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Oxidation processes play an integral role in many industries, but questions still remain regarding the mechanisms of carbon-hydrogen bond activation and oxidation in free-radical and catalyzed processes. Microkinetic modeling is a powerful tool capable of examining oxidation processes at the mechanistic level to gain understanding and guide catalyst applications. This thesis developed microkinetic models for oxidation of organic substrates using novel and industrially-relevant catalysts. Understanding the role of free-radical and catalyzed oxidation within a system is critical to knowing the effect of catalysts and predicting behavior when adapted to a new process. In this work, microkinetic models examined the oxidation of alcohols, alkenes, and alkylbenzenes using free radicals and various catalysts.

Microkinetic modeling was applied to the oxidation of 1,3-propanediol in order to explain the atypically high selectivity to acrolein for an uncatalyzed process. The developed free-radical model did not exhibit enough activity to explain the observed experimental conversion. An initial concerted dehydration reaction is the most probable mechanism of increasing the overall rate of reaction. The dehydration reaction leaves behind a double bond, and the allylic hydrogen is more likely to be initiated by free radicals. The investigation of this system showed that for oxidized starting materials concerted reactions may play an important role in directing selectivity.

The microkinetic model was then expanded to the oxidation of cyclooctene catalyzed by gold nanoparticles. There has been significant interest in determining the role of small gold nanoparticles in catalyzing reactions. In order to reveal the role of ~5-8 atom gold clusters, the free-radical model was first validated against experimental data. Net rate analysis revealed that alkoxy and peroxy radicals prefer to add to cyclooctene as opposed to abstract hydrogen, giving

rise to high (~80 %) selectivity to cyclooctene oxide. With the underlying chemistry defined, the role of gold nanoparticles was initiation of free radicals via hydrogen abstraction by superoxo gold species and hydroperoxide decomposition on gold sites. This makes gold nanoparticles interesting radical initiators, but they are not a plausible method for guiding selectivity of a system to epoxides.

The established cyclooctene model was amended to account for the addition of another substrate, ethylbenzene, and a new catalyst, Co/ZSM-5. This model provided the opportunity to investigate the effect of kinetically coupling of the slower oxidation of ethylbenzene with the active oxidation of cyclooctene. Net flux analysis revealed that under conditions that have a high concentration of ethylbenzene, alkoxy and peroxy radicals derived from cyclooctene have a higher tendency to abstract hydrogen, initiating ethylbenzene oxidation. The alkoxy and peroxy radicals are more important in initiating ethylbenzene and driving secondary reactions to acetophenone than the zeolite catalyst, showing that kinetic coupling is a viable method of improving activity.

Finally, direct epoxidation reactions catalyzed by Ti/SiO₂ were added to the extant free-radical model for studying oxidation of limonene. The complexity of limonene led to a far more complex free-radical behavior with diepoxide and 1,2-epoxide products being slightly preferred to a multitude of other minor products. For catalyzed oxidation, the system is highly selective to 1,2-limonene oxide, implying that the 1,2-double bond is the most vulnerable for oxidation in both cases. Examination of the mechanism revealed that the Ti/SiO₂ catalyst can be in multiple active states with differing activities, emphasizing the importance of catalyst structure on oxidation.

The microkinetic modeling framework established in this work can serve as a platform to investigate a variety of oxidation systems. When built upon, the effect of catalysts can be quantified, and predictions can be made in order to improve oxidation processes.

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Table of Contents

List of Figures.....	8
List of Tables	10
Chapter 1: Introduction and Background.....	12
1.1 Introduction to Oxidation Systems	12
1.2 Background for Microkinetic Modeling.....	14
1.3 Outline of Research	17
Chapter 2: Mechanistic Modeling of the Partial Oxidation of 1,3-Propanediol.....	20
2.1. Introduction	20
2.2. Partial Oxidation Mechanisms	22
2.3. Computational Methods	27
2.4. Results and Discussion	32
2.5. Conclusions	41
Chapter 3: Microkinetic Modeling of Homogeneous and Gold Nanoparticle-Catalyzed Oxidation of Cyclooctene	43
3.1. Introduction	43
3.2. Methods	49
3.3. Results and Discussion	59
3.4. Conclusions	70
Chapter 4: Microkinetic Modeling of the Co-Oxidation of Ethylbenzene and Cyclooctene Using Co/ZSM-5.....	72
4.1 Introduction	72
4.2. Methods	75
4.3 Computational Results and Discussion	83
4.4 Conclusions	94
Chapter 5: Mechanistic Modeling of Limonene Oxidation by Titanium Oxide Catalyst....	96
5.1 Introduction	96
5.2 Methods	98
5.3 Results and Discussion	108
5.4 Conclusions	121
Chapter 6: Summary and Future Perspectives.....	123
References.....	127
Appendices.....	143

List of Figures

Figure 1.1: Example of a single β -scission step in the automated network generation process..	15
Figure 2.1: Unimolecular routes and their putative cyclic transition states for (a) dehydrogenation and (b) dehydration reactions of 1,3-propanediol.	25
Figure 2.2: Bimolecular reactions facilitated by an OH-containing species (here shown as H ₂ O) and their putative cyclic transition states for (a) dehydrogenation and (b) dehydration reactions.	26
Figure 2.3: Dominant pathways leading to acrolein for the free-radical mechanism	33
Figure 2.4: Postulated mechanism for the conversion of 1,3-propanediol involving concerted reactions via the cyclic structures depicted in Figures 2.1 and 2.2.	35
Figure 2.5: Results of the model based on concerted reactions shown in Figure 2.4 compared to experimental data at various residence times.	36
Figure 2.6: Dominant pathway to acrolein in the combined free-radical and concerted mechanism	40
Figure 2.7: Results of the model based on a combined reaction mechanism compared to experimental data at various residence times.	40
Figure 3.1: Reaction scheme for key reactions leading to oxidation of cyclooctene with the competition between the two branches shown dictating the selectivity to epoxide and alcohol/ketone.	46
Figure 3.2: Catalytic mechanisms of radical initiation by gold: a) hydrogen abstraction by a gold superoxo species and b) hydroperoxide decomposition by gold species.	48
Figure 3.3: Results of homogeneous model compared to experimental data for a) 373 K, 0 mL TBHP, b) 373 K, 0.3 mL TBHP, c) 373 K, 1.5 mL TBHP, d) 363 K, 1.5 mL TBHP.....	61
Figure 3.4: Homogeneous reaction network for oxidation of cyclooctene to cyclooctene oxide, 2-cycloocten-1-ol, and 2-cycloocten-1-one (shown in bold).	63
Figure 3.5: Results of model compared to experimental data for AuNP-catalyzed cases at 373 K with a) 0.8 ng/mL Au and b) 26 ng/mL Au.	66

Figure 3.6: Au-catalyzed reaction network for oxidation of cyclooctene to cyclooctene oxide, 2-cycloocten-1-ol, and 2-cycloocten-1-one (shown in bold).	68
Figure 3.7: Populations of major Au species at short times based on the model results for runs with a) 0.8 ng/mL Au and b) 26 ng/mL Au.	70
Figure 4.1: Scheme for decomposition of a) 2-cycloocten-1-yl hydroperoxide and b) 1-phenylethyl hydroperoxide on Co sites.....	81
Figure 4.2: Model results for ethylbenzene oxidation in the two-component system	85
Figure 4.3: Model results for cyclooctene conversion in the two-component system	86
Figure 4.4: Parity plot of ratio of cyclooctene conversion to ethylbenzene conversion.	87
Figure 4.5: The mechanism of cyclooctene oxidation within the two-component oxidation system	90
Figure 4.6: Mechanism of ethylbenzene oxidation in the two-component oxidation system.	93
Figure 5.1: Limonene molecule with carbon-numbering convention.....	97
Figure 5.2: Mechanism of direct epoxidation of limonene by Ti/SiO ₂	102
Figure 5.3: Microkinetic model results for uncatalyzed free-radical limonene oxidation.....	109
Figure 5.4: Mechanism of free-radical epoxidation for limonene through peroxy intermediates.	110
Figure 5.5: Mechanism of free-radical epoxidation for limonene through alkoxy intermediates.	112
Figure 5.6: Mechanism for limonene diepoxide formation.	114
Figure 5.7: Model results for Ti/SiO ₂ -catalyzed oxidation of limonene.	118
Figure 5.8: Net flux for the catalyzed formation of epoxide products from limonene.	120

List of Tables

Table 2.1: List of reaction families included in the reaction mechanism for 1,3-propanediol conversion based on free-radical chemistry.....	23
Table 2.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the free-radical mechanistic model.....	29
Table 2.3: List of Arrhenius pre-exponential factors and Evans-Polanyi parameters used for each reaction family in the mechanistic model based on concerted reactions.	30
Table 2.4: Comparison of experimental conversion and product selectivity values to the microkinetic model results based on a free-radical mechanism.	34
Table 2.5: Activation energies of reactions in concerted mechanism with reaction numbers corresponding to the reactions shown in Figure 2.4.	37
Table 3.1: List of reaction families included in the reaction mechanism for cyclooctene oxidation based on free-radical chemistry.	51
Table 3.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the cyclooctene oxidation mechanistic model.	54
Table 3.3: Reaction mixtures for experimental cyclooctene oxidation runs.....	58
Table 3.4: Regressed values for the rate constants for initiation reactions involving gold species. Values from the literature of analogous reactions catalyzed by Co(II) that were used as initial guesses are provided as well for comparison.....	65
Table 4.1: List of reaction families included in the reaction mechanism for cyclooctene and ethylbenzene oxidation based on free-radical chemistry.	76
Table 4.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the mechanistic model of cyclooctene and ethylbenzene oxidation.....	79
Table 4.3: Pre-exponential factor values for reactions of ethylbenzene and its progeny that were obtained via regression to experimental data.	80
Table 4.4: Composition of experimental reaction mixtures for the co-oxidation of ethylbenzene and cyclooctene.....	83
Table 4.5: Values of rate coefficients for Co reactions and corresponding net flux at 1 h.....	89

Table 5.1: List of reaction families included in the uncatalyzed reaction mechanism for limonene oxidation based on free-radical chemistry. 99

Table 5.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the limonene oxidation mechanistic model based on free-radical chemistry. 104

Table 5.3: Rate coefficients for Ti-catalyzed reactions for the oxidation of limonene. 105

Table 5.4: Experimental reaction conditions for uncatalyzed limonene oxidation..... 107

Table 5.5: Experimental reaction conditions for limonene oxidation catalyzed by Ti/SiO₂ 107

Chapter 1: Introduction and Background

1.1 Introduction to Oxidation Systems

Oxidation chemistry is important to a variety of industries ranging from pharmaceuticals to polymers. Specifically, partial oxidation processes that can convert low value alkanes or alkenes to higher value products with alcohol, ketone, or epoxide functionality are of particular interest. As a result, industries are constantly looking to create processes that are cheaper, more efficient, and environmentally friendly.¹⁻³

The barrier to achieving these goals for oxidation processes is activation of stable carbon-hydrogen bonds in the most abundant petroleum- and biomass-derived feedstocks.⁴⁻⁶ This work will focus on two methods of carbon-hydrogen bond activation that have been receiving considerable interest of late: free radical-mediated initiation and catalyzed activation. Both of these reaction mechanisms are often occurring simultaneously with radical chemistry being the homogeneous background to the metal-catalyzed reactions.^{7,8} A challenge for each method is directing selectivity to desired products. While there has been much research into developing active and selective chemical processes for oxidation using free radicals or catalysts, many questions about the mechanisms of oxidation remain. By furthering the understanding of carbon-hydrogen bond activation and oxidation processes, opportunities to improve and apply catalysts to new systems may arise. The overarching goal of this work is to gain understanding of oxidation systems at a molecular level through the design of microkinetic models.

One question that remains in the realm of oxidation chemistry is the role of the intrinsic free-radical behavior of the substrate on a catalyzed system.^{5,9} A goal for introducing a catalyst to a system is to improve the activity or selectivity compared to the homogeneous behavior of the

substrate. There are many instances when the metal may be acting as a radical initiator either by activating oxidizers or substrate carbon-hydrogen bonds.^{4,10} As a result, it is important to quantify the contribution of the homogeneous uncatalyzed reactions, so that the true influence of a catalyst can be evaluated.

In addition to the effect of the intrinsic nature of the substrate on the overall system, the role of catalysts is dependent upon the type of material and catalyst structure.^{11–13} Catalysts have been shown to have the ability to activate the oxidant or perform direct oxidation, and both of these functions can occur in competition within a given system. In the case of this work, models that incorporate the function of nanoparticles, metal sites on zeolites, and metal oxides were developed to investigate various catalyst structures.

While bulk gold is inherently inactive for catalytic processes, Haruta et al. pioneered the use of gold nanoparticles as a catalyst for oxidation of small molecules.^{14–16} With the surge of research following the initial discovery, gold nanoparticles have been shown to exhibit unique size dependence,^{16,17} electronic effects,¹⁸ and support interactions.^{19–21} Several other publications then showed that gold nanoparticles can serve as catalysts for alkane oxidation reactions.^{22–24} Despite the significant research interest, there is still uncertainty about the mechanisms of oxidation employing these gold nanoparticles. The main hypothesis is that small gold nanoparticles, below approximately 14 atoms, have the ability to activate oxygen and decompose hydroperoxide species.¹⁷ While the effect of size and density functional theory quantification of energetics are beyond the scope of this work, the mechanism of oxidation on gold nanoparticles will be elucidated via microkinetic modeling.

Another set of materials that are of significant interest as catalysts and catalytic supports are zeolites, a group of porous structures. Zeolites often contain metal or acid sites capable of performing catalysis and have pores that may be able to impart shape selectivity.²⁵⁻²⁷ In this work, an oxidation model will be adapted to account for reactions governed by Co/ZSM-5 as a catalyst. Cobalt sites of this type have long been known to perform decomposition of alkyl hydroperoxides.²⁸⁻³⁰ The microkinetic model will be used to determine the role of the Co sites within the Co/ZSM-5 zeolite catalyst.

More traditionally, metal sites and metal oxides are employed as oxidation catalysts.^{11,12} These metal catalysts are often hypothesized to perform direct oxidation of substrate molecules. The structure of the active site has been proposed to have an impact on the rate of reaction and selectivity of a given catalyst.^{31,32} The presence of multiple active sites for a given catalyst makes modeling of the catalytic processes more challenging but could provide more insight to the role of catalysts. The structure of the active site could play an even larger role when steric hindrance could impart regioselectivity on a given substrate. The final model developed in this work will examine the mechanism of oxidation on a Ti/SiO₂ catalyst with two different active sites.

1.2 Background for Microkinetic Modeling

As mentioned, the basis of this dissertation will be microkinetic modeling, an approach to modeling that incorporates postulated rate expressions based on elementary steps, mass action kinetics, and reactor design equations in order to predict resultant product distributions. This approach depends on the reliable postulation of many different elementary reaction steps that will comprise a subset of the total reaction space for a type of chemistry. When producing this subset

of reactions, the goal is to encompass all of the kinetically-relevant elementary steps by including all previously proposed reaction mechanisms and multiple pathways to experimentally observed products. The scale at which this study seeks to examine the complex oxidation networks necessitates an automated method for systematically formulating elementary steps. This work employed, adapted, and expanded a previously developed reaction network generation tool.^{33–37}

Within the network generation framework, bonds and atoms of a molecule are stored as connectivity matrices. When a reactive moiety is identified within a molecule, a reactant sub-matrix is isolated and modified using a reaction matrix. The groups of elementary steps that perform the same type of chemistry are referred to as reaction families and share a reaction matrix. After the reactant sub-matrix is acted upon by the reaction matrix, a product sub-matrix is formed, and the product species are created if it is a unique reaction. An example of this process can be seen in Figure 1.1.

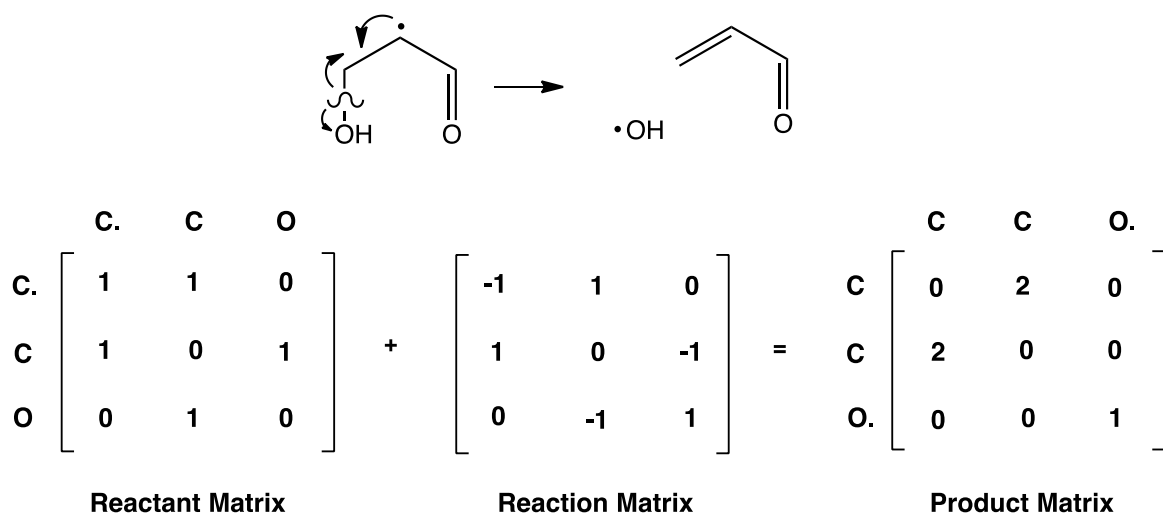


Figure 1.1: Example of a single β -scission step in the automated network generation process.

Following reaction network generation, a rate coefficient must be obtained for each of the elementary reaction steps. Each rate coefficient is assumed to be in the Arrhenius form, $k = A \exp(-E_A/RT)$, where A is the Arrhenius pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the temperature.³⁸ The Arrhenius pre-exponential factor is based on transition state theory and encapsulates the entropic contribution to the rate coefficient. Since each of the reactions within a given family should have approximately the same entropic change to the transition state, reaction families are assumed to have a common Arrhenius pre-exponential factor. When literature values are not available for a reaction activation barrier, the activation barrier may be estimated from the Evans-Polanyi relationship: $E_A = E_A^\circ + \alpha \Delta H_{rxn}$ where α and E_A° are constants for each reaction family and ΔH_{rxn} is the enthalpy of reaction for a specific reaction in the family.³⁹ In order to tabulate the enthalpy of reaction for all elementary steps, Benson's group additivity method, which states that each heavy atom center contributes the same amount to enthalpy of formation independent of the molecule the atom center is in, is employed.⁴⁰ The specific reaction families and the corresponding parameters employed by each network generation step for the individual models will be noted in each chapter.

With the rate coefficients tabulated, rate expressions based on mass action kinetics are compiled for all of the species within a model. The rate expressions are paired with the appropriate reactor design equation, and in the case of batch reactor or plug flow reactor, the balance equations are integrated to predict output product concentrations.⁴¹ Each of these predicted product distributions is validated by a set of experimental data, and parameter regression is often employed to refine the accuracy of the model. Regression is performed on the Arrhenius pre-exponential factors to account for changes in the phase from literature source to practical application and

deviations in the entropic contribution for a specific chemistry from the general case.⁴² A flowchart of this general procedure can be seen in Figure 1.2.

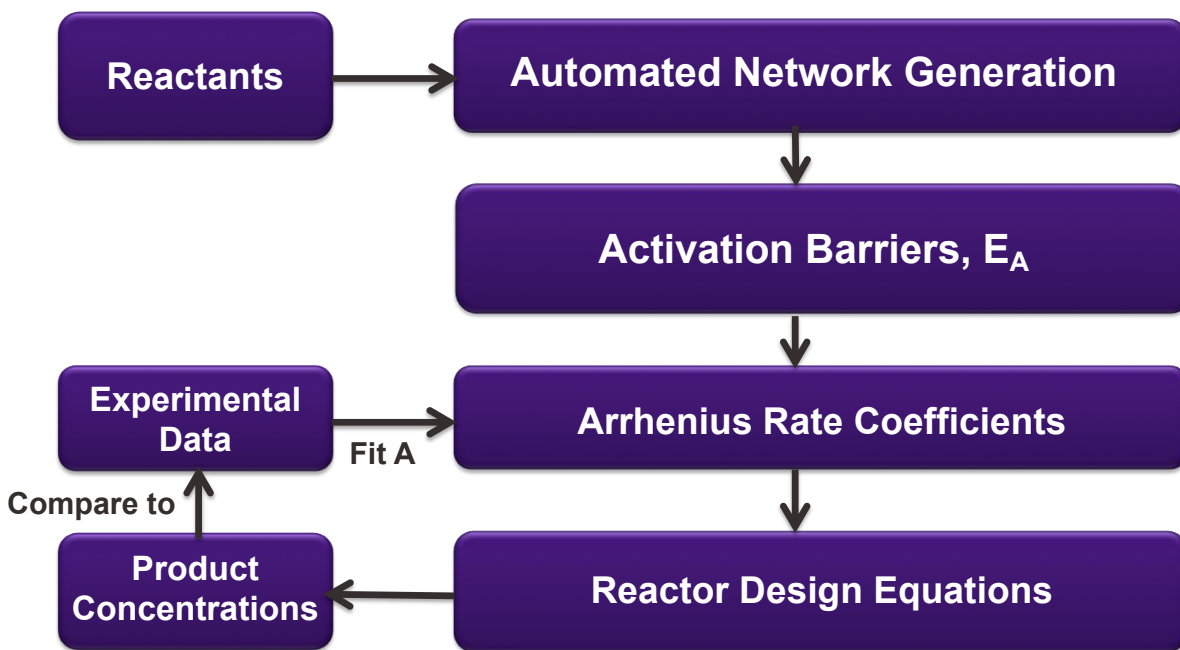


Figure 1.2: Flowchart for development and execution of a microkinetic model.

1.3 Outline of Research

In Chapter 2, a microkinetic model was developed to investigate uncatalyzed oxidation of 1,3-propanediol using molecular oxygen, which experimentally exhibited naturally high selectivity to acrolein. This work sought to compare and quantify the relative contributions of free-radical and concerted reaction mechanisms. The full mechanistic model tests the hypothesis of a free-radical mechanism that had been previously proposed, and this serves as evidence that postulated mechanisms without validation are not always accurate. The model revealed that for alcohol reactants a more complex concerted oxidation mechanism is more likely to capture the activity of the system.

The ensuing chapters detail the development of a free-radical microkinetic model for determination of the underlying chemistry occurring in the oxidation of alkenes and alkyl benzenes. For each case, different catalytic functionalities were added to the model in order to determine catalytic effects and expand our knowledge of the mechanisms of catalytic oxidation. Chapter 3 investigates cyclooctene oxidation using molecular oxygen catalyzed by gold nanoparticles. The oxidation of cyclooctene exhibits unique selectivity towards the epoxide product, cyclooctene oxide, compared to other cyclic alkenes. The model was able to determine that the high selectivity is a result of the preference for radical addition across substrate double bonds over hydrogen abstraction. Additionally, the gold nanoparticle catalysts were determined to be radical initiators through hydrogen abstraction by active superoxo gold species and decomposition of hydroperoxides.

Chapter 4 expands on the previous model to examine the mechanism of co-oxidation of ethylbenzene and cyclooctene catalyzed by Co/ZSM-5. Kinetic coupling of oxidation reactions represents an opportunity to catalyze a typically less active oxidation reaction without the use of extreme reaction conditions or expensive catalysts. This more complex model was able to capture the behavior of the two-substrate system at a variety of reaction mixture compositions. It was determined that the role of cyclooctene-derived radicals was to initiate the more stable ethylbenzene carbon-hydrogen bonds and abstract from 1-phenylethyl hydroperoxide to push selectivity towards acetophenone. The role of Co/ZSM-5 was predominantly to decompose 2-cycloocten-1-yl hydroperoxide, generating more radicals with the capability of initiating ethylbenzene and 1-phenylethyl hydroperoxide.

The model outlined in Chapter 5 examines the free radical and Ti/SiO₂-catalyzed oxidation of limonene. Limonene is an especially interesting molecule as it has two distinct double bonds, making it a candidate for determination of catalyst regioselectivity. The dual functionality of limonene leads to a comparably more complex model that accounts for greater than 2,000 species and 20,000 reactions. In addition, the model shows that Ti/SiO₂ catalyst is able to perform direct epoxidation and dominates the flux in the system. The model was able to investigate differences in catalyst activity between two proposed active sites.

Finally, Chapter 6 recaps the relevant conclusions from this work and proposes future directions. There is potential for the developed model to act as predictive tool to evaluate the improvement imparted by different catalysts and determine optimal reaction conditions for a given application.

Chapter 2: Mechanistic Modeling of the Partial Oxidation of 1,3-Propanediol

Material in this chapter is reproduced from the publication “Mechanistic modeling of the partial oxidation of 1,3-propanediol: Comparison of free-radical and concerted mechanisms” by Robert R.O. Brydon and Linda J. Broadbelt; *Ind Eng Chem Res*, **56** (23), 6599-6607.

2.1. Introduction

Partial oxidation processes are important to the chemical industry broadly, ranging in applications from fuels to polymers to pharmaceuticals. Ideally, oxidation can be carried out using molecular oxygen as a cheap and abundant oxidant and without the use of expensive or environmentally harmful catalysts, suggesting that an aerobic homogeneous process at low to moderate temperatures would be appealing. However, the relationship between conversion and selectivity towards partial oxidation products is typically inverse, limiting the yield of desired products.^{43–45}

There are examples of homogeneous oxidation processes where free-radical pathways are at play, but the temperature is typically elevated or radical initiators are added to ensure measurable rates of conversion.^{46,47} Examples of the homogeneous oxidation of various substrates include carbon monoxide,^{46,47} methane,^{47–49} and ethane.^{50,51} Unfortunately, radical intermediates, due to their high reactivity under these conditions, can undergo a variety of different reactions, often leading to low selectivity and an array of different products. While catalysts are a common strategy to lower reaction temperature or induce high product selectivity, it remains a challenge to design catalysts for the selective conversion of substrates and the concomitant use of molecular oxygen.^{52–}

With the recent surge of interest in biomass feedstocks and their products as platform chemicals,^{56–59} renewed attention has been focused on the low temperature partial oxidation of oxygenated hydrocarbons using homogenous chemistry involving oxygen as the oxidant. Both experimental^{46,50,51} and theoretical^{48,60,61} efforts have been put forth to study the conversion of oxygenates with varying degrees or types of oxygen functionalities. One example is the homogeneous aerobic oxidation of 1,3-propanediol investigated by Diaz et al.⁶² which is a counter-example to the typical diverse product spectrum observed for analogous systems. At 430 K, a conversion of 32.9% with 90% selectivity to acrolein with the balance going to formaldehyde, acetaldehyde, and carbon dioxide was achieved at a residence time of 18.6 s.⁶² The ~90% selectivity to acrolein is consistent at all tabulated conversions.⁶²

Radical mechanisms of low temperature oxidation are frequently invoked to rationalize observed product distributions and are a natural assumption for homogeneous conversion of hydrocarbons. However, recent work on biomass-derived intermediates reacted under homogeneous conditions suggests that concerted pathways are more likely for molecules containing oxygen functionality.^{63–66} Due to interactions of hydroxyl groups with neighboring oxygen atoms, reactions leading to high selectivities to particular reaction pathways have been mapped.⁶⁶

The work carried out here confronted the highly selective 1,3-propanediol experimental data of Diaz et al.⁶² with three possible reaction mechanisms: one based on free-radical reactions, another based on concerted chemistry, and finally one that was comprised of a combination of free-radical and concerted chemistry. The mechanisms were used in the formulation of mechanistic models with the rate parameters obtained from literature or, if not available, using parameter

estimation with reasonable bounds for the parameters known from theory or analogous reactions. The ability of the three competing mechanisms to capture quantitatively the yields of the major and minor products at different residence times was assessed.

2.2. Partial Oxidation Mechanisms

2.2.1 Radical-Mediated Pathways

The reaction mechanism based on free-radical chemistry was based on reaction families reported in the literature for oxidation chemistry. Primary initiation occurs via hydrogen abstraction from the substrate, 1,3-propanediol, by an oxygen molecule, forming an alkyl radical and a hydroperoxy radical.^{67,68} Initiation via bond fission of peroxide bonds formed in first rank and higher products was also included in the mechanism. Following initiation, propagation steps including oxygen addition, β -scission, and hydrogen transfer are possible.^{67,68} Termination of radical intermediates occurs via recombination and disproportionation reactions of radicals.⁶⁷ A full list of reaction families included and a prototypical example for each reaction family are provided in Table 2.1.

Table 2.1: List of reaction families included in the reaction mechanism for 1,3-propanediol conversion based on free-radical chemistry

Reaction Family	Example
<u>Initiation</u>	
Primary initiation	$\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HOO}\cdot$
Peroxy-bond fission	$\text{ROOR}' \rightarrow \text{RO}\cdot + \text{R}'\text{O}\cdot$
Hydroperoxide decomposition	$\text{RH} + \text{R}'\text{OOH} \rightarrow \text{R}\cdot + \text{R}'\text{O}\cdot + \text{H}_2\text{O}$
<u>Propagation</u>	
Oxygen addition	$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$
β -scission	$\cdot\text{ROOH} \rightarrow \text{R}=\text{O} + \cdot\text{OH}$
Oxygen-assisted β -scission	$\cdot\text{ROH} + \text{O}_2 \rightarrow \text{R}=\text{O} + \cdot\text{OOH}$
Hydrogen transfer	$\text{ROO}\cdot + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'\cdot$
<u>Termination</u>	
Disproportionation	$2 \text{ROO}\cdot \rightarrow \text{R}=\text{O} + \text{ROH} + \text{O}_2$
Recombination	$\text{R}\cdot + \text{R}'\cdot \rightarrow \text{RR}'$
<u>Concerted</u>	
Geminal diol dehydration	$\text{R}(\text{OH})(\text{OH}) \rightarrow \text{R}=\text{O} + \text{H}_2\text{O}$
Geminal peroxide-alcohol decomposition	$\text{R}(\text{OOH})(\text{OH}) \rightarrow \text{R}=\text{O} + \text{H}_2\text{O}$
Retro-Michael addition	$\text{R}-\text{R}'\text{OH} \rightarrow \text{R}=\text{R}' + \text{H}_2\text{O}$
Keto-enol isomerization	$\text{R}=\text{R}'\text{OH} \leftrightarrow \text{RR}'=\text{O}$

The reactions in Table 2.1 encompass all of the steps involving free radicals postulated by Diaz et al.⁶² to rationalize the observed product distribution. However, the authors also proposed

additional reactions to explain the degradation of unstable intermediates that would be classified as concerted reactions. Specifically, geminal diol dehydration and rapid degradation of 1-hydroxypropanal to acrolein via what Diaz et al. termed retro-Michael addition were postulated.⁶² An analogous geminal hydroperoxide-alcohol decomposition reaction with hydrogen peroxide as the leaving molecule was included in the model, as this moiety is hypothesized to be unstable as well. Enol to ketone isomerization was also included as the equilibrium relationship in this case would heavily favor the ketone.⁶⁹ While all observed products could be formed by only including free-radical reaction families, the types of rearrangements that were proposed to be facile by Diaz et al.⁶² were also included in the mechanistic model to investigate if these would play a significant role.

2.2.2 Concerted Pathways

Reaction families based on concerted chemistry were also derived from literature reports. Dehydrogenation and dehydration reactions involving cyclic transition states where bonds are formed and broken in concert with the release of an H₂ or H₂O molecule were included.^{70–73} These reactions were allowed to occur via unimolecular or assisted-bimolecular pathways.^{63,70,71} Unimolecular reactions occur via four-membered rings (Figure 2.1) leading to double bond formation and the release of H₂ or H₂O, while bimolecular reactions require a molecule with O-H functionality to aid in the reaction, forming a six-membered ring transition state (Figure 2.2). The molecule with the O-H group exchanges hydrogen atoms in the reaction but is regenerated to its original form, serving as a catalyst. The involvement of the second molecule in the reaction has been shown to lower activation enthalpy by up to 13 kcal/mol for dehydrogenation and up to 30

kcal/mol for dehydration.⁷¹ Whether the unimolecular and bimolecular routes are competitive will be a function of temperature and the concentration of the facilitating OH-containing species, which include the reactant, 1,3-propanediol, water, and any OH-containing products formed as a result of reaction.

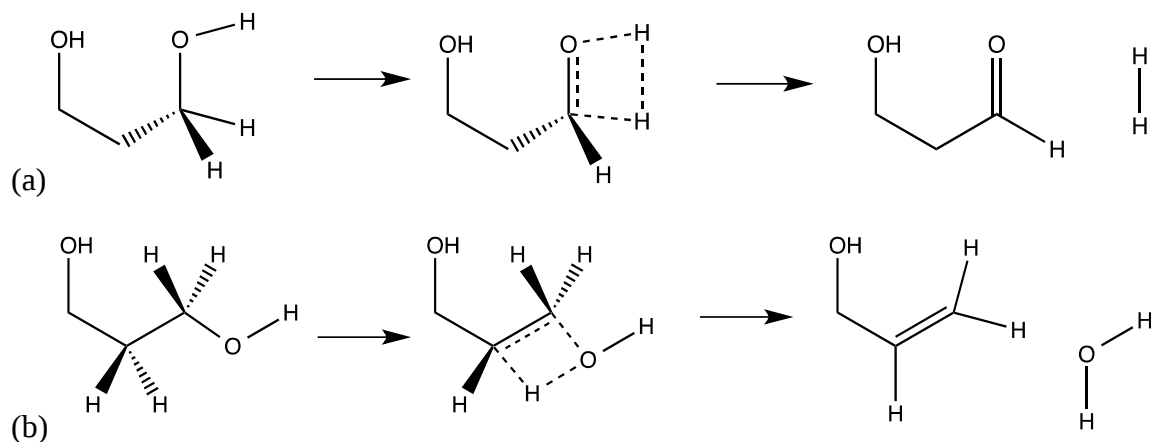


Figure 2.1: Unimolecular routes and their putative cyclic transition states for (a) dehydrogenation and (b) dehydration reactions of 1,3-propanediol. Adapted from the work of Westmoreland et al.^{70,71}

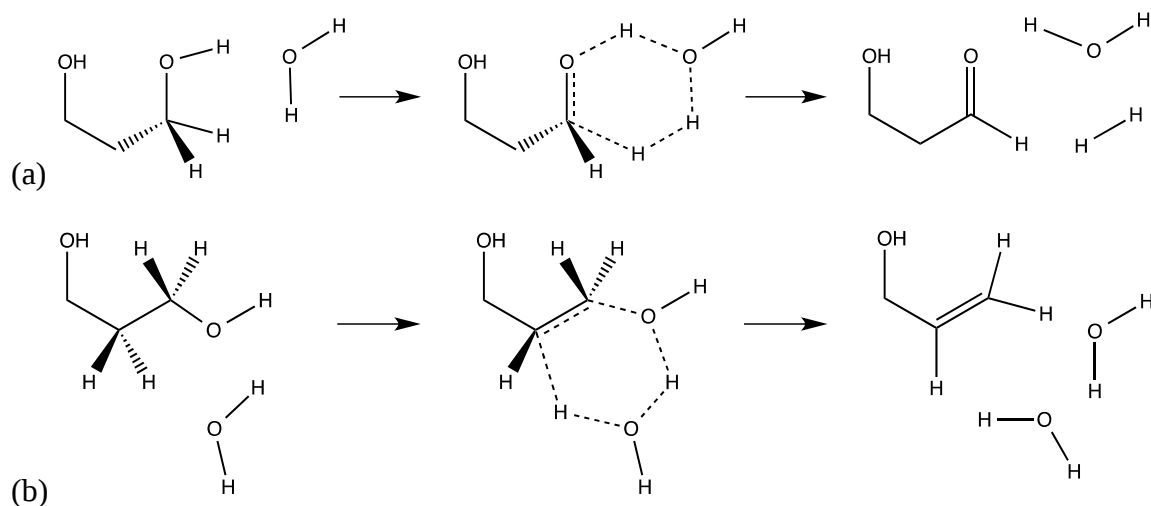


Figure 2.2: Bimolecular reactions facilitated by an OH-containing species (here shown as H₂O) and their putative cyclic transition states for (a) dehydrogenation and (b) dehydration reactions.

