider polymeric-forming chain reactions, such as hydrocarbon radical-radical carbon chain growth. We present our experimental results showing the reaction products resulting from 1-hexene oxidation, along with chemical kinetic modeling of the system showing product ratios as a function of time. Applicability of our observations to oxidation-promoted fouling in hydrocarbon fuels (i.e., formation of gum) and radical-promoted polymerizations will also be discussed.

Acknowledgments

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Acronyms and Abbreviations

°C	degrees Celsius
CDI	Chemical Dynamics Initiative
DFT	density functional theory
DNA	deoxyribonucleic acid
DOE	Department of Energy
DTBP	di-*tert*-butylperoxide
E_a	activation energy
K	Kelvin
kcal/mol	kilocalories per mole
MD	molecular dynamics
NEB	nudged-elastic band
PNNL	Pacific Northwest National Laboratory
psi	pound-force per square inch
psig	pounds per square inch gauge

Contents

Figures

Tables

1.0 Introduction

Autooxidation is ubiquitous, and includes organic oxidation processes in the atmosphere(Bianchi et al. 2019), polymerization/polymer degradation(Shelton 1978, Soucek, Khattab, and Wu 2012), and biological phenomena (i.e., oxidative stress on cell membrane lipids, DNA, and lipoproteins, which can lead to degenerative and inflammatory diseases, cancer, arteriosclerosis, etc.)(Shikama 1990, Simic 1980, Zerbinati and Iuliano 2017), and the fouling and gum formation in fuels(Alborzi et al. 2018, Pradelle et al. 2015, Watkinson and Wilson 1997). These processes are often well documented, with kinetic rates of reaction and product speciation empirically derived. But aside from a generally accepted mechanism, Figure 1, the processes are not well-understood beyond the first steps in a mechanism. In contrast, combustion is becoming a well-understood process, and is a good example for how largely free-radical reaction mechanisms can provide kinetic, thermodynamic, and physical properties of the system as a whole.

While there remain many research challenges, the process for fuel oxidation in the form of combustion is well-documented. Considerable progress has been made in tying reaction mechanisms and kinetics to fuel properties observable in internal combustion engines (for example: Mehl et al. 2006, Mehl et al. 2011, Westbrook et al. 2017). Briefly, during combustion oxidation typically occurs in two stages following an initiation step(Glassman 1996a, b). The first stage of oxidation typically occurs below 700 K and involves the creation of peroxy radicals, ROO· (where R is a generic alkyl group). The ROO· intermediate of first-stage oxidation can undergo an internal hydrogen transfer from an alkyl group within the same molecule to create a hydroperoxide radical, ·ROOH (Benson 1981). Site reactivity within a particular organic molecule is driven by the energy required to break a specific C-H bond, with 3º carbons favored over 2º, followed by 1º. This is largely because the strength of the C-H bond increases in the same order, with weaker C-H bonds being more reactive, but is in contrast to the accessibility of that hydrogen atom (Andersen and Carter 2003, Berkowitz, Ellison, and Gutman 1994). Following its creation, the ·ROOH radical can combine with O_2 to create a ·OOROOH radical. This radical can undergo a similar hydrogen transfer reaction to that of ROO·, and subsequently form one ·OH radical and an aldehyde or ketone peroxide. If the aldehyde/ketone peroxide dissociates via O–O scission of the peroxide group, another ·OH can be created. If a second ·OH is created, chain branching is said to occur. The creation of two highly reactive ·OH radicals can then lead to the creation of four radicals, and ultimately, an exponential increase in highly exothermic fuel molecule oxidation, which can lead to explosive combustion, or first-stage ignition.

Processes similar to the oxidation process described for combustion can be observed for other systems, although at lower temperatures, and slower reaction rates. Certain polymerization reactions and polymer degradation reactions have similar oxidation stages stemming from oxygen additions to form peroxy radicals, hydroperoxides, hydroperoxy radicals, and peroxides (see Figure 1). Molecular dynamics (MD) simulations have been applied to polymerization reactions in the condensed phase (for example: Enciso et al. 2018, Gissinger, Jensen, and Wise 2017, Okabe et al. 2016, Vandenbergh et al. 2016), generally with only one chemical substrate, with limited examples having an open system to allow for replenishing oxygen consumed in the solution (for example: Lv et al. 2017, Shanmugam, Xu, and Boyer 2017).

