

Mechanistic insight into the production of ethylene glycol and propylene glycol from biorenewable resources

by

Daniel George Lahr

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Program of Study Committee:
Brent H. Shanks, Major Professor
Peter Reilly
R. Dennis Vigil
Tom Richard
John Robyt

Iowa State University

Ames, Iowa

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ABSTRACT

The production of ethylene glycol and propylene glycol from biorenewable resources, i.e. sorbitol, has been parametrically examined numerous times. However, the current selectivity is too low to be economically feasible. In order to develop improved catalyst systems, a better understanding of the reaction mechanism is required. Sorbitol, due to its many functional groups is quite complex. Thus, in order to begin understanding of this system, analysis of the products is required. The study of the degradation of the product glycols and reaction of glycerol under hydrogenolysis conditions gives foundational insight. The effects of pH, competitive adsorption, and product degradation are determined for these smaller polyols. A mathematical model for the glycerol reaction and product degradation is developed which includes an instantaneous selectivity parameter, which is more accurate than an overall selectivity that does not account for product degradation. This foundation was built upon with an understanding of the effects sulfur has on the reaction. Sulfur, a known catalyst poison, lowers the reaction rate while increasing the selectivity toward propylene glycol. The limiting step in the reaction is proposed to be the catalytic diffusion of sulfur adatoms away from the adsorbed polyol during the dehydrogenation step. Finally, higher polyols are studied. The reaction rate of higher polyols is correlated to the configuration of the polyol. Analysis of the product distribution of various polyols shows that the decarboxylation reaction is occurring along with the retro-aldol reaction. A selectivity map is fitted to the product distribution to determine which hydroxyl groups are preferentially dehydrogenated. Sulfur decreases the dehydrogenation fraction of the primary alcohol group.

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I have had many fine undergraduates, but there are two in particular to which I am grateful. Aaron McKee was the hardest working of the bunch, eager to do just about anything in the lab. His mechanical expertise was immeasurably useful in repairing the HPLC or the reactor. Nathan Morris ran a majority of the reactions for the work in the second chapter. He also worked on a project to produce sorbitol from levoglucosan, a portion of the original plan of my research. His work proved to my satisfaction that the production of glycols from levoglucosan, which would come from corn stalk pyrolysis, was economically a poor idea.

Finally, I would especially like to thank my wife, Diane for supporting and encouraging me during my stay at Iowa State. She was very understanding during the times I seemed to live at Sweeney.

CHAPTER 1

INTRODUCTION

General Introduction

In the pursuit of producing value-added products from renewable resources, researchers have been able to produce ethylene glycol and propylene glycol from sorbitol via hydrogenolysis. Cornstarch can be broken down by enzymatic hydrolysis into glucose, which can be catalytically hydrogenated to sorbitol. The two glycols are excellent candidates for compounds to produce from renewable resources. They are both produced in large quantities for a high price. There are 6.7 billion pounds of ethylene glycol sold for \$0.35/lb and 1.1 billion pounds of propylene glycol sold for \$0.50/lb annually. They are also both currently produced using fossil fuel as the raw material. Hydration of propylene oxide and ethylene oxide give rise to the two glycols. Another reason for the production of glycols from biorenewable is their high oxygen content. Most renewable resources have an oxygen to carbon ratio close to one. It is advantageous to produce products from these resources that have a similar ratio. The glycols meet this specification; ethylene glycol has a ratio of 1.0 while propylene glycol has a ratio of 2/3. On the other hand, the production of paraffins like polyethylene from biorenewable resources wastes oxygen, about 50% of the weight of a typical biorenewable. The only hurdle left is to find a way to produce these compounds economically.

Structure of Polyols

The structure of a polyols consists of a chain of two to six carbon molecules, each having one hydroxyl group and one or two hydrogen atoms, depending on if the carbon atom

is in the primary or interior position. An example polyol, glycerol, is shown at the top of Figure 1.1. Additional CHOH groups can be added between the top primary alcohol group and the secondary alcohol group. Since these additional carbons will be chiral, this addition needs to be performed twice to account for both potential polyols formed. In the same manner as with sugar aldehydes beginning with glyceraldehyde, a tree of polyols can be formed starting with glycerol as shown in Figure 1.1. Unlike aldehydes, polyols have the same functional unit at both primary positions of the molecule. This reduces the number of total unique compounds due to planes of symmetry. For example, there are only six unique D-hexitols and three unique D-pentitols, while there are eight unique D-hexoses and four unique D-pentoses. All fully-hydroxylated aldehydes with three or more carbons are optically active, but not all polyols are optically active. Glycerol, erythritol, xylitol, ribitol, galactitol, and allitol are not optically active while the remaining polyols are optically active. The names of the polyols are the same as the aldehyde except with a different ending.

Hydrogenolysis Mechanism

There are a number of steps in the production of glycols from sorbitol. Sorbitol, glycerol, ethylene glycol, and propylene glycol are shown in Figure 1.2. The mechanism to break the six-carbon molecule down to two or three carbon molecule is complex.¹ First sorbitol is dehydrogenated to an aldehyde or ketone, depending on which hydrogens are removed. This molecule can then react via the retro-aldol mechanism. This is shown in Figure 1.3. There is a hydroxyl attack on the β -hydroxyl group, the hydroxyl group two carbons from the dehydrogenated oxygen. This leads to a specific carbon-carbon bond cleavage as shown. Since sorbitol is fully hydroxylated and at least 3 carbons long, any

carbon-carbon bond can be broken by this mechanism. Compounds that do not have hydroxyl groups that are two carbons away from each other cannot react under this mechanism. Therefore, glycerol can react under this mechanism to form ethylene glycol. However, neither glycol can react in this manner, because the only two hydroxyl groups in each compound are adjacent to each other. In order to produce propylene glycol, glycerol is dehydrated. The mechanism for this reaction is shown in Figure 1.4. A hydroxyl group attacks the hydrogen one position from the aldehyde. This frees the β -hydroxyl group to break into solution, leaving a molecule with two double bonds to be reduced by the catalyst to form propylene glycol. The dehydration mechanism requires a hydrogen atom one position away from the oxidized oxygen. Another reaction that is known to occur at high pH and high temperature is the decarboxylation reaction. This mechanism is shown in Figure 1.5. An oxidation occurs at the primary position followed by a carbon-carbon cleavage resulting in an aldehyde with one less carbon than the previous aldehyde and carbon dioxide.

From Figures 1.2 and 1.3, it is apparent that it would be beneficial to specifically break the middle carbon-carbon bond of sorbitol to produce two 3-carbon molecules (glyceraldehyde and dihydroxyacetone) that both could reduce to glycerol. Glycerol could then react to form ethylene glycol or propylene glycol. If other carbon-carbon bonds break, there is the potential for a large loss due to the single carbon molecules formed.

Sorbitol has six alcohol groups that can be dehydrogenated. There are many different products that can be produced depending on the hydroxyl group oxidized. This is shown in Figure 1.6. The initial dehydrogenation of sorbitol can produce six intermediate products. These products can react via decarboxylation or retro-aldol to form smaller aldehydes or ketones. The decarboxylation reactions are labeled in Figure 1.6, while the remaining

cleavage reactions via are the retro-aldol reaction. These smaller intermediates formed from a carbon-carbon cleavage can react further in the same manner or can be reduced back to a polyol. Figure 1.6 only shows the reduction of the smaller intermediates back to polyols. All three five-carbon polyols, both four-carbon polyols, glycerol and ethylene glycol can be formed from sorbitol with one dehydrogenation step, one carbon-carbon cleavage step, and the subsequent reduction.

Literature Review

Much of the work in this area looked at the empirical outcomes of changing process variables. Process variables that are usually examined are process temperature, metal catalyst used, and co-catalyst or base used. A typical example is a patent from Schuster.² The majority of the patent describes the process for making the catalyst. The remaining portion mentions process conditions (T, P, time, etc) with six example reactions. The differences between the reactions are either the metal catalyst used, which is a combination of five metals, or the co-catalyst used, such as magnesium oxide or calcium oxide. Results are given in a weight percent of organic material remaining in the liquid phase, of which 60 percent is propylene glycol. Over 30% of the original organic weight that began as sucrose had degraded to gases and were not detected. Two other patents from Schuster are similar in respect that the majority of the discussion involves the catalyst used in the reaction.^{3,4} There are also six sequential patents from Gubitosa that also discuss the production of catalysts to be used in this reaction.⁵⁻¹⁰ A variety of different metals are used as blends. These are palladium, platinum, rhodium, ruthenium, and tin. Compared to Schuster, there are many more reaction examples given with different variables examined. Process variables studied

include the catalyst to sorbitol molar ratio, base to sorbitol molar ratio, reaction temperature, pressure, special velocities or reaction time, and catalyst used. There is little, if any, discussion about the results however. These studies simply report the results obtained.