Adapted from the work of Westmoreland et al.^{70,71}

Literature sources propose two different schemes of C₃ decomposition to form the minor products formaldehyde and acetaldehyde. The first possibility is carbon-carbon bond breaking in the dehydrogenation product, 3-hydroxypropanal, by retro-aldol decomposition to form formaldehyde and acetaldehyde directly.^{63,74,75} Alternatively, 1,3-propanediol can decompose through cyclic Grob fragmentation to form ethylene, formaldehyde, and water.^{64,71} Each of these fragmentation pathways were considered in the concerted mechanism. Formaldehyde can then decompose further, in an O₂-rich environment, to form CO₂ and H₂.^{76,77}

2.3. Computational Methods

2.3.1 Mechanism Generation

To facilitate construction of the full reaction mechanism given the free-radical reaction families in Table 2.1, the NetGen program created by Broadbelt and coworkers was employed.^{33–}

³⁷ The NetGen structure takes input molecules, identifies reactive moieties, and creates products in accordance with the elementary reaction steps in Table 2.1. The implementation of the reaction families is subject to reaction rules, which limit the application of reaction families to certain structural moieties and combinations of reactants. In this work, reaction families were restricted to align with the product slate and degree of oxidation observed per the following reaction rules: formation of vinyl radicals was prevented, and oxygen addition may occur only once to a given carbon atom in a molecule. In addition, the generation of a mechanism for free-radical oxidation of 1,3-propanediol would be infinite if external termination criteria were not applied. To limit mechanism growth, termination criteria requiring reactants to contain fewer than four carbon atoms and be lower than rank two were imposed. The concerted reaction mechanism was sufficiently concise that it was constructed manually.

2.3.2 Kinetic Parameter Determination

To specify the rate coefficients for each reaction in the mechanism for either the free-radical or concerted chemistry, a combination of literature values was used either without adjustment or with perturbations determined by parameter regression within specified bounds. All rate coefficients were assumed to be of Arrhenius form: $k = A \exp(-E_A/RT)$, where A is the Arrhenius pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and

T is the temperature. The Arrhenius pre-exponential factors, derived from transition state theory, for the free-radical reactions were specified based on the reaction family approach, where a single value of A is assumed to hold for all reactions in the family. The assumption of a constant pre-exponential factor for all reactions in a given family is not perfect due to variations of the entropic contribution among specific reactions and allows for fitting over a narrow range of values. Values tabulated in the work of Pfaendtner et al.⁶⁷ and Khan et al.⁷⁸ were used in this work as the initial parameters. For the concerted reactions, values of the pre-exponential factors were constant and taken from the work of Zhou et al.⁶⁴, also following the reaction family approach. The initial values for all pre-exponential factors used in the free-radical mechanistic model are summarized in Table 2.2, and the values used in the concerted reaction model are summarized in Table 2.3.

Table 2.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the free-radical mechanistic model. All values were culled from the work of Pfaendtner et al.⁶⁷ except when noted.

Reaction Family	A [$\text{s}^{-1}/\text{M}^{-1} \text{s}^{-1}$]	E _A ⁰ [kcal/mol]	α
Primary initiation	10 ¹³	0	1
Peroxy bond fission	10 ¹⁵	0	1
Hydroperoxide decomposition	10 ⁶	24.6	-0.09
Oxygen addition	10 ⁸	0	0
β -scission by alkoxy radical	10 ¹⁴	9.5	0.85
β -scission by carbon-centered radical	10 ¹⁴	14.24	0.76
Oxygen-assisted β -scission ^a	10 ¹⁰	14.45	0.7
Hydrogen transfer alkoxy radical from alkane	10 ⁷	11.9	0.91
Hydrogen transfer alkylperoxy radical from alkane	10 ⁷	3.05	1.1
Disproportionation	10 ⁶	0	0
Recombination	10 ⁸	0.85	0
Geminal diol dehydration ^b	10 ¹⁵	0	0
Geminal peroxide-alcohol decomposition ^b	10 ¹⁵	0	0
Retro-Michael addition ^b	10 ¹⁵	0	0
Keto-enol isomerization ^b	10 ¹⁵	0	0

^aValues for this reaction from the work of Khan et al.⁷⁸

^bValues for the denoted facile reactions were set at sufficiently high values to approximate rapid rearrangements.

Table 2.3: List of Arrhenius pre-exponential factors and Evans-Polanyi parameters used for each reaction family in the mechanistic model based on concerted reactions. The activation energy values shown for dehydration and dehydrogenation are for reaction 1 and reaction 2, respectively, in Figure 2.4, while the activation energies for the other reactions in these two families are calculated using the corresponding α and Δ (ΔH_{rxn}) values.

Reaction Family	A [$s^{-1}/M^{-1} s^{-1}$]	α	E _A [kcal/mol]	
Dehydration	2×10^{15}	1.4	37.9 ^a	32.9 ^b
Dehydrogenation	1.5×10^{13}	1.2	30.1 ^a	23.7 ^b
Retro-aldol condensation ⁶³	1×10^{12}	-	30.9	
Cyclic Grob fragmentation	1.5×10^{15}	-	52.5	
Formaldehyde decomposition ⁷⁶	2×10^{13}	-	28.2	
CO ₂ formation ⁷⁷	2.5×10^9	-	47.1	

^aValue for unimolecular dehydration and dehydrogenation reactions of 1,3-propanediol obtained from parameter fitting.

^bValue for bimolecular dehydration and dehydrogenation reactions of 1,3-propanediol obtained from parameter fitting.

To calculate the values of the activation energies when they were not available in the literature, structure-reactivity relationships were used for the free-radical reactions, one for each reaction family. Evans-Polanyi relationships, where there is a linear relationship between activation energy and enthalpy of reaction, were used: $E_A = E_A^\circ + \alpha \Delta H_{rxn}$ where α and E_A° are constants for each reaction family and ΔH_{rxn} is the enthalpy of reaction for a specific reaction in the family.³⁹ The enthalpies of reaction were calculated from the enthalpies of formation for the reactants and products, which were calculated using Benson's group additivity method.⁴⁰ The values of E_A° and α for each radical reaction family are summarized in Table 2.2.

For the concerted reaction families, there were no Evans-Polanyi relationships available, but the Evans-Polanyi approach still applied. For one reaction in each family, E_A was a fitted

parameter, and the activation energies of the other reactions in the same family were related through $\Delta E_A = \alpha \Delta(\Delta H_{rxn})$. The value of α for dehydration was obtained by fitting an Evans-Polanyi relationship based on activation enthalpy values for reactions in the work of Zhou et al.⁶⁴ and the dehydration reactions of methanol, ethanol, 1-propanol, and 2-propanol as reported in the work of Westmoreland et al.^{70,71} For dehydrogenation reactions, the only available data set for creation of an Evans-Polanyi relationship came from Westmoreland et al.^{70,71} The resultant values for α are shown in Table 2.3, and the associated regressions can be seen in Appendix 1. Frequency factors and activation energies for retro-aldol condensation,⁶³ cyclic Grob fragmentation,⁶⁴ formaldehyde decomposition,⁷⁶ and CO₂ formation⁷⁷ were fixed at values taken from literature. Overall, this approach resulted in four adjustable parameters: the E_A values for dehydrogenation and dehydration reactions of 1,3-propanediol for both the unimolecular and bimolecular cases, with the E_A values for the bimolecular reactions constrained to be lower than the corresponding unimolecular reaction within the bounds set by literature reports. Parameter estimation was used to regress the model results against the experimental data for conversion and product yields at all five residence times that were experimentally reported.

2.3.3 Mechanistic Modeling

For each mechanism, rate equations were formulated based on elementary rate laws and mass action kinetics. The rate equations were then coupled with design equations for a plug-flow reactor. To model the conditions studied experimentally by Diaz et al.⁶², the following quantities were specified: 430 K, 0.28 kPa 1,3-propanediol and 0.89 kPa O₂ at the inlet, He diluent added bringing the total pressure to ambient pressure, and a reactor volume of 9 mL. The design equations

were numerically integrated using DASSLSO⁷⁹ to a set of final residence times corresponding to data points in the work of Diaz et al.⁶² allowing for direct comparison of the quantified product yields. The model results were then compared to the experimental values based on the reactant conversion and product selectivity to acrolein, acetaldehyde, formaldehyde, and CO₂.

2.4. Results and Discussion

2.4.1 Free-Radical Mechanism

The reaction mechanism that was generated based on free-radical chemistry was composed of 6,223 unique forward reactions and 195 species. Figure 2.3 shows the predominant pathways comprising the mechanistic model based on elementary steps involving free radicals. The two major pathways share an initiation step (Reaction 1), which involves hydrogen abstraction from either one of the α -carbon atoms of the two hydroxyl groups by O₂. The α -carbon radical then primarily reacts via one of two reactions: oxygen-assisted β -scission breaking an oxygen-hydrogen bond (Reaction 2) or addition of O₂ (Reaction 4). The oxygen-assisted β -scission product, 3-hydroxypropanal, will undergo a facile reaction characterized as retro-Michael addition (Reaction 3) by Diaz et al.¹ to form acrolein. The oxygen addition product, a peroxy radical, is then allowed to abstract hydrogen from any hydrogen-containing substrate (Reaction 5). The product of peroxy-radical hydrogen abstraction is allowed to undergo a number of different reactions including peroxy-bond fission and hydroperoxide decomposition but will only rapidly decompose to 3-hydroxypropanal (Reaction 6). The lack of a kinetically competitive carbon-carbon bond breaking reaction versus the oxygen-assisted β -scission reaction, shown as Reaction 2, precludes the formation of the experimentally observed minor products.

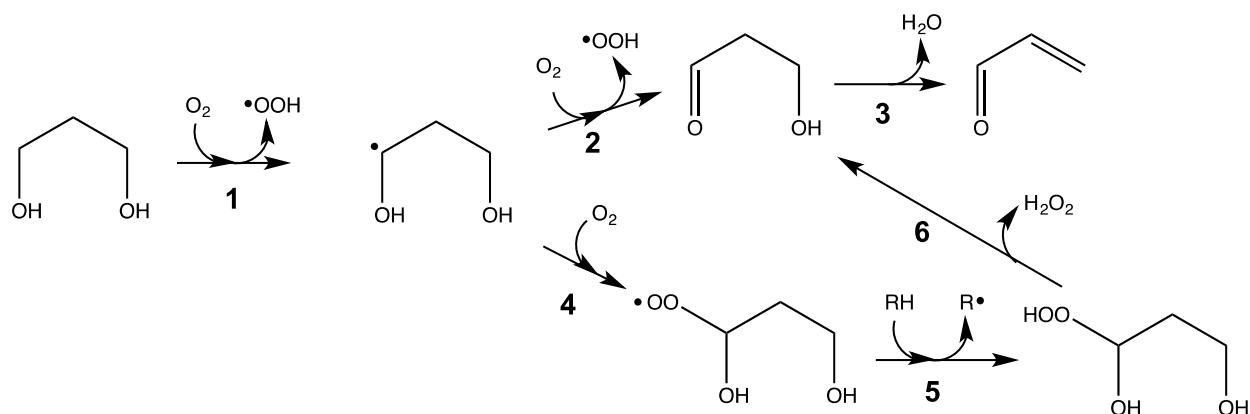


Figure 2.3: Dominant pathways leading to acrolein for the free-radical mechanism.

While the pathways are in agreement with the routes hypothesized by Diaz et al.⁶² involving free-radical chemistry, the mechanistic model results are not able to rationalize the high conversion or selectivity to minor products seen in the experimental results of Diaz et al.⁶² The conversion and selectivity data is summarized in Table 2.4, with insignificant selectivity to the minor products that were experimentally observed. The model predicts that the conversion is negligible; at 430 K, the initiation step, with a constant rate of 8.4×10^{-17} M/s for space times from 0.01 s to 18.6 s, does not create a sufficient concentration of radicals to effectively start consumption of the substrate via chain propagation. It is also important to note that when the pre-exponential factor for initiation was increased to a value outside its theoretical upper limit, effectively mimicking an unknown initiation mechanism (e.g., wall effects, contaminant, etc.), conversion still does not reach a significant value, as there is insufficient chemistry to extend the free-radical chain to high kinetic chain lengths.

Table 2.4: Comparison of experimental conversion and product selectivity values to the microkinetic model results based on a free-radical mechanism.

			Selectivity [%]			
Data Set		Conversion [%]	Acrolein	Acetaldehyde	Formaldehyde	CO ₂
τ =11.9 s	Exp.	23.1	91	6.8	2.0	0.2
	Model	8 x 10 ⁻⁸	98	0	0	0
τ =18.6 s	Exp.	32.9	90	6.0	1.8	2.0
	Model	1 x 10 ⁻⁷	98	0	0	0

2.4.2 Concerted Mechanism

The network created for the concerted mechanism through dehydrogenation and dehydration reactions that were postulated to be major reaction types is comparatively simple. The complete network (Figure 2.4) includes nine reactions and 13 species. Both pathways to acrolein involve one dehydrogenation and one dehydration step, with the order reversed between the two pathways. As discussed in Section 2.3.2, the activation energies of the first dehydration (Reaction 1) and dehydrogenation (Reaction 2) reactions of 1,3-propanediol were fit against experimental data with the model containing both unimolecular and bimolecular reactions. The ability of the model based on concerted chemistry to capture the experimental data is shown in the parity plot in Figure 2.5, and the resultant activation energies for each reaction are shown in Table 2.5.

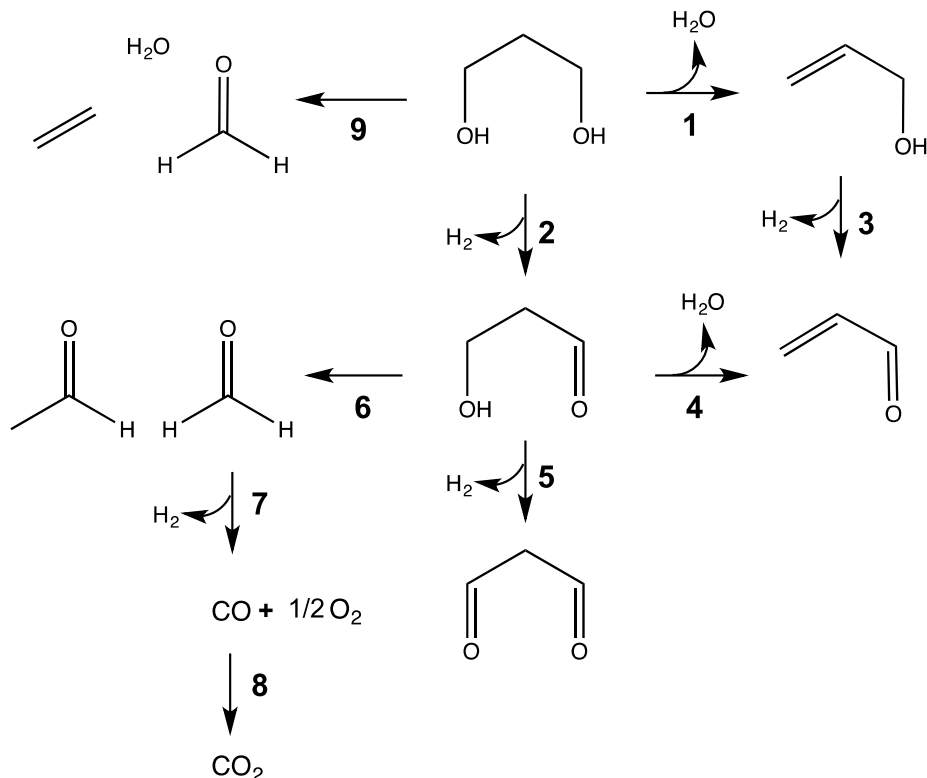


Figure 2.4: Postulated mechanism for the conversion of 1,3-propanediol involving concerted reactions via the cyclic structures depicted in Figures 2.1 and 2.2.

The results shown in Figure 2.5 and the parameter values tallied in Table 2.5 suggest that concerted pathways are a more viable candidate compared to free-radical reactions as the dominant route for conversion of 1,3-propanediol and the high selectivity to acrolein at low temperature. The values for the activation energies for the unimolecular and bimolecular dehydration reactions are in line with the values from the computational work of Zhou et al.⁶⁴ and reports by others⁶³ for analogous dehydration reactions, and net rate analysis reveals that both unimolecular and bimolecular pathways contribute to the observed chemistry. It is also consistent with related literature that the lowering of the activation energy due to the OH-containing catalyst in the bimolecular reaction compared to the unimolecular case is no greater than 7 kcal/mol, consistent

with literature values reporting decreases as much as 7 kcal/mol for a dehydration reaction.⁶³ While the unimolecular reaction rates are consistently about an order of magnitude faster than their bimolecular counterparts, it is noted that there was a degree of correlation between pairs of fitted parameters, revealing that if the bimolecular pathways were allowed to have a broader range of deviation from their unimolecular counterparts, then their rates could have been more competitive in the final net rate analysis. This observation provides inspiration for future studies focusing on experimental characterization of intermediates or quantum chemical studies outside the scope of this research that could be used to conclusively determine in what proportion each concerted mechanism should be invoked.

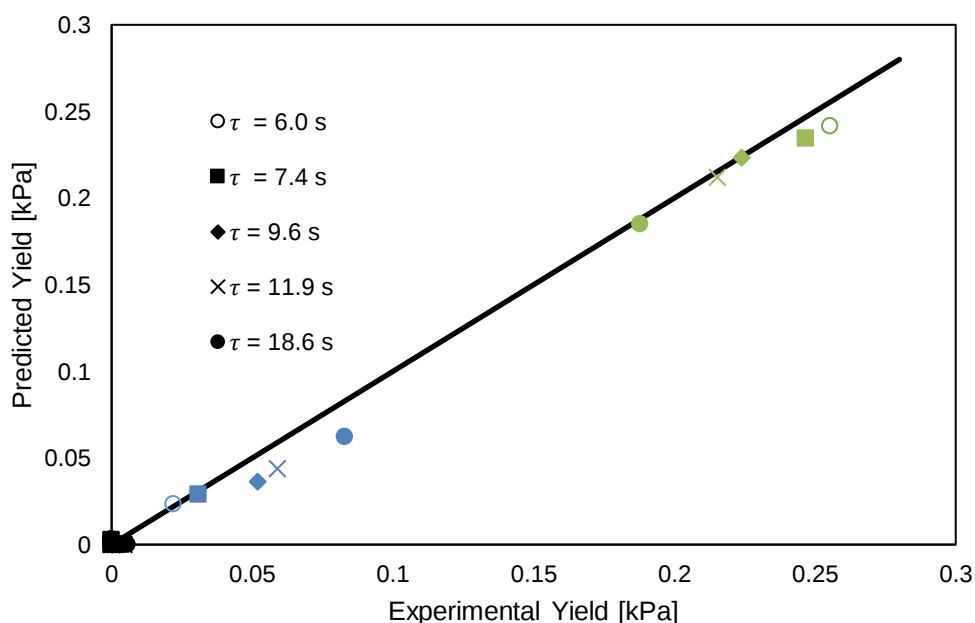


Figure 2.5: Results of the model based on concerted reactions shown in Figure 2.4 compared to experimental data at various residence times. Green markers represent outlet partial pressures of 1,3-propanediol, blue markers represent outlet partial pressures of acrolein, and black markers correspond to concentrations of acetaldehyde, formaldehyde, or CO₂.

Table 2.5: Activation energies of reactions in concerted mechanism with reaction numbers corresponding to the reactions shown in Figure 2.4.

Reaction	Activation Barriers	
	Unimolecular E_A [kcal/mol]	Bimolecular E_A [kcal/mol]
1	37.9	32.9
2	30.1	23.7
3	23.5	17.1
4	29.7	24.7
5	46.4	40.0
6	30.9	
7	28.2	
8	47.1	
9	52.5	

It is noteworthy that the model predicts that the rate of dehydrogenation of 1,3-propanediol is about two orders of magnitude faster than dehydration with values of 7.0×10^{-7} M/s and 8.8×10^{-9} M/s at a space time of 0.01 s, respectively. This is consistent with the hypothesis from Diaz et al.⁶² that 1-hydroxypropanal is the main intermediate that can then undergo rapid dehydration to form acrolein. However, the concerted model has a notable shortcoming. The activation energy values for dehydrogenation deviate significantly from the values for activation enthalpy in the work of Westmoreland et al.⁷⁰ that were used for the development of the Evans-Polanyi correlation employed in this work (shown in Appendix 1). Further quantum mechanical calculations would be needed to fully investigate the dependence of the barrier of concerted dehydrogenation on structure, but it is unlikely that structure would have such a dramatic effect on lowering the activation energies for concerted dehydrogenation so significantly. Another shortcoming of the concerted mechanism is its inability to incorporate any dependence of O_2 on the formation of

acrolein, which is observed in the experimental data. In the concerted mechanism, the role of O₂ is solely contained in carbon monoxide oxidation. The experimental work of Diaz et al.⁶² included an investigation of the dependence of the rate of formation of acrolein on O₂ pressure. While reaction orders derived from exit concentrations need to be carefully rationalized due to changes in the pressure of various components as a function of space time and induction periods that are characteristic of homogeneous oxidation chemistry, the formation rate of acrolein was shown to be weakly dependent on the O₂ pressure, hypothesized to be 1/2 order, and strongly dependent on 1,3-propanediol pressure, put forth as 3/2 order.

2.4.3 Combined Free-Radical and Concerted Mechanism

To address the shortcomings of the free-radical model and the concerted model, a combined model was formulated, consisting of both free-radical pathways and concerted routes. Because it was shown that the concerted dehydrogenation reactions did not carry significant reaction flux unless the activation barriers were reduced to physically unreasonable values, these reactions were removed from the combined model. Limited parameter estimation was carried out, primarily focusing on the effect of the pre-exponential factor for initiation.

The resultant model is able to capture the conversion of the reactant and the selectivities to the products with significant contributions from both the free-radical and concerted chemistries. Figure 2.6 shows the dominant pathway to acrolein, which involves both concerted reactions and free-radical steps, with a key dehydration reaction of 1,3-propanediol leading to a more labile intermediate containing allylic hydrogens that can be readily initiated. Figure 2.7 provides a parity plot showing the agreement of the model results with the experimental data, revealing a better

overall fit than that shown in Figure 2.5 for concerted chemistry alone, even when the activation energy for dehydrogenation in that model was allowed to go well below a reasonable bound set by theoretical calculations. The rate of initiation of the dehydration product of 1,3-propanediol (Reaction 2) is 2×10^{-7} M/s at a residence time of 0.01 s, which is faster than the rate of initiation of 1,3-propanediol by 4 orders of magnitude, showing that the concerted chemistry aids the conversion of the reactant and leads to a species that is more labile for radical-based pathways, allowing for the formation of radicals in the system. However, it is important to note that the fitting of parameters leading to the agreement shown in Figure 2.7 did lead to a frequency factor for initiation that was unreasonably high, i.e., three orders of magnitude higher than its initial value. Thus, while the agreement is clearly improved and captures all of the major features of the reaction, this does suggest that there is still some extrinsic factor (e.g., wall effects, contamination, etc.) that is not accounted for in the model. However, as noted above, a model based on exclusively free-radical reactions was still not able to capture the experimental data, even with the increased pre-exponential factor for initiation, as the conversion was still almost negligible, only 0.05 % at a residence time of 18.6 s. This supports the conjecture that the first dehydration step is crucial to enhancing the radical-based portions of the combined mechanism and that a model that combines concerted and free-radical chemistry is serviceable.

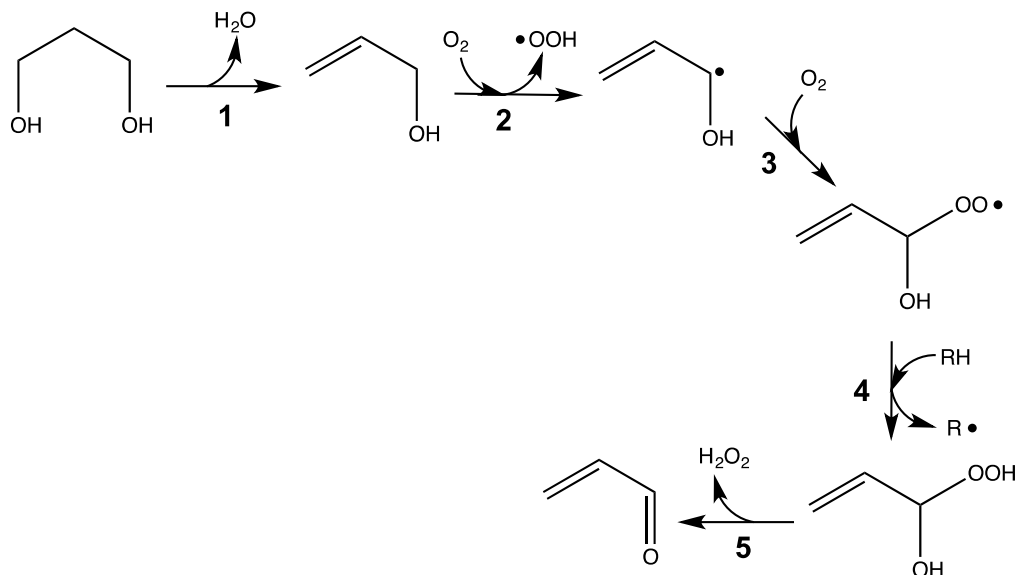


Figure 2.6: Dominant pathway to acrolein in the combined free-radical and concerted mechanism

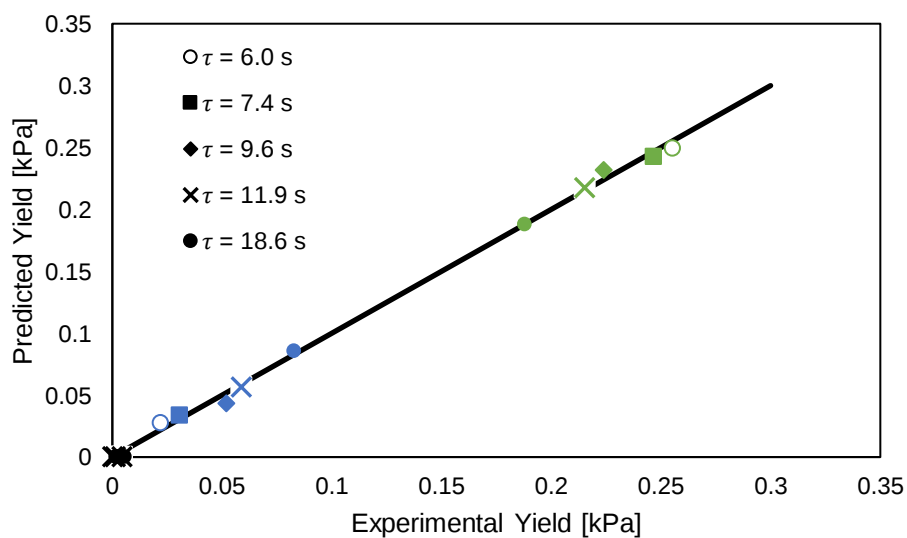


Figure 2.7: Results of the model based on a combined reaction mechanism compared to experimental data at various residence times. Green markers represent outlet partial pressures of 1,3-propanediol, blue markers represent outlet partial pressures of acrolein, and black markers correspond to concentrations of acetaldehyde, formaldehyde, or CO_2 .

To further explore the performance of the combined mechanism, simulations were carried out in which the initial pressures of the reactants (1,3-propanediol and O₂) were varied. For the rate of formation of acrolein, the resultant reaction orders were roughly 3/2 for 1,3-propanediol and 1/4 for O₂, consistent with the values reported experimentally, albeit a direct comparison may not be possible given that the reaction orders are highly variable depending whether the induction period is incorporated, or overall rates of formation based on the yields of the products at the outlet are used. Overall, the combined mechanism is promising in its ability to reflect all facets of the experimental data reported, but future investigation on the contributions of enhanced initiation rates leading to the formation of radicals is warranted.

2.5. Conclusions

A mechanistic model based on free-radical chemistry alone was unable to justify the conversion and selectivity data that was experimentally observed, revealing that for low-temperature partial oxidation of 1,3-propanediol, radical-mediated pathways in isolation are negligible. In contrast, a model formulated based on concerted dehydrogenation and dehydration reactions, considering both unimolecular and bimolecular reactions assisted by OH-containing species, could achieve the experimental activity, but when the activation energies for dehydrogenation reactions were allowed to be lowered to values substantially lower than the range predicted by theory. In addition, the concerted mechanism only incorporated O₂ in the reaction leading to carbon monoxide. These observations suggested that a combined mechanism based on both free-radical and concerted reactions without a direct dehydrogenation pathway was viable. The concerted dehydration of 1,3-propanediol allows for more facile initiation of the radical chain

reactions. The combined mechanism was able to capture the experimental trends more effectively than either of the individual models, albeit with an initiation pre-exponential factor that is higher than that suggested by theory. This suggests that future experimental comparisons in which external initiators are added or different substrates that would not lead to the formation of sites for allylic abstraction could be very enlightening.

Chapter 3: Microkinetic Modeling of Homogeneous and Gold Nanoparticle-Catalyzed Oxidation of Cyclooctene

Material in this chapter is reproduced from the publication “Microkinetic modeling of homogeneous and gold nanoparticle-catalyzed oxidation of cyclooctene” by Robert R.O. Brydon, Anyang Peng, Linping Qian, Harold H. Kung, and Linda J. Broadbelt; *Ind Eng Chem Res*, **57** (14), 4832-4840.

3.1. Introduction

Oxidation is an important chemical process in many far-ranging industries. Specifically, epoxidation processes are employed in the production of paints, plasticizers, curing agents, and many more commercial products.⁸⁰ Ethylene oxide and propylene oxide are the most widely produced epoxides in industry, with processes relying on heterogeneous catalysts and running at low conversion.⁸¹ Ideally, an oxidation catalyst would selectively generate epoxide even when extended to high conversion. One reaction process that has shown inherent selectivity to the epoxide product is the oxidation of *cis*-cyclooctene. The *cis* conformation of cyclooctene is the lowest energy conformer and will be referred to henceforth as cyclooctene.⁸² In this work, cyclooctene oxidation is used as a probe reaction to investigate the radical mechanism that gives rise to the high epoxide selectivity.

Recent work from Qian et al.⁸³ has shown the potential of gold nanoparticles (AuNPs) formed from gold salt precursors to catalyze oxidation of cyclooctene without greatly affecting the selectivity. AuNPs are not postulated to participate actively in direct epoxidation, but rather only serve as a promoter of initiation of radicals via two distinct mechanisms.^{84–86} Overall, this work seeks to explain the underlying homogeneous mechanism of cyclooctene oxidation and the effect

of AuNP catalysis through microkinetic modeling results compared quantitatively to experimental data.

3.1.1 Cyclooctene Oxidation

Cyclooctene oxidation has shown high selectivity to epoxide under a number of different reaction conditions. In work from Mahajan et al.,⁸⁰ cyclooctene homogeneous oxidation using O₂ was shown to exhibit high selectivity to the epoxide, consistently above 80 %, at conversions up to 26 %. A separate study from Alshammari et al.⁸⁷ using tert-butyl hydroperoxide as a radical initiator revealed that cyclooctene had over 65 % selectivity to epoxide at 0.2 % conversion after 24 h at 363 K. While cyclooctene has high selectivity to epoxide, cyclic alkenes of different ring sizes preferentially form hydroperoxide, alcohol, and ketone products.^{87,88} This work sought to employ a radical initiator, tert-butyl hydroperoxide, and O₂ at a constant concentration to drive the conversion and observe the resultant behavior of the system.

The mechanism that gives rise to the uniquely high selectivity for cyclooctene epoxide has been investigated previously using computational approaches. A density functional theory study showed that a peroxy or alkoxy radical prefers to add across the double bond of cyclooctene rather than abstract hydrogen, which was postulated to be due to the poor overlap between the σ_{C-H} and $\pi_{C=C}$ orbitals.⁸⁹ These addition steps give rise to peroxy,^{89,90} ROOR'•, or ether bond,^{87,21} ROR'•, intermediates that can then undergo cyclic epoxidation reactions. Both of the addition steps involving peroxy or alkoxy radicals have been proposed individually and purported to have similar energetics, but they have not been tested simultaneously against experimental data quantitatively. The participation of two facile epoxidation reactions could contribute to the high selectivity observed. It is hypothesized that the less competitive reaction of hydrogen abstraction by the

peroxy and alkoxy radicals gives rise to the formation of the minor products. This overall scheme can be seen in Figure 3.1. A microkinetic model was used to determine the relative rates of radical addition and hydrogen abstraction reactions that rationalized the conversion and selectivity to products that were observed experimentally.