Aspects of polymer-forming reactions can be seen in the complex chemical mixture that makes up gasoline at room temperatures. These reactions produce a polymeric material commonly referred to as gum, varnishes or lacquers, and are fueled mainly by the presence of olefins in the gasoline. While there has been considerable empirical work in defining the kinetics for this process, and for the initial steps in the reaction mechanism, the complexity of the fuel mixture, the low-temperature reactions, as well as the continuous, but slow, addition of oxygen, makes study beyond the first steps in oxidation, challenging (for example:Ashraful et al. 2014, Batts and Fathoni 1991, Czarnocka, Matuszewska, and Odziemkowska 2015, Dunn 2002, Le Pera 1966, Lin and Chiu 2009, Pradelle et al. 2015). Gum formation, as result of autooxidation, is of increasing relevance with trends toward vehicle electrification. For electric vehicles with range-extender engines, it is conceivable that the fuel could remain in a fuel tank for months at a time before being consumed, allowing sufficient time for gum to build up, which can be deleterious to engine operation.

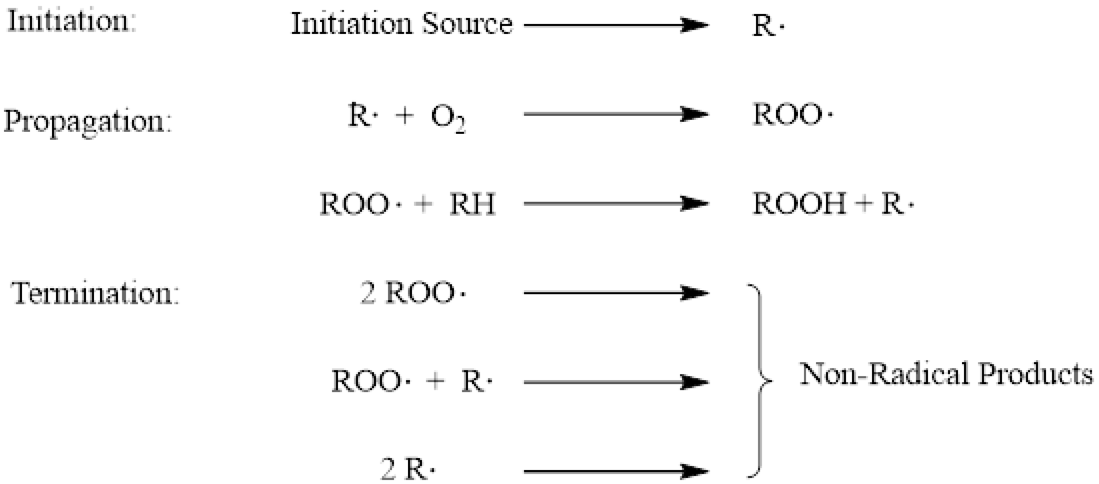

Figure 1. General reaction scheme for autooxidation.

Further examples where autooxidation can be studied include the formation of partially oxidized deposits on interior surfaces of internal combustion engines, or the formation of soot from combustion, where a strongly oxidizing environment is necessary for efficient and complete fuel burn. Thus, further fundamental investigation of the mechanisms of autooxidation that result in soot, and other polymerization products, is needed to formulate strategies to prevent formation of these byproducts.

To make the problem on studying autooxidation in complex organic biphasic systems more tractable, a stepwise approach was taken in conducting laboratory experiments and computational simulations, as shown in Figure 2. Gum formation is a common process that occurs in gasoline as a result of olefin oxidation and subsequent crosslinking to form polymeric materials. These polymeric materials can be soluble or insoluble and are called gum. Model systems using surrogate gasoline mixtures can serve as a test bed for condensed-phase reaction conditions, using organic peroxides to initiate the oxidation process as a homogeneous system. These systems are sensitive to oxygen, initiator (peroxide), substrate (olefin) concentrations, and temperature. Biphasic systems were used to provide diffusion-limited conditions.