Sohounloue et al performed early work studying the catalytic hydrogenolysis of sorbitol.¹¹ They showed that temperature and pH affected the selectivity of products. The selectivity toward ethylene glycol remains constant with temperature changes while the selectivity toward propylene glycol increases with temperature. The mechanism used to explain the catalytic carbon-carbon cleavage in sugar alcohols was first proposed in this paper. There is much discussion about the statistical possibilities that occur, depending on which of the three hydroxyl groups is initially dehydrogenated. (Sorbitol has a plane of symmetry, ignoring stereochemistry, which is not important in the final products; there are only three unique possibilities.) There will be more three-carbon molecules formed if the second hydroxyl group is attacked preferentially, as opposed to if all hydroxyl groups were attacked equally. However, the pH was only measured initially, and not measured throughout the reaction to ensure the pH level remained constant. The molarity of the base added is 25% of what is added in the studies discussed in this thesis with the reaction time lasting twice as long. The base chosen in this study was calcium oxide, which dissolves poorly. As the base is consumed by acid production reactions, which are common under the reaction conditions, the remaining solid dissolves. Without enough base present, the pH level will drop from 12 to below 7. This is shown by Chang et al.¹² The study mentioned that the pH before a reaction containing calcium oxide was 12.5. This dropped to 5.3 at the end of the reaction. As with the earlier paper, the pH through the reaction was not studied. The pH could have dropped sharply at the beginning, sharply near the end or gradually throughout the reaction.

This work is typical of the empirical studies performed. The following variables were changed individually: temperature, hydrogen pressure, catalyst amount, catalyst type, agitation rate, and metal oxide or base added. Data was shown how the sorbitol reaction rate or selectivity to glycerol was affected by these changes.

Tronconi et al¹³ made a mathematical model of the hydrogenolysis of sorbitol. They determined that the reaction of sorbitol was first order in sorbitol and second order in catalyst amount, in the form of a Langmuir-Hinshelwood model. They also gave a model with 6 compounds, one of which was an intermediate. The reactions of glycerol to form either glycol, lactic acid to propylene glycol, and propylene glycol to lactic acid were all modeled as first order non-catalytic steps. However, all of these reactions require a catalyst, and the reactions of polyols are limited by the catalytic step. The model is shown in Figure 1.7. Equation 1 models the rate, r_1 , while Equation 2 models the remaining constants.

$$r_1 = k_1 (C_{NaOH})^2 \frac{C_s}{(1 + K.C_s)^2} \quad (1)$$

$$r_i = \exp\left(a_i - \frac{b_i}{T}\right) C_i \quad (2)$$

where C_i is the concentration of the reactant or the base, T is the reaction temperature, k_1 is the sorbitol rate constant, and K is the inhibition constant. Both constants are functions of temperature in the form of Equation 2, removing the concentration term. There are a number of concerns with this model. Only one reaction rate is modeled catalytically, even though the authors state that all require a metal catalyst to proceed. There is no mention of possible inhibition caused by the products adsorbing on the catalyst. There is no model for the degradation products. According to the model, the only products that should be found are

sorbitol, ethylene glycol, propylene glycol, glycerol and lactic acid. However, the best data given showed 30% of the overall selectivity was toward, presumably, degradation products.

Montassier et al¹⁴ studied the effect sulfating ruthenium has on the reaction rate and selectivity of products. Sulfur poisons the reaction, slowing the rate. However, the selectivity of the reaction toward propylene glycol increased dramatically from 0.12 without sulfur to 0.8 with one mole of sulfur added per mole of ruthenium catalyst. The pH of this reaction began at 6.0; thus it is unlikely to have changed drastically during the reaction. The low pH will lead to lower reaction rates in this system. This work also mentions that ruthenium modified with sulfur is still known to hydrogenate. Therefore, hydrogenation of aldehydes like xylose is not affected to the extent of the hydrogenolysis of glycerol.

Wang et al¹⁵ performed an important study confirming the reaction mechanisms for hydrogenolysis. Three different mechanisms had been proposed to explain the carbon-carbon cleavage of polyols; the retro-aldol, retro-Claisen, and retro-Michael mechanisms. They showed that the retro-aldol mechanism is the correct reaction mechanism in multiple ways. Specific compounds were shown as unreactive that are predicted to react under either one of the final two mechanisms. For example, a molecule that cannot go through the dehydrogenation mechanism according to the retro-aldol mechanism, 2, 4-dimethyl-2, 4-pentanediol, did not dehydrate. This shows that the initial dehydrogenation of the hydroxyl group is an essential portion of the dehydration mechanism. A total of seven compounds consistently reacted in ways that support the retro-aldol mechanism for C-C cleavage and dehydration mechanism for C-O cleavage. Evidence against the other two mechanisms was presented.

Brand et al¹⁶ studied the surface diffusion of hydrogen on a Ru(001) surface as a function of sulfur loading. The surface diffusion coefficient of hydrogen is $9 \times 10^{-7} \text{ cm}^2/\text{s}$ without sulfur, while this value drops by a factor of 30 to $3 \times 10^{-8} \text{ cm}^2/\text{s}$ with the sulfur coverage is 0.25. The reduction in the diffusion coefficient was also correlated to the number of adsorption sites each the sulfur adatom blocked, which is ten. Ten sites correspond to an effective blocking radius for sulfur of 2.7Å, while its actual radius is 2.0Å. The larger effective blocking radius is attributed to long range electronic effects.

The different conformations of higher polyols may lead to different adsorption potentials for each polyol. Koshikawa et al¹⁷ studied the adsorption of sugars onto hydrous zirconium and hydrous iron oxide surfaces. It was found that sugars with a particular configuration adsorbed onto the metal better than others. For example, the Langmuir constant for ribose adsorption onto zirconium is 35 while for arabinose this constant is 7. The adsorption potential is higher for sugars with the 2nd, 3rd, and 4th carbons in the axial, equatorial, and axial positions respectively. The strength of adsorption was also correlated to the fraction of conformations that have any three oxygen atoms enclosed by a circle of radius 1.6Å. Replacement of hydroxyl groups with hydrogen lowered the adsorption potential. However, mannitol is the only polyol studied. This work was compared to work done by Angyal¹⁸ who measured the complexation between Ca (II) and a variety of sugars, including many polyols. The degree of complexation of cyclic sugars correlated with the adsorption of sugars onto metals. The corresponding polyol-sugar pairs did not correlate well with the degree of complexation. Ribose has the highest degree of complexation amongst the sugars while ribitol was the lowest. The degree of complexation among polyols is a function of configuration as well. Polyols which have hydroxyl groups all on the same side like ribitol

complexed poorly, while polyols that have hydroxyl groups on opposite sides like xylitol complexed well. Xylitol complexed better with Ca (II) than arabitol because there are two hydroxyl group inversions. (The 2nd hydroxyl group is on the right side, the 3rd is on the left, the 4th is on the right)

Methodology

As Figure 1.6 shows, the path to the highest selectivity of three carbon molecules is through the dehydrogenation of the secondary alcohol group. A retro-aldol cleavage of fructose or sorbose produces two three-carbon molecules that can be reduced to glycerol. A question arises; why not use fructose as a raw material? The main reason for using fructose as a raw material is the milder reaction condition. The retro-aldol and reduction reactions can occur at low temperatures, 40°C, but the retro-aldol reactions need to be enhanced with a strong base such as KOH. The dehydrogenation step requires higher temperatures around 200°C. While fructose is more expensive than sorbitol, the cheaper processing step may account for this difference. The main problems with this method are the low potential selectivity toward product as well as the lack of potential catalyst control of this selectivity. This is shown in Figure 1.8. The idea behind this approach is to split fructose and subsequently reduce the three-carbon molecules produced. However, a balance between the cleavage reactions and the reduction reaction is required. This is because fructose can be reduced to mannitol and sorbitol, and the three-carbon molecules can react further. If there is too much catalyst all of the ketone is reduced to the polyol. Too much base leads to too many cleavage reactions. Miller et al performed a parametric study to try to optimize the base to catalyst ratio to give the largest selectivity toward three-carbon products. The best

result had a conversion of 68% with a selectivity toward three-carbon molecules of 50%. While 50% is a nice selectivity, there is concern with this method about the large range of products produced. Figure 1.8 gives many of the products formed; however, there are many more acids, aldehydes, and alcohols that can be produced due to the very high pH.

The methodology of producing glycols is the hydrogenolysis of sorbitol. While any alcohol group can be dehydrogenated, it is feasible to choose a catalyst that selectively dehydrogenates the secondary alcohol group. The pH of the system is lower, which will lower the product distribution and the reaction rate. The pH is also another variable that can be tuned to improve selectivity. Starting with sorbitol also allows for more interesting catalyst questions to be answered, because the initial step as well as intermediate steps is on the catalyst instead of only the final step.