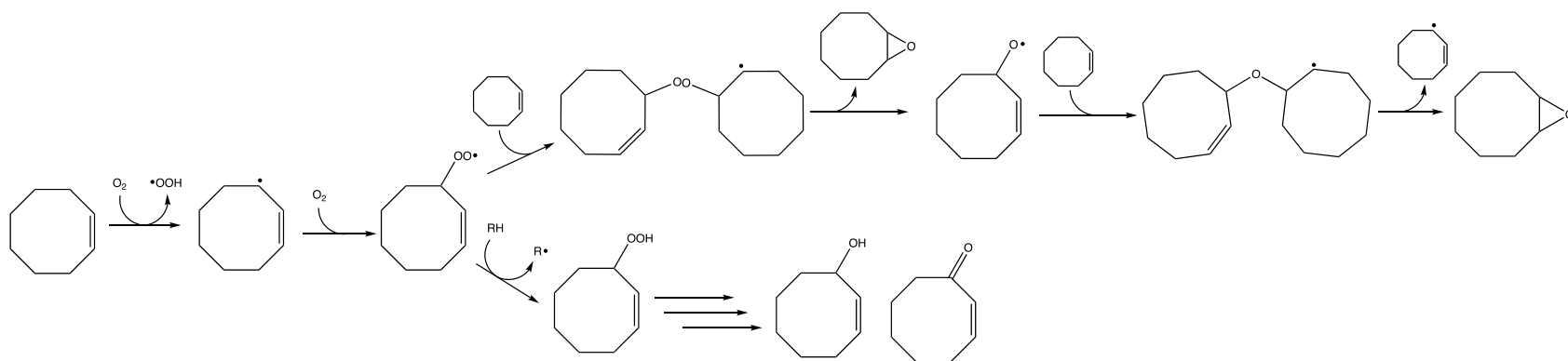


Figure 3.1: Reaction scheme for key reactions leading to oxidation of cyclooctene with the competition between the two branches shown dictating the selectivity to epoxide and alcohol/ketone.

3.1.2 Gold Nanoparticle Catalysis

Bulk gold is not typically reactive, exhibiting very low activity for catalysis unless augmented by a support^{91,19} or a high concentration of Au sites with low coordination.^{92–94} The work of Haruta et al.¹⁴ inspired an increase in the investigation of AuNPs due to their unique size-dependent catalysis,^{16,17} electronic effects,¹⁸ and support interactions.^{21,19,20} An interesting application of AuNPs is catalysis of oxidation reactions. The potential for catalysis is highly dependent on the size of Au clusters and on the support.^{91,95–97} Typically, small AuNPs with sufficiently low coordination number have shown the greatest potential to interact with O₂ and catalyze oxidation systems.¹⁷

Literature sources have suggested that the function of small AuNPs in oxidation reactions is to catalyze radical initiation.^{84,86} Two possible radical initiation mechanisms catalyzed by AuNPs are shown in Figure 3.2. Figure 3.2a shows a cycle where an oxygen atom adsorbs to a small AuNP to form a superoxo species on gold. The viability of superoxo species on AuNPs has been suggested in the literature based on density functional theory calculations using clusters as small as 4 atoms and up to 14 atoms.¹⁷ The superoxo gold species act as a radical that can abstract hydrogen from substrates and initiate radical oxidation; this role as a radical initiator has also been proposed for superoxo Co⁹⁰ and Cu species.^{98,99} The resultant hydroperoxide bound to gold is not active in catalysis, but it is proposed that it dissociates to regenerate the bare AuNP and form a hydroperoxy radical.

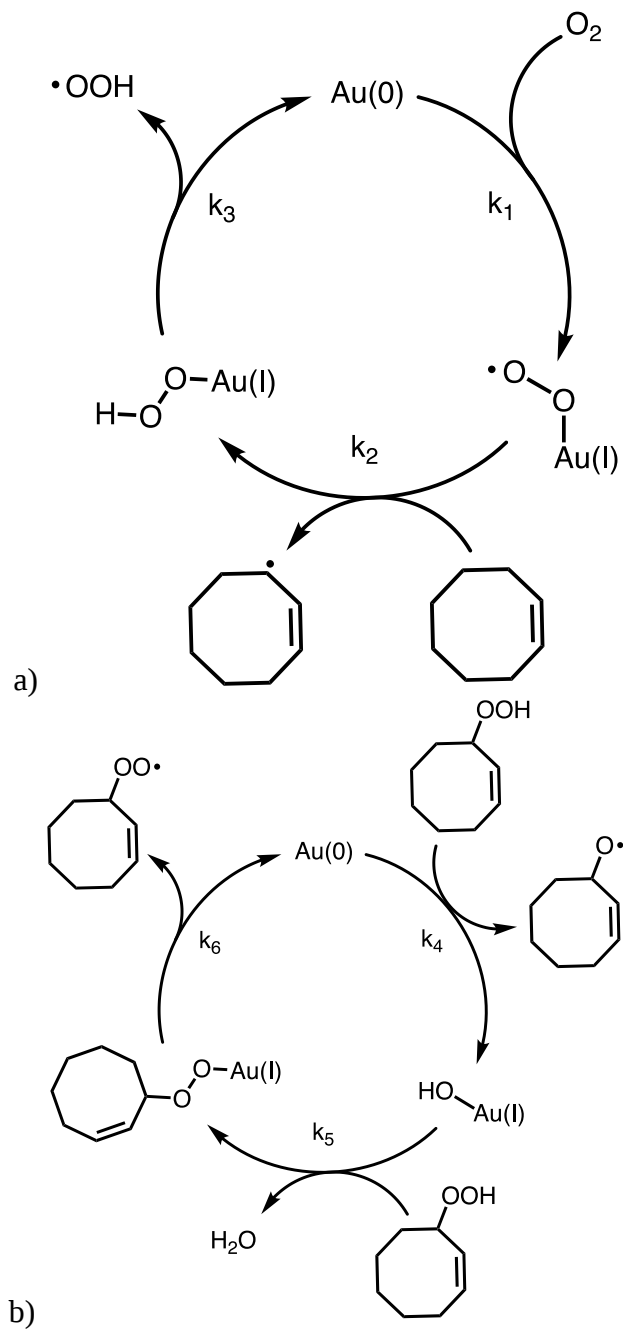


Figure 3.2: Catalytic mechanisms of radical initiation by gold: a) hydrogen abstraction by a gold superoxo species and b) hydroperoxide decomposition by gold species.

The second function of AuNPs in oxidation is hypothesized to be the activation of hydroperoxide species via the mechanism shown in Figure 3.2b.^{85,20} This scheme was inspired by radical Fenton chemistry that was proposed by Spier et al.¹⁰⁰ in work investigating hydroperoxide decomposition on Co(II). The first step is the fission of the peroxy bond by the AuNP, releasing an alkoxy radical and forming a bond between the AuNP and hydroxyl group. Another equivalent of hydroperoxide can interact with AuOH, releasing water and forming an AuOOR species. The alkylperoxy species comprising AuOOR can desorb from the Au nanoparticle to form a peroxy radical and regenerate AuNP.

The goal of the present study is to use microkinetic modeling to evaluate the relative contributions of these two functions in the oxidation of cyclooctene by comparison of net rate analyses with experimental data. To date, there has been no evidence that AuNPs interacting with O₂ will perform a direct epoxidation reaction, so only the mechanisms of radical initiation by AuNPs will be considered.

3.2. Methods

3.2.1 Computational Methods

3.2.1.1 Mechanism Generation

The first step for development of the microkinetic model was application of automated mechanism generation to delineate the elementary reaction steps based on postulated reaction families. This work employed NetGen, software developed by Broadbelt et al.^{33–37} In this application of NetGen, reaction families involving typical elementary steps for oxidation were used and applied to the moieties comprising the input reactants and their progeny. A complete list

of the elementary reaction families for the oxidation system used in this work can be found in Table 3.1. To maintain a manageable model size and eliminate reactions that are not kinetically favorable, the following set of reaction rules was applied to each of the families: vinyl radicals were not allowed to form and oxygen may only add to the same molecule once to prevent over-oxidation. In addition, the generation process is infinite without the application of termination criteria due to chemistries leading to high molecular weight species. The termination criteria used in this case were that reactants must contain 16 carbon atoms or fewer and be no more than first rank, leading to second rank products as those with the highest rank.

Table 3.1: List of reaction families included in the reaction mechanism for cyclooctene oxidation based on free-radical chemistry. R, R', and R'' represent alkyl/alkoxy groups or hydrogens, and R>O represents an epoxide.

Reaction Family	Example
<u>Initiation</u>	
Primary initiation	$\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HOO}\cdot$
Peroxy-bond fission	$\text{ROOR}' \rightarrow \text{RO}\cdot + \text{R}'\text{O}\cdot$
Hydroperoxide decomposition	$\text{RH} + \text{R}'\text{OOH} \rightarrow \text{R}\cdot + \text{R}'\text{O}\cdot + \text{H}_2\text{O}$
<u>Propagation</u>	
Oxygen addition	$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$
β -scission	$\cdot\text{ROOH} \rightarrow \text{R}=\text{O} + \cdot\text{OH}$
Hydrogen transfer	$\text{ROO}\cdot + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'\cdot$ $\text{RO}\cdot + \text{R}'\text{H} \rightarrow \text{ROH} + \text{R}'\cdot$ $\text{R}\cdot + \text{R}'\text{H} \rightarrow \text{RH} + \text{R}'\cdot$
Addition	$\text{ROO}\cdot + \text{R}'=\text{R}'' \rightarrow \text{ROOR}'\text{-R}''\cdot$ $\text{RO}\cdot + \text{R}'=\text{R}'' \rightarrow \text{ROR}'\text{-R}''\cdot$
Epoxidation	$\text{R}'\text{OOR}\cdot \rightarrow \text{R}'\text{O}\cdot + \text{R}>\text{O}$ $\text{R}'\text{OR}\cdot \rightarrow \text{R}'\cdot + \text{R}>\text{O}$
<u>Termination</u>	
Disproportionation	$2 \text{ROO}\cdot \rightarrow \text{R}=\text{O} + \text{ROH} + \text{O}_2$ $2 \text{RO}\cdot \rightarrow \text{R}=\text{O} + \text{ROH}$
Recombination	$\text{R}\cdot + \text{R}'\cdot \rightarrow \text{RR}'$

3.2.1.2 Kinetic Parameter Determination

In order to predict the temporal evolution of the concentrations of each species, each of the reactions postulated by the network generation process needs an associated rate constant. When available, literature values for the rate constant, activation energy, or Arrhenius pre-exponential factors were used. The activation energies for a peroxy radical performing hydrogen abstraction from cyclooctene and adding to the double bond in cyclooctene were taken from a density functional theory study by Neuenschwander et al.⁸⁹ For epoxidation through an ether bond intermediate, the same Evans-Polanyi relationship as in the peroxy bond epoxidation reaction was employed with the increase in enthalpy of reaction accounting for the difference in rate coefficients. In both of these cases, an Arrhenius pre-exponential factor was not provided, so these specific reactions were assumed to have the same pre-exponential factor as the other reactions of the same family. For the reactions mediated by AuNPs, the initial estimates of the rate constants were taken from the work of Oakley et al.⁹⁰ on radical initiation by Co(II), and fitting was permitted over a range of three orders of magnitude to allow for possible activity differences between Co and Au. The desorption rate coefficient for both peroxy species from the AuNPs was set at a constant value of 0.5 s^{-1} , taken from Oakley et al.⁹⁰

For all reaction families, rate constants were assumed to be in the Arrhenius form, $k = A \exp(-E_A/RT)$, where k is the rate coefficient, A is the Arrhenius pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the temperature.³⁸ Each reaction within an elementary reaction family is assumed to have the same pre-exponential factor, assuming that $\Delta S^\ddagger$, the change in entropy between the reactants and transition state, is approximately the same for each member of the family. Table 3.2 contains the Arrhenius pre-exponential factors for

all oxidation reaction families that were either directly taken from the literature (see Pfaendtner et al.⁶⁷ and Oakley et al.¹⁰¹) or adjusted to account for the fact that bimolecular reactions in the liquid phase may have pre-exponential factors that are two to three orders of magnitude lower,¹⁰² and small further changes within two orders of magnitude based on parameter optimization. The subset of parameters that were adjusted is delineated in Table 3.2, and the results are discussed in Section 3.3.1.

Table 3.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the cyclooctene oxidation mechanistic model. All values culled from the work of Pfaendtner et al.⁶⁷ except when noted.

Reaction Family	A [$\text{s}^{-1}/\text{M}^{-1} \text{s}^{-1}$] ^a	E _A ⁰ [kcal/mol]	α
Primary initiation	$2.8 \times 10^{10} \text{ c}$	0	1
Peroxy bond fission	$2.4 \times 10^{15} \text{ c}$	0	1
Hydroperoxide decomposition	$7.4 \times 10^5 \text{ c}$	24.6	-0.09
Oxygen addition	1.0×10^8	0	0
β -scission by alkoxy radical	1.0×10^{14}	9.5	0.85
β -scission by carbon-centered radical	1.0×10^{14}	14.24	0.76
Hydrogen transfer by alkyl radical	$2.3 \times 10^4 \text{ c}$	9.1	0.3
Hydrogen transfer by alkoxy radical	$5.3 \times 10^4 \text{ c}$	11.9	0.91
Hydrogen transfer by peroxy radical	$1.0 \times 10^6 \text{ c}$	3.05	1.1
Addition	$4.9 \times 10^7 \text{ c}$	14.24	0.24
Epoxidation ^b	$3.0 \times 10^{12} \text{ c}$	21.4	0.51
Disproportionation	$1.0 \times 10^5 \text{ c}$	0	0
Recombination	1.0×10^8	0.85	0

^aFirst-order reactions have the units s^{-1} and second-order reactions have the units $\text{M}^{-1}\text{s}^{-1}$ for the Arrhenius pre-exponential factor.

^bValue taken from the work of Oakley et al.¹⁰¹

^cDenotes a regressed value. Error ranges for all fitted parameters were approximately half an order of magnitude.

When activation energies are not available for a specific elementary step from the literature, they may be determined from linear scaling relationships, such as the Evans-Polanyi relationship, $E_A = E^\circ_A + \alpha \Delta H_{rxn}$, where α and E°_A are constants for each reaction family and ΔH_{rxn} is the enthalpy of reaction for a specific reaction in the family.³⁹ Values for α and E°_A are reported in Table 3.2. Enthalpies of reactions were tabulated for each reaction using the enthalpies of

formation of the reactant(s) and product(s) obtained from experimental databases when available or the Benson group additivity method.⁴⁰

3.2.1.3 Model Execution

Once rate constants were determined on-the-fly for each reaction, rate expressions for all species in the systems were formulated based on elementary rate laws and mass action kinetics, and the rate laws were coupled with reactor design equations for a constant volume batch reactor. Because O₂ was bubbled into the system, the concentration of O₂ was assumed to be constant at the saturation limit for O₂ in cyclooctane, the most analogous solvent for which a value was available in the literature, which was 1.1×10^{-3} mol fraction.¹⁰³ The resultant set of differential equations was integrated via DDASAC.⁴¹ Parameter fitting was performed using GREG⁴² by minimizing the residual sum of squares for concentrations of cyclooctene, cyclooctene oxide, 2-cycloocten-1-ol, 2-cycloocten-1-one, and 2-cycloocten-1-yl hydroperoxide at a series of reaction times using experimental data from both tert-butyl hydroperoxide (TBHP) and AuNP-catalyzed runs simultaneously. The model converged once the residual sum of squares did not change more than 10^{-5} from one step to the next. The starting value for the concentration of cyclooctene was set at either 7.0 M or 6.1 M, depending on the reaction conditions. The initial value for TBHP varied between 0 M and 0.7 M. The concentration of AuNPs used was either 6.1×10^{-9} M or 1.2×10^{-7} M. Due to the narrow particle size distribution for the AuNPs, a single value of a rate constant that quantified a given step catalyzed by AuNPs was assumed.

3.2.2 Experimental Methods, authored by Anyang Peng

3.2.2.1 Chemicals and Materials

To carry out the experimental runs, the chemicals and materials used and their specifications were the following: $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (≥ 99.9 % trace metals basis, Sigma Aldrich), fumed silica (CAB-O-SIL-90, Cabot Corporation), ethylenediamine (≥ 99 % ReagentPlus, Sigma Aldrich), ethanol (200 grade, DeconTM Labs), decane (≥ 99 % ReagentPlus, Sigma Aldrich), *cis*-cyclooctene (95%, Alfa Aesar), potassium hydroxide (reagent grade, 90 %, Sigma Aldrich), sodium sulfate (FCC/USP grade, Fisher Chemical), tetrahydrofuran (> 99 %, Sigma Aldrich), tert-butyl hydroperoxide (~ 5.5 M in decane, Sigma Aldrich), triphenylphosphine (> 98.5 %, Sigma Aldrich), EM Quant peroxide test strips, and syringe filters (PVDF membrane, 0.25 mm/0.2 μm , Acrodisc).

Before use, cyclooctene was purified to remove the manufacturer-added stabilizer. In general, 50 mL of commercial cyclooctene was mixed with 50 mL of 3 M KOH solution and stirred vigorously for 10 min. After stirring, cyclooctene was recovered by separation. The cyclooctene was then washed with another 50 mL of KOH solution and twice washed with 50 mL of distilled deionized (DDI) water in the same manner. The recovered cyclooctene was dried in a flask with anhydrous sodium sulfate overnight. Finally, the cyclooctene was distilled using an oil bath at around 180 °C while collecting the sample at 145 °C.

3.2.2.2 Catalyst Preparation

Au/SiO_2 : The precursor used to generate solubilized Au clusters, which were the actual catalyst, was prepared in a similar procedure as that reported by Zhu et al.¹⁰⁴ In general, 0.5 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was dissolved in a mixture containing 10 mL of ethanol and 2 mL of water and

stirred for 5 min before the addition of 0.23 mL of ethylenediamine (en = ethylenediamine) to achieve an en/Au ratio of 2.65. The resulting mixture was stirred for 10 min, and the precipitate ($\text{Au(en)}_2\text{Cl}_3$) was collected by filtration and washed with 300 mL of ethanol. 46.3 mg of as prepared $\text{Au(en)}_2\text{Cl}_3$ was dissolved in 26 mL of DDI water to form a 4.2 mM solution. 1 g of fumed silica was added to the solution at 40 °C while the mixture was stirred. The pH of the resulting mixture was adjusted to 9 by dropwise addition of 0.75 M en solution (in DDI water), and the mixture was stirred at room temperature for 2 h. The suspension was filtered and the solid was washed with 500 mL of DDI water and re-dispersed in 200 mL of DDI water at 40 °C. Finally, the as-formed Au/SiO_2 was collected by filtration, washed with another 500 mL of DDI water, and dried overnight. Before use, Au/SiO_2 was calcined in a U-tube under O_2/O_3 flow (~ 300 cc/min) with a ramping rate of 0.12 °C/min until 150 °C and held at 150 °C for 0.5 h. After calcination, the resulting powder was light yellow in color and had a Au loading of 1.2 wt.% with an average particle size around 2 nm.

Solubilized Au clusters: The solubilized Au clusters were prepared according to the procedure developed by Qian et al.⁸³ In general, 10 mL of purified *cis*-cyclooctene (COE), 1 mL of decane and 80 mg Au/SiO_2 were added to a three-necked cylindrical reactor. The mixture was sonicated for 15 min and equilibrated under N_2 for 20 min prior to reaction. The reaction was carried out under O_2 flow (30 cc/min) at 100 °C. After 20 hours, Au/SiO_2 was removed by hot filtration with a syringe filter, and the filtrate was collected. The as-prepared filtrate was characterized to contain small gold clusters with a narrow cluster size distribution ranging from single atoms to ~ 0.7 nm clusters. Details on the characterization of the AuNPs are included in the Appendix 2.

3.2.2.3 Reactions

All reactions were conducted in a three-necked cylindrical reactor equipped with a fine frit glass disperser tube (Chemglass Sciences) and a condenser maintained at -10 °C. Before each reaction, the reactor and disperser were soaked in Aqua regia overnight, thoroughly washed with DDI water and ethanol, and dried in an oven at 150 °C. In a typical reaction, the reaction mixture was loaded into the reactor together with a teflon-coated magnetic stirrer. After the reaction set up was assembled, the reaction mixture was stabilized under N₂ flow for 20 min in a pre-heated oil bath. The reaction was started by supplying constant O₂ flow at 30 cc/min. 0.2 mL of the reaction mixture was taken at different time intervals, diluted with anhydrous THF and analyzed by gas chromatography (Agilent 6890 GC equipped with a FID with DB-624 capillary column 30 m × 0.25 mm × 0.25 μm) immediately. The compositions of the reaction mixtures are listed in Table 3.3. Results are only reported below for reactions using solubilized AuNP clusters as the catalyst.

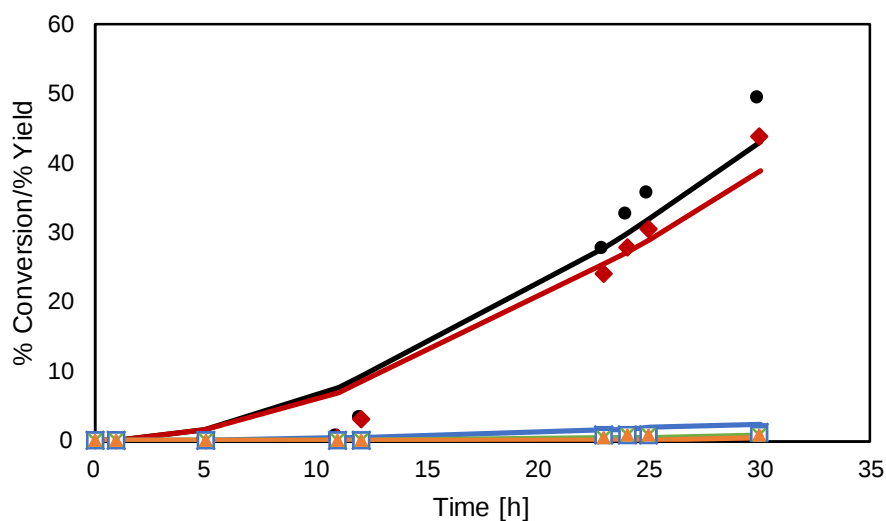
Table 3.3: Reaction mixtures for experimental runs

Run	Substrate	Initiator	Standard
0 mL TBHP	10 mL cyclooctene	None	1 mL decane
0.3 mL TBHP	10 mL cyclooctene	0.3 mL TBHP	1 mL decane
1.5 mL TBHP	8.9 mL cyclooctene	1.5 mL TBHP	0.9 mL decane
Solubilized Au Clusters	8 mL cyclooctene	2 mL Au cluster solution	0.8 mL decane

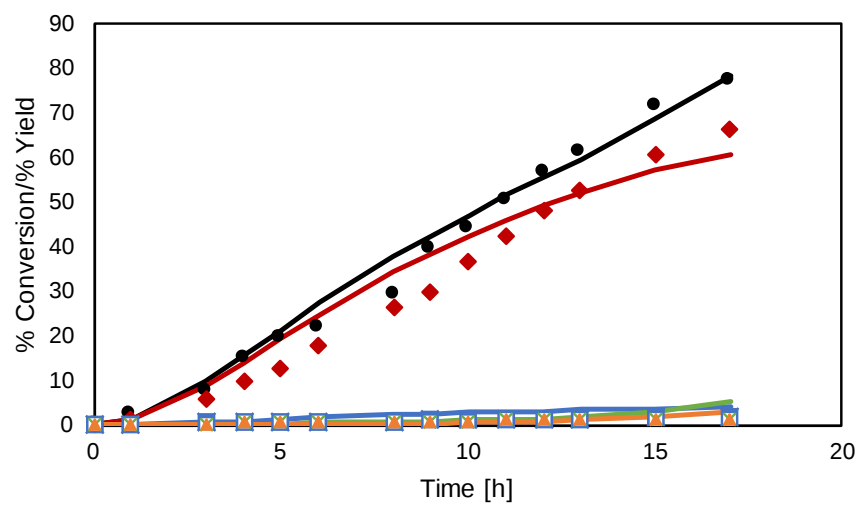
3.3. Results and Discussion

3.3.1 Model of Homogeneous Oxidation

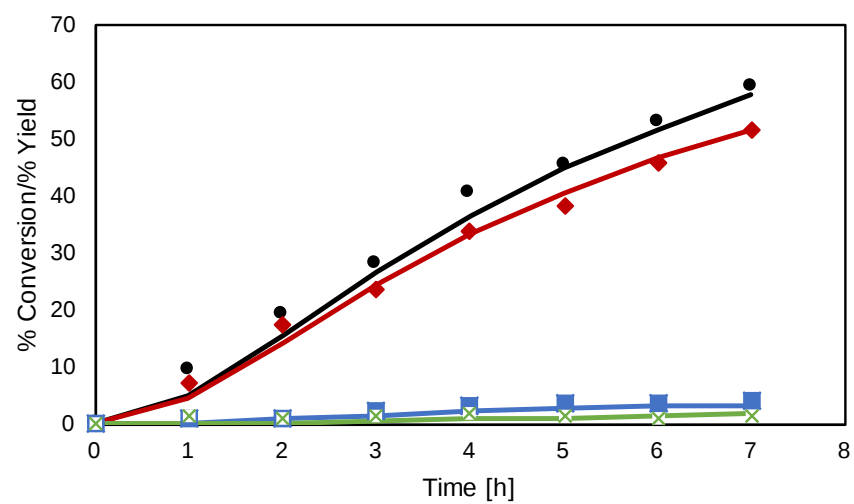
The mechanism generation step resulted in a network made up of 128 species, 90 forward/reverse reaction pairs, and 291 unique forward reactions. Comparison of the experimental data using tert-butyl hydroperoxide as the initiator and the best fit of the microkinetic model results at the various temperatures and initiator concentrations can be seen in Figure 3.3. The values of the pre-exponential factors that were fit to achieve the agreement are shown in Table 3.2 and fall within expected ranges for liquid-phase oxidation reactions. The model is able to capture the reactant conversion and the yields of the major and minor products well over a range of conditions. It is particularly noteworthy that experimental data at different temperatures was captured with no adjustment in any activation energy values.



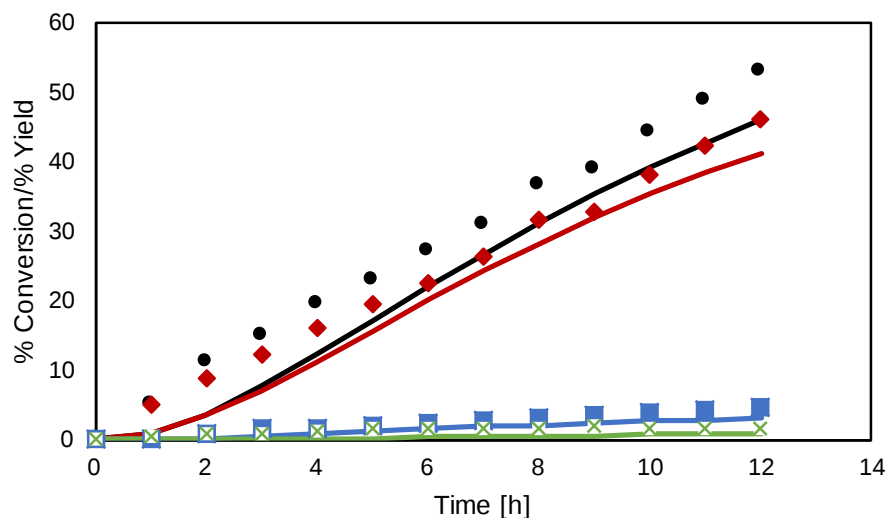
a)



b)



c)



d)

Figure 3.3: Results of homogeneous model compared to experimental data for a) 373 K, 0 mL TBHP, b) 373 K, 0.3 mL TBHP, c) 373 K, 1.5 mL TBHP, d) 363 K, 1.5 mL TBHP. Experimental data are shown in symbols, and the model results are shown as lines of corresponding colors. The data plotted are conversion of cyclooctene (●) and yields of the products: cyclooctene oxide (◆), 2-cycloocten-1-ol (■), 2-cycloocten-1-one (×), and 2-cycloocten-1-yl hydroperoxide (▲). Note the differences in timescale for each of the plots.

The model results were then analyzed to identify key reaction steps and dominant reaction fluxes. The network of major reactions that lead to the formation of the epoxide, alcohol, ketone, and hydroperoxide products is shown in Figure 3.4 with the rates at 1 h for the 373 K, 0 mL TBHP and 373 K, 0.3 mL TBHP cases. The fastest initiation step is bimolecular decomposition of TBHP with cyclooctene, forming an alkoxy radical and an allylic radical. This allylic radical then readily adds oxygen for formation of a peroxy radical. The peroxy radical can then undergo two possible reactions, addition across a double bond or hydrogen abstraction. The addition step is energetically

favorable, based on the work of Neuenschwander et al.,⁸⁹ which is a property that is unique to cyclooctene compared to other cyclic alkenes. The result of the addition step is a bicyclic radical intermediate with a peroxy bond bridge. This intermediate then undergoes a unimolecular epoxidation reaction, sometimes called Twigg rearrangement,⁸⁹ forming the epoxide product and an alkoxy radical. The alkoxy radical also has the ability to add across a double bond to form a bicyclic radical with a bridging ether bond. The bicyclic ether can also perform unimolecular epoxidation to form an epoxide and regenerate the allylic radical to close the cycle. The inclusion of two favorable addition steps leading to intermediates that can directly form the epoxide product results in the high selectivity to epoxide seen in the experimental results.

When the peroxy radical formed from oxygen addition performs hydrogen abstraction, the hydroperoxide product, 2-cycloocten-1-yl hydroperoxide, is formed. This hydroperoxide can initiate via peroxy bond fission or form a radical via hydrogen abstraction from the α -carbon. The alkoxy radicals formed either in the epoxidation cycle or by peroxy bond fission may also abstract hydrogen to form the alcohol product, 2-cycloocten-1-ol. The alkoxy radical and the α -carbon radical can both perform β -scission to form 2-cycloocten-1-one. The most prevalent reactions that lead to the formation of minor products are hydrogen abstraction and β -scission of the alkoxy radical to form the alcohol and ketone products, respectively. At 1 h in the 0.3 mL TBHP, 373 K case, hydrogen abstraction is preferred over β -scission by just less than an order of magnitude, leading the model to predict the proper relative ratio of alcohol to ketone side products.

The competition between addition and hydrogen abstraction by the peroxy radical is a main determining factor of the product selectivity. For all homogeneous runs, the model results suggest that the rate of addition is three orders of magnitude greater than the rate of hydrogen abstraction, leading to the greater than 80 % selectivity to epoxide. When the peroxy or alkoxy radicals prefer to abstract hydrogen, the selectivity would shift toward the alcohol and ketone products as is observed experimentally for other cyclic alkenes. For example, it is proposed in the literature that hydrogen abstraction is more favorable in the case of cyclohexene oxidation, necessitating that a direct epoxidation catalyst be used to influence the selectivity towards the epoxide.^{87,89}

3.3.2 Model of Oxidation in the Presence of AuNP Catalysts

With the underlying homogeneous model validated against the experimental runs at a variety of conditions, the effect of AuNPs was quantified by using the homogeneous reactions

and their kinetic parameters without adjustment and by fitting the model results against experimental data with the addition of the catalytic cycles shown in Figures 3.2a and 3.2b with six adjustable parameters, k_1 through k_6 . The agreement of the model results for the AuNP-catalyzed cases can be seen in Figure 3.5, and the values of the regressed rate constants for reactions involving gold species are tabulated in Table 3.4. The model is successful in matching the experimental data in the induction period for both Au concentrations. The ability of the model to capture the radical chain propagation regime is very good for the 26 ng/mL Au case, and for the 0.8 ng/mL case, the deviation between the model results and the experimental data is less than 0.5 M, which is within the experimental error range.

Table 3.4: Regressed values for the rate constants for initiation reactions involving gold species. Values from the literature of analogous reactions catalyzed by Co(II) that were used as initial guesses are provided as well for comparison.

Reaction	Rate Constant (See Figure 3.2)	k [$s^{-1}/M^{-1} s^{-1}$] ^a	k for Co(II) analogous reactions ⁹⁰ [$s^{-1}/M^{-1} s^{-1}$]
$Au + O_2 \bullet \rightarrow AuOO\bullet$	k_1	6.0×10^1 ^b	6.7×10^{-1}
$AuOO\bullet + RH \rightarrow AuOOH + R\bullet$	k_2	7.4×10^{-3} ^b	5.0×10^{-5}
$AuOOH \rightarrow Au + \bullet OOH$	k_3	5.0×10^{-1}	5.0×10^{-1}
$Au + ROOH \rightarrow AuOH + RO\bullet$	k_4	7.7×10^1 ^b	5.0×10^{-1}
$AuOH + ROOH \rightarrow AuOOR + H_2O$	k_5	1.8×10^1 ^b	2×10^0
$AuOOR \rightarrow Au + ROO\bullet$	k_6	5.0×10^{-1}	5.0×10^{-1}

^aFirst-order reactions have the units s^{-1} and second-order reactions have the units $M^{-1}s^{-1}$ for the rate coefficients.