Developing a fundamental understanding of gum formation will offer a tractable starting point for investigating other autooxidation processes. In this work, a one-component surrogate gasoline comprised of 1-hexene is used. Because of the slow autooxidation process, even at elevated temperatures, oxidative radical reactions are initiated using a peroxide initiator, in this case di-

tert-butylperoxide. Herein we present the results observed for this surrogate gasoline both in laboratory studies and in simulated chemical reactions.

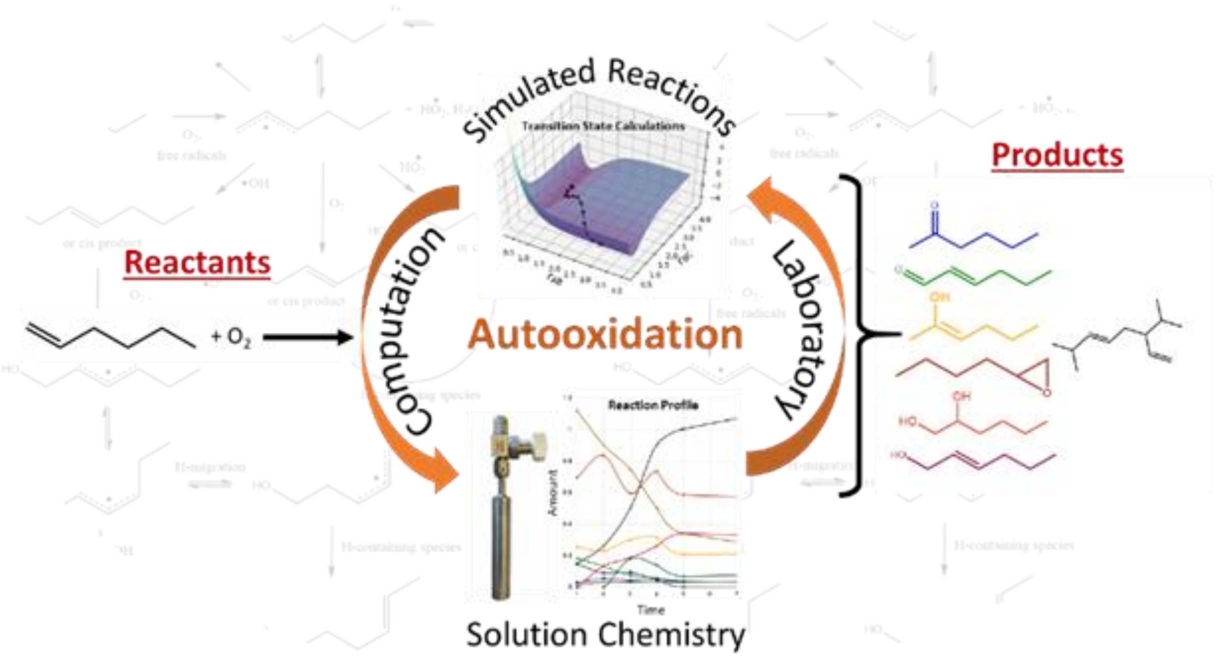

Figure 2. The oxidation of 1-hexene is being studied using a combination of laboratory and simulated experiments. These studies work synergistically and iteratively, each providing feedback to the other. The resulting developed from understanding the detailed mechanistic pathways will allow the prediction of products across a range of temperatures and pressures.

2.0 Methods

Laboratory work was carried out in stainless steel batch reactors. The reactors were loaded with known amounts of 1-hexene as the substrate, di-*tert*-butylperoxide as the initiator, and benzene as an internal standard. The reactors were then pressurized with dry air and heated in an oven for the required time. The reactors were then removed, and product distributions were observed and quantified using gas chromatography and a mass selective detector.

Density functional theory (DFT) calculations were performed using NWChem quantum chemistry code (Valiev et al. 2010). Transition state structures for intermediate and product species were calculated using nudged-elastic band (NEB) and zero temperature string methods (Jónsson, Mills, and Jacobsen 1998, Weinan, Ren, and Vanden-Eijnden 2002). These structures were then used to compute reaction rates. Global kinetics for the identified chemical reactions were then modeled using a zero-dimensional batch reactor and Cantera software (Goodwin et al. 2018).