Motivations

There are many areas to improve on the previous work. Chapter 2 discusses three of these areas; pH, product degradation, and competitive adsorption. While it is generally acknowledged that the pH of the system is important, only the impact of base selection has been discussed and not the effect of pH value. The decarboxylation reaction consumes hydroxyl groups; thus the pH can drop as the reaction proceeds. Control of the pH during the reaction is important to understand the effect pH has on the hydrogenolysis reaction. Another area is the effect reaction products have on the reaction rate of raw materials, namely competitive adsorption. Since the products are similar in configuration to the products, except smaller, it is expected that they would also adsorb onto the catalyst potentially lowering the reaction rate as the reaction proceeds. The adsorption of products

leads to another area that has not been explored, namely the degradation of products. Ignoring the degradation of products can lead to errors in measuring the actual selectivity of the reaction. This study is done on the products, ethylene glycol and propylene glycol, and glycerol instead of the raw materials. This reaction system is complex and the study of the smaller products will give a foundation to future study of larger compounds.

Chapter 3 discusses the effect of temperature and sulfur on the hydrogenolysis reaction. Studying the behavior of glycols and glycerol as a function of temperature and sulfur leads to insights on the adsorption of these molecules on the catalyst. Also, it is well known that the addition of sulfur reduces the reaction rate while increases the selectivity toward propylene glycol. Sulfur is a known catalyst poison, but the mechanism for the dehydration of glycerol toward propylene glycol occurs in the solution phase. The mechanism for the increased selectivity toward propylene glycol is not discussed and needs to be better understood. This study is also done using ethylene glycol, propylene glycol, and glycerol. Understanding how sulfur affects the reaction is crucial in the rational design of catalysts. Again, with a complex system, this understanding needs a foundation gained by using the smaller products.

Chapter 4 begins to understand the hydrogenolysis reaction of higher polyols. As mentioned earlier, the adsorption potential of a polyol is a function of its configuration. Also, compound that adsorb better onto catalyst will like react faster. Thus, the relative reaction rates of higher polyols can be correlated to their configuration. Since the reaction rate of a polyol will increase with more hydroxyl groups adsorbed onto the catalyst, the differing reaction rates can also give insight into the adsorbed conformation of the polyols.

Chapter 5 adapts the existing reaction mechanism and maps the flow of carbon in the hydrogenolysis reaction. Previous research has discussed the role of the retro-aldol mechanism in the hydrogenolysis of higher polyols. Another reaction that is known to occur at these conditions is the decarboxylation reaction. Analysis of the hydrogenolysis reaction products shows that the decarboxylation reaction can not be ignored in analyzing the reaction pathway as well showing that there is little dehydrogenation of the interior alcohol groups. A selectivity map is also generated to predict the relative dehydrogenation rates of alcohol groups as well as the relative contributions of the retro-aldol and decarboxylation reactions. The addition of sulfur increases the relative dehydrogenation rate of the secondary alcohol while lowering the rate of the primary alcohol group.

The goal of the previous research was largely to optimize empirically the production of glycerol, ethylene glycol, and propylene glycol. The goal of this current work instead is to develop a deeper understanding of the reaction mechanism of polyol hydrogenolysis. Conditions were chosen to help gain insight into this mechanism, not to necessarily obtain the best selectivity. This gained understanding will help rationally design catalysts for this reaction, which will optimize the production of these value-added compounds.

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Figure 1.1: Structures and names of three-carbon to six-carbon polyols

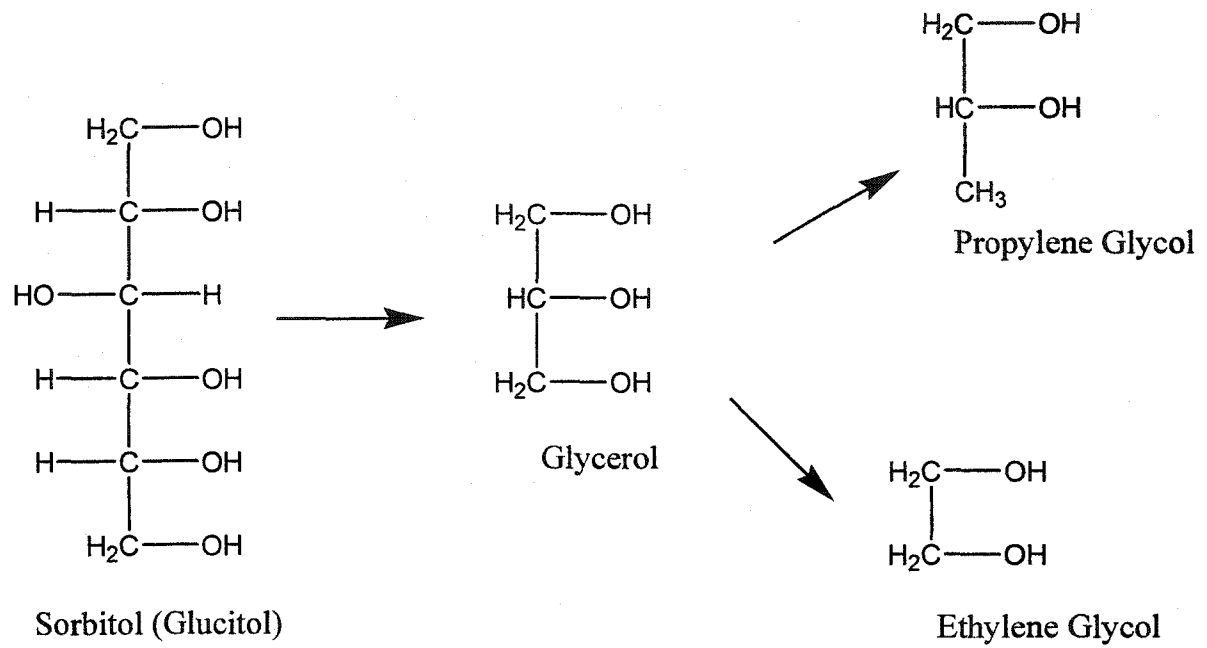


Figure 1.2: Schematic of Compounds Involved in Production of Glycols

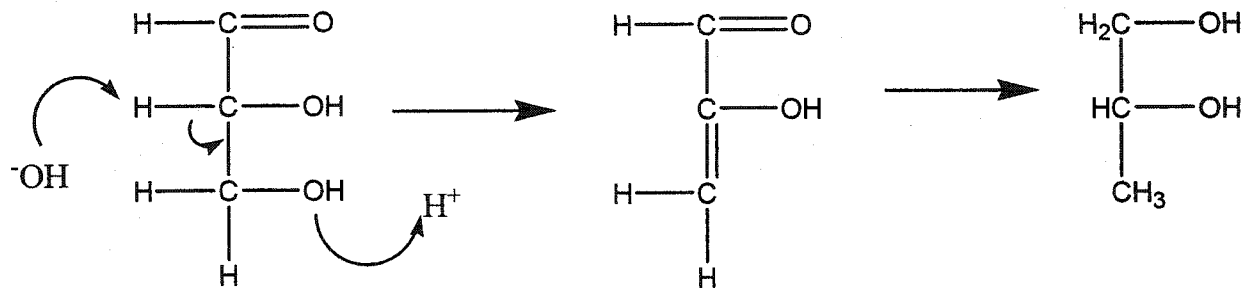


Figure 1.3: Dehydration and Subsequent Reduction of Glyceraldehyde to Propylene Glycol

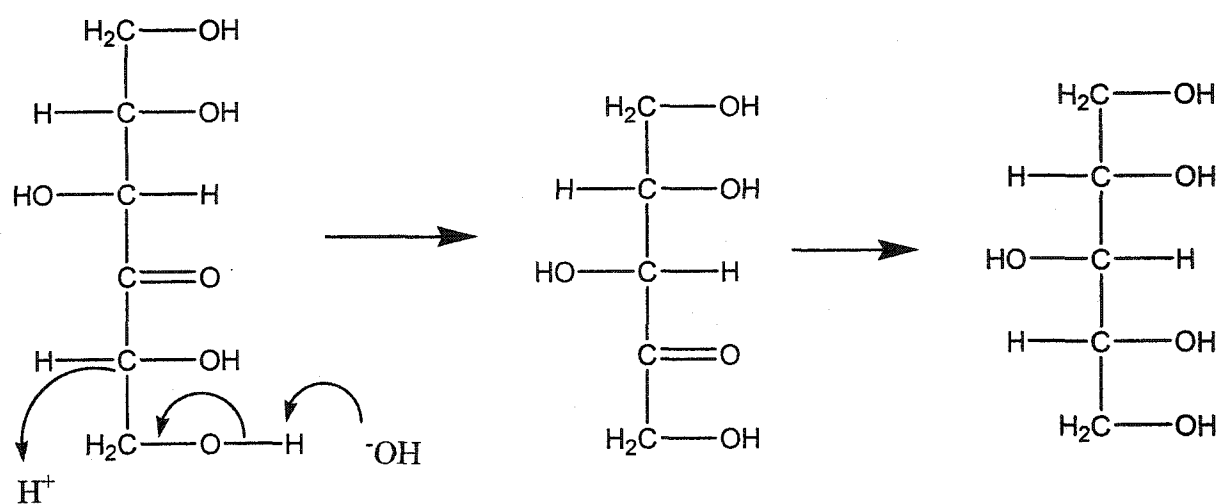


Figure 1.4: Schematic of the Retro-Aldol Mechanism Followed by Reduction to Polyol