^bDenotes a regressed value

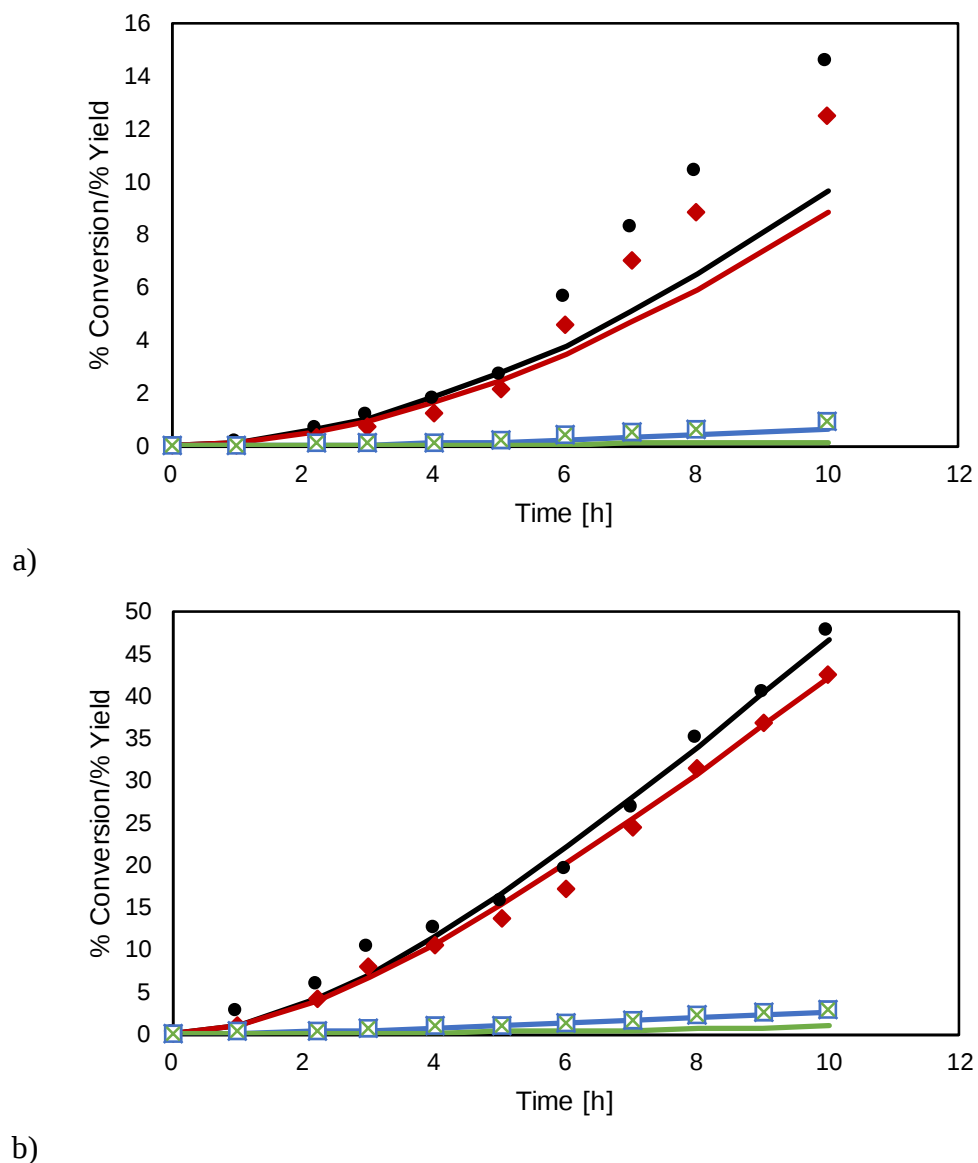


Figure 3.5: Results of model compared to experimental data for AuNP-catalyzed cases at 373 K with a) 0.8 ng/mL Au and b) 26 ng/mL Au. Experimental data are shown in symbols, and the model results are shown as lines of the corresponding color. The data plotted are conversion of cyclooctene (●) and yields of the products: cyclooctene oxide (◆), 2-cycloocten-1-ol (■), and 2-cycloocten-1-one (×).

The mechanism invoked in the AuNP-catalyzed model is depicted in Figure 3.6 with the net reaction rates at 1 h for both concentrations of AuNP. It is striking that the same epoxidation cycle as in the homogeneous case dominates the consumption of the reactant and the formation of products. However, the epoxidation cycle in this case is initiated primarily by the AuNP-catalyzed reactions. Hydrogen abstraction by superoxo gold species creates allylic radicals at a higher rate than the homogeneous primary initiation reaction by at least an order of magnitude at 1 s for both Au concentrations. At short times, the hydroperoxide decomposition cycle does not contribute significantly to initiation, but as more hydroperoxide product is formed, the rate steadily increases. It is only after approximately 6 h in the 26 ng/mL Au run that hydroperoxide decomposition by Au is proceeding at a faster rate than either homogeneous or AuNP-catalyzed primary initiation.

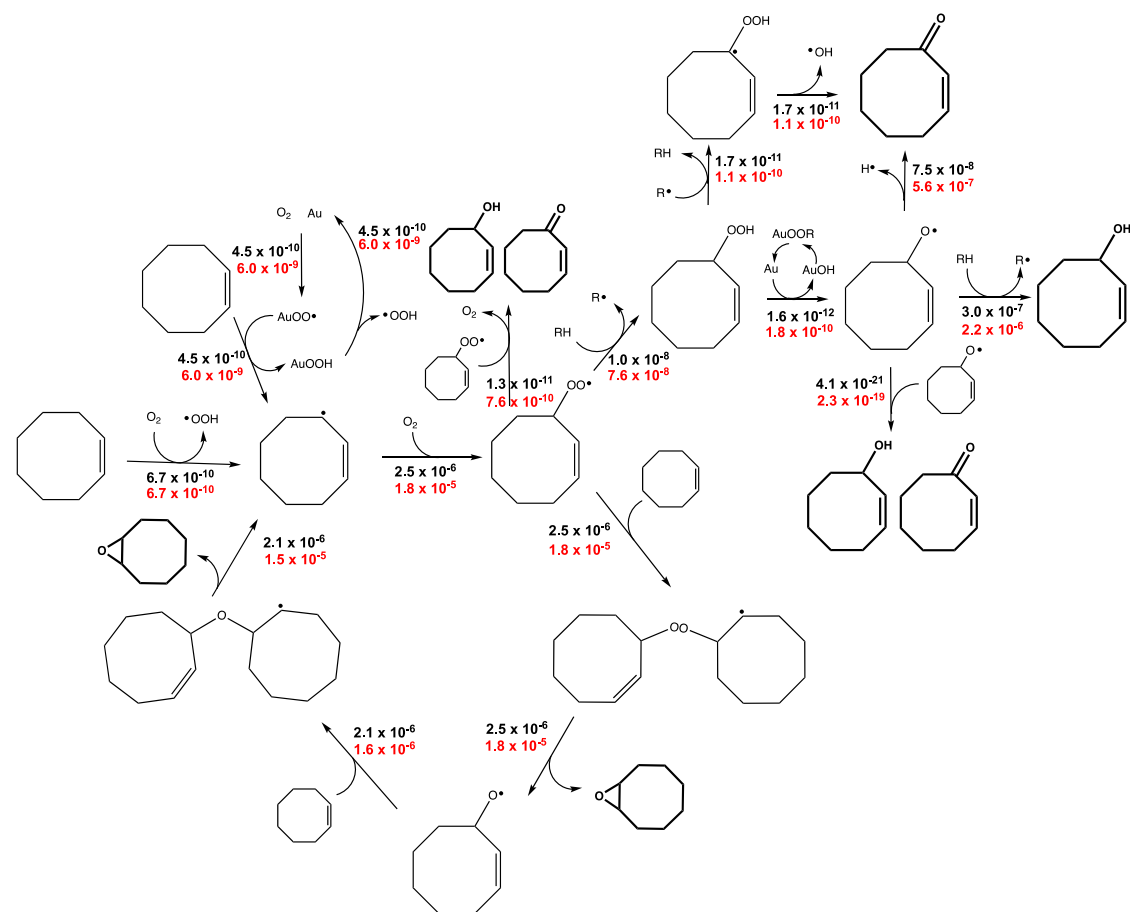
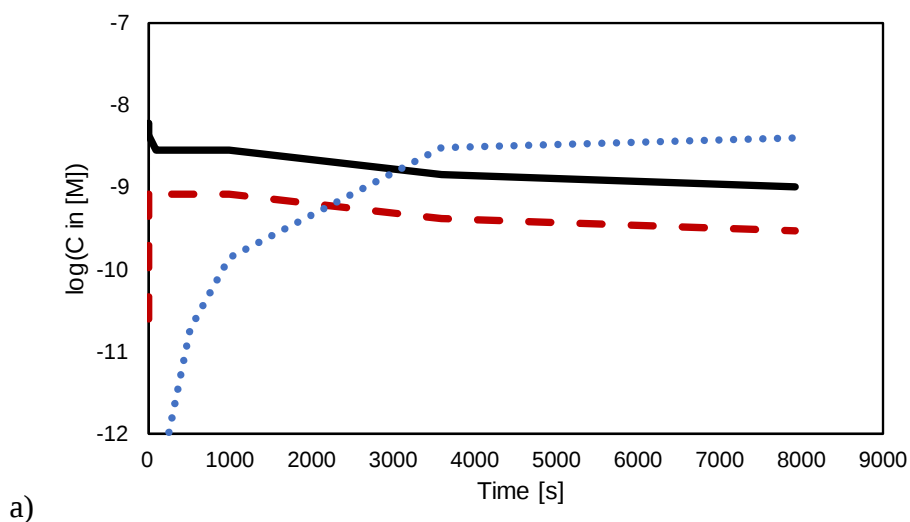


Figure 3.6: Au-catalyzed reaction network for oxidation of cyclooctene to cyclooctene oxide, 2-cycloocten-1-ol, and 2-cycloocten-1-one (shown in bold). Net rates of reaction at 1 h for the 0.8 ng/mL Au (in black) and 26 ng/mL Au (in red) cases are shown corresponding to the nearest reaction arrow in M/s. Note that the model was comprised of many additional reactions not shown here, which only reproduces key reactions with the dominant fluxes.

These temporal trends are further illuminated by monitoring the concentrations of Au species as a function of time, as seen in Figure 3.7. The concentrations of bare AuNPs (Au), superoxo gold ($\text{AuOO}\bullet$), and the first intermediate in the hydroperoxide decomposition cycle (AuOH) are specifically shown here as the dominant Au species, although the model tracked all forms of Au. Very quickly, as short as 100 s, $\text{AuOO}\bullet$ reaches a maximum concentration with O_2 complexing to the bare nanoparticles. As higher concentrations of hydroperoxides emerge, the rate of formation of AuOH increases, shuttling Au towards AuOH and resulting in a decrease in the active $\text{AuOO}\bullet$ state. On the timescale of an hour, AuOH dominates the speciation of Au, signifying that a transition from the induction period to radical chain oxidation has occurred.



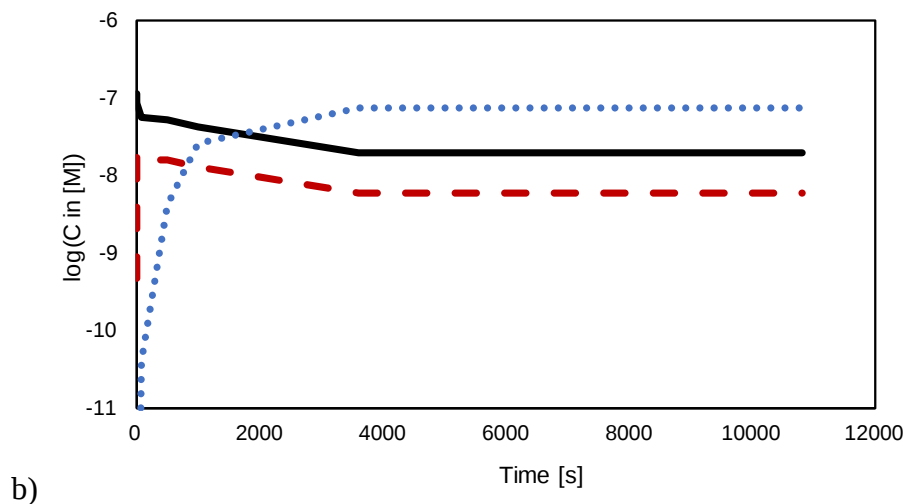


Figure 3.7: Populations of major Au species at short times based on the model results for runs with a) 0.8 ng/mL Au and b) 26 ng/mL Au. The populations shown are bare Au in solid black, AuOO. in dashed red, and AuOH in dotted blue lines.

The ability of the model to capture the role of AuNPs on the rates and product selectivities has important implications. It suggests that the role of the AuNPs is as a radical initiator with no need to include any additional role of AuNP as a catalyst, e.g., as a facilitator of a direct epoxidation pathway. It is possible that other catalysts, e.g., other metals or metal oxides, could function as promoters of additional reactions, but the homogeneous model that was built here can still be used as a foundation on which catalytic routes can be imposed.

3.4. Conclusions

The results of the microkinetic model developed for homogeneous and AuNP-catalyzed oxidation of cyclooctene matched the experimental results well at a variety of conditions. Analysis of resultant net rates showed that the unique preference of cyclooctene for addition across the

double bond by peroxy and alkoxy radicals drives the reaction into the radical epoxidation cycle. This cycle includes two epoxidation reactions through different bond types, leading to the high epoxide selectivity in this specific case. When hydrogen abstraction is favorable as is postulated for other cyclic alkenes, a direct epoxidation catalyst would be needed to obtain comparable epoxide selectivity.

The model accounting for catalysis by AuNPs and its ability to capture the experimental data suggest that AuNPs function solely as radical initiators. At short times, initiation by superoxo gold species performing hydrogen abstraction dominates compared to either homogeneous initiation or hydroperoxide decomposition mediated by AuNPs. As greater concentrations of hydroperoxides are produced, the rate of decomposition of hydroperoxides by AuNPs increases until it is faster than initiation by superoxo gold species, with the crossover point at approximately 6 h. The AuNP reactions contribute in both the induction period and the chain propagation phase leading to a faster transition to chain propagation and increasing the overall rate of reaction.

Chapter 4: Microkinetic Modeling of the Co-oxidation of Ethylbenzene and Cyclooctene Using Co/ZSM-5

4.1 Introduction

Selective partial oxidation processes play an important role in many industries from pharmaceuticals to plastics. While the use of O₂ as a cheap, abundant, and eco-friendly oxidant in these processes would be ideal, barriers often exist to utilizing O₂ in industrial processes. One of the main challenges is the difficulty of activating stable carbon-hydrogen bonds with O₂ and common metal catalysts. A strategy that could be implemented to increase reaction rate is to kinetically couple multiple oxidation reactions.¹⁰⁵ In this co-oxidation scheme, a kinetically-limited partial oxidation reaction would be facilitated by the simultaneous partial oxidation of another substrate. While effective in increasing the rate of oxidation for a slower oxidation reaction, there are other considerations when attempting co-oxidation, such as tuning reaction conditions and catalysts to ensure that both reactants are active and create products that are stable. The task of finding compatible reaction conditions for multiple substrates can be especially difficult when oxidation is carried out through a radical mechanism. Due to the complexity of the co-oxidation systems, this work sought to produce a microkinetic model that elucidates an underlying co-oxidation mechanism and the role of a cobalt-zeolite catalyst.

This work examines the co-oxidation of ethylbenzene and cyclooctene using O₂ as the oxidant and catalyzed by Co/ZSM-5 at 100 °C. The oxidation of cyclooctene has been investigated in both experimental and computational studies, both without catalyst and in the presence of gold nanoparticles.^{83,106} When uncatalyzed, the oxidation of cyclooctene exhibited an induction period of up to 12 hours followed by a radical chain propagation phase characterized by increased

consumption of the substrate. The homogeneous oxidation showed consistently ~80 % selectivity to the epoxide product, cyclooctene oxide, at ~50 % conversion with the balance going to approximately equal amounts of 2-cycloocten-1-ol and 2-cycloocten-1-one. When gold salts were added as catalysts for the cyclooctene reaction, the length of the induction period and the rate in the chain propagation region changed, but the high selectivity to epoxide was consistent. Following the reaction, the active form of gold was characterized via TEM to be gold nanoparticle (AuNP) clusters of 5-8 atoms, a size that is small enough to be active in catalysis. The microkinetic model that was developed was able to rationalize that the high selectivity to epoxide relative to alcohol and ketone products was due to the preference for peroxy and alkoxy radicals to add across the substrate double bond as opposed to abstracting hydrogen. Addition across the double bond by a peroxy radical forms an $\text{ROOR}'\bullet$ species, from which a radical epoxidation reaction may occur to form the epoxide and an alkoxy radical. The resultant alkoxy radical may perform radical addition to form an alkyl radical next to an ether bond, $\text{ROR}'\bullet$, which will then undergo epoxidation to form another epoxide equivalent and generate an active alkyl radical, feeding back into the reaction cycle. This series of addition and subsequent epoxidation reactions completes an epoxidation cycle with hydrogen abstraction reactions giving rise to side reactions that form the minor products. In addition, the model determined that the role of the AuNPs was most likely to act as a radical initiator via two mechanisms: hydrogen abstraction by a superoxo intermediate and hydroperoxide decomposition. There was no evidence that the gold nanoparticles performed any direct epoxidation reactions.

For ethylbenzene oxidation, higher temperatures are often required to drive the conversion compared to the case of cyclooctene oxidation.¹⁰⁷ In contrast to the cyclooctene system, the

oxidation of ethylbenzene does not involve the radical addition reactions mentioned, leading to the more traditionally expected oxidation products: alcohol, ketone, and hydroperoxide. Ethylbenzene oxidation shows high selectivity to the ketone product, acetophenone, so a mechanism based on rapid termination leading to one equivalent of ketone and alcohol, 1-phenylethanol, is not sufficient in this case.¹⁰⁸ Literature suggests that the ketone and alcohol are formed via decomposition of the primary hydroperoxide product.^{107,109} The introduction of active cyclooctene-derived radicals should increase the rate of initiation of ethylbenzene and hydrogen abstraction from 1-phenylethyl hydroperoxide, increasing the rate of consumption of ethylbenzene and the rate of secondary reactions that will form the alcohol and ketone major products.

In addition to illuminating the mechanism by which the two substrates interact, the model sought to explain the role of the Co/ZSM-5 catalyst. A previous study of the oxidation of ethylbenzene to acetophenone using a Co/SBA-15 catalyst showed that upon removal of Co via hot filtration the reaction rate decreased sharply, illustrating the importance of the metal sites.¹¹⁰ In industrial applications, the oxidation of ethylbenzene is carried out using Co catalysts.¹¹¹ However, these processes can be improved upon as they often involve harsh conditions, including the use of acids and bromides. Ideally, Co/ZSM-5 would prove to be an active ethylbenzene oxidation catalyst that can operate under more benign conditions. Previous work with Co/ZSM-5 has been shown to activate methane carbon-hydrogen bonds, showing that it has the potential to catalyze the weaker carbon-hydrogen bonds in ethylbenzene.^{112–114}

4.2. Methods

4.2.1 Mechanism Generation

The goal of the computational study is to test the hypotheses for the mechanism for the cyclooctene and ethylbenzene oxidation system through development of a full microkinetic model. The first step of the process was to implement automated network generation to postulate relevant reactions for the two-component system. This work employed an automated network generator developed by Broadbelt et al.^{33–37} The network generation step involves finding reactive moieties within starting materials and their progeny and then applying types of elementary reactions to unfurl individual steps. The elementary reactions of the same type are grouped into reaction families. The reaction families used in this work are prototypical of radical oxidation processes, and a complete list can be found in Table 4.1.^{67,78} Without termination criteria, the reaction network would grow infinitely and become computationally intractable as new reactive moieties will continuously be produced. As a result, the following termination criteria were set on a carbon number and rank basis: products with only 16 carbon atoms or fewer were allowed to form, no tertiary or higher rank reactions were allowed for the progeny of ethylbenzene, and no secondary reactions or higher were allowed for the progeny of cyclooctene other than hydroperoxides. In addition to the termination criteria, the model did not allow for the formation of vinyl or methyl radicals or for the addition of oxygen to already oxidized species to avoid creating molecules that were not observed experimentally.

Table 4.1: List of reaction families included in the reaction mechanism for cyclooctene and ethylbenzene oxidation based on free-radical chemistry. R, R', and R'' represent alkyl/alkoxy groups or hydrogens, and R>O represents an epoxide.

Reaction Family	Example
<u>Initiation</u>	
Primary initiation	$\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HOO}\cdot$
Peroxy-bond fission	$\text{ROOR}' \rightarrow \text{RO}\cdot + \text{R}'\text{O}\cdot$
Hydroperoxide decomposition	$\text{RH} + \text{R}'\text{OOH} \rightarrow \text{R}\cdot + \text{R}'\text{O}\cdot + \text{H}_2\text{O}$
<u>Propagation</u>	
Oxygen addition	$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$
β -scission	$\cdot\text{ROOH} \rightarrow \text{R}=\text{O} + \cdot\text{OH}$
Hydrogen transfer	$\text{ROO}\cdot + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'\cdot$ $\text{RO}\cdot + \text{R}'\text{H} \rightarrow \text{ROH} + \text{R}'\cdot$ $\text{R}\cdot + \text{R}'\text{H} \rightarrow \text{RH} + \text{R}'\cdot$
Addition	$\text{ROO}\cdot + \text{R}'=\text{R}'' \rightarrow \text{ROOR}'\text{-R}''\cdot$ $\text{RO}\cdot + \text{R}'=\text{R}'' \rightarrow \text{ROR}'\text{-R}''\cdot$
Epoxidation	$\text{R}'\text{OOR}\cdot \rightarrow \text{R}'\text{O}\cdot + \text{R}>\text{O}$ $\text{R}'\text{OR}\cdot \rightarrow \text{R}'\cdot + \text{R}>\text{O}$
<u>Termination</u>	
Disproportionation	$2 \text{ROO}\cdot \rightarrow \text{R}=\text{O} + \text{ROH} + \text{O}_2$ $2 \text{RO}\cdot \rightarrow \text{R}=\text{O} + \text{ROH}$ $2 \text{R}\cdot\text{-OH} \rightarrow \text{R-OH} + \text{R}=\text{O}$
Recombination	$\text{R}\cdot + \text{R}'\cdot \rightarrow \text{RR}'$

4.2.2 Kinetic Parameter Determination

For evaluating the temporal evolution of all of the species, a rate coefficient is needed for each of the postulated reactions generated during the automated network generation step.

Literature values for rate coefficients, activation energies, and Arrhenius pre-exponential factors were used in the model when available. When kinetic parameters were not available from literature, the values were approximated within the model based on structure-reactivity relationships. For each of the postulated reactions, the rate expression is represented in Arrhenius form, $k = A \exp(-E_A/RT)$, where k is the rate coefficient, A is the Arrhenius pre-exponential factor, E_A is the activation barrier, R is the universal gas constant, and T is the temperature.³⁸

The activation barrier, when not available in literature, was calculated using the Evans-Polanyi relationship, $E_A = E^\circ_A + \alpha \Delta H_{rxn}$, where α and E°_A are constants for each reaction family and ΔH_{rxn} is the enthalpy of reaction for a specific reaction in the family.³⁹ Enthalpies of reaction were tabulated for each reaction from enthalpies of formation for reactant(s) and product(s) obtained from experimental databases or Benson's group additivity method. Reactions within a given family have been shown to share Arrhenius pre-exponential factors and Evans-Polanyi coefficients. The Arrhenius pre-exponential factors and Evans-Polanyi parameters for the conversion of cyclooctene and its progeny were determined previously in the work of Brydon et al.¹⁰⁶ and have been treated as constant values in this model. A complete list of the cyclooctene parameters can be found in Table 4.2. Certain kinetic parameters for reactions involving ethylbenzene and its progeny were regressed to better capture the behavior of the system, and these values are denoted in Table 4.3. A previous investigation on the oxidation of ethylbenzene showed that the barrier for hydrogen abstraction by a peroxy radical from the substrate is ~2 kcal/mol higher than the barrier for hydrogen abstraction from the hydroperoxide product. In order to more accurately capture this within the model, the abstraction from ethylbenzene (denoted Primary in Table 4.3) and abstraction from hydroperoxide and alcohol products (denoted Secondary in Table

4.3) have two different pre-exponential factors. Additionally, the model accounted for disproportionation with two sub-families: cross-disproportionation between a cyclooctene-derived radical and an ethylbenzene-derived radical and self-disproportionation between two ethylbenzene-derived radicals.

Table 4.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the mechanistic model of cyclooctene and ethylbenzene oxidation. All cyclooctene-related values taken from the work of Brydon et al.⁶⁷ Pre-exponential factors for reactions involving ethylbenzene are regressed when listed or set to the same reaction family values as for cyclooctene. E_A^0 and α values were fixed in all cases at the values used by Brydon et al.¹⁰⁶ for cyclooctene oxidation.

Reaction Family	A for Cyclooctene Reactions [s ⁻¹ /M ⁻¹ s ⁻¹] ^a	E_A^0 [kcal/mol]	α
Primary initiation	2.8×10^{10}	0	1
Peroxy bond fission	2.4×10^{15}	0	1
Hydroperoxide decomposition	7.4×10^5	24.6	-0.09
Oxygen addition	1.0×10^8	0	0
β -scission by alkoxy radical	1.0×10^{14}	9.5	0.85
β -scission by carbon-centered radical	1.0×10^{14}	14.24	0.76
Hydrogen transfer by alkyl radical	2.3×10^4	9.1	0.3
Hydrogen transfer by alkoxy radical	5.3×10^4	11.9	0.91
Hydrogen transfer by peroxy radical	1.0×10^6	3.05	1.1
Addition	4.9×10^7	14.24	0.24
Epoxidation ^b	3.0×10^{12}	21.4	0.51
Disproportionation	1.0×10^5	0	0
Recombination	1.0×10^8	0.85	0

^aFirst-order reactions have the units s⁻¹ and second-order reactions have the units M⁻¹s⁻¹ for the Arrhenius pre-exponential factor.

^bValue taken from the work of Oakley et al.¹⁰¹

Table 4.3: Pre-exponential factor values for reactions of ethylbenzene and its progeny that were obtained via regression to experimental data.

Reaction Family	A for Ethylbenzene Reactions [s ⁻¹ /M ⁻¹ s ⁻¹] ^a
Primary initiation	1 x 10 ¹²
Hydroperoxide decomposition	1 x 10 ³
Hydrogen transfer by peroxy radical	Primary: 1.3 x 10 ⁴ Secondary: 1.3 x 10 ⁵
Hydrogen transfer by alkoxy radical	8.1 x 10 ⁴
Disproportionation by carbon-centered radical	3.4 x 10 ⁴
Disproportionation by oxygen-centered radical	Cross: 1 x 10 ⁴ Self: 1 x 10 ¹⁰

^aFirst-order reactions have the units s⁻¹ and second-order reactions have the units M⁻¹s⁻¹ for the Arrhenius pre-exponential factor.

^bPrimary refers to hydrogen abstraction from an ethylbenzene molecule and secondary refers to hydrogen abstraction from a 1-phenylethyl hydroperoxide or 1-phenylethanol molecule

^cCross refers to the disproportionation of a cyclooctene-derived radical and an ethylbenzene-derived radical. Self refers to disproportionation of two ethylbenzene-derived radicals.

Due to its ability to decompose hydroperoxide species, Co/ZSM-5 was considered to decompose 2-cycloocten-1-yl hydroperoxide and 1-phenylethyl hydroperoxide. The scheme implemented for both Co-mediated hydroperoxide decomposition cycles can be seen in Figure 4.1, with these reactions formulated based on Fenton-type chemistry.¹⁰⁰ The value of the rate coefficients for Co-catalyzed hydroperoxide decomposition were initialized to the values for the same reactions on Au and regressed individually to fit the data and account for differences in activity for the two hydroperoxides. The ZSM-5 zeolite was determined to not affect the catalysis by a blank experimental run, and therefore, no effect of the support on the chemistry was incorporated in the model.

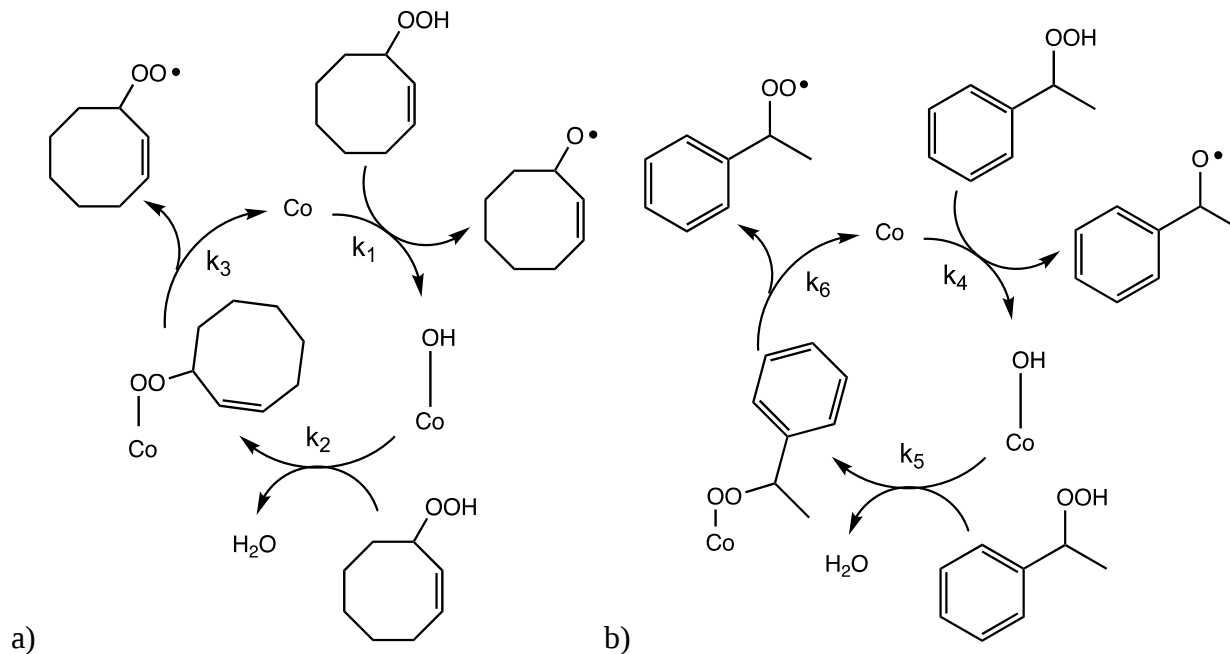


Figure 4.1: Scheme for decomposition of a) 2-cycloocten-1-yl hydroperoxide and b) 1-phenylethyl hydroperoxide on Co sites.

4.2.3 Model Execution

Once rate coefficients for all of the reactions were tabulated, rate expressions for all species were formulated using elementary rate laws and mass action kinetics. The rate laws were coupled with the reactor design equation for a constant volume batch reactor, and the balance equations were integrated using a modified Newton's method.⁴¹ Parameter regression was performed by minimizing the residual sum of squares for concentrations of ethylbenzene, 1-phenylethanol, 1-phenylethanone, and 1-phenylethyl hydroperoxide at all reaction times for the different cyclooctene and ethylbenzene runs simultaneously.⁴² The model was deemed to have converged when the residual sum of squares did not change more than 10^{-5} between one iteration to the next. The initial concentrations of ethylbenzene, cyclooctene, cyclooctene oxidation products, and tert-

butyl hydroperoxide were set according to the experimental conditions listed in the following section. Since O₂ is bubbled into the system, the concentration of O₂ in the model was set as a constant at the saturation point of O₂ in cyclooctane, the closest solvent where data was available, which was 1.1×10^{-3} mol fraction.

4.2.4 Experimental Methods

The full experimental details and procedures can be found in Appendix 3. Each reaction was run in a batch reactor with O₂ bubbled in at a rate of 30 cm³/min; increasing the bubbling rate was verified to have a negligible effect on the rate of oxidation. The temperature was set and maintained at 373 K for each trial. The reaction mixtures were composed of varying amounts of ethylbenzene, cyclooctene reaction mixture, pure cyclooctene, and Co. The cyclooctene reaction mixture was produced by running the reaction with cyclooctene and oxygen until ~50 % conversion, then sampling the resultant mixture. This reactant mixture is assumed to contain about 50 % cyclooctene, 40 % cyclooctene oxide, 4 % 2-cycloocten-1-ol, 4 % 2-cycloocten-1-one, and 2 % 2-cycloocten-1-yl hydroperoxide. The composition is based on the previous work on cyclooctene oxidation and the consistent selectivities that were observed at ~50 % conversion. An inert internal standard of 1 mL of decane was added to each reaction mixture as well. The Co/ZSM-5 was 5 wt% Co loading. Table 4.4 lists the compositions of all of the reaction mixtures used as trials for regression of the model parameters.

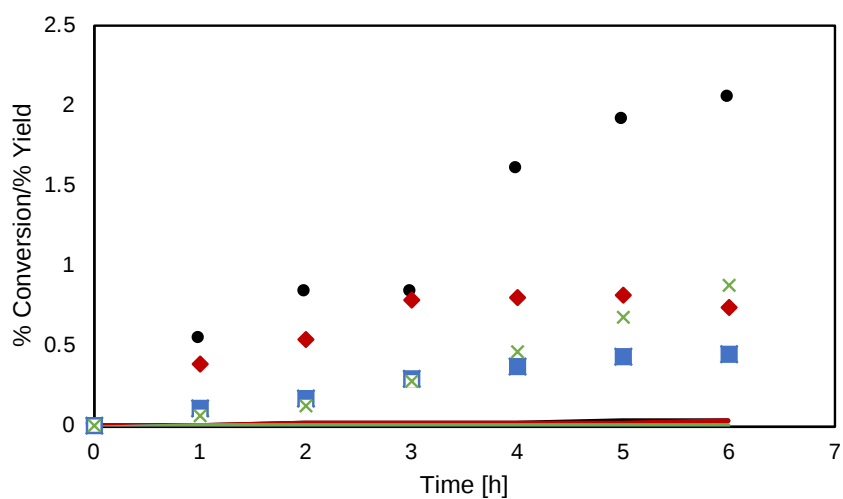
Table 4.4: Composition of experimental reaction mixtures for the co-oxidation of ethylbenzene and cyclooctene. Included in each trial is an additional internal standard of 1 mL decane.