3.0 Results/Discussion

For the associated laboratory work needed to understand the oxidation of 1-hexene in the condensed phase, a series of batch reactor experiments were conducted, varying temperature, oxygen partial pressure, and amount of peroxide used as an initiator. To initiate the reactions di-*tert*-butylperoxide (DTBP) was selected from several peroxide candidates based on its low O–O bond scission temperature and predictable reaction products. Without an initiating peroxide, autooxidation reactions occurred at a rate that was too slow to be useful in this study. Reaction conditions ranged from 125-175 °C, 10-30 psi O_2, and lasted up to about 20 hours. To deconvolve purely thermal reactions from those initiated by the peroxide decomposition, reaction times were shortened, and temperatures were maintained low. Gas chromatography was used to separate the reaction products and mass spectrometry was used to identify dominant reaction product structures. Overall, about a dozen products were identified and tracked as a function of time, temperature, O_2 partial pressure, and peroxide concentration. A sample chromatogram is shown in Figure 3.

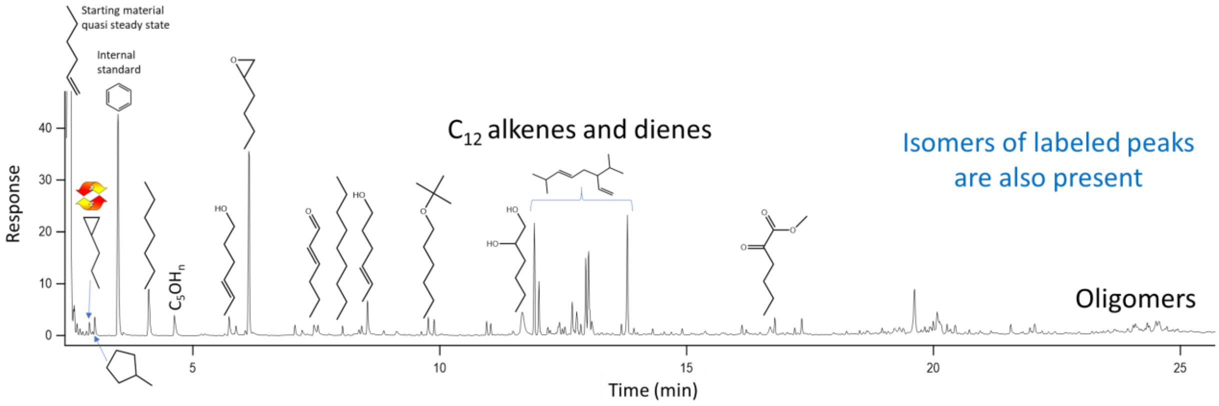

Figure 3. Gas chromatogram of reaction mixture from batch reactors. Major oxidation products of 1-hexene were speciated using a mass spectral library. This reaction was carried out in a batch reactor at 150 °C and 20 psi P_{O2}.

Computation work initially focused on revising the kinetic mechanism proposed by Mehl et al. for the combustion of 1-hexene (Mehl et al. 2008), adapting the mechanism for condensed-phase radical processes. During this adaptation process, the computation team and laboratory team worked together to ensure that observed or predicted species were present in the laboratory experiments as well as present in the detailed mechanism. Ultimately the detailed mechanism was developed and is shown in Figure 4.

Even while the mechanism was being developed, Nudged Elastic Band (NEB)/String Calculations were used to identify the minimum energy pathways between products and reactants to define the energy of the transition state for each elementary step. To date 14 of 23 transition states for the mechanism shown in Figure 4 have been calculated. For the remainder, estimates have been used to provide the necessary reaction entropies, Arrhenius kinetic parameters, and fits for heat capacity, enthalpy and entropy needed for the Cantera reaction simulation software.

Simulated chemical reactions in a zero-dimensional batch reactor were undertaken, using Cantera reaction simulation software with gradually increasing complexity. Increasing complexity includes adding subsets of the detailed kinetic mechanism and updating the mechanism to accommodate diffusion-limited kinetics.