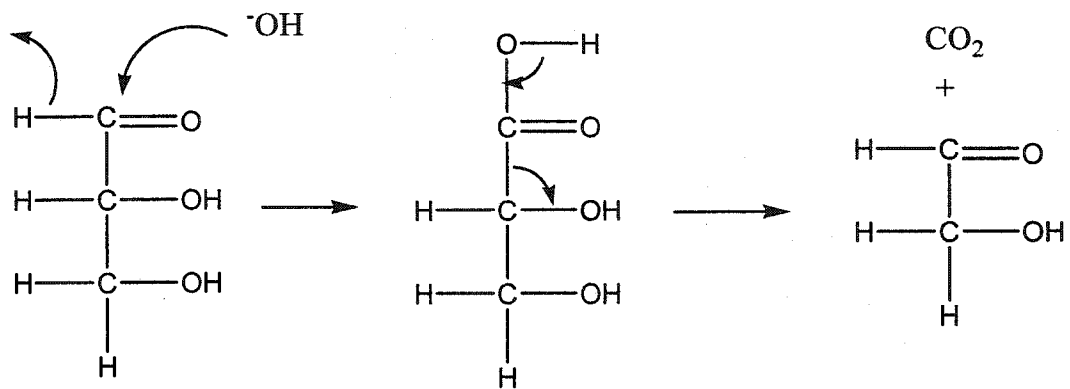


Figure 1.5: Decarboxylation of Glyceraldehyde to Glycol Aldehyde

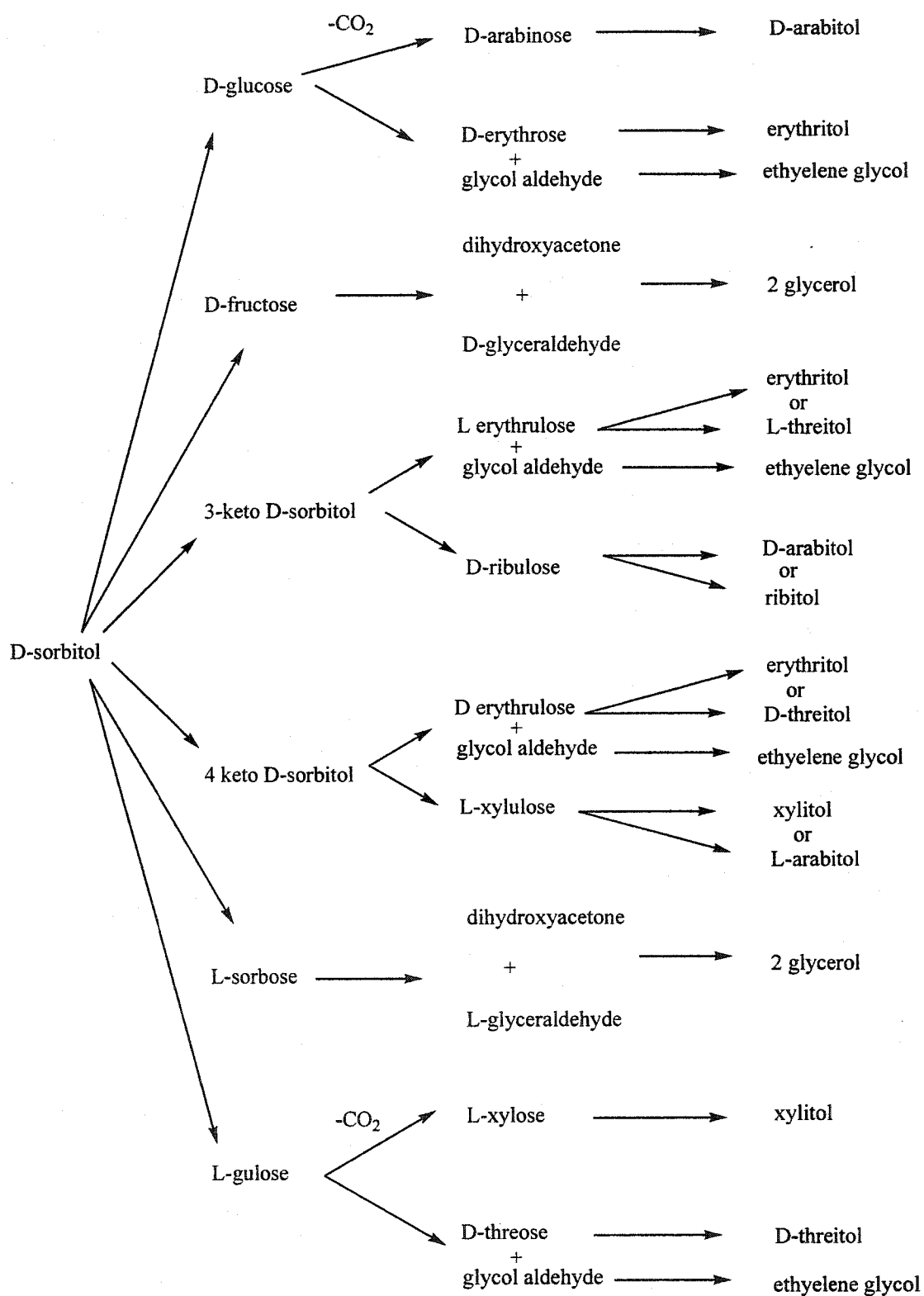


Figure 1.6: Potential Products Produced from Sorbitol via Retro-Aldol or Decarboxylation Reactions after an initial Dehydrogenation Step