Trial	Amount of Ethylbenzene	Amount of Cyclooctene Reaction Solution	Amount of Pure Cyclooctene Added	Amount of Decane	Amount of Co/ZSM-5
1	7 mL	3 mL	0 mL	0mL	0 mg
2	7 mL	1 mL	0 mL	2 mL	32 mg
3	7 mL	1 mL	1 mL	1 mL	32 mg
4	7 mL	1 mL	2 mL	0 mL	32 mg

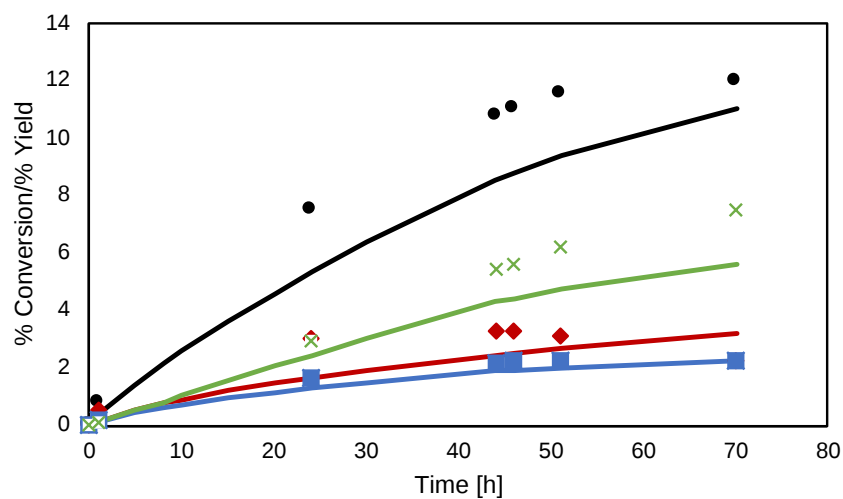
4.3 Computational Results and Discussion

The generation of the reaction network for the co-oxidation of ethylbenzene and cyclooctene yielded a model that included 695 species, 134 forward/reverse reaction pairs, and 3,673 unique forward reactions. For the uncatalyzed baseline with ethylbenzene and cyclooctene reaction solutions, the absolute errors between the concentration values from the model compared to those from experiment were less than 0.1 M, well within the experimental error. The results of the model including the role of the catalyst match the experimental data at a variety of reaction conditions, and the agreement is shown in Figure 4.2. The model is able to capture reactant conversion and product yields within experimental error for each of the trials. The regressed values of pre-exponential factors for several reaction families involving ethylbenzene and its progeny are within the expected range. It is noted that the rate coefficients for disproportionation are pushed to their theoretical upper bounds to maintain the proper amount of activity in the system. These regressed values are higher than the equivalent reactions for cyclooctene, as it is hypothesized that the ethylbenzene oxidation is much less active than cyclooctene oxidation due to the propensity for termination reactions. One possible explanation for this high rate of disproportionation would

be that confinement within the zeolite pores keeps local radical density higher than expected. Further investigation beyond the scope of this work would be needed to evaluate the role of the zeolite microstructure within this system.



a)



b)

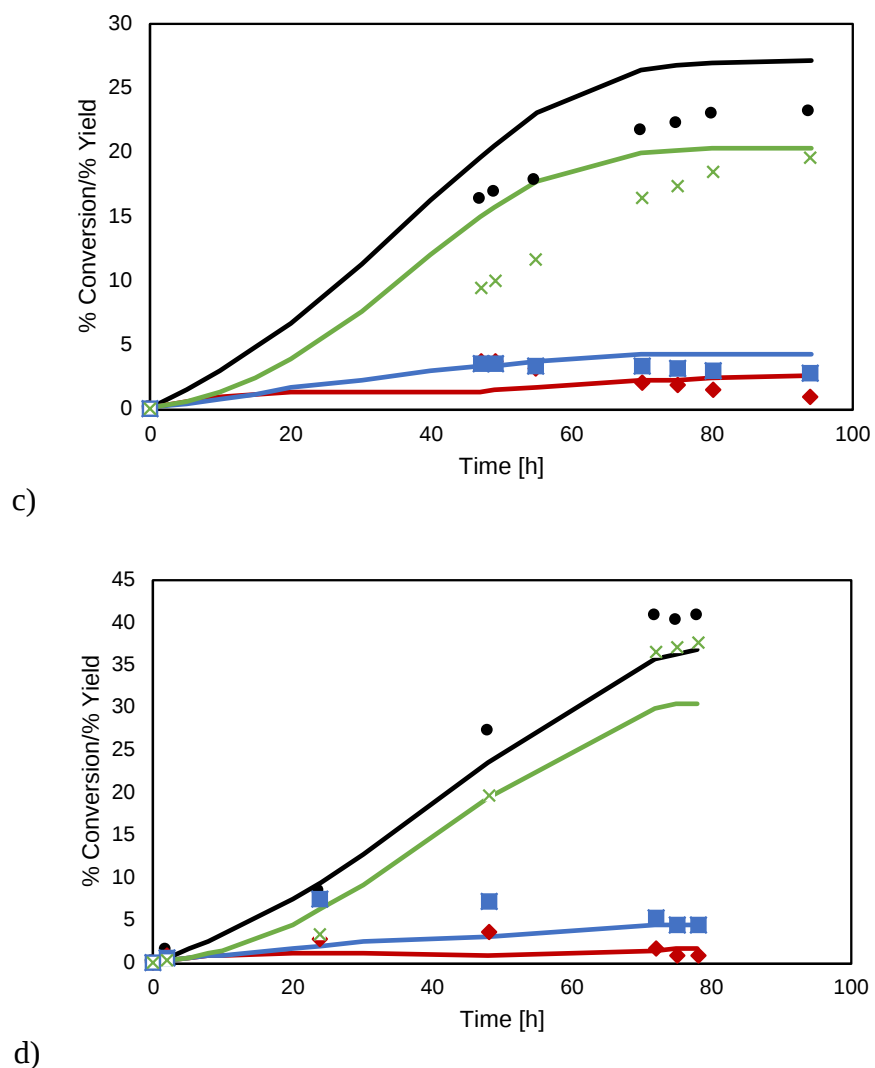


Figure 4.2: Model results for ethylbenzene oxidation in the two-component system with the following conditions: a) uncatalyzed with 3 mL cyclooctene reaction solution and Co-catalyzed systems with b) 1 mL cyclooctene reaction solution, c) 1 mL cyclooctene reaction solution and 1 mL pure cyclooctene, and d) 1 mL cyclooctene reaction solution and 2 mL pure cyclooctene. Experimental data are shown in symbols, and the model results are shown as lines of the corresponding color. The data plotted are conversion of ethylbenzene (●) and yields of the products: 1-phenylethyl hydroperoxide (♦), 1-phenylethanol (■), and acetophenone (×).

As anticipated from the kinetic coupling effect of the co-oxidation, as the amount of cyclooctene in the system was increased, the activity of ethylbenzene oxidation increased. In concert with the rate enhancement of the ethylbenzene system, the chain propagation rate of cyclooctene oxidation was suppressed as a higher ratio of the concentration of ethylbenzene to cyclooctene reaction solution and pure cyclooctene was obtained, as illustrated in Figure 4.3.

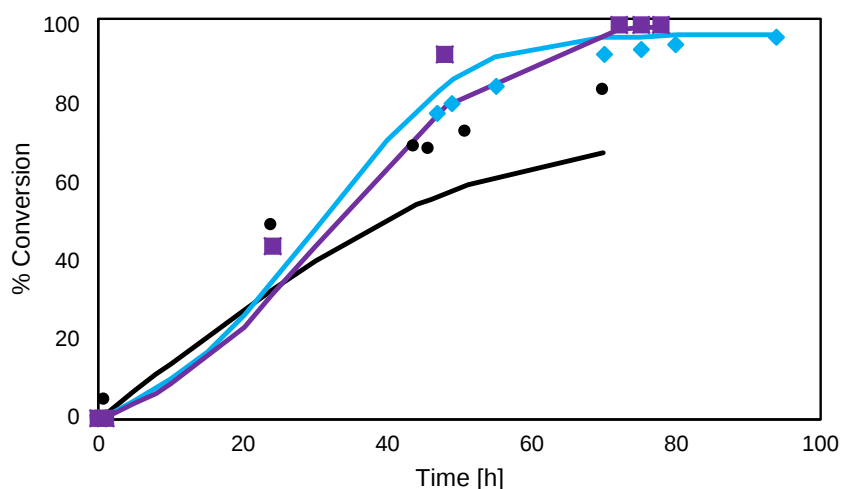


Figure 4.3: Model results for cyclooctene conversion in the two-component system. The data plotted represents the following trials: 7 mL ethylbenzene to 1 mL cyclooctene reaction solution (●), 7 mL ethylbenzene to 1 mL cyclooctene reaction solution and 1 mL pure cyclooctene (◆), and 7 mL ethylbenzene to 1 mL cyclooctene reaction solution and 2 mL pure cyclooctene (■).

An important metric to consider in terms of the model's effectiveness as a predictive tool is the ratio of conversion of cyclooctene to conversion of ethylbenzene. If the relative rates are captured by the model, one can predict the promotion of the rate of ethylbenzene oxidation at new reaction conditions by simply knowing the oxidation rate of cyclooctene. This metric was validated on a system with 5 mL of ethylbenzene and 5 mL of pure cyclooctene, and the complete results

can be seen in Figure 4.4. The performance of the model in terms of the ratio of conversion of cyclooctene to the conversion of ethylbenzene improves at long times, especially in the 1 mL cyclooctene case.

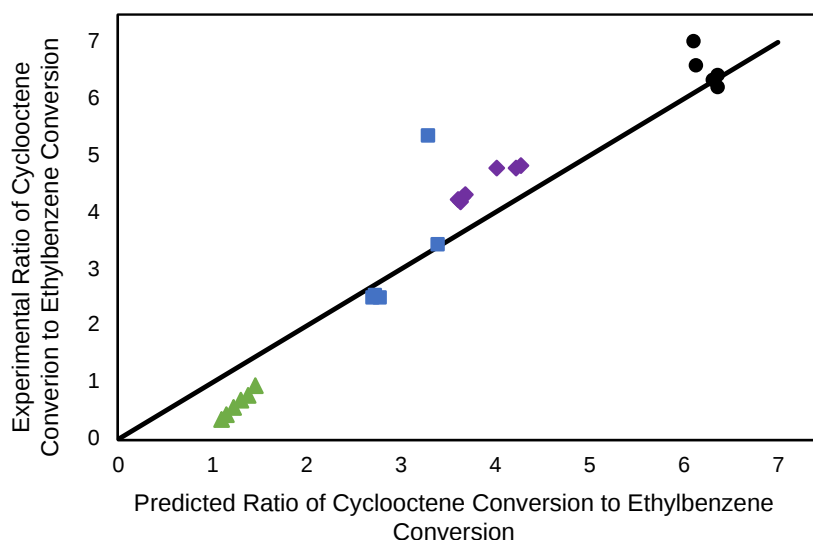


Figure 4.4: Parity plot of ratio of cyclooctene conversion to ethylbenzene conversion. Data points corresponds to time points in the 1 mL cyclooctene reaction solution (●), 1 mL cyclooctene reaction solution and 1 mL pure cyclooctene (◆), 1 mL cyclooctene reaction solution and 2 mL pure cyclooctene (■), and 5 mL pure cyclooctene (▲) trials.

The net rate analysis of this system indicates that a truly synergistic co-oxidation is occurring, where the kinetically-favorable cyclooctene reactions facilitate the oxidation of ethylbenzene. Previous work on the oxidation of cyclooctene indicated that the majority of the flux in the system was contained in a series of addition reactions with alkoxy or peroxy radical intermediates adding across the double bond of the substrate. The bicyclic intermediate that was formed underwent subsequent epoxidation reactions through an ether or peroxy bond cleavage

mechanism. The minor reactions within the system were hydrogen abstraction by an alkoxy or peroxy radical of the allylic hydrogen atoms of cyclooctene. This scheme can be seen in Figure 4.5. When ethylbenzene is present, a higher proportion of the alkoxy or peroxy radicals is diverted to the path of hydrogen abstraction, as increasing the ethylbenzene to cyclooctene ratio increases the ratio of abstractable hydrogen atoms to double bonds. In addition, the hydrogen atoms in ethylbenzene are more easily abstracted by peroxy and alkoxy radicals compared to the allylic hydrogen atoms in cyclooctene, due to poor overlap between the σ_{C-H} and $\pi_{C=C}$ orbitals in cyclooctene.⁸⁹ Another source of peroxy and alkoxy radicals of cyclooctene and their progeny is the decomposition of 2-cycloocten-1-yl hydroperoxide by the Co species. Because there is 2-cycloocten-1-yl hydroperoxide present in the starting cyclooctene reaction solution, the catalytic cycle is active even at short times in generating radicals. The fit values for rate coefficients and net fluxes for two different reaction conditions for the Co reactions can be seen in Table 4.5.

Table 4.5: Values of rate coefficients for Co reactions and corresponding net flux at 1 h for Trial 1: 1 mL cyclooctene reaction solution only and Trial 2: 1 mL cyclooctene reaction solution, 2 mL pure cyclooctene. The abbreviation COE represents a functionalized cyclooctene molecule, and EB represents a functionalized ethylbenzene molecule.

Reaction	Rate Constant (See Figure 4.1)	k [s ⁻¹ /M ⁻¹ s ⁻¹] ^a	Net Flux at 1 h	
			Trial 1	Trial 2
Co + COE-OOH → CoOH + COE-O•	k ₁	2.1 x 10 ¹ ^b	2.9 x 10 ⁻⁷	1.5 x 10 ⁻⁶
CoOH + COE-OOH → CoOOR + H ₂ O	k ₂	2.9 x 10 ⁰ ^b	2.9 x 10 ⁻⁷	1.5 x 10 ⁻⁶
CoOO-COE → Co + COE-OO•	k ₃	5.0 x 10 ⁻¹	2.9 x 10 ⁻⁷	1.5 x 10 ⁻⁶
Co + EB-OOH → CoOH + EB-O•	k ₄	5.6 x 10 ⁻¹⁰ ^b	1.2 x 10 ⁻¹⁷	1.2 x 10 ⁻¹⁷
CoOH + EB-OOH → CoOOR + H ₂ O	k ₅	8.8 x 10 ⁻¹¹ ^b	1.3 x 10 ⁻¹⁷	1.3 x 10 ⁻¹⁷
CoOO-EB → Co + EB-OO•	k ₆	5.0 x 10 ⁻¹	1.3 x 10 ⁻¹⁷	1.3 x 10 ⁻¹⁷

^aFirst-order reactions have the units s⁻¹ and second-order reactions have the units M⁻¹ s⁻¹ for the rate coefficients. Net fluxes have units of M s⁻¹

^bDenotes a regressed value

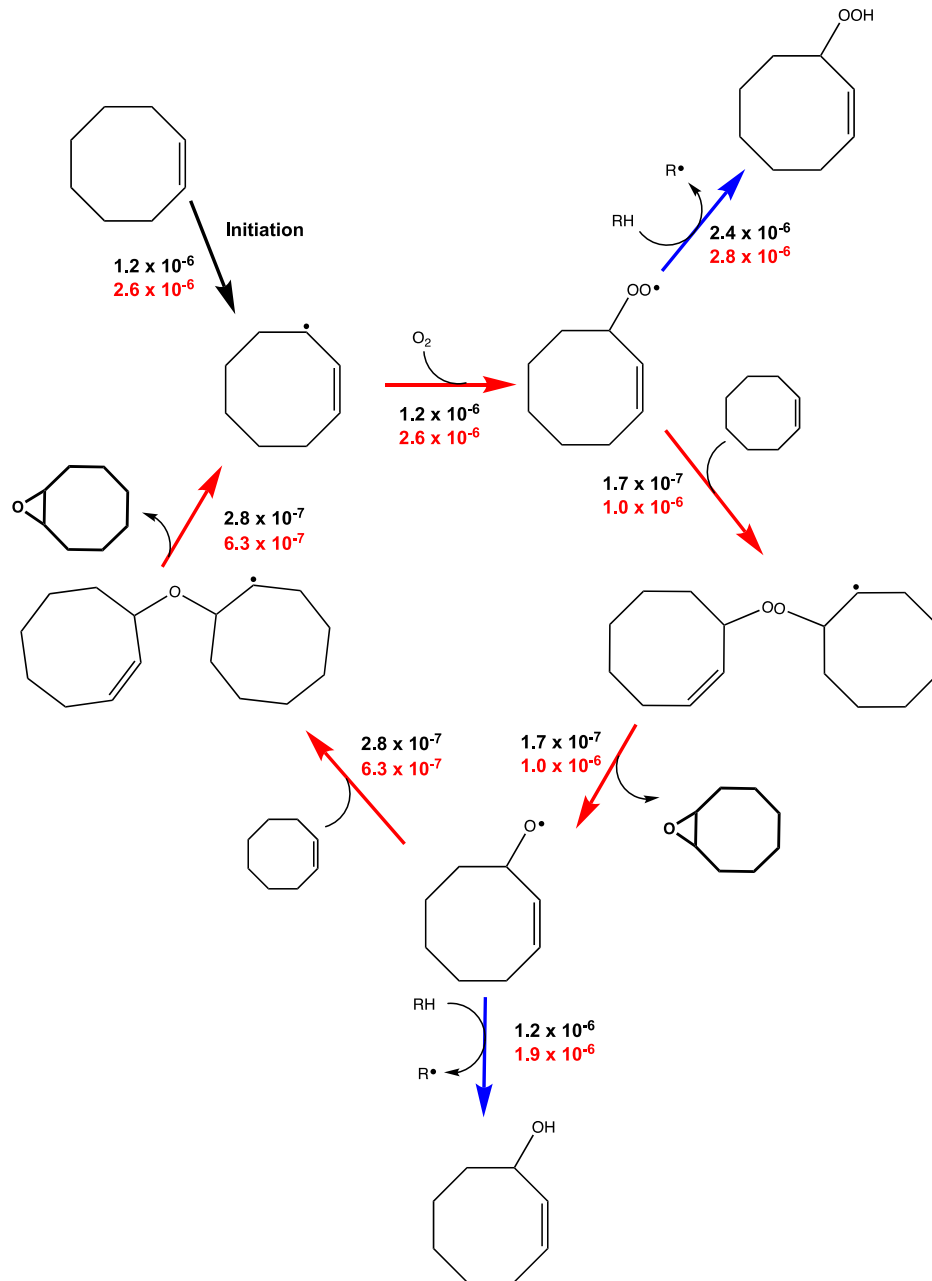


Figure 4.5: The mechanism of cyclooctene oxidation within the two-component oxidation system. Red arrows represent steps in the epoxidation cycle, and blue arrows are diversion steps that can initiate ethylbenzene. The net fluxes in M s^{-1} through each of these steps for the 1 mL cyclooctene reaction solution trial at 1 h are shown in black, and the net fluxes for the 1 mL cyclooctene reaction solution, 2 mL pure cyclooctene at 1 h are shown in red.

With the decreased tendency towards radical addition as the concentration of cyclooctene is decreased, the alkoxy and peroxy radicals derived from cyclooctene initiate ethylbenzene via hydrogen abstraction. Once initiated, the ethylbenzene radical readily adds O_2 to form a peroxy radical. Hydrogen abstraction by the resultant ethylbenzene peroxy radical gives rise to a significant amount of the minor product, 1-phenylethyl hydroperoxide. Once 1-phenylethyl hydroperoxide is formed, there are two competing secondary reactions: the α -hydrogen may be abstracted or the hydroperoxide can re-initiate either via a Co-catalyzed reaction or homogeneous decomposition. The preferred pathway under these conditions is for the α -hydrogen abstraction of 1-phenylethyl hydroperoxide, the product of which proceeds to perform β -scission to form the major product, acetophenone. When 1-phenylethyl hydroperoxide undergoes bimolecular decomposition, the resultant alkoxy radical abstracts hydrogen from ethylbenzene or the other sources of labile hydrogen to form the other minor product, 1-phenylethanol. The alcohol product may also undergo a secondary reaction, where its α -hydrogen is abstracted, followed by two equivalents reacting via carbon-centered disproportionation to form one equivalent of 1-phenylethanol and acetophenone, although this is a minor contributor to the flux in the system towards acetophenone. It is of note that in contrast to the neat cyclooctene system, the ethylbenzene-derived peroxy radical has a higher tendency to disproportionate leading to the creation of 1-phenylethanol, acetophenone, and O_2 . This termination reaction is competitive with hydrogen abstraction by the peroxy radical throughout the reaction time. The model predicts that 1-phenylethyl hydroperoxide is not decomposed by the Co sites. An experimental trial using 1-phenylethyl hydroperoxide as the starting material exhibited negligible conversion when Co/ZSM-

5 was introduced. The ethylbenzene oxidation mechanism with its corresponding net fluxes can be seen in Figure 4.6.

The model results and net rate analysis provide evidence that the role of cyclooctene in this system is to activate the carbon-hydrogen bonds in the ethylbenzene substrate. A vast majority of the initiation of ethylbenzene comes from hydrogen abstraction by molecules that are diverted from the cyclooctene oxidation system. In fact, cyclooctene plays more of a role in facilitating the ethylbenzene reaction than the Co catalyst, according to the net fluxes. The rate of hydrogen abstraction by a cyclooctene alkoxy or peroxy radical from 1-phenylethyl hydroperoxide is orders of magnitude greater than decomposition of 1-phenylethyl hydroperoxide via the Co-catalyzed route. Note, however, that the effect of Co on the entire system cannot be discounted, as the decomposition of 2-cyclooctene-1-yl hydroperoxide plays an important role in generating the important alkoxy and peroxy radical species that perform hydrogen abstraction, especially at short times.

4.4 Conclusions

The microkinetic model developed for analyzing the co-oxidation of ethylbenzene and cyclooctene using molecular oxygen and Co/ZSM-5 catalyst is able to match the observed experimental data for conversion and selectivity. As anticipated, the model matched the trend that when more cyclooctene is added to the system, the rate of oxidation of ethylbenzene increases. Analysis of the flux in the system showed that the overall reaction proceeds via formation of 1-phenylethyl hydroperoxide, and subsequent secondary reactions form acetophenone and 1-phenylethanol. The hydrogen abstraction reaction from 1-phenylethyl hydroperoxide by cyclooctene-derived alkoxy and peroxy radicals plays a major role in driving the activity and selectivity towards acetophenone, the predominant product. The presence of cyclooctene-derived

radicals is more important in terms of driving this integral secondary reaction than the Co catalyst. Overall, this work suggests that the strategy of co-oxidation to improve the activity of a less reactive substrate has merit and deserves further investigation as a catalytic scheme.

Chapter 5: Mechanistic Modeling of Free-radical and Ti/SiO₂-catalyzed Oxidation of Limonene

5.1 Introduction

In order to supplement or replace petroleum-derived polymer processes, the polymer industry has been searching for green alternatives. One possible green feedstock is limonene, a cheap and abundant raw material that can be found in the peels of citrus fruit and obtained via separation from citrus oil.^{115,116} Limonene may be oxidized to its epoxide products, 1,2-limonene oxide and 8,9-limonene oxide, using various transition metal oxide catalysts. When limonene oxide is subsequently polymerized in the presence of carbon dioxide, the resultant poly(limonene carbonate) has desirable physical properties, which shows the potential for limonene to be used as a biomass-derived alternative to traditional monomers for polymers.^{115,117}

Limonene contains two double bonds, an internal 1,2- and an external 8,9-double bond, that exhibit considerable steric differences. A limonene molecule with the accepted carbon-numbering convention is shown in Figure 5.1. The two distinct double bonds within limonene make it an ideal regioselectivity probe for direct epoxidation catalysts. Previous studies on the epoxidation of limonene using acidic oxides have illustrated that the regioselectivity of the reaction can be highly dependent on the catalyst structure.^{8,118–123} Typically, for electrophilic oxidation mechanisms on supported metal oxides, increased alkyl substitution at the double bond will lead to higher reactivity, as illustrated by studies on both 4-vinyl-1-cyclohexene and limonene.^{124,125} In the case of limonene, the preference for the triply-substituted internal 1,2-limonene oxide can range from 3:1 to 10:1 compared to the external doubly-substituted 8,9-limonene oxide.^{8,119,120} However, there are cases when support sterics influence the regioselectivity and the production of

8,9-limonene oxide can be driven to excess.^{121–123} These direct epoxidation routes have been shown to be in competition with radical oxidation mechanisms that can give rise to significant amounts of allylic oxidation products.^{126,127} The underlying homogeneous radical chemistry is most likely present in the catalyzed studies even when not fully reported, as shown by other studies on the oxidation of alkenes.^{126–128}

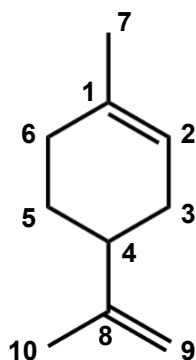


Figure 5.1: Limonene molecule with carbon-numbering convention.

While the oxidation of limonene and other alkenes using supported and bulk metal oxide catalysts has been studied, there remain questions about the relative roles of catalyst structure, reaction conditions, and intrinsic reactivity of the substrate on the observed conversion and selectivity. This work represents a collaborative computational and experimental study with the goal of elucidating the mechanism(s) of limonene oxidation over titanium on silica using tert-butyl hydroperoxide (TBHP) as the oxidant at various reaction conditions. Prior to the catalytic study, the intrinsic behavior of limonene oxidation was investigated through creation of a free-radical microkinetic model validated by experimental data. The microkinetic model based on radical chemistry alone was then augmented to include two postulated Ti-catalyzed direct epoxidation cycles involving distinct active sites.

5.2 Methods

5.2.1 Computational Methods

5.2.1.1 Reaction Network Generation

The first step in creating the full microkinetic model for limonene oxidation was to postulate a set of elementary reactions. The network generation was performed by an automated method developed by Broadbelt et al.^{33–37} Automated network generation relies on the concept of elementary reaction families, where reactions of the same canonical type are grouped. For the homogenous model, the reaction families are based on typical radical oxidation families and are listed in Table 5.1.⁶⁷ The radical reaction families were subject to the following reaction rules to prevent the formation of products that were not experimentally observed: vinyl radicals were not allowed to form, and oxygen was only allowed to add to a given molecule once to prevent over-oxidation. In order to maintain a computationally reasonable network size while still capturing all postulates for the radical mechanism, most primary products were not allowed to undergo secondary reactions, and only molecules containing fewer than 20 carbons were allowed to react. Secondary reactions were allowed for the primary hydroperoxide products of limonene, as these were not quantified experimentally, and for 1,2-limonene oxide and 8,9-limonene oxide, as a high selectivity was observed for 1,2-8,9 limonene diepoxide.

Table 5.1: List of reaction families included in the uncatalyzed reaction mechanism for limonene oxidation based on free-radical chemistry. R, R', and R'' represent alkyl/alkoxy groups or hydrogens, and R>O represents an epoxide.

Reaction Family	Example
<u>Initiation</u>	
Primary initiation	$\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HOO}\cdot$
Peroxy-bond fission	$\text{ROOR}' \rightarrow \text{RO}\cdot + \text{R}'\text{O}\cdot$
Hydroperoxide decomposition	$\text{RH} + \text{R}'\text{OOH} \rightarrow \text{R}\cdot + \text{R}'\text{O}\cdot + \text{H}_2\text{O}$
<u>Propagation</u>	
Oxygen addition	$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$
β -scission	$\cdot\text{ROOH} \rightarrow \text{R}=\text{O} + \cdot\text{OH}$
Hydrogen transfer	$\text{ROO}\cdot + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'\cdot$ $\text{RO}\cdot + \text{R}'\text{H} \rightarrow \text{ROH} + \text{R}'\cdot$ $\text{R}\cdot + \text{R}'\text{H} \rightarrow \text{RH} + \text{R}'\cdot$
Addition	$\text{ROO}\cdot + \text{R}'=\text{R}'' \rightarrow \text{ROOR}'\text{-R}''\cdot$ $\text{RO}\cdot + \text{R}'=\text{R}'' \rightarrow \text{ROR}'\text{-R}''\cdot$
Epoxidation	$\text{R}'\text{OOR}\cdot \rightarrow \text{R}'\text{O}\cdot + \text{R}>\text{O}$ $\text{R}'\text{OR}\cdot \rightarrow \text{R}'\cdot + \text{R}>\text{O}$
<u>Termination</u>	
Disproportionation	$2 \text{ROO}\cdot \rightarrow \text{R}=\text{O} + \text{ROH} + \text{O}_2$ $2 \text{RO}\cdot \rightarrow \text{R}=\text{O} + \text{ROH}$
Recombination	$\text{R}\cdot + \text{R}'\cdot \rightarrow \text{RR}'$

Due to the limited number of catalyzed oxidation reactions possible on Ti, the reactions were tabulated manually. The reactions implemented for the direct epoxidation cycle on the bulk Ti sites were inspired by several literature sources.^{31,118} The first step of the cycle is physisorption

of the oxidant, TBHP, on a tri-coordinated Ti site. Following physisorption, there is a chemisorption step where the TBHP binds to the active site. This active species comprised of TBHP on Ti species can then react with limonene to form either the 1,2-limonene oxide or 8,9-limonene oxide. Activation barriers for formation of 1,2-limonene oxide and 8,9-limonene oxide have been reported for Al_2O_3 as 8 kcal/mol and 13 kcal/mol, respectively.¹²⁹ This relative difference in activation barrier for the formation of 1,2-epoxide versus 8,9-epoxide was assumed to apply to other catalysts and was included in the model as a constraint, with the absolute kinetic rate of each pathway being set by the regressed pre-exponential factors. Following the reaction to form epoxide products, tert-butanol is formed and may either remain physisorbed to the Ti site or desorb and regenerate a bare Ti site. There is also a reaction proposed by Yoon et al.⁷ that allows for two equivalents of TBHP to interconvert with two equivalents of tert-butanol and an oxygen molecule. This proposed catalytic cycle involving the bulk Ti lattice sites will be referred to as Cycle 1.

The reactions in Cycle 1 do not encompass all of the possible Ti-catalyzed reactions for this system. There is a possibility of a secondary direct epoxidation cycle involving an active site that has been modified by tert-butanol, as inspired by the work of Notestein et al.^{31,32} on oxidation by metallocalixarene catalysts. In order to enter this second catalytic cycle, a physisorbed tert-butanol will chemisorb to the Ti site, releasing water and forming a new active site with a bulkier tert-butyl group within the framework. The reaction can then proceed by physisorption, followed by chemisorption of a TBHP molecule. The active TBHP on Ti species can then oxidize limonene to either the 1,2-epoxide or 8,9-epoxide. The remaining tert-butanol can either occupy the modified

Ti site or desorb and return an active site. This catalytic cycle involving a tert-butyl-modified active site will be referred to as Cycle 2.

While the 10 forward and reverse reaction pairs in the direct epoxidation cycle are active, the underlying radical chemistry will be considered as well. It has been proposed that the chemisorbed TBHP on Ti may also decompose via a radical mechanism,⁷ and two radical initiation reactions will be considered as well in the model. This will allow the model to quantify the relative contributions towards the activity and selectivity of the direct epoxidation reaction and the intrinsic radical behavior of limonene oxidation. The full catalytic reaction scheme can be seen in Figure 5.2.

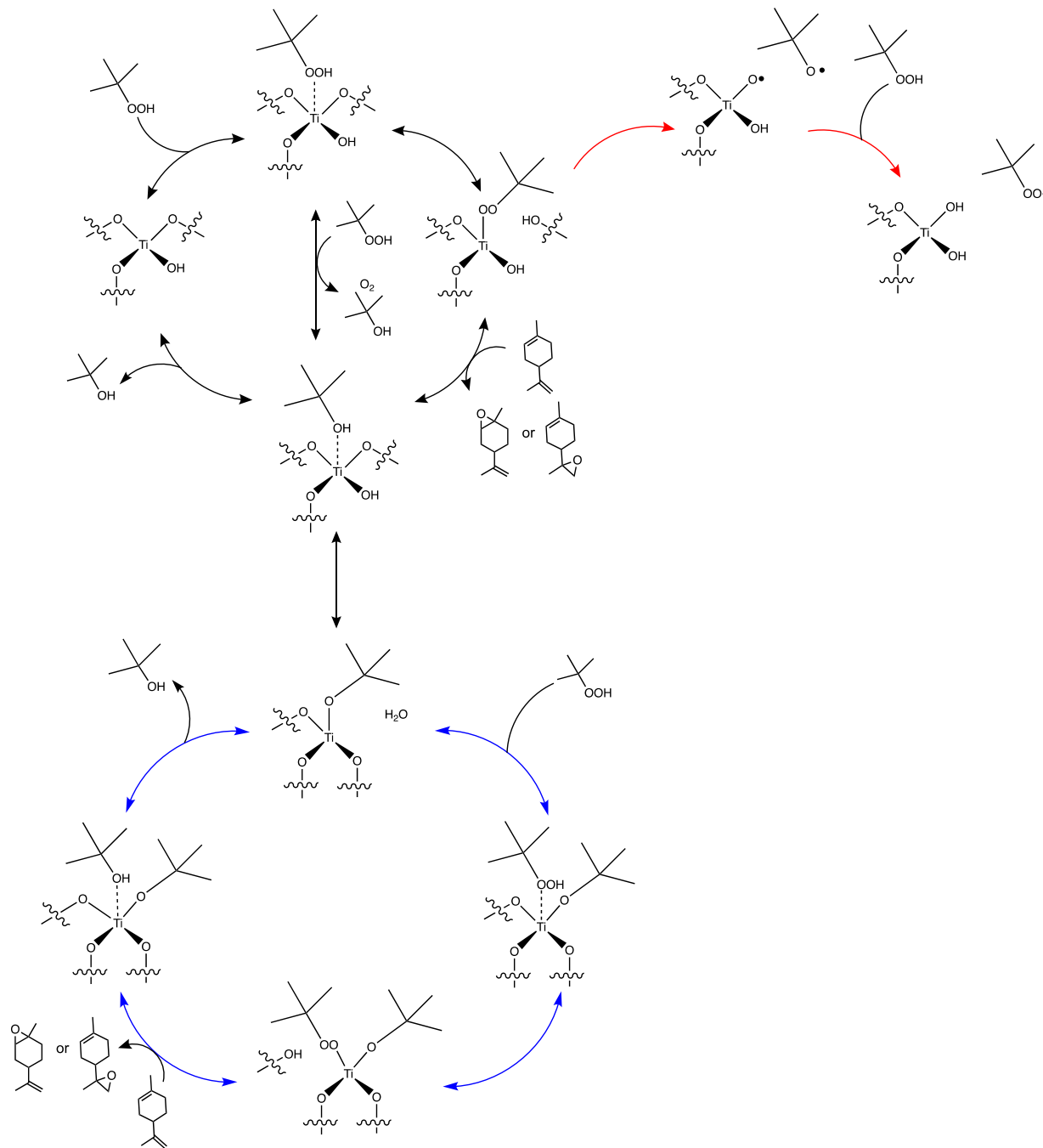


Figure 5.2: Mechanism of direct epoxidation of limonene by Ti/SiO₂. Arrows in black will be referred to as Cycle 1, blue as Cycle 2, and red as radical hydroperoxide decomposition.

5.2.1.2 Parameter Estimation and Regression

For implementation of a microkinetic model, each of the proposed reactions in the mechanism requires a rate coefficient. In order to tabulate a rate coefficient for each reaction on-the-fly for the radical mechanism as created by automated network generation, rate coefficients were assumed to be in the Arrhenius form, $k = A \exp(-E_A/RT)$, where k is the rate coefficient, A is the Arrhenius pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the temperature.³⁸ Values for the pre-exponential factor are taken as constant for each reaction with a given family. Activation barriers are obtained from literature when available or otherwise tabulated via the Evans-Polanyi relationship for a given family, $E_A = E_A^\circ + \alpha \Delta H_{rxn}$, where α and E_A° are constants for each reaction family and ΔH_{rxn} is the enthalpy of reaction for a specific reaction in the family.³⁹ Additionally, enthalpies of reaction are either obtained from literature or Benson's group additivity method.⁴⁰ Values for the Arrhenius pre-exponential factors and Evans-Polanyi parameters used in this work can be seen in Table 5.2. In addition, it was observed experimentally that the 1,2-8,9-limonene dioxide was formed in greater yield than initial models predicted. As a result, the reaction family approach for addition across the double bond was subdivided into two sub-families, with one specifically for the formation of the diepoxide, lowering the barrier by 4.1 kcal/mol for addition to an epoxide product. The amount by which the reaction barrier for secondary addition was lowered was determined by parameter regression. Several other values for Arrhenius pre-exponential factors were regressed in order to improve model performance and are noted in Table 5.2. The regression of pre-exponential factors is carried out to account for the change to the liquid phase from the initial gas phase values and to account for the fact that the pre-exponential factor is an estimate for all reactions in a family, when

indeed there are small changes in the difference between the entropy of the transition state and the entropy of the reactant from one reaction to another within a given family.