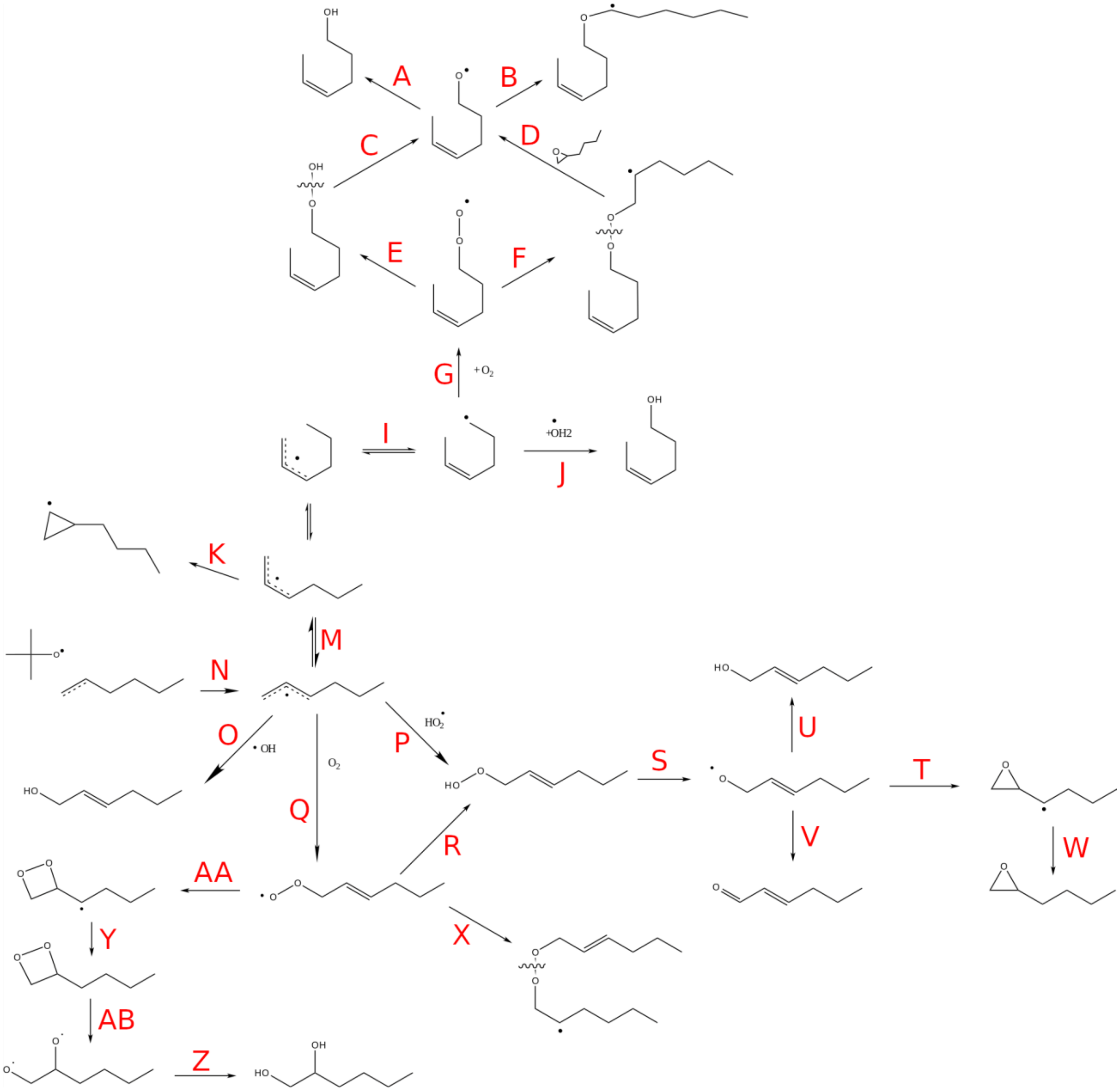

Figure 4. Proposed mechanism for the autoxidation of 1-hexene. Elementary reaction steps have been labeled with letters. Corresponding activation energies calculated at PNNL are listed in Table 1.