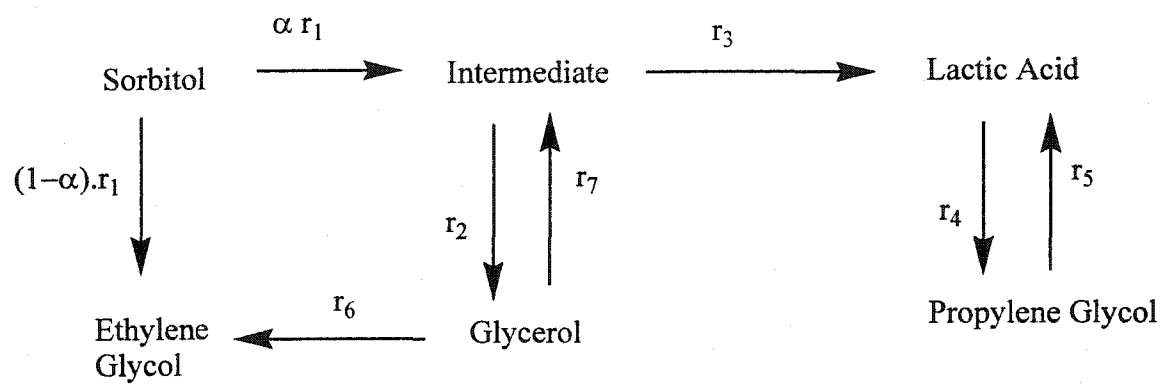


Figure 1.7: Reaction Scheme Proposed by Tronconi et al

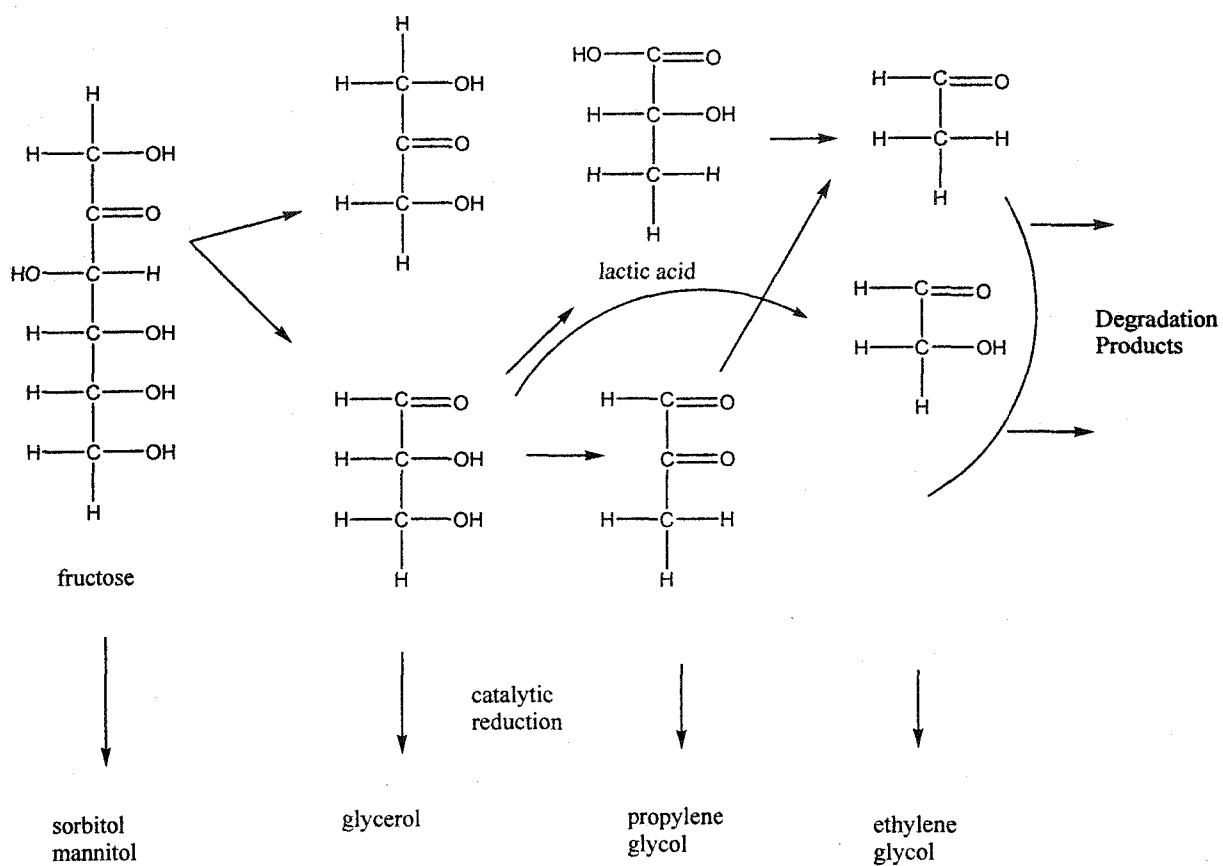


Figure 1.8: Products Produced From Fructose at Low Temperature and High pH

CHAPTER 2

Kinetic Analysis of the Hydrogenolysis of Lower Polyhydric Alcohols: Glycerol to Glycols

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Daniel G. Lahr and Brent H. Shanks*
Department of Chemical Engineering*
Iowa State University
Ames, IA 50011, USA
Email: bshanks@iastate.edu

Abstract

The production of ethylene glycol and propylene glycol from higher polyhydric alcohols has been parametrically examined numerous times. However, efforts to develop improved catalyst systems require a better understanding of the reaction mechanism. Glycerol conversion to the glycols represents an initial system for developing an improved mechanistic understanding of the conversion of the more complex higher polyhydric alcohols. Batch reactor studies with ruthenium on carbon catalysts were performed at two pH levels to obtain kinetic data. Langmuir-Hinshelwood type models were developed from the experimental data to describe the hydrogenolysis of glycerol into ethylene and propylene glycol as well as further degradation of the glycols. Detailed information on the competitive adsorption coefficients for the reaction species was determined, which led to conclusions about the limitations of previous parametric analysis.

Keywords: Hydrogenolysis; Glycerol reaction; Propylene glycol and ethylene glycol production

Introduction

The catalytic production of ethylene glycol and propylene glycol from higher polyols such as sorbitol and xylitol has been studied over the past decades.¹⁻⁷ The goal of this research was largely to optimize empirically the production of glycerol, ethylene glycol, and propylene glycol. The highest selectivities reported for the reaction of sorbitol to ethylene glycol and propylene glycol are approximately 65%, which is not high enough to be commercially viable.¹⁻⁵ Past work has focussed on catalyst modifications, type of base co-catalyst, and control of process variables as a means to improve the selectivity to glycols. However, these techniques do not lead to a mechanistic understanding of the reaction, which can be used for rational development of improved catalyst systems. For rational development to occur, a deeper knowledge of the reaction mechanism needs to be developed.

For improved understanding, efforts need to be directed into the mechanism of the hydrogenolysis as well as interactions between the reactants and the catalysts, which include both metals for the dehydrogenation/hydrogenation and hydroxyl groups for C-C and C-O cleavage. Missing from previously reported work are important mechanism features such as the effects of pH, competitive adsorption, and degradation of the reaction products on the overall reaction rates. While it is generally acknowledged that the pH of the system is important; only the impact of base selection (CaO, NaOH, KOH, etc) and not the effect of pH value has been discussed.⁷⁻⁸ In addition, a mechanistic understanding of the of the key reaction steps in the overall reaction has not been developed. For example, a model was developed with sorbitol as the substrate reacting to form glycerol, ethylene glycol, and propylene glycol.⁹ However, other than the reaction of sorbitol, all other steps are modeled

as elementary first order non-catalytic steps. As a result, potentially important mechanistic details such as competitive adsorption were not factored into the model.

The hydrogenolysis of higher polyols; sorbitol, xylitol, and glycerol, to form ethylene glycol and propylene glycol is reported to have multiple steps.¹⁰ The polyol is first dehydrogenated by the catalyst to an aldehyde or ketone. The product of dehydrogenation undergoes either a C-C or a C-O cleavage. The overall reaction sequence leading to C-C cleavage, known as the retro-aldol mechanism, or C-O cleavage, which occurs by dehydration, are both affected by base catalysis and go through a number of intermediates. The product(s) of either mechanism contain two olefinic bonds, which are subsequently hydrogenated by the metal catalyst. The metal catalyst is both a hydrogenating and dehydrogenating catalyst; therefore, the formation of the aldehydes and ketones is reversible.

To begin to unravel the mechanism of the complex hydrogenolysis reaction, only glycerol, ethylene glycol and propylene glycol were used in the current study. The primary reason to use these compounds as opposed to sorbitol and xylitol is to begin the development of a mechanistic model for the overall hydrogenolysis reaction by understanding the reaction network for the smaller polyols. If only sorbitol and/or xylitol were examined, the degradation of the glycols would not be considered, missing the impact of this degradation on the overall selectivity, thereby biasing this parameter too low. In addition, potential competitive adsorption of the glycols with the higher polyhydric alcohols could be important in the overall reaction. Incorrect conclusions about the reaction rate, especially the reaction order, of higher order polyols can be drawn if the only information is found from these polyols. An accurate determination of the reaction order requires knowledge of competitive adsorption. An additional motivation for this work is the potential value of understanding the

hydrogenolysis of glycerol to propylene glycol and ethylene glycol. In the production of biodiesel, glycerol is formed in large quantities as a byproduct. As the production of biodiesel increases, technologies will need to be developed to produce products from glycerol. Thus, understanding the mechanism in the production of glycols from glycerol could become industrially important.

The goal of this work was to develop a mechanistic model for the glycerol reaction portion of the hydrogenolysis process to ultimately help maximize yields to the desired glycols. A schematic of the model framework is shown in Figure 2.1. Discussion of the pH and competitive adsorption effects on this reaction system are included. The model presented here discusses the production of ethylene glycol and propylene glycol from glycerol.

Experimental

Glycerol, ethylene glycol, and 1,2 propylene glycol (all 99%+) were purchased from Acros Organics and diluted with deionized water for these experiments. Hydrogen (99.992% purity) was used as well as two bases, calcium oxide (96%) and calcium carbonate (99%), both of which came from Acros Organics. The catalyst purchased from Activated Metals & Chemicals, Inc. is 5 wt% ruthenium supported on activated carbon. The catalyst is handled in a powder which is about 50 wt% water.

All reactions were performed in a 100mL batch reactor (Autoclave Engineers) equipped with a stirrer, an electric temperature controller, and a sample port for liquid samples. For a typical reaction, a 10 wt% (1.5 M) solution of reactant; e.g. glycerol, ethylene glycol, propylene glycol, or a combination of the above, was added with 5 wt% Ru/C catalyst

(1.5 or 3.0 mM Ru), and a base for maintaining constant pH. Use of 0.4M CaO held the pH at 11.7, while CaCO_3 held the pH near 8.0. Measurements of each sample taken throughout the reaction shown that pH did not vary significantly with time. The reaction vessel was flushed with low-pressure nitrogen followed by low-pressure hydrogen. Next, the system is pressured with 70 bar H_2 and heated to reaction temperature. Two initial samples were taken and the pressure was increased to 100 bar. The stirring speed was set to 500 rpm. Experiments at higher mixing speed showed no change in reaction performance; therefore, there were no mass transfer limitations at this speed. The temperature, pressure, and mixing speed were held constant during the reaction.

Samples were taken in 15-minute intervals for 75 minutes. The samples were cooled to room temperature (20°C) to facilitate pH measurement. After the pH was measured, the sample was diluted with 60 wt% acetonitrile in water until the sample contained 40 wt% acetonitrile. The samples were analyzed by a HC-75 Ca^{++} cation exchange column from Hamilton with an RI detector. The column was run using a mobile phase of 40 wt% acetonitrile in water.