Table 5.2: List of Arrhenius pre-exponential factors and Evans-Polanyi constants used for each reaction family in the limonene oxidation mechanistic model based on free-radical chemistry.

Reaction Family	A [$\text{s}^{-1}/\text{M}^{-1} \text{s}^{-1}$] ^a	E _A ⁰ [kcal/mol]	α
Primary initiation	$1 \times 10^{10} \text{ }^b$	0	1
Peroxy bond fission	$1 \times 10^{11} \text{ }^b$	0	1
Hydroperoxide decomposition	1×10^6	24.6	-0.09
Oxygen addition	1×10^8	0	0
β -scission by alkoxy radical	$1 \times 10^{13} \text{ }^b$	9.5	0.85
β -scission by carbon-centered radical	1×10^{14}	14.24	0.76
Hydrogen transfer by alkyl radical	$1 \times 10^6 \text{ }^b$	9.1	0.3
Hydrogen transfer by alkoxy radical	$2.8 \times 10^5 \text{ }^b$	11.9	0.91
Hydrogen transfer by peroxy radical	$1 \times 10^4 \text{ }^b$	3.05	1.1
Addition	$5.0 \times 10^5 \text{ }^b$	14.24	0.24
Epoxidation ^b	$1.7 \times 10^9 \text{ }^b$	21.4	0.51
Disproportionation	$1 \times 10^8 \text{ }^b$	0	0
Recombination	1×10^8	0.85	0

^aFirst-order reactions have the units s^{-1} and second-order reactions have the units $\text{M}^{-1}\text{s}^{-1}$ for the Arrhenius pre-exponential factor.

^bValues taken from the work of Oakley et al.¹⁰¹

In order to reduce the computational time required for running the catalyzed model, the full free-radical mechanism was simplified based on net rate analysis to obtain a smaller mechanism that contained the most kinetically-relevant reactions. Free-radical reactions were eliminated based on the results of the homogeneous model if their net flux was below a threshold of 10^{-10} M/s . For the Ti/SiO₂-catalyzed reactions, a rate coefficient was assigned to each reaction. Initial values were selected based on typical catalyzed reactions reported for adsorption, reactions on surfaces, and

desorption. The values for each of the rate coefficients for the catalyzed reactions can be seen in Table 5.3 with values that were regressed noted.

Table 5.3: Rate coefficients for Ti-catalyzed reactions for the oxidation of limonene.

Cycle 1		
Reaction	Forward Rate Coefficient^a	Reverse Rate Coefficient^a
Physisorption of TBHP	$5.2 \times 10^{-2}{}^b$	$1.6 \times 10^{-1}{}^b$
Chemisorption of TBHP	1×10^3	1×10^{-1}
Limonene oxidation to 1,2-limonene oxide	$3.6 \times 10^4{}^b$	1×10^{-4}
Limonene oxidation to 8,9-limonene oxide	$1.2 \times 10^7{}^b$	1×10^{-4}
Desorption of t-butanol	$9.8 \times 10^3{}^b$	$9.0 \times 10^{-8}{}^b$
TBHP to t-butanol	1×10^0	1×10^{-1}
Chemisorption of tert-butanol	$1.2 \times 10^2{}^b$	$1.5 \times 10^{-7}{}^b$
Cycle 2		
Physisorption of TBHP	$1.1 \times 10^3{}^b$	1×10^{-1}
Chemisorption of TBHP	$2.1 \times 10^2{}^b$	1×10^{-1}
Limonene oxidation to 1,2-limonene oxide	$1.2 \times 10^{-1}{}^b$	1×10^0
Limonene oxidation to 8,9-limonene oxide	$8.4 \times 10^{-4}{}^b$	1×10^{-1}
Desorption of tert-butanol	$3.0 \times 10^{-2}{}^b$	$8.6 \times 10^3{}^b$
Radical Hydroperoxide Decomposition		
Alkoxy radical formation	$1.3 \times 10^{-3}{}^b$	-
Peroxy radical formation	$4.9 \times 10^{-5}{}^b$	-

^aRate coefficients are in the units of s^{-1} for unimolecular reactions and $\text{M}^{-1} \text{s}^{-1}$ for bimolecular reactions

^bDenotes a regressed value

5.2.1.3 Model Execution

With rate coefficients tabulated for each reaction, rate expressions were formulated for each reaction based on elementary rate laws and mass action kinetics. These rate expressions

were coupled with reactor design equations for each species based on a batch reactor and integrated via a modified Newton's method.⁴¹ Regression was performed to minimize the residual sum of squares for the concentration of limonene, 1,2-limonene oxide, 8,9-limonene oxide, and TBHP at times corresponding to experimental data points for all trials.⁴² The model converged when the residual sum of squares did not change by more than 10^{-5} between iterations. The initial concentrations of limonene and TBHP were initialized according to the experimental conditions for a given trial. For the homogeneous runs, O₂ was bubbled into the system, so the model set the concentration of O₂ as a constant with a mol fraction of 1.2×10^{-3} , which is the solubility of O₂ in cyclohexane the most comparable solvent where data was available.

5.2.2 Experimental Methods

Full experimental details and procedures can be found in Appendix 4. It is important to note at this point the reaction conditions that were initialized within the model, as these will differentiate among the experimental cases. Each of the homogeneous uncatalyzed reactions were run in a batch reactor with the only solvent being decane to keep the reactor volume constant. Oxygen was bubbled through the reaction mixture at a rate of 1 cm³/s. The temperature and concentration of TBHP as the initiator were varied to test their impact on reaction kinetics. Table 5.4 lists the reaction conditions for the homogeneous trials that were used in validation of the free-radical model.

Table 5.4: Experimental reaction conditions for uncatalyzed limonene oxidation.

Trial	Temperature	Amount of Limonene	Amount of TBHP	Amount of Decane
1	65 °C	14 mL	1 mL	0 mL
2	75 °C	14 mL	1 mL	0 mL
3	75 °C	14 mL	0.2 mL	0.8 mL

Additionally, several trials were performed using Ti/SiO₂ catalysts and used to aid the development of the catalyzed model. Each of these reactions were performed in acetonitrile and/or decane within a batch reactor. The oxidant for these trials was TBHP, as O₂ was shown to be inactive when the catalyst was used. The model was regressed using four trials with varying temperature, concentration of TBHP, and concentration of tert-butanol in order to span the reaction space. The model was then validated against an additional trial at an intermediate concentration of TBHP. For the trial run with tert-butanol, a pre-treatment with tert-butanol was performed in an attempt to force the active site to that driving Cycle 2, but there is evidence that this capping process is not irreversible. The reaction conditions for runs used in the development and validation of the catalyzed model are shown in Table 5.5.

Table 5.5: Experimental reaction conditions for limonene oxidation catalyzed by Ti/SiO₂.

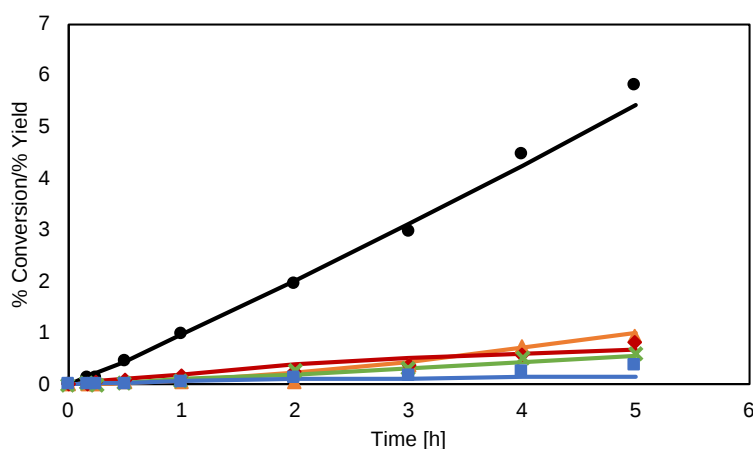
Trial	Temperature	Amount of limonene	Amount of TBHP	Amount of acetonitrile, decane, tert-butanol	Amount of Ti/SiO₂
1	55 °C	0.16 mL	0.2 mL	4.6 mL, 0 mL, 0 mL	108.1 mg
2	65 °C	0.16 mL	0.2 mL	4.6 mL, 0 mL, 0 mL	106.7 mg
3 ^a	65 °C	0.16 mL	0.6 mL	3 mL, 1.2 mL, 0 mL	102.5 mg
4	65 °C	0.16 mL	1.8 mL	3 mL, 0 mL, 0 mL	102.6 mg
5	65 °C	0.16 mL	0.2 mL	0 mL, 0 mL, 4.6 mL	70.4 mg

^aTrial used for the validation of the model after regression was carried out using the other trials.

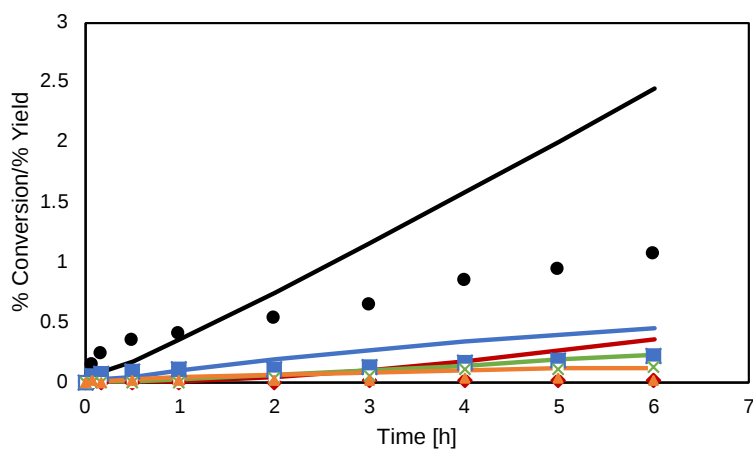
5.3 Results and Discussion

5.3.1 Homogeneous Model

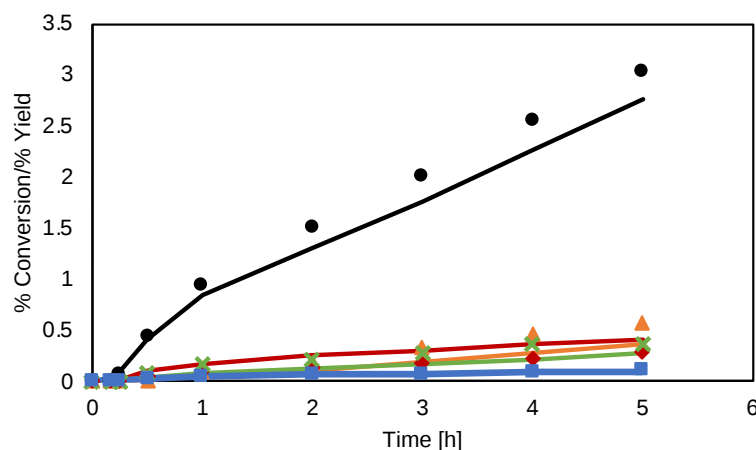
The network generated for the uncatalyzed oxidation of limonene contained 2,136 species, 1,132 reversible reactions and 20,291 unique forward reactions. The agreement between the model results and experimental data for conversion of the reactant and major product yields is shown in Figure 5.3. The model is able to capture the free-radical oxidation of limonene at multiple temperatures and initiator concentrations. The regressed pre-exponential factors are within the expected range and are comparable to previous values for the oxidation of cyclooctene.



a)



b)



c)

Figure 5.3: Microkinetic model results for uncatalyzed free-radical limonene oxidation with the following conditions: a) 75 °C, 1 mL TBHP b) 348 °C, 0.2 mL TBHP, and c) 338 °C, 1 mL TBHP. Experimental data are shown in symbols, and the model results are shown as lines of the corresponding color. The data plotted are conversion of limonene (●) and yields of the products: 1,2-epoxide (◆), 8,9-epoxide (■), C₃-alcohol (×), and diepoxide (▲).

Net rate analysis reveals a more complex system than in the case of either cyclooctene or ethylbenzene oxidation. There are three competing sites where hydrogen is abstracted at a significant rate: carbon atoms at positions 3, 4, and 6. Following hydrogen abstraction, oxygen will add rapidly to the resultant alkyl radical. For limonene, the next step is consistently radical addition to one of the double bonds in the substrate. Addition to the 1,2-double bond is consistently preferred by a factor of about three compared to addition to the 8,9-double bond. This forms bicyclic intermediates with a bridging peroxy bond in the β -position to the alkyl radical, which will then undergo epoxidation reactions. This preference for addition to the 1,2-double bond and

subsequent epoxidation explains the higher regioselectivity to 1,2-limonene oxide. This scheme can be seen in Figure 5.4.

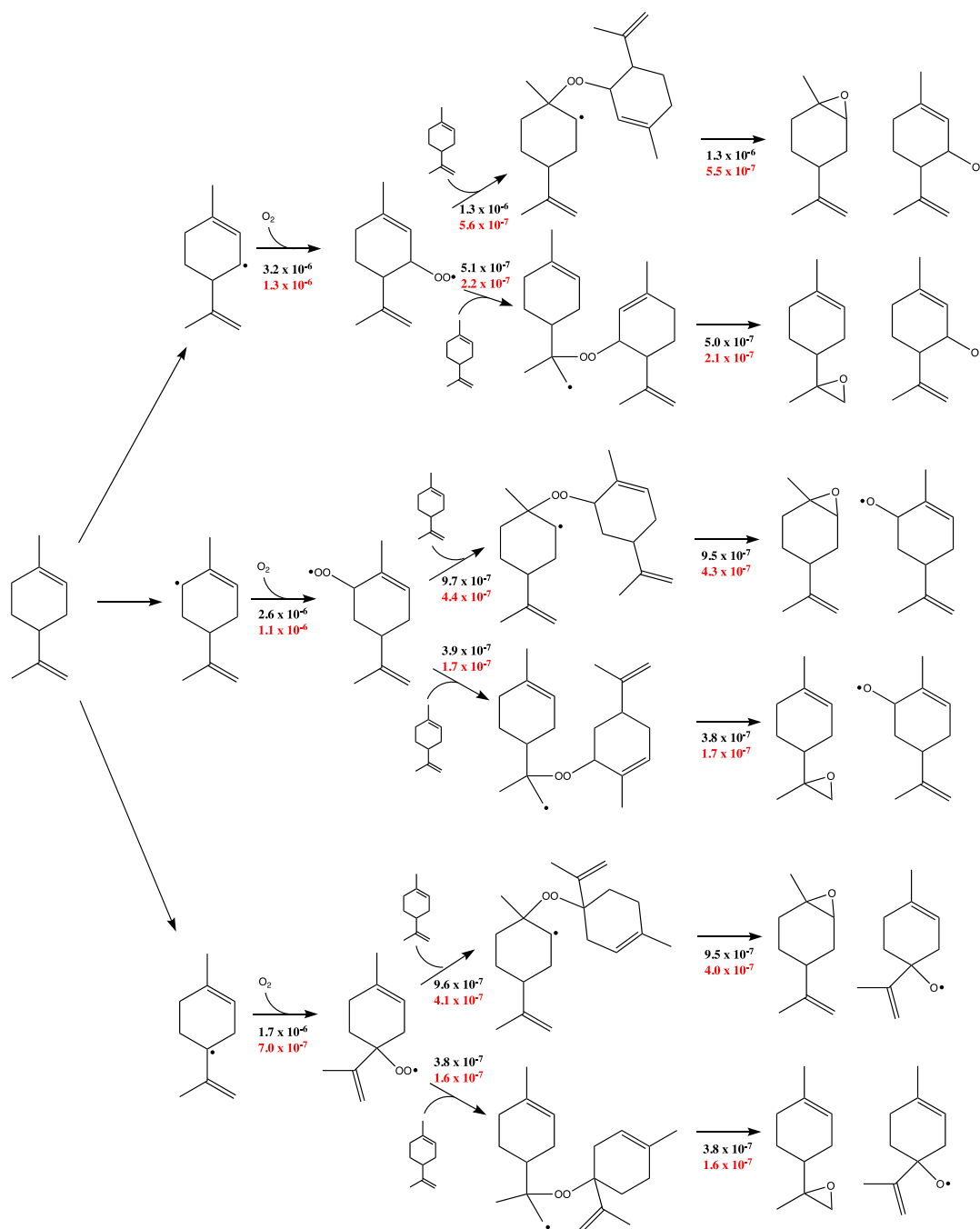


Figure 5.4: Mechanism of free-radical epoxidation for limonene through peroxy intermediates.

Net fluxes are shown for 75 °C, 1 mL TBHP (black) and 65 °C, 1 mL TBHP (red) in M/s.

Following epoxidation through the peroxy intermediate, an alkoxy radical remains active in the system. The alkoxy radical prefers to add to the limonene substrate as well, but both addition reactions are more favorable and proceed essentially without an activation barrier. This leads to an equal rate of production of 1,2- and 8,9-limonene oxide through the ether bond intermediate. This implies that the overall preference to 1,2-limonene oxide in terms of selectivity is a result of the peroxy bond epoxidation reaction. The epoxidation reaction via an ether bond intermediate regenerates an active alkyl radical, thereby closing the epoxidation cycle. This second portion of the reaction mechanism can be seen in Figure 5.5.

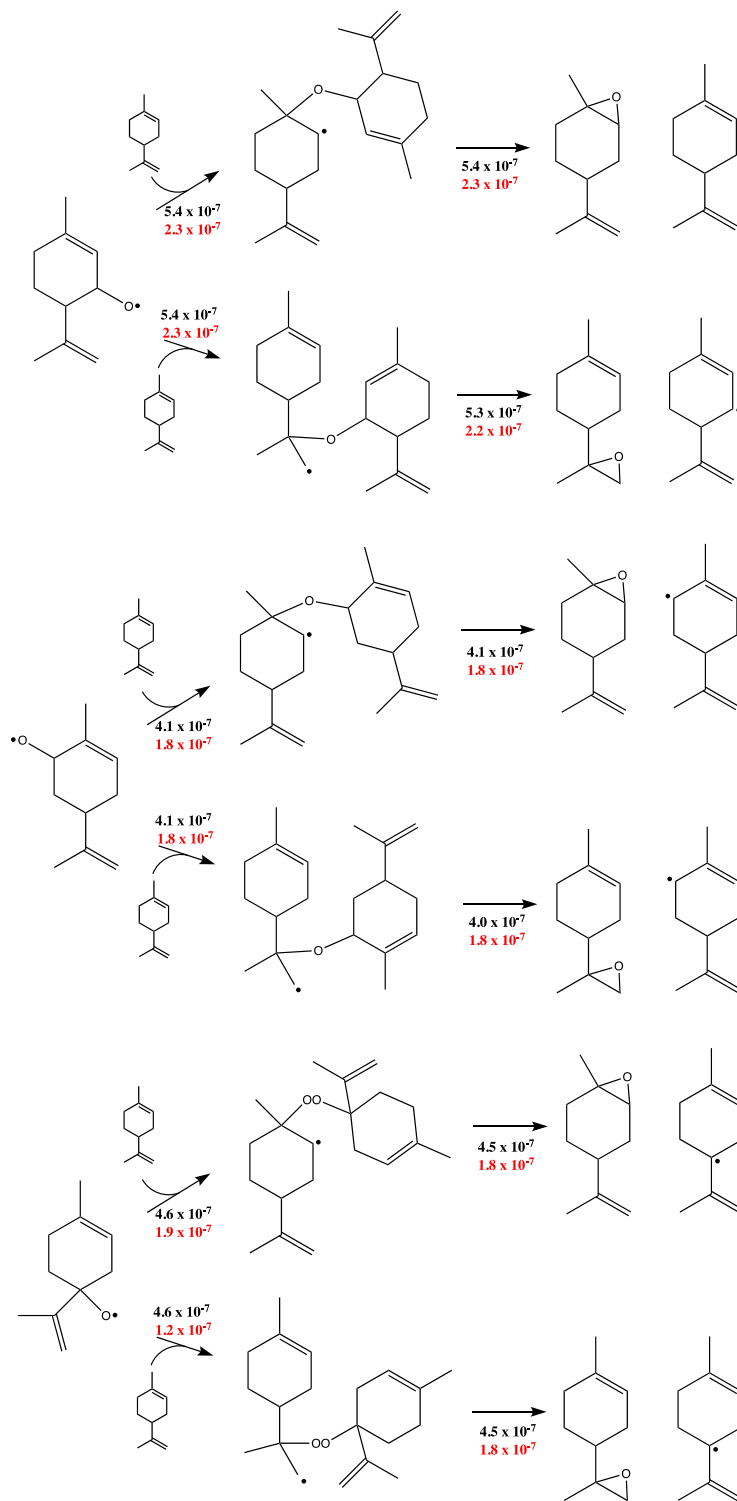


Figure 5.5: Mechanism of free-radical epoxidation for limonene through alkoxy intermediates.

Net fluxes are shown for 75 °C, 1 mL TBHP (black) and 65 °C, 1 mL TBHP (red) in M/s.

The final part of the reaction mechanism with flux values comparable to those noted above is the set of addition reactions and subsequent epoxidation steps that lead to the formation of 1,2-8,9-limonene diepoxide. As observed in the experimental data at times longer than three hours, the product with the highest selectivity is the diepoxide. The secondary reactions of the three main peroxy radicals of limonene adding to the remaining double bonds in 1,2- or 8,9-limonene oxide are able to justify this observed behavior. The diepoxide formation reactions and the corresponding net fluxes can be seen in Figure 5.6.

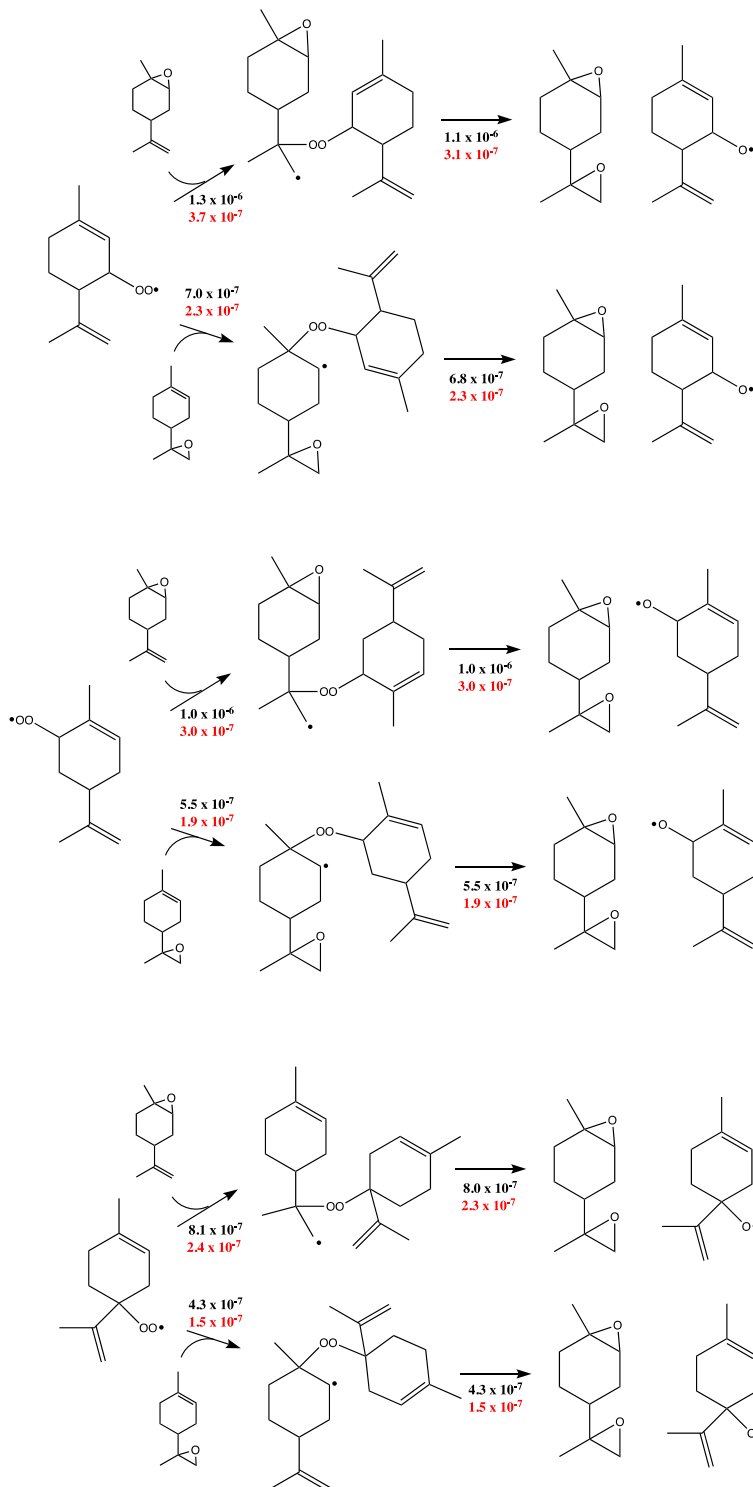


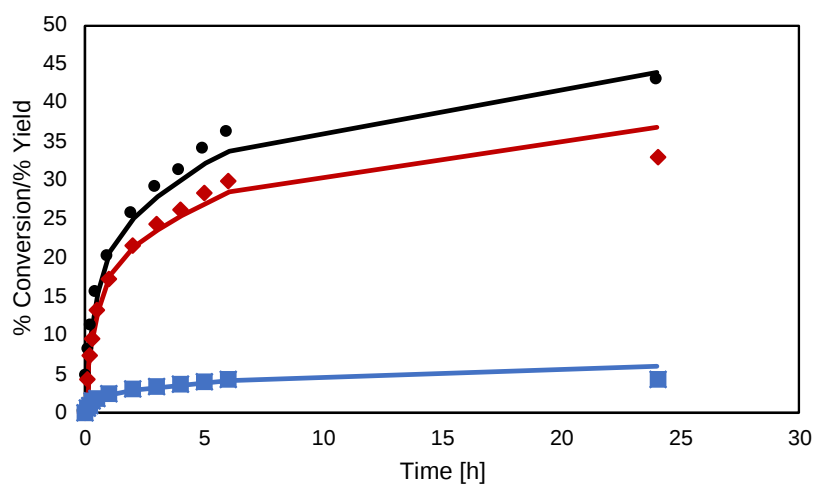
Figure 5.6: Mechanism for limonene diepoxide formation. Net fluxes are shown for 75 °C, 1 mL TBHP (black) and 65 °C, 1 mL TBHP (red) in M/s.

The formation of minor products, alcohol and ketone progeny of limonene, occurs from hydrogen abstraction by the peroxy or alkoxy radicals at the various carbon positions. None of these reactions has a net flux greater than 3×10^{-7} M/s for the 75 °C, 1 mL TBHP trial, lower than all reactions in the epoxidation cycle. The reaction with the highest net flux is hydrogen abstraction by the alkoxy radical at the C₃-position for formation of C₃-alcohol. This is consistent with the experimental observation that C₃-alcohol is the most prevalent minor product, as seen in the plots in Figure 5.3.

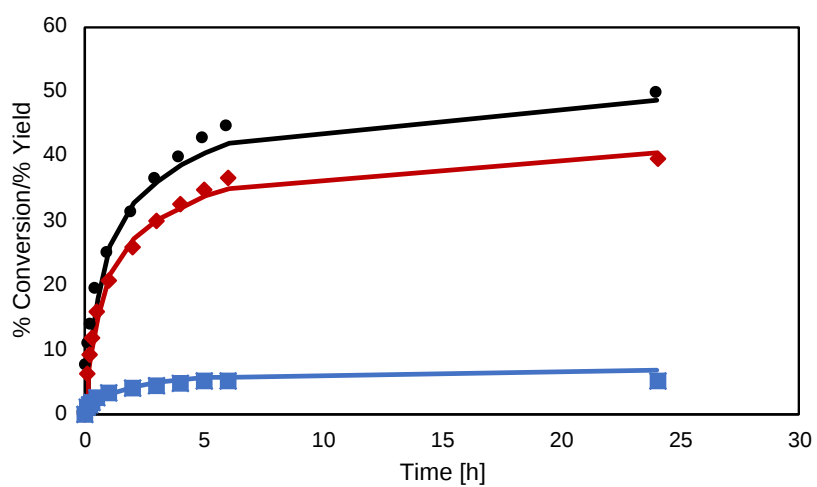
The model constructed for the homogeneous oxidation of limonene is successful in matching the experimental data for the most prevalent products. The net flux analysis that the preference for radical addition reactions generates an epoxidation cycle and drives high selectivity to 1,2-epoxide, 8,9-epoxide, and diepoxide. However, this complex system with many competing pathways does not yield any one product in a significant amount, a maximum selectivity of ~18 % diepoxide at 6 h, making this less than ideal for use in a practical process.

5.3.2 Catalyzed Model

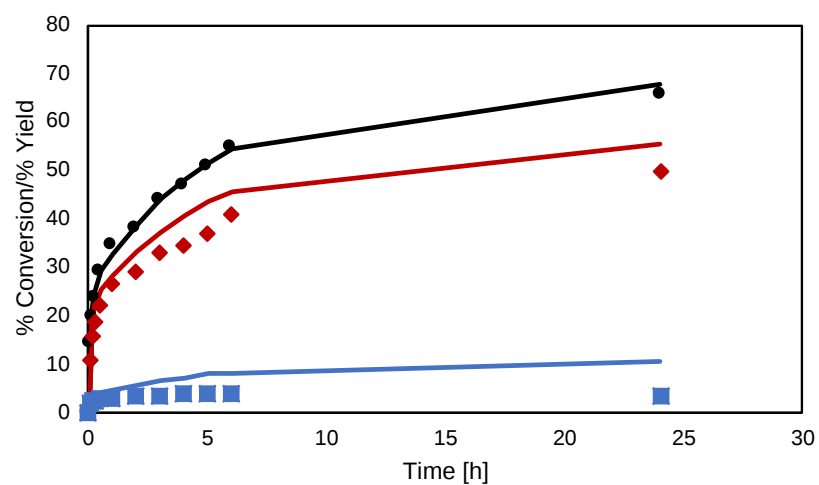
The Ti/SiO₂-catalyzed model featured the set of catalyzed reactions laid out in Figure 5.2 and a reduced set of free-radical reactions. In total, the catalyzed model included 752 species, 191 forward/reverse reaction pairs, and 2,360 unique forward reactions. The model results based on the regressed trials show excellent agreement with the experimental data, and the model results for the validation trial slightly overpredict conversion but are within experimental error, capturing product selectivity well. The agreement of the model results to experimental data for conversion, yield of 1,2-limonene oxide, and yield of 8,9-limonene oxide is shown in Figure 5.7.



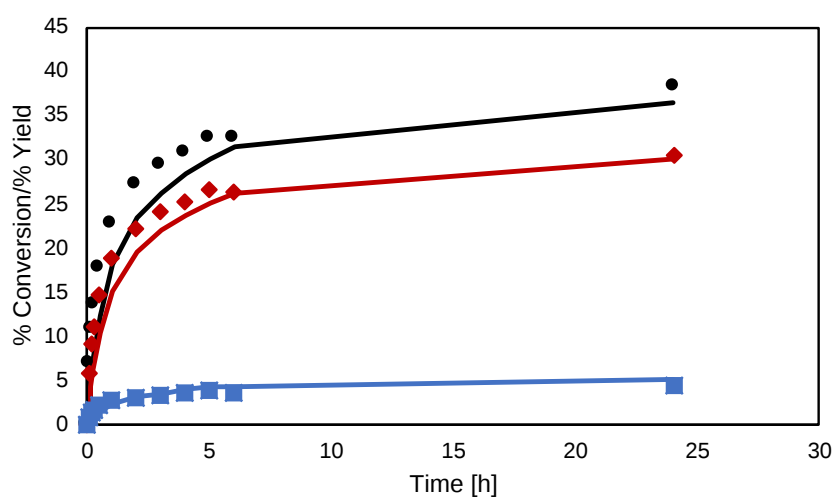
a)



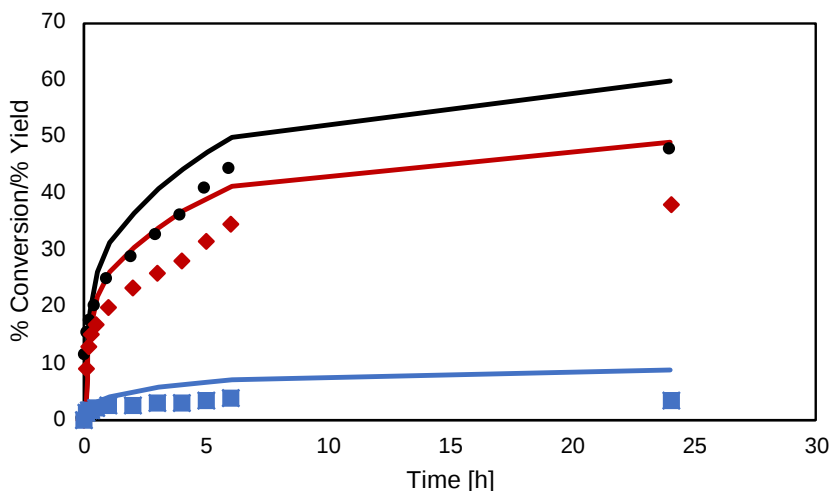
b)



c)



d)



e)

Figure 5.7: Model results for Ti/SiO₂-catalyzed oxidation of limonene. Experimental data points are shown in symbols, and model results are shown as lines of the corresponding color. The data plotted represents the following trials: a) 55 °C, 1.1 TBHP:1 limonene, b) 65 °C, 1.1 TBHP:1 limonene, c) 65 °C, 9.9 TBHP:1 limonene, d) 65 °C, 1.1 TBHP:1 limonene:1 tert-butanol, e) 65 °C, 3.3 TBHP:1 limonene. Note that the model was regressed for a) - d) and validated against e). The data plotted are conversion of limonene (●), yield of 1,2-limonene oxide (◆), and yield of 8,9-limonene oxide (■).

Net flux analysis revealed that a vast majority of the activity in the system is contained within the catalyzed reactions, as anticipated. Although there is a catalyzed radical formation pathway with a net flux of 1.1×10^{-6} M/s, the radical mechanism does not significantly contribute to the overall conversion in the system, as it is alkyl hydrogen abstraction that regenerates limonene. The highest net flux for an uncatalyzed oxidation reaction in this system is 5.0×10^{-8} M/s, which is for the addition of the alkoxy radical of TBHP to the 1,2-double bond of limonene. One key factor

that reduces free-radical oxidation is the absence of O_2 in the system, and the facile oxygen addition to alkyl radicals is the first step in the epoxidation cycle. Without O_2 in the system to drive the epoxidation cycle, alkyl radicals formed following epoxidation via an ether bond intermediate may only abstract from the substrate, which is not a productive step for oxidation of limonene.