Figure 5 shows the time-dependent concentrations for selected reactants and products using a subset of the completed mechanism. These are shown by the solid lines, while results from each of the laboratory batch reactor experiments is shown as a colored dot. The simulated chemical reaction profiles can be seen to be tracking the experimental data sufficiently well to suggest that the approach is sound.

Subsequently, additional elements of the kinetic mechanism were introduced. This significantly increased the complexity of the Cantera simulation, and some problems were identified. For example, the olefin, 1-hexene, was observed to decrease in concentration, but should remain relatively constant since the reaction were run assuming 1-hexene concentration to be pseudo-steady state. Additionally, the epoxy radical is not a long-lived radical and should be reacting immediately with 1-hexene to generate additional hexenyl radicals for reaction. This is a diffusion-limited reaction step. Also, DTBP appears to be reacting too quickly. This could signal inappropriate Arrhenius preexponential factor, or O-O scission activation energy. Once these potential errors are corrected, additional scrutiny of product distributions will be required.

At the conclusion of formal project funding, Cantera simulations were in progress. Suitable simulations will be needed prior to publishing this work.

Table 1. Activation energies (E_a) calculated as part of this project for the corresponding elementary reaction steps in the proposed kinetic mechanism, shown in Figure 4.

	E_a (kcal/mole)*			E_a (kcal/mole)*	
Elementary Step	PNNL	Diffusion-Limited	Elementary Step	PNNL	Diffusion-Limited
A			O		1.5
B			P		1.5
C			Q		1.5
D	17.08		R		
E			S	24.682	
F			T	8.79	
G		1.5	U	9.257	
H		1.5	V	51.027	
I			W	14.856	
J		1.5	X	29.126	
K	52.74		Y	10.807	
L	36.457		Z		
M		1.5	AA	1.925	
N		1.5	AB	4.931	

*Activation energies for steps not shown in this table were obtained from various works in the chemical literature.

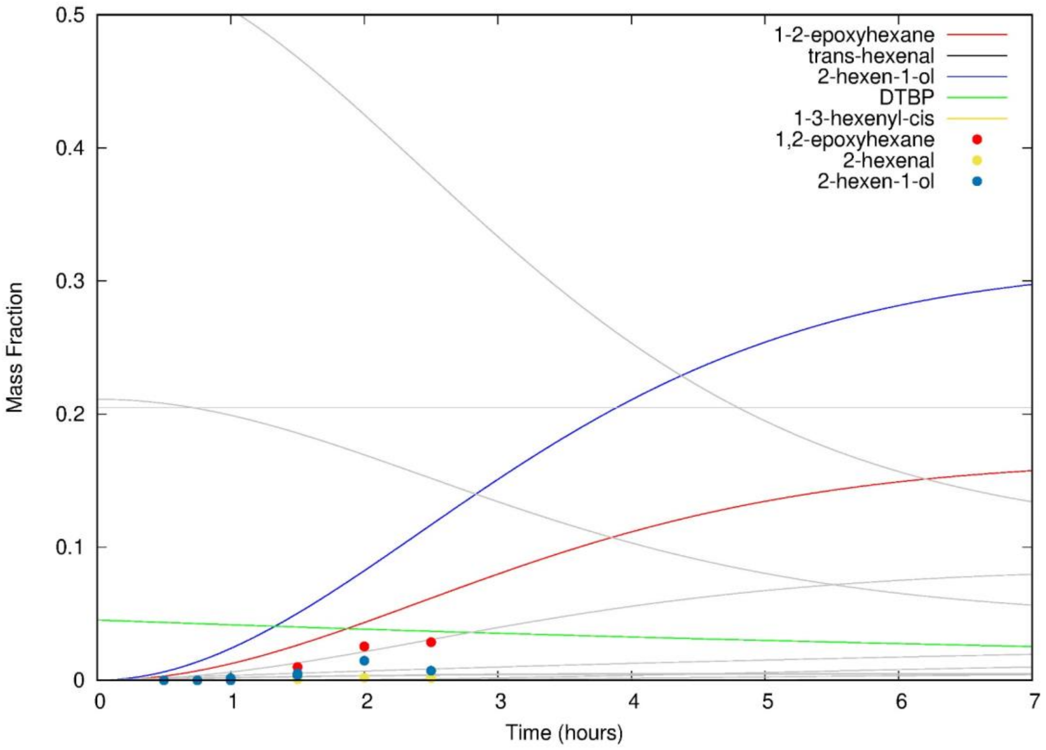

Figure 5. Cantera zero-dimensional batch reactor simulations and empirical data at 125 °C and 100 PSIG using a subset of the proposed reaction mechanism.