Kinetic Study of Ethylene Glycol and Propylene Glycol Degradation

Ethylene glycol and propylene glycol will react further under hydrogenolysis conditions. Therefore, to understand the selectivity to the desired glycols the degradation rates of ethylene glycol and propylene glycol must be considered. To determine these degradation rates, the individual reaction behavior of ethylene glycol and propylene glycol was evaluated at each pH level. Initial concentrations of each glycol ranged from 2.5-10 wt% (0.3-1.5 M). While the base reaction conditions were performed at 500 rpm, reaction

data were also obtained at 1000 rpm. No difference in reaction rates was found between the two mixing levels, so the system was not limited by external diffusion. For both ethylene glycol and propylene glycol, the degradation rate remained constant throughout the concentration range. The data for each reaction gave linear fits with R^2 values greater than 0.95. Shown in Figures 2.2 and 2.3 are the degradation rates for the ethylene glycol and propylene glycol, respectively, as a function of the initial concentration of the glycol. Since the reaction rate was independent of initial concentration, the degradation reaction was zero order for the range of glycol concentrations considered. This zero order reaction rate suggests that the catalyst was nearly saturated with glycols even at low concentrations. The average reaction rates for ethylene glycol and propylene glycol were 40 mol/kgcat·s and 50 mol/kgcat·s, respectively. These rates are of sufficient magnitude to necessitate the incorporation of glycol degradation in a glycerol hydrogenolysis model.

To determine whether the glycols compete for reactive sites on the catalyst, ethylene glycol and propylene glycol were introduced to the reactor at varying weight ratios from 1:3 to 3:1. The same temperature, pressure, and catalyst amount were used as in the pure component degradation experiments. The degradation rate was subsequently determined from the slope of the concentration versus time plot. Since there was excess glycol in all of these reactions, the catalyst would still be saturated and the zero-order kinetics discussed above would fit the data. Table 2.1 shows the degradation rates of both glycols in these mixtures compared to the rate of each glycol reacting alone. The fractional turnover is the fraction of the catalyst reactivity that was utilized in degrading each glycol. Assumed in this analysis was that the total activity was directly proportional to the total weight of catalyst in the reaction system. The total turnover of each reaction from Table 2.1 is within 20% error

of unity further indicating that the overall turnover was not significantly influenced by varying the glycol concentration.

As seen in Table 2.1, the fractional turnover for ethylene glycol was significantly higher than propylene glycol. The turnover ratio between glycols ranged from 2:1 to 30:1 depending on the initial glycol concentration. Even though propylene glycol degraded at a slightly faster rate than ethylene glycol, propylene glycol was less competitive for active sites than ethylene glycol. Therefore, previously reported selectivities for glycols, especially ethylene glycol, in the hydrogenolysis reaction of polyhydric alcohols could then be too low since these calculations did not include the degradation of glycols.

Previous work has indicated that either polyol will adsorb to ruthenium through oxygen.¹¹ Therefore, one could speculate that the presence of the non-oxygenated end in propylene glycol may cause it to be partially repelled by the catalytic surface, thus, decreasing its binding energy, which would allow ethylene glycol to adsorb more readily on the surface sites.

The catalytic degradation of the glycols may proceed through the conversion of a hydroxyl group into a ketyl or aldehyde group, depending on if an interior or exterior oxygen is dehydrogenated, as has been implicated in the production of glycols via hydrogenolysis.^{5,10} The electron density on ethylene glycol is balanced, while on propylene glycol, the electron density is shifted toward the hydroxyl end, allowing for an easier hydroxyl to aldehyde conversion. This effect may explain the slightly higher degradation rate for propylene glycol. However, it should be noted that the statistical probability that the difference between the two individual degradation rates was significant was only 70%.

To model the degradation reaction for the glycols, the following reaction steps were included, which are analogous to steps that have been proposed for polyols under these reaction conditions. Each glycol adsorbs on the catalyst and reacts to form an aldehyde or ketone. The aldehyde or ketone species desorbs and is subsequently degraded by hydroxyl attack in the basic solution. According to past research, C-C and C-O cleavage steps in the degradation of higher polyols to lower polyols are catalyzed by bases, thus the pH of the system affects the overall rate.¹⁰ Other reaction pathways are also likely to be pH dependant. In the reactor studies with either propylene glycol or ethylene glycol, no other liquid products (i.e., no aldehydes or ketones) were detected by the HPLC. In addition, the initial concentration of glycol did not affect the degradation rate. These two facts lead to the conclusion that Equation 2 represents the limiting step. Furthermore, since the degradation rate of the glycols did not change with time; the side products that were produced did not appreciably affect the degradation rate. Therefore, the following model was used for ethylene glycol with the same model structure also used for propylene glycol



where EG is the ethylene glycol, S is the catalytic site, EG' is the aldehyde formed by dehydrogenation of ethylene glycol, and X represents the degradation products. The degradation products were not measured or identified. However, these species do not affect the mechanism because the limiting step occurs prior to productions of the degradation

products. It is important to note that the dehydrogenation of EG to EG' is reversible and from the Gibbs Free Energy data the equilibrium concentration of glycol is strongly favored under the conditions used in the experiment.

A model was developed to describe the degradation of both ethylene glycol and propylene glycol assuming Langmuir–Hinshelwood kinetics. Competitive adsorption occurs between the glycols, which affects their relative degradation rates; this competition was addressed in the denominator of the two glycol rate equations using glycol inhibition constants as shown in Equation 5.

$$-r_{iG} = \frac{k'_{iG}(iG)}{k_{EG}EG + k_{PG}PG + 1} \quad (5)$$

where r_{iG} is the degradation rate for the glycol ($i = E$ for ethylene glycol and P for propylene glycol), k'_{iG} is degradation rate constant, iG the respective concentrations of the glycols, and k_{EG} and k_{PG} the respective adsorption constants for the glycols. The constants found in Equation 5 were obtained by a regression fit to the degradation data. Shown in Table 2.2 are the values for the rate constants determined from fitting the model given in Equation 5 to degradation data at each pH level (11.7 and 8.0). The adsorption constants in the denominator did not vary significantly for the two different pH conditions, so these constants were fit over both sets of data. Each of the glycols was found to degrade at about double the rate per gram of catalyst at the higher pH level, which is reflected in the values of the degradation rate constants. These results are consistent with the model given in Equations 1-4 in which only the reaction of the aldehyde to degradation products is expected to be pH dependent.

Kinetic Study of Glycerol Conversion

The reaction behavior of glycerol at the standard test conditions was first determined for an initial 5 wt% concentration of glycerol. Subsequent runs were performed with 5 wt% glycerol and either 5 wt% ethylene glycol, 5 wt% propylene glycol, or 2.5 wt% of each glycol. These data are shown in Figure 2.4. The two runs in which ethylene glycol was present demonstrated that the reaction rate of the glycerol decreased in proportion to the amount of ethylene glycol added. In contrast, the addition of propylene glycol had minimal effect on the reaction rate of the glycerol. The inhibitory effect, particularly of ethylene glycol, demonstrates the need to include competitive adsorption in the rate equation for the reaction of glycerol.

The reaction pathway was assumed to be similar for glycerol to that used for the glycols above in which the glycerol was first dehydrogenated to an aldehyde or ketone. In this case, the oxidized species can react via a C-C or C-O cleavage from the retro-aldol or dehydration reaction, respectively, which would be expected to be pH dependent. The pH dependant steps can either lead to products that are subsequently hydrogenated to glycols or to other side products.

Initial rate data for the reaction of glycerol in the absence of the glycols was obtained by varying the initial glycerol concentration. A plot of $\ln (dG/dt)$ versus $\ln (G)$, where G is the glycerol concentration, as shown in Figure 2.5, gave a positive slope. For a 99% confidence interval, the slope was found to be in the range of 0.45-0.99. This concentration dependence of the glycerol reaction rate was in contrast to the zero order rates found for degradation of the glycols.

The glycerol reaction data were first fit by regression analysis to the model given by Equation 6,

$$-r_G = \frac{k'_G G}{k_G G + k_{EG} EG + k_{PG} PG + 1} \quad (6)$$

where r_G is the glycerol reaction rate for the glycol, k'_G is glycerol reaction rate constant, and k_G is the adsorption constant for glycerol. The values used for k_{EG} and k_{PG} in the analysis were those given in Table 2.2 from the ethylene and propylene glycol degradation experiments. It is interesting to note that performing the regression analysis again while allowing these adsorption constants to be simultaneously determined gave similar values that did not affect the R-squared value of the resulting model. Using Equation 6, a plot of $1/(dG/dt)$ versus $1/G$ yielded an unreasonable result in that the initial rate data gave a negative value for k'_G with a 92% certainty that the value was significant compared to zero. Since a negative rate constant is not possible, an improved model was developed in which the reaction order with respect to the glycerol concentration was simultaneously determined during the k'_G and k_G estimation. The resulting equation:

$$-r_G = \frac{k'_G G^{1.5}}{k_G G + k_{EG} EG + k_{PG} PG + 1} \quad (7)$$

was found to yield a significantly improved fit to the data and to provide values for the constants that gave reasonable initial rate values. In addition, Equation 7 was consistent with the reaction order found from the initial rate data for glycerol conversion. The values of the model constants, k'_G and k_G , as determined from regression analysis of the glycerol reaction data are given in Table 2.3 for the Equation 6 and 7 glycerol models.

Shown in Figure 2.6 is a parity plot for the two models under the high pH conditions. As can be seen from the figure, the model based on Equation 6 gives clear curvature in the parity plot at the higher reaction rates. In contrast, the Equation 7 model has no curvature and yields better agreement between the observed and simulated results. Unfortunately, the mechanistic reason for the 1.5 order for the glycerol reaction term is not clear. However, it should be noted that the model is providing an overall reaction description for the glycerol reaction and undoubtedly does not capture all of the steps in the detailed reaction mechanism. The 1.5 reaction order may be explained by a reaction intermediate between the glycerol and glycols.