The fluxes in the catalyzed reaction cycles reveal that both forms of the active site play a role in the oxidation of limonene. At short times, the flux is mainly in Cycle 1 with the tri-coordinated Ti/SiO_2 performing direct epoxidation of limonene. The net flux to 1,2-limonene oxide is almost an order of magnitude greater than for the formation 8,9-limonene oxide. As the reaction progresses, there is a crossover point to where the flux is predominantly in Cycle 2. By 2 h, the majority of the flux in the system is now in the second cycle. Cycle 2 exhibits overall activity that is an order of magnitude lower than the maximum flux observed in the first cycle. The same preference for formation of 1,2-limonene oxide versus 8,9-limonene oxide is observed for the second active site, showing that steric hindrance from the tert-butyl group does not impart a regioselectivity shift. The rate through the second cycle reaches a maximum around 1 h, and then deactivation starts to decrease the flux through both cycles. The mechanism of deactivation at the reaction conditions that were studied is flux to the free-radical decomposition pathway. As noted, the anaerobic free-radical pathway is not productive in oxidizing limonene with TBHP since the epoxidation cycle cannot be sustained. The net fluxes over time for the reactions that form 1,2-limonene oxide and 8,9-limonene oxide for both catalytic cycles are shown in Figure 5.8.

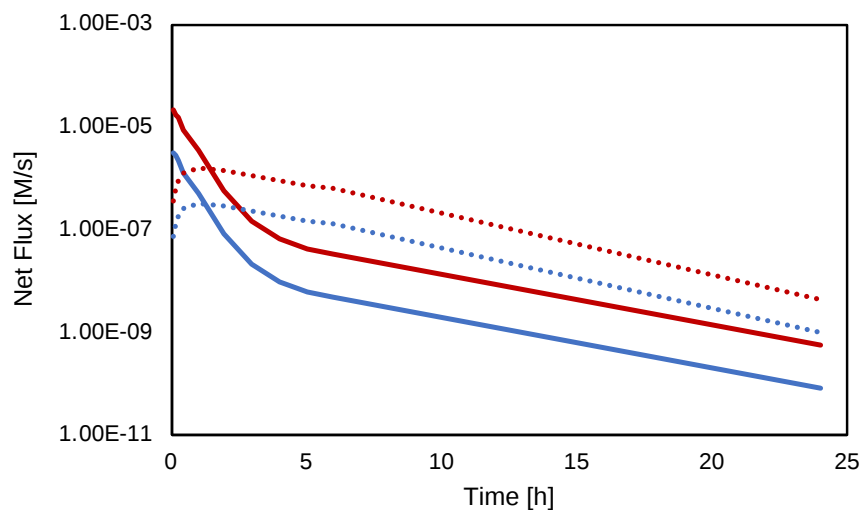


Figure 5.8: Net flux for the catalyzed formation of epoxide products from limonene. Red lines represent the net flux to 1,2-limonene oxide via the direct oxidation of limonene, and blue lines represent the net flux to 8,9-limonene oxide via the direct oxidation of limonene. Solid lines indicate the flux for these reactions in Cycle 1, and dotted line show the flux for these reactions in Cycle 2.

The net flux analysis provides insight into the mechanism that gives rise to the conversion behavior that is experimentally observed and captured by the model which contains three distinct regimes. In all cases, there is a rapid initial oxidation by the cycle with the bulk Ti/SiO_2 active site for times up to 1 h. The rate of oxidation then begins to decrease between 1 h to 6 h as the net flux through reactions involving the second active site are slower by approximately an order of magnitude. Finally, the catalyst is deactivated by the radical decomposition of TBHP at times greater than 6 h.

The models for both free-radical chemistry and Ti/SiO₂-catalyzed conversion are consistent in their preference for formation of 1,2-limonene oxide. The intrinsic nature of limonene and its more vulnerable 1,2-double bond does have an effect on the behavior of the catalyzed mechanism. Further investigation is needed into the effect of catalyst structure as the tert-butyl group in Cycle 2 is not bulky enough to shift the regioselectivity of the process.

5.4 Conclusions

While the microkinetic model developed for the free-radical oxidation showed that limonene has relatively high selectivity epoxide products, the product distribution is still diverse due to the voluminous number of feasible reactions through a complex reaction and confirms that free-radical oxidation is not viable for practical application. The Ti/SiO₂-catalyzed mechanism is a far more selective process with nearly 100 % of the conversion going to either 1,2- or 8,9-limonene oxide via direct epoxidation of limonene by the catalyst. The free-radical mechanism that is in competition with the direct epoxidation routes and is fueled by decomposition of TBHP by the catalyst proceeds at a far slower rate, mainly due to the lack of O₂ in the system which would be needed to drive the radical epoxidation cycle. Up to 1 h, direct epoxidation catalyzed by bulk supported-Ti sites occurs rapidly. As the reaction progresses, there is a shift in the dominant active site as tert-butanol chemisorbs on Ti, and the reaction slows by about an order of magnitude in this secondary cycle. The catalyst then deactivates as more TBHP is decomposed and the reaction becomes inactive beyond 6 h. The catalytic cycles for both of the active sites prefer to form 1,2-limonene oxide at about 82 % selectivity at long times. Higher selectivity to 1,2-limonene oxide in both the free-radical and catalyzed cases shows that the 1,2-double bond is the more

susceptible for oxidation. Further research would be required to impart a regioselectivity shift towards the 8,9-limonene oxide.

Chapter 6: Summary and Future Perspectives

There are several important conclusions that can be drawn from the development of microkinetic models for oxidation systems with increasing complexity. In terms of homogeneous oxidation, the first model, outlined in Chapter 2, exhibited that for the oxidation of alcohols a more complex reaction mechanism with concerted reactions may be occurring. The mechanism that included only radical pathways is not active enough to justify the experimentally observed data. A combined model with both concerted and free-radical pathways is the most likely scenario in order to justify the observed activity and O₂ dependence.

Chapter 3 moved into the realm of creating a model for free radical and catalyzed alkene oxidation. For the case of cyclooctene oxidation, the epoxide product, cyclooctene oxide, is preferred to the alcohol, ketone, and hydroperoxide products. This tendency to form epoxide comes from the preference for radical addition across the substrate double bond as opposed to hydrogen abstraction. In addition, the model confirmed the hypothesis that the role of gold nanoparticle catalysts was most likely to be activation of O₂ and decomposition of hydroperoxides to initiate free radicals. With this knowledge, gold nanoparticles do not make for a promising candidate for directing epoxidation in oxidation of other alkenes, but only would be attractive in additional cases where the intrinsic nature of the substrate causes a preference for radical addition.

In Chapter 4, an expanded microkinetic model strove to explain the method of carbon-hydrogen bond activation for ethylbenzene, which does not exhibit high reactivity when oxidized. This model was developed and validated for the co-oxidation of ethylbenzene and cyclooctene using Co/ZSM-5 catalysts. There is evidence that when ethylbenzene and cyclooctene are co-oxidized these reactions are kinetically coupled, increasing the rate of ethylbenzene oxidation. The

net rate analysis showed that cyclooctene-derived alkoxy and peroxy radicals are pulled out of the epoxidation cycle and served as initiators of ethylbenzene by abstracting hydrogen. The presence of cyclooctene with the power of its radical progeny to abstract hydrogen from ethylbenzene proved to be more effective in driving activity and selectivity to acetophenone than hydroperoxide decomposition by Co/ZSM-5.

Finally, the developed free-radical microkinetic modeling approach was applied to the oxidation of limonene and adapted to account for a direct epoxidation catalyst, as detailed in Chapter 5. The primary pathways for free-radical oxidation were epoxidation cycles similar to the one observed for cyclooctene oxidation. However, there are two different double bonds in limonene that can undergo radical addition, and three hydrogen positions that can be initiated, making this system far more complex and leading to a decrease in selectivity to any one product. In order to improve the selectivity of the process, a Ti/SiO₂ catalyst was introduced, which has the capability of performing direct epoxidation. The direct epoxidation of limonene occurs rapidly on bare Ti/SiO₂, but then transitions to a new active site that incorporates tert-butanol after approximately 2 hours. The secondary active site exhibits a slower rate of oxidation, which highlights the importance of catalyst structure on activity. Both of the active sites are consistent with the free-radical mechanism in that they both prefer to oxidize the 1,2-double bond of limonene, implying that intrinsic stability of the bond plays a role in determining catalyst selectivity.

The free-radical model has been adapted for the oxidation of alkenes, alcohols, and alkylaromatics. For more classes of molecules that are dissimilar to those that were analyzed using the previously developed models, it would be prudent to adapt the model using the same methods outlined in this work before making predictions. The selective oxidation of alkanes remains a

difficult challenge in industry due to the stability of alkyl bonds.^{2,11} One possible extension of the model with experimental collaboration is to the diamondoid cycloalkane, adamantane. Modeling adamantane provides a unique challenge in the complexity of its structure: three fused cyclohexane rings lead to a variety of unique hydrogen positions that will exhibit different potentials for abstraction. This makes adamantane an interesting probe for carbon-hydrogen activation and subsequent functionalization of alkanes.

For chemical systems with analogous functionalities to the molecules examined in the already validated models, there are several options for application of the developed free-radical model. With a reliable model for determining free-radical activity and selectivity for the oxidation of organic molecules, the baseline homogeneous chemistry for a reaction can be determined. This could lead to the microkinetic model being used as a tool to determine the improvement that a catalyst imparts on an oxidation system. While there are often unforeseen physical complications that necessitate the model to be adjusted, the parameters for these cases can be used for at least a rough estimate for reactivity and selectivity.

When the free-radical or catalyzed models are validated against a wide range of experimental properties, the developed model could also function as a way to screen and optimize reaction conditions. Throughout the work detailed here, the model has been shown to be able to match experimental data at a variety of initiator concentrations, catalyst concentrations, and temperatures. Predictions can be made for conversion and yields of products at different reaction conditions, eliminating the cost of materials and time for experimentation. By systematically varying the reaction conditions, a volcano plot for the yield of the desired product(s) could be produced as a tool for finding optimal reaction conditions.

While the framework for modeling of free-radical oxidation has been validated by a number of different substrates, the catalysts have been added on a case by case basis. The most ambitious direction for this work would be to build in general catalyst functionality. Since gold nanoparticle and cobalt-functionalized zeolite catalysts function as radical initiators, a metric for the affinity of molecular oxygen and hydroperoxides to metal sites is needed to generalize the catalyst function. Density functional theory could be used to determine the binding energy of oxygen or hydroperoxides to the metal sites, and then ideally that could be correlated to activity of a system. The task of generalizing the direct epoxidation catalyst may be even more challenging, but the strategy could remain the same. If a metric could be determined via density functional theory calculations for the interaction of the active form(s) of the catalyst, then this could be related to activity and selectivity of a catalyst.

The development of a microkinetic model that can be readily adapted to many oxidation systems would be ideal for industrial applications, reducing the need for trial and error that may waste time and resources. The belief is that the model built in this work can act as a basic framework to be built upon for achieving that goal. Even in its current state the model has been able to provide new insight into mechanisms of oxidation and actionable conclusions for practical applications.

References

- (1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.
- (2) Teles, J. H.; Hermans, I.; Franz, G.; Sheldon, R. A. Oxidation. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley VCH: Weinheim, 2015; pp 1–103.
- (3) Centi, G.; Cavani, F.; Trifiro, F. *Selective Oxidation by Heterogeneous Catalysis*, 1st ed.; Kluwer Academic/Plenum Publishers: New York, 2001.
- (4) Labinger, J. A.; Bercaw, J. E. Understanding and Exploiting C-H Bond Activation. *Nature* **2002**, *417* (6888), 507–514.
- (5) Yi, H.; Zhang, G.; Wang, H.; Huang, Z.; Wang, J.; Singh, A. K.; Lei, A. Recent Advances in Radical C-H Activation/Radical Cross-Coupling. *Chem. Rev.* **2017**, *117* (13), 9016–9085.
- (6) Segawa, Y.; Maekawa, T.; Itami, K. Synthesis of Extended π -Systems through C-H Activation. *Angew. Chemie - Int. Ed.* **2015**, *54* (1), 66–81.
- (7) Yoon, C. W.; Hirsekorn, K. F.; Neidig, M. L.; Yang, X.; Tilley, T. D. Mechanism of the Decomposition of Aqueous Hydrogen Peroxide over Heterogeneous TiSBA15 and TS-1 Selective Oxidation Catalysts: Insights from Spectroscopic and Density Functional Theory Studies. *ACS Catal.* **2011**, *1* (12), 1665–1678.
- (8) Charbonneau, L.; Kaliaguine, S. Epoxidation of Limonene over Low Coordination Ti in Ti-SBA-16. *Appl. Catal. A Gen.* **2017**, *533*, 1–8.
- (9) Mellouki, A.; Le Bras, G.; Sidebottom, H. Kinetics and Mechanisms of the Oxidation of Oxygenated Organic Compounds in the Gas Phase. *Chem. Rev.* **2003**, *103* (12), 5077–5096.
- (10) Dadyburjor, D. B.; Jewur, S. S.; Ruckenstein, E. Selective Oxidation of Hydrocarbons on

- Composite Oxides. *Catal. Rev.* **1979**, *19* (2), 293–350.
- (11) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. Recent Advances in Transition Metal Catalyzed Oxidation of Organic Substrates with Molecular Oxygen. *Chem. Rev.* **2005**, *105* (6), 2329–2363.
- (12) Grant, J. T.; Venegas, J. M.; McDermott, W. P.; Hermans, I. Aerobic Oxidations of Light Alkanes over Solid Metal Oxide Catalysts. *Chem. Rev.* **2018**, *118* (5), 2769–2815.
- (13) Liu, L.; Corma, A. Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. *Chem. Rev.* **2018**, *118* (10), 4981–5079.
- (14) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature Far below 0 °C. *Chem. Lett.* **1987**, *16* (2), 405–408.
- (15) Haruta, M. Novel Catalysis of Gold Deposited on Metal Oxides. *Catal. Surv. from Japan* **1997**, *1* (1), 61–73.
- (16) Hayashi, T.; Tanaka, K.; Haruta, M. Selective Vapor-Phase Epoxidation of Propylene over Au/TiO₂ Catalysts in the Presence of Oxygen and Hydrogen. *J. Catal.* **1998**, *178* (2), 566–575.
- (17) Barrio, L.; Liu, P.; Rodriguez, J. A.; Campos-Martin, J. M.; Fierro, J. L. G. Effects of Hydrogen on the Reactivity of O₂ toward Gold Nanoparticles and Surfaces. *J. Phys. Chem. C* **2007**, *111* (51), 19001–19008.
- (18) Daniel, M. C. M.; Astruc, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size Related Properties and Applications toward Biology, Catalysis and Nanotechnology. *Chem. Rev.* **2004**, *104*, 293–346.
- (19) Sanchez, A.; Abbet, S.; Heiz, U.; Schneider, W.-D.; Häkkinen, H.; Barnett, R. N.; Landman,

- U. When Gold Is Not Noble: Nanoscale Gold Catalysts. *J. Phys. Chem.* **1999**, *103* (48), 9573–9578.
- (20) Yesmurzayeva, N. N.; Nurakhmetova, Z. A.; Tatykhanova, G. S.; Selenova, B. S.; Kudaibergenov, S. E. Catalytic Activity of Gold and Silver Nanoparticles Supported on Zinc Oxide. *Supramol. Catal.* **2015**, *2* (1), 1–8.
- (21) Bawaked, S.; Dummer, N.; Dimitratos, N.; Bethell, D.; He, Q.; Kiely, C.; Hutchings, G. Solvent-Free Selective Epoxidation of Cyclooctene Using Supported Gold Catalysts. *Green Chem.* **2009**, *13*, 127–134.
- (22) Lu, G. M.; Zhao, R.; Qian, G.; Qi, Y. X.; Wang, X. L.; Suo, J. S. A Highly Efficient Catalyst Au/MCM-41 for Selective Oxidation Cyclohexane Using Oxygen. *Catal. Letters* **2004**, *97* (September), 115–118.
- (23) Biella, S.; Rossi, M. Gas Phase Oxidation of Alcohols to Aldehydes or Ketones Catalysed by Supported Gold. *Chem Commun.* **2003**, *39*, 378–379.
- (24) Zhu, K.; Hu, J.; Richards, R. Aerobic Oxidation of Cyclohexane by Gold Nanoparticles Immobilized upon Mesoporous Silica. *Catal. Letters* **2005**, *100* (3–4), 195–199.
- (25) Clerici, M. G.; Domine, M. E. Oxidation Reactions Catalyzed by Transition-Metal-Substituted Zeolites. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M. G., Kholdeeva, O. A., Eds.; John Wiley & Sons, Inc., 2013.
- (26) Vanelderen, P.; Vancauwenbergh, J.; Sels, B. F.; Schoonheydt, R. A. Coordination Chemistry and Reactivity of Copper in Zeolites. *Coord. Chem. Rev.* **2013**, *257* (2), 483–494.

- (27) Weitkamp, J. Zeolites and Catalysis. *Solid State Ionics* **2000**, *131* (1), 175–188.
- (28) Dean, M. H.; Skirrow, G. The Cobalt-Catalyzed Decomposition of Tert-Butyl Hydroperoxide. *Trans. Faraday Soc.* **1958**, *54*, 849–862.
- (29) Richardson, W. H. Metal Ion Decomposition of Hydroperoxides. III. Intermediates in Cobalt Salt Catalyzed Decomposition of t-Butyl Hydroperoxide. *J. Org. Chem.* **1965**, *30* (8), 2804–2808.
- (30) Saussine, L.; Brazi, E.; Robine, A.; Mimoun, H.; Fischer, J.; Weiss, R. Cobalt(III) Alkylperoxy Complexes. Synthesis, X-Ray Structure, and Role in the Catalytic Decomposition of Alkyl Hydroperoxides and in the Hydroxylation of Hydrocarbons. *J. Am. Chem. Soc.* **1985**, *107* (12), 3534–3540.
- (31) Notestein, J. M.; Solovyov, A.; Andrini, L. R.; Requejo, F. G.; Katz, A.; Iglesia, E. The Role of Outer-Sphere Surface Acidity in Alkene Epoxidation Catalyzed by Calixarene-Ti(IV) Complexes. *J. Am. Chem. Soc.* **2007**, *129* (50), 15585–15595.
- (32) Morlanés, N.; Notestein, J. M. Grafted Ta-Calixarenes: Tunable, Selective Catalysts for Direct Olefin Epoxidation with Aqueous Hydrogen Peroxide. *J. Catal.* **2010**, *275* (2), 191–201.
- (33) Broadbelt, L. J.; Stark, S. M.; Klein, M. T. Computer Generated Reaction Networks: On-the-Fly Calculation of Species Properties Using Computational Quantum Chemistry. *Chem. Eng. Sci.* **1994**, *49* (24), 4991–5010.
- (34) Broadbelt, L. J.; Stark, S. M.; Klein, M. T. Computer-Generated Pyrolysis Modeling: On-the-Fly Generation of Species, Reactions, and Rates. *Ind. Eng. Chem. Res.* **1994**, *33* (4), 790–799.

- (35) Broadbelt, L. J.; Stark, S. M.; Klein, M. T. Termination of Computer-Generated Reaction Mechanisms: Species Rank-Based Convergence Criterion. *Ind. Eng. Chem. Res.* **1995**, *34*, 2566–2573.
- (36) Broadbelt, L. J.; Stark, S. M.; Klein, M. T. Computer Generated Reaction Modelling: Decomposition and Encoding Algorithms for Determining Species Uniqueness. *Comput. Chem. Eng.* **1996**, *20* (2), 113–129.
- (37) Susnow, R. G.; Dean, A. M.; Green, W. H.; Peczak, P.; Broadbelt, L. J. Rate-Based Construction of Kinetic Models for Complex Systems. *J. Phys. Chem. A* **1997**, *101* (20), 3731–3740.
- (38) Arrhenius, S. A. Über Die Dissociationswärme Und Den Einfluß Der Temperatur Auf Den Dissociationsgrad Der Elektrolyte. *Z. Phys. Chem* **1889**, *4*, 96–116.
- (39) Evans, M. G.; Polanyi, M. Further Considerations on the Thermodynamics of Chemical Equilibria and Reaction Rates. *Trans. Faraday Soc.* **1936**, *32*, 1333–1360.
- (40) Benson, S. *Thermochemical Kinetics*; John Wiley and Sons, 1976.
- (41) Stewart, W. E.; Caracotsios, M.; Sorensen, J. P. Double Precision Differential-Algebraic Sensitive Analysis Code. Madison, WI 1997.
- (42) Stewart, W. E.; Caracotsios, M.; Sorensen, J. P. Generalized Regression Software (GREG). Madison, WI 1997.
- (43) Sawatari, N.; Yokota, T.; Sakaguchi, S.; Ishii, Y. Alkane Oxidation with Air Catalyzed by Lipophilic N-Hydroxyphthalimides without Any Solvent. *J. Org. Chem.* **2001**, *66* (23), 7889–7891.
- (44) Lin, M. M. Selective Oxidation of Propane to Acrylic Acid with Molecular Oxygen. *Appl.*

- Catal. A Gen.* **2001**, 207 (1–2), 1–16.
- (45) Labinger, J. A. Oxidative Coupling of Methane: An Inherent Limit to Selectivity? *Catal. Letters* **1988**, 1 (11), 371–375.
- (46) Holgate, H. R.; Tester, J. W. Oxidation of Hydrogen and Carbon Monoxide in Sub- and Supercritical Water: Reaction Kinetics, Pathways, and Water Density Effects. 1. Experimental Results. *J. Phys. Chem.* **1994**, 98 (3), 800–809.
- (47) Dryer, F. L.; Glassman, I. High-Temperature Oxidation of CO and CH₄. *Symp. Combust.* **1973**, 14 (1), 987–1003.
- (48) Zanthoff, H.; Baerns, M. Oxidative Coupling of Methane in the Gas Phase. Kinetic Simulation and Experimental Verification. *Ind. Eng. Chem. Res* **1990**, 29 (1), 2–10.
- (49) Tjatjopoulos, G. J.; Vasalos, I. A. Reaction-Path Analysis of a Homogeneous Methane Oxidative Coupling Mechanism. *Appl. Catal. A, Gen.* **1992**, 88 (2), 213–230.
- (50) Driscoll, D. J.; Lunsford, J. H. Gas-Phase Radical Formation during the Reactions of Methane, Ethane, Ethylene, and Propylene over Selected Oxide Catalysts. *J. Phys. Chem.* **1985**, 89, 4415–4418.
- (51) Dagaut, P.; Cathonnet, M.; Boettner, J. C. Kinetics of Ethane Oxidation. *Int. J. Chem. Kinet.* **1991**, 23 (5), 437–455.
- (52) Hutchings, G. J. Methane Activation by Selective Oxidation. *Top. Catal.* **2016**, 59 (8–9), 658–662.
- (53) Schlögl, R. Selective Oxidation: From a Still Immature Technology to the Roots of Catalysis Science. *Top. Catal.* **2016**, 59, 1461–1476.
- (54) Schuchardt, U.; Cardoso, D.; Sercheli, R.; Pereira, R.; Da Cruz, R. S.; Guerreiro, M. C.;

- Mandelli, D.; Spinacé, E. V.; Pires, E. L. Cyclohexane Oxidation Continues to Be a Challenge. *Appl. Catal. A Gen.* **2001**, *211* (1), 1–17.
- (55) Lunsford, J. H. Catalytic Conversion of Methane to More Useful Chemicals and Fuels: A Challenge for the 21st Century. *Catal. Today* **2000**, *63* (2–4), 165–174.
- (56) Meng, X.; De Jong, W.; Kudra, T. A State-of-the-Art Review of Pulse Combustion: Principles, Modeling, Applications and R&D Issues. *Renew. Sustain. Energy Rev.* **2016**, *55*, 73–114.
- (57) Isikgor, F. H.; Becer, C. R. Lignocellulosic Biomass: A Sustainable Platform for Production of Bio-Based Chemicals and Polymers. *Polym. Chem.* **2015**, *6*, 4497–4559.
- (58) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-Phase Catalytic Processing of Biomass-Derived Oxygenated Hydrocarbons to Fuels and Chemicals. *Angew. Chemie - Int. Ed.* **2007**, *46* (38), 7164–7183.
- (59) Davda, R. R.; Shabaker, J. W.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. A Review of Catalytic Issues and Process Conditions for Renewable Hydrogen and Alkanes by Aqueous-Phase Reforming of Oxygenated Hydrocarbons over Supported Metal Catalysts. *Appl. Catal. B Environ.* **2005**, *56* (1–2 SPEC. ISS.), 171–186.
- (60) Marinov, N. M. Kinetic Model for High Temperature Ethanol Oxidation. *Int. J. Chem. Kinet.* **1999**, *31* (3), 183–220.
- (61) Li, L.; Chen, P.; Gloyna, E. F. Generalized Kinetic Model for Wet Oxidation of Organic Compounds. *AIChE J.* **1991**, *37* (11), 1687–1697.
- (62) Díaz, E.; Sad, M. E.; Iglesia, E. Homogeneous Oxidation Reactions of Propanediols at Low Temperatures. *ChemSusChem* **2010**, *3* (9), 1063–1070.

- (63) Seshadri, V.; Westmoreland, P. R. Concerted Reactions and Mechanism of Glucose Pyrolysis and Implications for Cellulose Kinetics. *J. Phys. Chem. A* **2012**, *116* (49), 11997–12013.
- (64) Zhou, X.; Nolte, M. W.; Mayes, H. B.; Shanks, B. H.; Broadbelt, L. J. Experimental and Mechanistic Modeling of Fast Pyrolysis of Neat Glucose-Based Carbohydrates. 1. Experiments and Development of a Detailed Mechanistic Model. *Ind. Eng. Chem. Res.* **2014**, *53* (34), 13274–13289.
- (65) Mayes, H. B.; Broadbelt, L. J. Unraveling the Reactions That Unravel Cellulose. *J. Phys. Chem. A* **2012**, *116* (26), 7098–7106.
- (66) Mayes, H. B.; Nolte, M. W.; Beckham, G. T.; Shanks, B. H.; Broadbelt, L. J. The Alpha-Bet(a) of Glucose Pyrolysis: Computational and Experimental Investigations of 5-Hydroxymethylfurfural and Levoglucosan Formation Reveal Implications for Cellulose Pyrolysis. *ACS Sustain. Chem. Eng.* **2014**, *2* (6), 1461–1473.
- (67) Pfaendtner, J.; Broadbelt, L. J. Mechanistic Modeling of Lubricant Degradation. 1. Structure-Reactivity Relationships for Free-Radical Oxidation. *Ind. Eng. Chem. Res.* **2008**, *47* (9), 2886–2896.
- (68) Porter, N. A.; Caldwell, S. E.; Mills, K. A. Mechanisms of Free Radical Oxidation of Unsaturated Lipids. *Lipids* **1995**, *30* (4), 277–290.
- (69) Chiang, Y.; Kresge, A. J.; Schepp, N. P. Temperature Coefficients of the Rates of Acid-Catalyzed Enolization of Acetone and Ketonization of Its Enol in Aqueous and Acetonitrile Solutions. Comparison of Thermodynamic Parameters for the Keto-Enol Equilibrium in Solution with Those in the Gas Phase. *J. Am. Chem. Soc.* **1989**, *111* (3), 3977–3980.

- (70) Westmoreland, P.; Fahey, P. Dehydration and Dehydrogenation Kinetics of Oh Groups in Biomass Pyrolysis. *Chem. Eng. Trans.* **2016**, *50*, 73–78.
- (71) Fahey, P. J. Alcohol and Saccharide Model-Compound Pyrolysis Experiments to Improve Understanding of Cellulose Pyrolysis [Dissertation], North Carolina State University, 2015.
- (72) Laino, T.; Tuma, C.; Curioni, A.; Jochowitz, E.; Stolz, S. A Revisited Picture of the Mechanism of Glycerol Dehydration. *J. Phys. Chem. A* **2011**, *115* (15), 3592–3595.
- (73) Nimlos, M. R.; Blanksby, S. J.; Qian, X.; Himmel, M. E.; Johnson, D. K. Mechanisms of Glycerol Dehydration. *J. Phys. Chem. A* **2006**, *110* (18), 6145–6156.
- (74) Zhou, X.; Nolte, M. W.; Mayes, H. B.; Shanks, B. H.; Broadbelt, L. J. Experimental and Mechanistic Modeling of Fast Pyrolysis of Neat Glucose-Based Carbohydrates. 2. Validation and Evaluation of the Mechanistic Model. *Ind. Eng. Chem. Res.* **2014**, *53* (34), 13290–13301.
- (75) Paine, J. B.; Pithawalla, Y. B.; Naworal, J. D.; Thomas, C. E. Carbohydrate Pyrolysis Mechanisms from Isotopic Labeling. Part 1: The Pyrolysis of Glycerin: Discovery of Competing Fragmentation Mechanisms Affording Acetaldehyde and Formaldehyde and the Implications for Carbohydrate Pyrolysis. *J. Anal. Appl. Pyrolysis* **2007**, *80* (2), 297–311.
- (76) Vandooren, J.; de Guertechin, L. O.; Van Tiggelen, P. J. Kinetics in a Lean Formaldehyde Flame. *Combust. Flame* **1986**, *64* (2), 127–139.
- (77) Tsang, W.; Hampson, R. F. Chemical Kinetic Data Base for Combustion Chemistry. Part I. Methane and Related Compounds. *J. Phys. Chem. Ref. Data* **1986**, *15* (3), 1087–1222.
- (78) Khan, S. S.; Broadbelt, L. J. Automated Mechanism Generation. Part 2: Application to Atmospheric Chemistry of Alkanes and Oxygenates. *J. Atmos. Chem.* **2009**, *63* (2), 157–

186.

- (79) Maly, T.; Petzold, L. R. Numerical Methods and Software for Sensitivity Analysis of Differential-Algebraic Systems. *Appl. Numer. Math.* **1996**, *20* (60), 57–59.
- (80) Mahajan, S. S.; Sharma, M. M.; Sridhar, T. Uncatalyzed Oxidation of Cyclooctene. *Ind. Eng. Chem. Res.* **2005**, *44* (5), 1390–1395.
- (81) Kobe, J. M.; Evans, W. E.; June, R. L.; Lemanski, M. F. Epoxidation - Industrial. In *Encyclopedia of Catalysis*; John Wiley and Sons, 2002.
- (82) Favini, G.; Buemi, G.; Raimondi, M. Molecular Conformation of Cyclenes. I. Cyclohexene, Cycloheptene, Cis- and Trans-Cyclooctene, Cis- and Trans-Cyclononene. *J. Mol. Struct.* **1968**, *2* (2), 137–148.
- (83) Qian, L.; Wang, Z.; Beletskiy, E. V; Liu, J.; Santos, H. J.; Li, T.; Rangel, M. C.; Kung, M. C.; Kung, H. H. Stable and Solubilized Active Au Atom Clusters for Selective Epoxidation of Cis-Cyclooctene with Molecular Oxygen. *Nat. Commun.* **2017**, *8*, 1–8.
- (84) Mikami, Y.; Dhakshinamoorthy, A.; Alvaro, M.; García, H. Catalytic Activity of Unsupported Gold Nanoparticles. *Catal. Sci. Technol.* **2013**, *3* (1), 58–69.
- (85) He, W.; Zhou, Y. T.; Wamer, W. G.; Hu, X.; Wu, X.; Zheng, Z.; Boudreau, M. D.; Yin, J. J. Intrinsic Catalytic Activity of Au Nanoparticles with Respect to Hydrogen Peroxide Decomposition and Superoxide Scavenging. *Biomaterials* **2013**, *34* (3), 765–773.
- (86) Hereijgers, B. P. C.; Weckhuysen, B. M. Aerobic Oxidation of Cyclohexane by Gold-Based Catalysts: New Mechanistic Insight by Thorough Product Analysis. *J. Catal.* **2010**, *270* (1), 16–25.
- (87) Alshammari, H.; Miedziak, P. J.; Knight, D. W.; Willock, D. J.; Hutchings, G. J. The Effect

- of Ring Size on the Selective Oxidation of Cycloalkenes Using Supported Metal Catalysts. *Catal. Sci. Technol.* **2013**, 3 (6), 1531–1539.
- (88) Mahajani, S. M.; Sharma, M. M.; Sridhar, T. Uncatalysed Oxidation of Cyclohexene. *Chem. Eng. Sci.* **1999**, 54 (18), 3967–3976.
- (89) Neuenschwander, U.; Hermans, I. The Conformations of Cyclooctene: Consequences for Epoxidation Chemistry. *J. Org. Chem.* **2011**, 76 (24), 10236–10240.
- (90) Oakley, L. H.; Casadio, F.; Shull, K. R.; Broadbelt, L. J. Microkinetic Modeling of the Autoxidative Curing of an Alkyd and Oil-Based Paint Model System. *Appl. Phys. A Mater. Sci. Process.* **2015**, 121 (3), 869–878.
- (91) Guzman, J.; Gates, B. C. Simultaneous Presence of Cationic and Reduced Gold in Functioning MgO-Supported CO Oxidation Catalysts: Evidence from X-Ray Absorption Spectroscopy. *J. Phys. Chem. B* **2002**, 106 (31), 7659–7665.
- (92) Singh, S.; Li, S.; Carrasquillo-Flores, R.; Alba-Rubio, A. C.; Dumesic, J. A.; Mavrikakis, M. Formic Acid Decomposition on Au Catalysts: DFT, Microkinetic Modeling, and Reaction Kinetics Experiments. *AIChE J.* **2014**, 60 (4), 1303–1319.
- (93) Shang, C.; Liu, Z. P. Origin and Activity of Gold Nanoparticles as Aerobic Oxidation Catalysts in Aqueous Solution. *J. Am. Chem. Soc.* **2011**, 133 (25), 9938–9947.
- (94) Janssens, T. V. W.; Clausen, B. S.; Hvolbæk, B.; Falsig, H.; Christensen, C. H.; Bligaard, T.; Nørskov, J. K. Insights into the Reactivity of Supported Au Nanoparticles: Combining Theory and Experiments. *Top. Catal.* **2007**, 44 (1–2), 15–26.
- (95) Teranishi, M.; Naya, S. I.; Tada, H. Temperature- and pH-Dependence of Hydrogen Peroxide Formation from Molecular Oxygen by Gold Nanoparticle-Loaded Titanium(IV)

- Oxide Photocatalyst. *J. Phys. Chem. C* **2016**, *120* (2), 1083–1088.
- (96) Campbell, C. T.; Sharp, J. C.; Yao, Y. X.; Karp, E. M.; Silbaugh, T. L. Insights into Catalysis by Gold Nanoparticles and Their Support Effects through Surface Science Studies of Model Catalysts. *Faraday Discuss.* **2011**, *152*, 227–239.
- (97) Naya, S.; Teranishi, M.; Kimura, K.; Tada, H. A Strong Support-Effect on the Catalytic Activity of Gold Nanoparticles for Hydrogen Peroxide Decomposition. *ChemComm* **2011**, *47* (11), 3230–3232.
- (98) Bollinger, J. M.; Krebs, C. Enzymatic C–H Activation by Metal–superoxo Intermediates. *Curr. Opin. Chem. Biol.* **2007**, *11* (2), 151–158.
- (99) Chen, P.; Bell, J.; Eipper, B. A.; Solomon, E. I. Oxygen Activation by the Noncoupled Binuclear Copper Site in Peptidylglycine α -Hydroxylating Monooxygenase. Reaction Mechanism and the Role of the Noncoupled Nature of the Active Site. *Biochemistry* **2004**, *43* (19), 5735–5747.
- (100) Spier, E.; Neuenschwander, U.; Hermans, I. Insights into the Cobalt(II)-Catalyzed Decomposition of Peroxide. *Angew. Chemie - Int. Ed.* **2013**, *52* (5), 1581–1585.
- (101) Oakley, L. H.; Casadio, F.; Shull, K. R.; Broadbelt, L. J. Theoretical Study of Epoxidation Reactions Relevant to Hydrocarbon Oxidation. *Ind. Eng. Chem. Res.* **2017**, *56* (26), 7454–7461.
- (102) Denisov, E. T. *Liquid-Phase Reaction Rate Constants*; Plenum Press: New York, 1974.
- (103) Wilcock, R. J.; Battino, R.; Wilhelm, E. The Solubility of Gases in Liquids 10. The Solubility of He, Ne, Ar, Kr, N₂, O₂, CO, CO₂, CH₄, CF₄, and SF₆ in Cyclooctane at 289 to 313 K. *J. Chem. Thermodyn.* **1977**, *9* (2), 111–115.