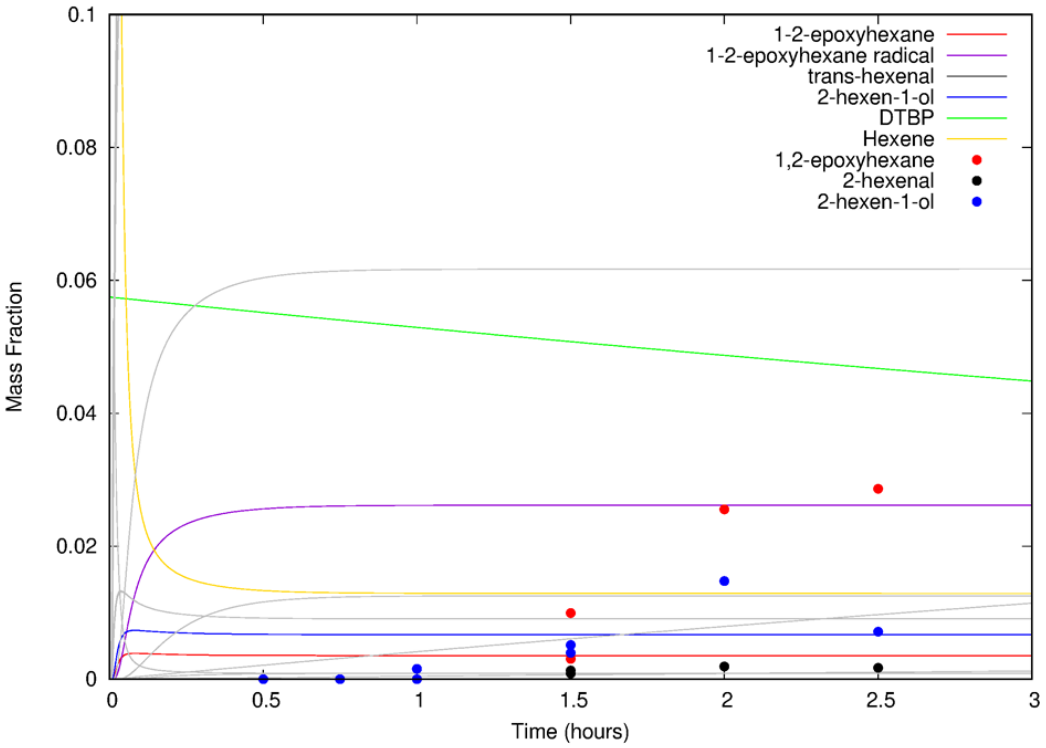

Figure 6. Cantera zero-dimensional batch reactor simulations and empirical data at 125 °C and 100 PSIG using the full, proposed reaction mechanism.

4.0 Conclusions

A one-component surrogate fuel, 1-hexene, was used to investigate gum formation in gasoline under conditions designed to promote autooxidation. To make the problem of studying autooxidation in complex organic biphasic systems more tractable, a stepwise approach was taken in conducting laboratory experiments and computational simulations, as shown in Figure 2. These experiments were carried out in parallel and were found to be synergistic as laboratory and computational studies identified and supported production of the reaction products, suggesting that the mechanism proposed in Figure 4 provided a good basis to undertake simulating chemical reactions to match observed products and time-dependent concentrations.

Initial Cantera reaction simulations using a subset of the kinetic mechanism provided results commensurate with laboratory experiments. However, as additional complexity was introduced into the simulation, several shortcomings were observed. These can likely be overcome with additional work in exercising the Cantera reaction simulation platform.

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