Equations with the similar form to Equation 7 were derived for ethylene glycol and propylene glycol in the presence of glycerol to represent the degradation of each glycol as well as their production from glycerol. While the accumulation of the glycols was directly measured, this accumulation is the difference between their production from glycerol and their degradation. The degradation kinetics as well as the inhibition constants in the denominator was determined as discussed previously. Therefore, the glycol production reaction can be accommodated by simply introducing a selectivity factor to the two glycol equations as shown in Equation 8,

$$-r_{iG} = \frac{k_{iG}iG - s_{iG}k'_G G^{1.5}}{k_G G + k_{EG} EG + k_{PG} PG + 1} \quad (8)$$

where the iG concentrations correspond to $i = E$ for ethylene glycol and P for propylene glycol and the s_{iG} factors are the respective selectivity factors. The selectivity factors are defined simply as the fraction of the glycerol converted into ethylene glycol or propylene

glycol. Since glycerol can also react to form chemical species other than the desired glycols, the selectivity factors for the glycols will not necessarily sum to a value of one.

By regression fit of the two selectivity parameters, s_{iG} , to the glycerol reaction data, an estimate of the overall selectivity for the glycerol reaction to each glycol was determined. This approach is an improvement over previous models for the hydrogenolysis of higher polyols that do not account for the degradation of ethylene glycol and propylene glycol under hydrogenolysis conditions. The effect of pH on reaction rates and selectivities were made by separately fitting the rate constants in the models to data at each pH level. The resulting model parameters at the two pH conditions are given in Table 4 as well as the resulting R-squared value between the model and experimental data.

Discussion

In the glycerol and glycol reactions, the initial step is a reaction in which two atoms of hydrogen are removed from the molecule to form an intermediate. However, this intermediate could not be measured directly in solution due to its high reactivity. The intermediate can be re-hydrogenated or pass through a reaction cascade to form multiple molecules (e.g., ethylene glycol, propylene glycol, etc.). Due to the inability to measure the intermediate species concentration, the overall reactions of the glycerol and glycols were each modeled as a single irreversible step.

The effect of hydrogen on these reactions was not explicitly included in the model since hydrogen was not a limiting reactant in the reaction. As noted previously, the final step in the production of ethylene glycol or propylene glycol is a hydrogenation step. If hydrogen is not found in abundance on the catalyst, this may be a limiting step. However, the

concentrations of the glycol precursors also have low values. These concentrations can be assumed approximately similar to the concentration of glyceraldehyde. A quick estimate for the glyceraldehyde concentration is found by assuming equilibrium with glycerol and estimating the Gibbs Free Energy difference in producing an aldehyde from an alcohol. From this estimation the maximum glyceraldehyde concentration expected in the bulk is about $4\text{E-}6$ M. The saturated hydrogen concentration in the aqueous bulk phase has been determined at lower pressures.¹³ The hydrogen concentration was found to linearly increase with pressure up to 50 bar. If the results are extrapolated to 100 bar, the estimated hydrogen concentration is 0.05 M, four orders of magnitude higher than the aldehyde. Thus, hydrogen was likely not to be the limiting reagent under the reaction conditions used for the current study. In addition, previous reports have stated that hydrogen does not appear to cover a large amount of the catalyst surface under reaction conditions similar to those used here.¹²⁻¹³

Comparison of the reaction results as a function of pH led to several insights into the glycerol reaction. The portion of the glycerol reaction leading to degradation products increased more as a function of pH increase than did the glycol degradation. The instantaneous selectivity toward glycols was 0.45 at low pH and 0.28 at the higher pH. However, the entire difference was found in the loss of selectivity toward ethylene glycol. The selectivity toward propylene glycol was not a function of pH. As such, the 5-fold increase observed for the glycerol reaction at the higher pH was correlated with a reaction rate for the production of propylene glycol that was also five times higher at the higher pH. In contrast, the production of ethylene glycol was less than doubled at the higher pH.

Shown in Figure 7 are the reaction pathways occurring in the reaction system. As seen in the figure, all of the fluxes through the reaction pathways increase with pH. As

described in the mechanism, glycerol and the glycols react reversibly to form an aldehyde, which desorbs from the catalyst into solution. However, the aldehydes are more stable under low pH conditions. Their reactivity was therefore higher in the calcium oxide solution than in the calcium carbonate solution, due to the higher hydroxide concentration. The selectivity factor found for the production of propylene glycol is independent of pH, which means the selectivity toward the production of propylene glycol does not vary as a function of pH in its reaction from glycerol. The primary contribution to the propylene glycol production rate is simply the net flux toward glyceraldehyde. In contrast, the selectivity to ethylene glycol does decrease with pH. This effect is likely due to conversion of a reactive intermediate between glyceraldehyde and ethylene glycol that removes some material from the glycol pathway to a degradation product pathway.

Even though the glycerol reaction order in the final rate equation does not correspond to a simple model predicted by Langmuir-Hinshelwood kinetics, the model still provides important information about the competitive adsorption of the three compounds. As mentioned earlier, ethylene glycol has a higher affinity for adsorption sites than propylene glycol, while glycerol has twice the affinity of ethylene glycol. This result is conceptually similar to that reported by Zhang et al. for a lactic acid – propylene glycol mixture in which propylene glycol was found to adsorb less readily than lactic acid.¹² The competitive adsorption is important when considering an appropriate model of the system. This competition will cause the reaction rate of glycerol to change with the production of glycols. Ignoring the competitive adsorption leads to poor assumptions when determining the correct model describing the reaction system.

Temperature effects were not incorporated into this phase of model development. Of course, temperature will have an effect on the reaction rates of all of the compounds and the activation energies for the reactions will affect the relative increase of the rates of the various reaction pathways. The most important temperature effect to still be characterized is the impact temperature has on glycol selectivity, since a quite a number reaction pathways are possible. A change in temperature will undoubtedly change all of these rates and, hence, the selectivities toward the glycols would likely depend greatly on the reaction temperature.

Conclusions

A model describing the glycerol to glycols reaction was developed that incorporates competitive adsorption of all three compounds, accounts for pH effects on the reaction rates, and predicts the instantaneous selectivity toward both glycols. The reaction rates of all three compounds were affected by pH. The instantaneous selectivity to propylene glycol did not change with pH, while the selectivity to ethylene glycol did. Propylene glycol appeared to have a lower affinity for active sites on the metal catalyst compared to glycerol and ethylene glycol, which competed relatively equally for sites. Even with the range of side reactions that occur, the fit of the model was quite good over a wide range of concentrations.

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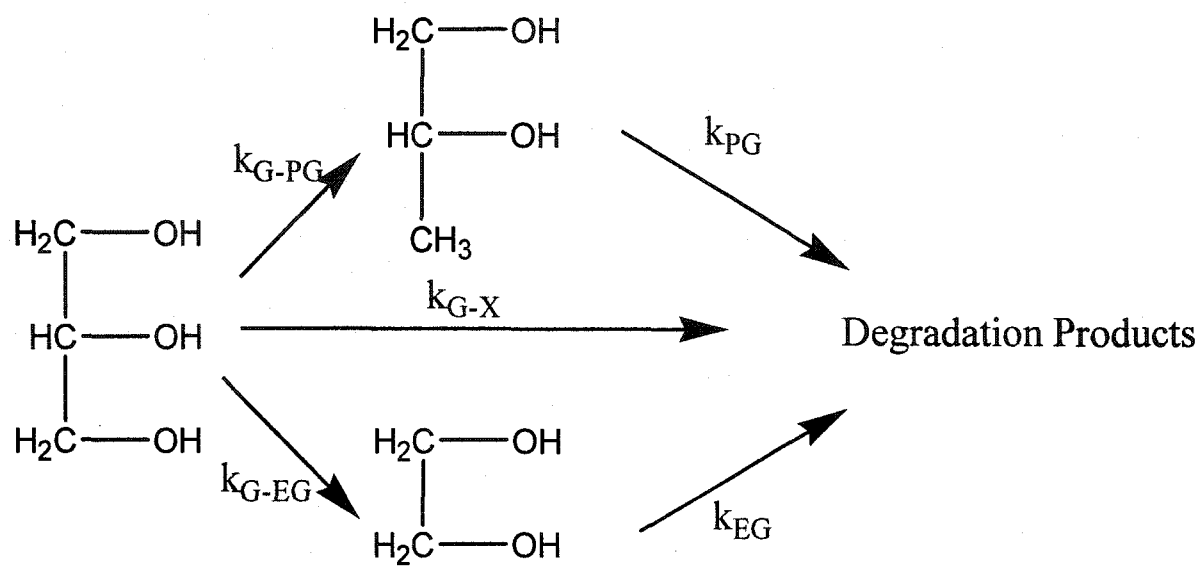


Figure 2.1: Schematic of the modeled reaction pathways.