- (104) Zhu, H.; Ma, Z.; Clark, J. C.; Pan, Z.; Overbury, S. H.; Dai, S. Low-Temperature CO Oxidation on Au/fumed SiO₂-Based Catalysts Prepared from Au(en)₂Cl₃ Precursor. *Appl. Catal. A Gen.* **2007**, 326 (1), 89–99.
- (105) LaMarca, C.; Libanati, C.; Klein, M. T. Design of Kinetically Coupled Complex Reaction Systems. *Chem. Eng. Sci.* **1990**, 45 (8), 2059–2065.
- (106) Brydon, R. R. O.; Peng, A.; Qian, L.; Kung, H. H.; Broadbelt, L. J. Microkinetic Modeling of Homogeneous and Gold Nanoparticle-Catalyzed Oxidation of Cyclooctene. *Ind. Eng. Chem. Res.* **2018**, 57 (14), 4832–4840.
- (107) Hermans, I.; Peeters, J.; Jacobs, P. A. Autoxidation of Ethylbenzene: The Mechanism Elucidated. *J. Org. Chem.* **2007**, 72 (8), 3057–3064.
- (108) Russell, G. A.; Glen, B. Y. Deuterium-Isotope Effects in the Autoxidation of Alkyl Hydrocarbons. Mechanism of the Interaction of Peroxy Radicals. *J. Am. Chem. Soc.* **1957**, 79 (14), 3871–3877.
- (109) Neuenschwander, U.; Hermans, I. Thermal and Catalytic Formation of Radicals during Autoxidation. *J. Catal.* **2012**, 287, 1–4.
- (110) Ma, H.; Xu, J.; Chen, C.; Zhang, Q.; Ning, J.; Miao, H.; Zhou, L.; Li, X. Catalytic Aerobic Oxidation of Ethylbenzene over Co/SBA-15. *Catal. Letters* **2007**, 113 (3–4), 104–108.
- (111) Gavrichkov, A. A.; Zakharov, I. V. Critical Phenomena in Ethylbenzene Oxidation in Acetic Acid Solution at High Cobalt (II) Concentrations. **2005**, 54 (8), 1878–1882.
- (112) Beznis, N. V.; Van Laak, A. N. C.; Weckhuysen, B. M.; Bitter, J. H. Oxidation of Methane to Methanol and Formaldehyde over Co-ZSM-5 Molecular Sieves: Tuning the Reactivity and Selectivity by Alkaline and Acid Treatments of the Zeolite ZSM-5 Agglomerates.

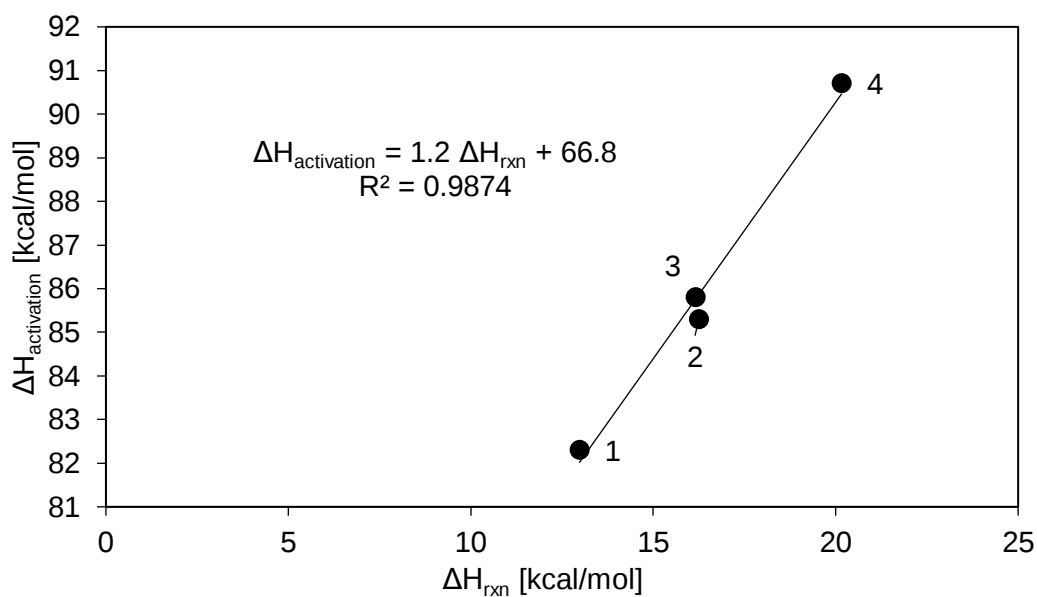
- Microporous Mesoporous Mater.* **2011**, *138* (1–3), 176–183.
- (113) Beznis, N. V.; Weckhuysen, B. M.; Bitter, J. H. Partial Oxidation of Methane over Co-ZSM-5: Tuning the Oxygenate Selectivity by Altering the Preparation Route. *Catal. Letters* **2010**, *136* (1–2), 52–56.
- (114) Kung, M. C.; Lin, S. S.-Y.; Kung, H. H. In Situ Infrared Spectroscopic Study of CH₄ Oxidation Over Co-ZSM-5. *Top. Catal.* **2012**, *55* (1–2), 108–115.
- (115) Hauenstein, O.; Reiter, M.; Agarwal, S.; Rieger, B.; Greiner, A. Bio-Based Polycarbonate from Limonene Oxide and CO₂ with High Molecular Weight, Excellent Thermal Resistance, Hardness and Transparency. *Green Chem.* **2016**, *18* (3), 760–770.
- (116) Jongedijk, E.; Cankar, K.; Buchhaupt, M.; Schrader, J.; Bouwmeester, H.; Beekwilder, J. Biotechnological Production of Limonene in Microorganisms. *Appl. Microbiol. Biotechnol.* **2016**, *100* (7), 2927–2938.
- (117) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. Alternating Copolymerization of Limonene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* **2004**, *126* (37), 11404–11405.
- (118) Bregante, D. T.; Flaherty, D. W. Periodic Trends in Olefin Epoxidation over Group IV and V Framework-Substituted Zeolite Catalysts: A Kinetic and Spectroscopic Study. *J. Am. Chem. Soc.* **2017**, *139* (20), 6888–6898.
- (119) Cagnoli, M. V.; Casuscelli, S. G.; Alvarez, A. M.; Bengoa, J. F.; Gallegos, N. G.; Samaniego, N. M.; Crivello, M. E.; Ghione, G. E.; Pérez, C. F.; Herrero, E. R.; Marchetti, S. G. “Clean” Limonene Epoxidation Using Ti-MCM-41 Catalyst. *Appl. Catal. A Gen.* **2005**, *287* (2), 227–235.
- (120) Gallo, A.; Tiozzo, C.; Psaro, R.; Carniato, F.; Guidotti, M. Niobium Metallocenes Deposited

- onto Mesoporous Silica via Dry Impregnation as Catalysts for Selective Epoxidation of Alkenes. *J. Catal.* **2013**, 298, 77–83.
- (121) Suslick, K. S.; Cook, B. R. Regioselective Epoxidations of Dienes with Manganese(III) Porphyrin Catalysts. *J. Chem. Soc. Chem. Commun.* **1987**, No. 3, 200–202.
- (122) Van Der Waal, J. C.; Rigutto, M. S.; Van Bekkum, H. Zeolite Titanium Beta as a Selective Catalyst in the Epoxidation of Bulky Alkenes. *Appl. Catal. A Gen.* **1998**, 167 (2), 331–342.
- (123) Muratsugu, S.; Tada, M. Molecularly Imprinted Ru Complex Catalysts Integrated on Oxide Surfaces. *Acc. Chem. Res.* **2013**, 46 (2), 300–311.
- (124) Sheldon, R. A. Synthetic and Mechanistic Aspects of Metal-Catalysed Epoxidations with Hydroperoxides. *J. Mol. Catal.* **1980**, 7 (1), 107–126.
- (125) Sheng, M. N.; Zajacek, J. G. Hydroperoxide Oxidations Catalyzed by Metals. III. Epoxidation of Dienes and Olefins with Functional Groups. *J. Org. Chem.* **1970**, 35 (6), 1839–1843.
- (126) Thornburg, N. E.; Thompson, A. B.; Notestein, J. M. Periodic Trends in Highly Dispersed Groups IV and V Supported Metal Oxide Catalysts for Alkene Epoxidation with H₂O₂. *ACS Catal.* **2015**, 5 (9), 5077–5088.
- (127) El-Korso, S.; Khaldi, I.; Bedrane, S.; Choukchou-Braham, A.; Thibault-Starzyk, F.; Bachir, R. Liquid Phase Cyclohexene Oxidation over Vanadia Based Catalysts with tert-Butyl Hydroperoxide: Epoxidation versus Allylic Oxidation. *J. Mol. Catal. A Chem.* **2014**, 394, 89–96.
- (128) Lane, B. S.; Burgess, K. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, 103 (7), 2457–2473.

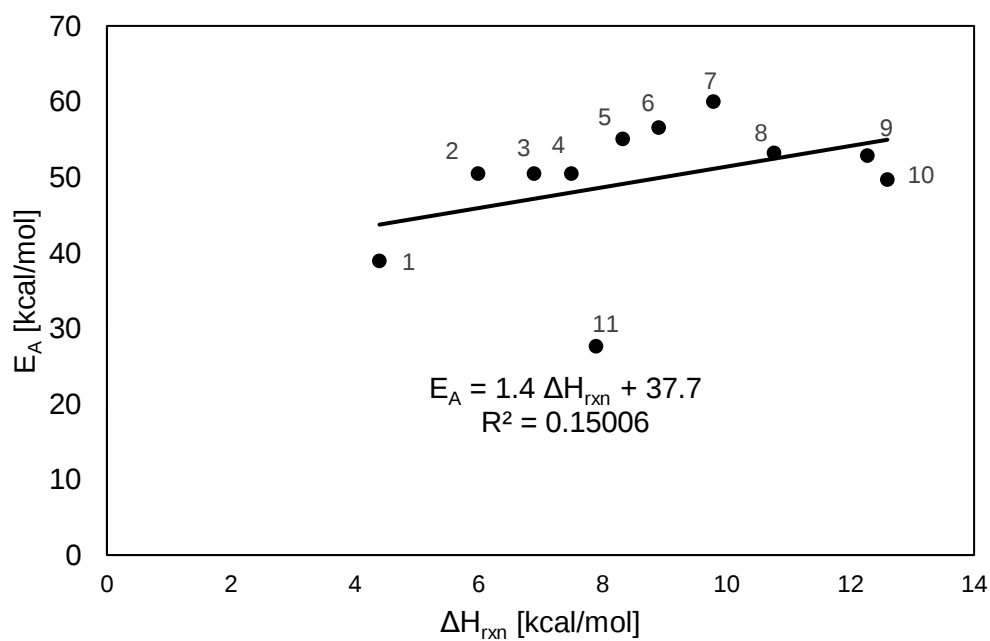
- (129) Bonon, A. J.; Kozlov, Y. N.; Bahú, J. O.; Filho, R. M.; Mandelli, D.; Shul'pin, G. B.
Limonene Epoxidation with H_2O_2 Promoted by Al_2O_3 : Kinetic Study, Experimental Design.
J. Catal. **2014**, 319, 71–86.

Appendices

Appendix 1: Scaling relations for concerted dehydration and dehydrogenation reactions

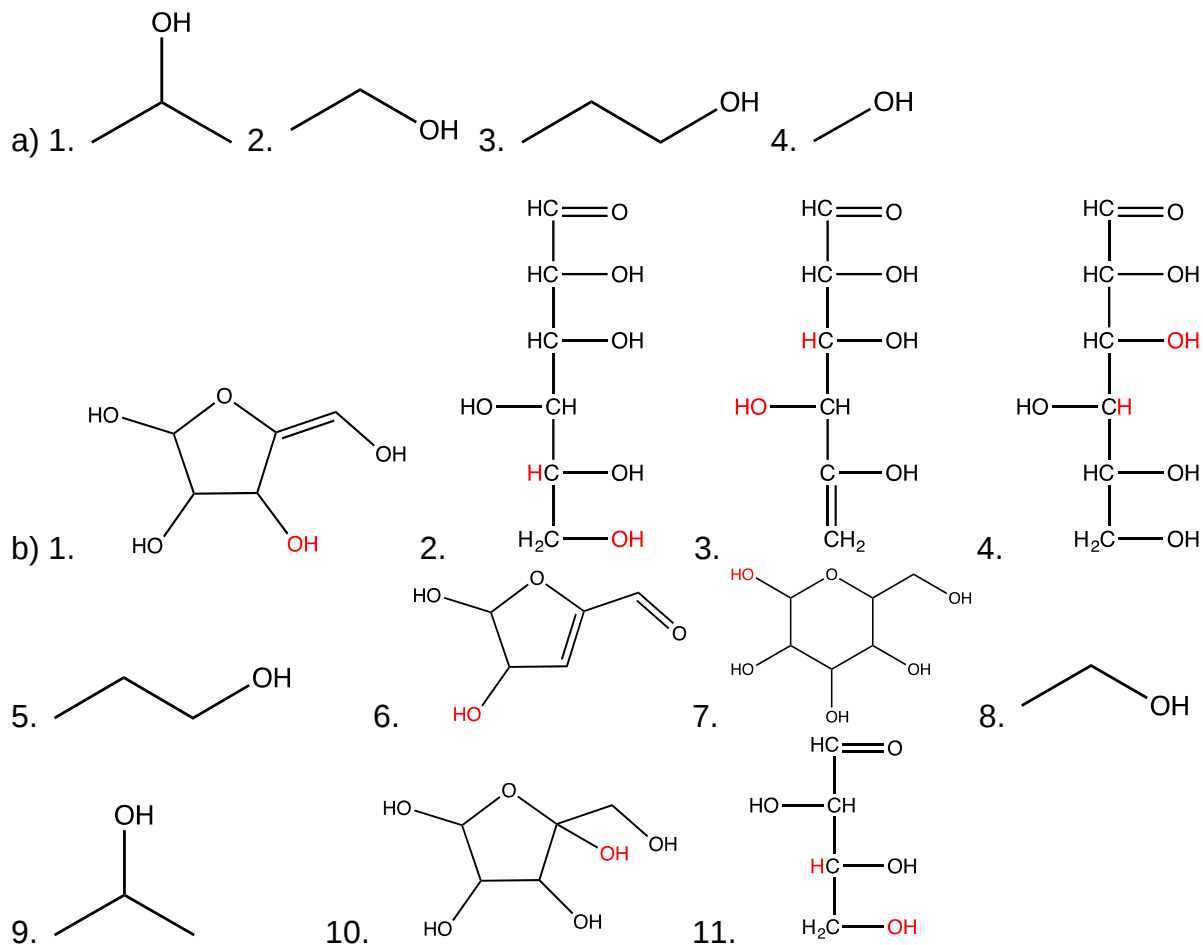


(a)



(b)

Figure A.1: Analogy to Evans-Polanyi relationship correlating ΔH_{rxn} to $\Delta H_{\text{activation}}$ for (a) unimolecular dehydrogenation and Evans-Polanyi relationship for (b) unimolecular dehydration. The corresponding molecules used for the above relationships can be seen below with the leaving oxygen and hydrogen atoms highlighted in red.



Appendix 2: Further experimental details for the oxidation of cyclooctene using gold nanoparticles, as recreated from the Supplementary Information for “Microkinetic modeling of homogeneous and gold nanoparticle-catalyzed oxidation of cyclooctene” by Robert R.O. Brydon, Anyang Peng, Linping Qian, Harold H. Kung, and Linda J. Broadbelt; *Ind Eng Chem Res*, **57** (14), 4832-4840.

A2.1 Experimental Characterization

A2.1.1 Emission and excitation spectra

The spectra of the reaction solutions were analyzed using Photon Technology International Model QM-2. The emission spectrum was collected by first determining the wavelength of the excitation light that would yield the maximum emission intensity. Once determined, then the emission spectrum was collected using this excitation wavelength. Excitation spectrum was generated by monitoring the fluorescence emission at the wavelength of the emission peak while varying the excitation wavelength. When sample was diluted, HPLC grade THF or ethanol was used.

A2.1.2 ICP

Au solution concentration after a reaction was determined using Thermo iCAP Q Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Before the measurement, the organic in 1 mL of the sample was burnt at 850 °C for 4 h in a muffle furnace. Then, 0.2 mL concentrated HNO₃ and 0.2 mL concentrated HCl were added to dissolve the Au species. After that, the solution was transferred to a volumetric flask and diluted to a total volume of 10 mL with Milli-Q water.

A2.1.3 TEM

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a JEOL ARM-200F aberration-corrected STEM (AC-STEM) operated at 200 kV with a nominal spatial resolution of 0.08 nm in the STEM mode. The TEM/STEM samples were prepared by dipping the lacey carbon covered copper TEM grid directly into the ethanol diluted filtrate solution that contained the Au nanoclusters. After drying, the filtrate formed a thin polymer film that hung over the holes of the lacey carbon film. The filtrate coated TEM grid was inserted into the microscope for observation.

A2.1.4 GC product analysis

Samples of the reaction mixture were analyzed using Agilent 6890 GC equipped with a flame ionization detector with DB-624 capillary column. Cyclooctene, cyclooctene oxide, cyclooctanol (analogue of 2-cycloocten-1-ol), cyclooctanone (analogue of 2-cycloocten-1-one) and cyclooctane-1,2-diol were purchased and used as standards to calibrate the sensitivity factors of the products. Small unidentified peaks were observed with overall area close to 5% of the total carbon at 50% conversion. The intensity of such peaks appeared to increase when cyclooctane-1,2-diol was deliberately added to the reaction solution, which suggests that these minor peaks could be high degree oxidation products formed along the diol oxidation pathway including cyclooctane-1,2-dione and suberic acid. However, the quantification of such oxidation products was not possible due to the similarity of their retention time.

A2.2 Additional Experimental Details

A2.2.1 Titration for peroxides

Triphenylphosphine (5 μ M in dichloromethane or ethanol) was added to 0.1 mL of the sample continuously until the peroxide test paper (EMD chemicals Inc. 0.5-25 ppm range) color turned colorless indicating the absence of peroxide. Since peroxide test paper may not be sensitive to polymeric hydroperoxide, KI and starch test was also used to verify the absence of polymeric hydroperoxide. 1 mL of a solution of 0.09 M KI and 0.011 wt% starch indicator was added to 1 mL of a sample that had been treated with triphenylphosphine. After sonicating for 10 mins, no dark blue color was observed, indicating peroxides had been completely removed by triphenylphosphine.

Appendix 3: Experimental details for the co-oxidation of ethylbenzene and cyclooctene, as performed and written by Anyang Peng, Mayfair Kung, and Harold Kung for the publication “Cyclooctene-3-hydroperoxide mediated selective C-H bond activation via co-oxidation” by Anyang Peng, Robert Brydon, Linda Broadbelt, Mayfair Kung, and Harold Kung; [in preparation].

A3.1 Chemicals and Materials

HAuCl₄•3H₂O (≥99.9% trace metals basis, Sigma Aldrich), fumed silica (CAB-O-SIL90, Cabot Corporation), ethylenediamine (≥99% ReagentPlus, Sigma Aldrich), ethanol (200 grade, Decon™ Labs), cobalt(II) nitrate hexahydrate (≥98%, Sigma Aldrich), Nano H-ZSM-5 (P-26, ACS Material), decane (≥99% ReagentPlus, Sigma Aldrich), cis-cyclooctene (95%, Alfa Aesar), ethylbenzene (99.8% anhydrous, Sigma Aldrich), acetophenone (99% ReagentPlus, Sigma Aldrich), 1-phenylethanol (98%, Sigma Aldrich), hydrogenperoxide (30% aqueous solution, Fisher Chemical), potassium hydroxide (reagent grade, 90%, Sigma Aldrich), sodium sulfate (FCC/USP grade, Fisher Chemical), tetrahydrofuran (>99%, Sigma Aldrich), tert-butyl hydroperoxide (~5.5M in decane, Sigma Aldrich), triphenylphosphine (>98.5%, Sigma Aldrich), D-chloroform (99.8 atom% D, Sigma Aldrich), HCl (38% wt/wt, Fisher Chemical), HNO₃ (68%~70% wt/wt, Fisher Chemical), EM Quant peroxide test strips, syringe filter (PVDF membrane, 0.25mm/0.2μm, Acrodisc).

A3.2 Catalyst Preparation and Characterization

A3.2.1 Co-ZSM-5 Preparation and Characterization

Nano H-ZSM-5 was calcined in a U-tube under O₂/O₃ flow (~300cc/min) with a ramping rate of 2°C/min till 200°C and held at 200°C for 1 hour to remove residual templates. Co/ZSM-5 was

prepared by incipient wetness. For example a 5 wt.% loading Co/ZSM-5 was prepared by adding a 0.72M cobalt (II) nitrate solution (250 mg of cobalt(II) nitrate hexahydrate in 1.2 mL DDI water) to 1g of Nano H-ZSM-5 while carefully rotating the beaker. The slurry was dried under a lamp and a uniform pink powder was formed. The as formed powder was then loaded into a linear calcination tube and purged under argon flow (100cc/min) for 1 hour to minimize humidity. The as prepared catalyst was then calcined under oxygen flow (60cc/min) with a ramping rate of 10°C/min to 450° (held at 250°C, 350°C, 450°C for 1 hour each). The obtained Co/ZSM-5 has a cobalt loading of 5 wt.%. Two other loadings, 3 wt. and 7 wt.% were also prepared. All three catalysts were characterized by H₂-TPR, XRD, XPS and UV-vis.

A3.2.2 Preparation of COE filtrate generated via auto-oxidation of COE (Auto-COE)

The COE filtrate was in-situ generated from homogeneous cyclooctene epoxidation reaction according to the procedure developed by Qian et. al. ^[6] Prior to reaction, cis-cyclooctene was purified to remove the manufacturer-added stabilizer. In general, 50mL of 3M KOH solution was added to 50mL of cis-cyclooctene in a flask. After sufficient mixing and vigorous stirring, the organic layer was collected by separation. This procedure was repeated with another 50mL of 3M KOH and two other 50mL of DDI water. The cis-cyclooctene was then dried with sodium sulfate overnight. To completely remove the stabilizer, the dried cis-cyclooctene was distilled in an oil bath at around 180 °C and the fraction came out at 145 °C was collected. 10mL of purified cis-cyclooctene and 1mL of decane were mixed in a reactor. The cyclooctene epoxidation reaction was conducted under oxygen flow (30cc/min) at 100°C and the conversion was monitored by GC. Once the desired conversion (50 % ± 10 %, unless specified) was reached, the reaction mixture

was collected. This solution contains a certain amount of oxidation products including cyclooctene oxide, cyclooctene 3-hydroperoxide, 2-cycloocten-1-ol, 2-cycloocten-1-one and trace amounts of 1,2-cyclooctanediol.

A3.3 Catalyst Activity Test

A3.3.1 General Procedure

Ethylbenzene oxidation reactions were conducted in a 3-necked cylindrical reactor equipped with a fine frit glass disperser tube (Chemglass Sciences) and a condenser maintained at -10°C in dark. In a typical reaction, 7mL of ethylbenzene, 1mL of decane and 3mL of filtrate (Auto-COE) were loaded into the reactor together with a teflon-coated magnetic stirrer (32 mg of Co/ZSM-5; unless specified usually 5% Co loading ZSM-5 was used). After the reaction set up was assembled, the reaction mixture was stabilized under N_2 flow for 20 min in a pre-heated oil bath. Once the temperature of the condenser and oil bath were stabilized, constant O_2 flow was supplied at 30cc/min. 0.1mL of the reaction mixture was taken at different time intervals (syringe filter was used when solid catalysts were involved), dissolved in 0.7mL of D-chloroform and analyzed by ^1H -NMR.

A3.3.2 Products Identification and Quantification

Aliquots of the reaction mixture were diluted with THF and analyzed by GC-MS spectrometry (Agilent GC-7890A, MS-5975). Acetophenone (AcP) and 1-phenylethanol (PEA) were identified to be the dominant products. ^1H -NMR and ^{13}C -NMR (400 MHz Agilent DD2-MR400 system) were employed to further confirm the product identities. 1-Phenylethyl hydroperoxide (PEHP),

which was not detected by GC-MS because of its thermal instability, was identified by NMR to be another dominant product. All three products were quantified by ^1H -NMR using decane as the internal standard. After calibrating the evaporating loss, no carbon imbalance was observed.

A3.4 Stoichiometry Experiment

Reactions were set up as described in the catalytic activity test section. 32mg of Co-IMP-5 was used in each reaction. Auto-COE filtrate used in these reactions were derived from the same COE oxidation reaction (50% cyclooctene conversion). 1mL of the Auto-COE solution and 7mL of ethylbenzene were used in each case. Additional amount of COE (0mL, 1mL and 2mL) was added to the mixture. In all three reactions, the total volume of the reaction mixture was kept at 11mL by varying the amount of decane introduced to the mixture. (1mL of the Auto-COE solution contains $\sim 3.8\text{mmol}$ cyclooctene epoxidation products including $\sim 0.3\text{mmol}$ cyclooctene 3-hydroperoxide)

A3.5 Quantification of Hydroperoxide

The concentration of hydroperoxide was quantified by two titration methods: A) Triphenylphosphine (PPh_3) titration. 0.1M of PPh_3 (in ethylbenzene) was used to titrate unknown hydroperoxide samples and the end point was identified with a EM Quant peroxide test strip. ^{31}P -NMR was used to confirm the complete removal of hydroperoxide species. B) iodometric titration. 0.2mL of sample was mixed together with 1mL of CHCl_3 /acetic acid (V:V = 1:2) and 6mL of 1M KI solution. The mixture was stirred in dark for 2h and then titrate with 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of a few drops of starch solution. The end point was reached when the mixture became colourless.

Appendix 4: Experimental details and procedures for oxidation of limonene using Ti/SiO₂ catalysts as prepared by Alex Ardagh and Justin Notestein for the publication, “Limonene epoxidation over Lewis acidic M-SiO₂” by Alex Ardagh, Robert Brydon, Linda Broadbelt, and Justin Notestein; [in preparation].

A4.1 Catalyst synthesis

Ti-SiO₂ was prepared by grafting Cp*TiCl₃ to wide pore SiO₂ using a method adapted from prior sources [18, 26-27]. Wide pore SiO₂ was dried at 463 K under dynamic vacuum (< 50 mTorr) overnight for 18 h prior to use for all catalysts. The dried support was then grafted with 50 mL anhydrous toluene solutions of Cp*TiCl₃ (Alfa Aesar) at RT under flowing N₂ on a Schlenk line. Metal loadings in solution were adjusted to deposit 0.20 M/nm² on the SiO₂ support. The mixture was stirred for 4 h, then the resulting light orange (Ti) powder was filtered and washed with 200 mL of toluene and hexanes. The powder was dried in air for 15 min then calcined at 823 K for 6 h with a 10 K/min ramp rate to yield Ti-SiO₂.

A4.2 Characterization

Nitrogen adsorption and desorption isotherms were collected using a Micromeritics ASAP 2010 instrument. Prior to analysis, samples were degassed at 463 K under dynamic vacuum (<5 mTorr) overnight for 16 h. The total surface area of the samples was calculated from the adsorption isotherm using the Rouquerol criteria modified BET method [32]. The mesopore size distribution was calculated from the desorption isotherm using the BJH method and micropore surface area was separated out from mesopore and external surface area using the t-plot. Metal content was determined from ICP-OES performed on a Thermo iCAP 7600 instrument calibrated with Ti, Nb, and Ta standards of known concentration. Catalyst samples were digested with 52 wt.% aqueous

HF (Macron Fine Chemicals) then diluted 10-fold with 1.0 wt.% HNO₃ (Fisher Chemical, TraceMetal grade, 67-70 wt.% aqueous) and shaken at 200 rpm at RT for 16 h overnight prior to analysis. X-ray diffraction (XRD) spectra were collected using a Rigaku ATXG X-ray diffractometer over the range 20-80° 2θ for TiO₂, Nb₂O₅, and Ta₂O₅ diffraction patterns using Cu Kα radiation.

Ambient diffuse reflectance UV-visible spectra were collected with a Shimadzu UV-3600 spectrophotometer equipped with a Harrick Praying Mantis diffuse reflectance accessory. Polytetrafluoroethylene (PTFE, Sigma-Aldrich) was used as the baseline white standard, and reflectance data were transformed to pseudo-absorbance using the Kubelka-Munk function $F(R)$.

$$F(R) = \frac{(1-R)^2}{2R} \propto \frac{k \text{ (molar absorption coefficient)}}{s \text{ (scattering coefficient)}} \quad (1)$$

All samples were diluted with PTFE to achieve similar $F(R) < 1.6$ to avoid non-linearity issues in the Kubelka-Munk transformation for highly absorbing samples. Pseudoabsorbance spectra were treated with Brown's simple exponential smoothing and a smoothing factor of 0.4 to increase signal to noise ratio at the expense of minor signal distortion [33]. Absorption edge energies were estimated from the x-intercept of a linear fit of the rising absorption edge in a plot of $(F(R)h\nu)^{1/2}$ for indirect transitions as in titania, niobia, and tantalum pentoxide.

A4.3 Epoxidation catalysis

Catalytic measurements were conducted in 20 mL glass vial batch reactors using 0.025-0.055 g catalyst. Acetonitrile (Fisher Chemical, Optima LC/MS grade, ≥99.9%) was used as the solvent. Limonene (Sigma-Aldrich, 97%) was passed over a column of activated Alumina N (Fisher Chemical, 60-325 mesh) immediately before use. Oxidants used included H₂O₂ (Sigma-

Aldrich, 50 wt.% aqueous, stabilized) and anhydrous TBHP (Sigma-Aldrich, ~5.5 M in decane, over molecular sieve 4 Å). Reactions were performed using oxidant: Limonene ratios spanning 11:1-1:11 with a constant total reactor volume of ~5 mL. Catalysts were calcined immediately before use in the reaction and were stored in a desiccator. Reactions were carried out under ambient pressure at 308-338 K with an 800-rpm shaker speed on a Glas-Col digital pulse mixer.

Epoxidation of Limonene with TBHP was also performed with the addition of catalyst poison/titrant phenylphosphonic acid (PPA, Sigma-Aldrich, 98%) over Ti-SiO₂ catalysts to assess the proportion of Lewis sites active for catalysis. A variable amount of a 50 mM PPA solution in mesitylene (Sigma-Aldrich, 98%) as solvent was added to the reactor, spanning 0-200% stoichiometric amounts of the total metal content across a series of identical batch reactors. PPA was added to the reaction mixture and allowed to titrate for 30 min before TBHP was added. Products were analyzed using a Shimadzu GC-2010 with a capillary column (TR-1) and flame ionization detector (FID) or a Shimadzu GCMS-QP2010 SE with a capillary column (ZB-624) and mass spectrometer (MS).

Ag powder (Alfa-Aesar, -120+325 mesh, atomized, 99% metals basis) was added to vials containing H₂O₂ to decompose the peroxide before analysis. Conversion was measured relative to an injected GC standard consisting of a 0.2 M limonene solution in acetonitrile with mesitylene added as an internal standard. Negligible limonene conversion was observed at 338 K in the absence of catalyst. A limonene epoxide standard injected into the GC-FID and GC-MS showed only small amounts of isomerization due to interactions with the inlet liner, amounting to ~0.01% conversion. The mass balance is defined with respect to carbon as the sum of known C₁₀ species

present in each GC sample divided by the Limonene present in the GC standard. Mass balances closed to 89-101 mol% for all reactions at conversions spanning 0-50%.

Experimental tests for internal diffusion limitations were performed with the wide pore Ti-SiO₂ catalyst in the epoxidation of limonene with TBHP. 500 mg Ti-SiO₂ was finely ground for 15 min using an agate mortar and pestle (Walter Stern). The powder was then passed through a No. 325 mesh sieve (Advantech Manufacturing) and the retained fraction was discarded. The fraction that passed was then finely ground again for 15 min, loaded into a 1 mL syringe (BD Medical), passed through a 0.7-micron filter (Whatman), and the retained fraction was discarded. The recovered fraction (~18 mg) was then calcined at 823 K for 6 h with a 10 K/min ramp rate to yield FG Ti-SiO₂.

Recycle tests were performed for the Ti-SiO₂ catalyst to test for permanent deactivation when applied in epoxidation with aqueous H₂O₂. Freshly calcined Ti-SiO₂ was used in the reaction for 6 hours. The catalyst was recovered via vacuum filtration, then washed with 50 mL acetonitrile and methanol (Sigma-Aldrich, ACS Reagent, ≥99.8%). The recovered spent catalyst was dried in air for 15 min, then was dried in a glass oven at 393 K for 1 h. After drying, the spent catalyst was recalcined at 823 K for 6 h with a 10 K/min ramp rate to yield S/R Ti-SiO₂.