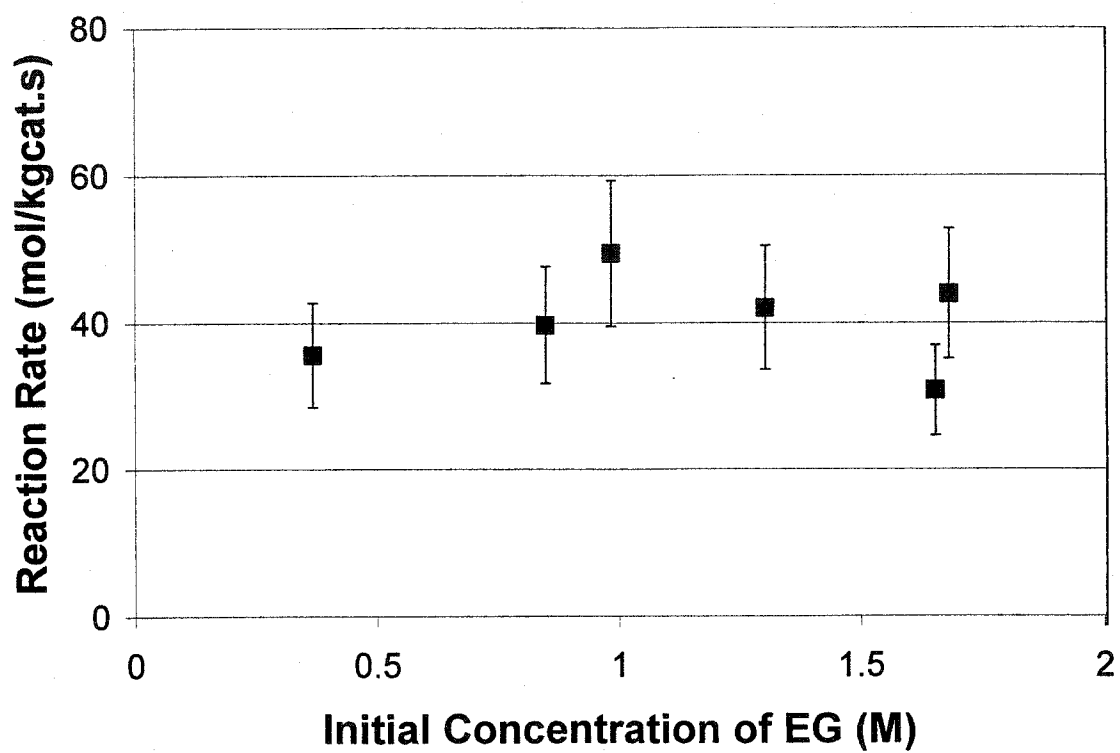


Figure 2.2: Ethylene glycol reaction rate as a function of initial ethylene glycol concentration.

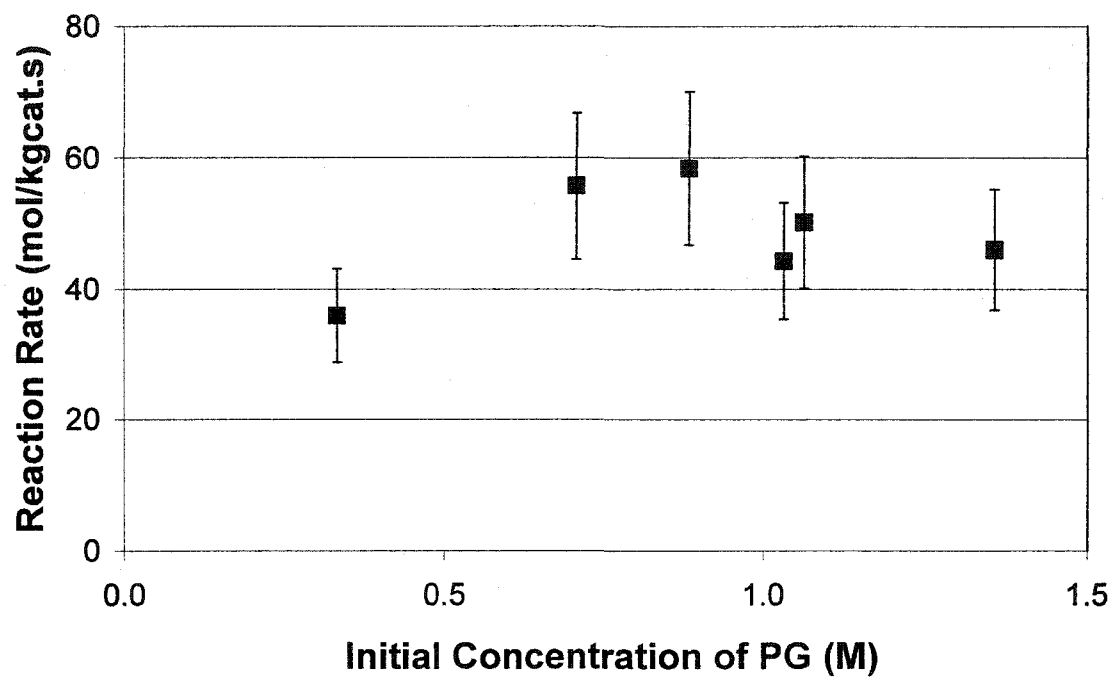


Figure 2.3: Propylene glycol reaction rate as a function of initial propylene glycol concentration.

Reaction Number	Ethylene Glycol wt%	Propylene Glycol wt%	Fractional Turnover (EG)	Fractional Turnover (PG)	Total Turnover
1	2.5	2.5	0.84	0.16	0.99
2	5.0	5.0	0.70	0.24	0.93
3	2.5	5.0	0.83	0.36	1.19
4	2.5	7.5	0.56	0.28	0.84
5	5.0	2.5	1.03	0.09	1.12
6	7.5	2.5	0.95	0.03	0.97

Table 2.1: Competitive adsorption between ethylene glycol and propylene glycol.

	High pH	Low pH
k'_{EG} (L/min.kgcat)	6300	3700
k'_{PG} (L/min.kgcat)	1800	750
k_{EG} (L/mol)	21	21
k_{PG} (L/mol)	4.0	4.0
R squared	0.84	0.82

Table 2.2: Regression results for the glycol degradation equations.

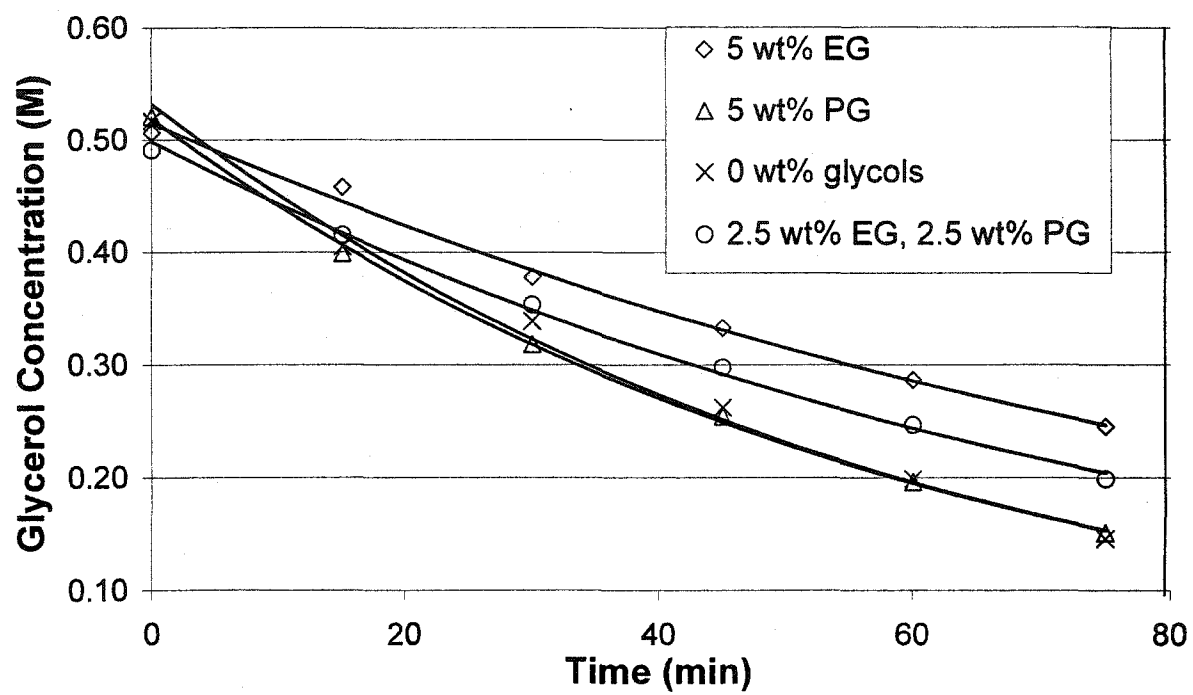


Figure 2.4: Glycerol reaction as a function of glycol concentration.

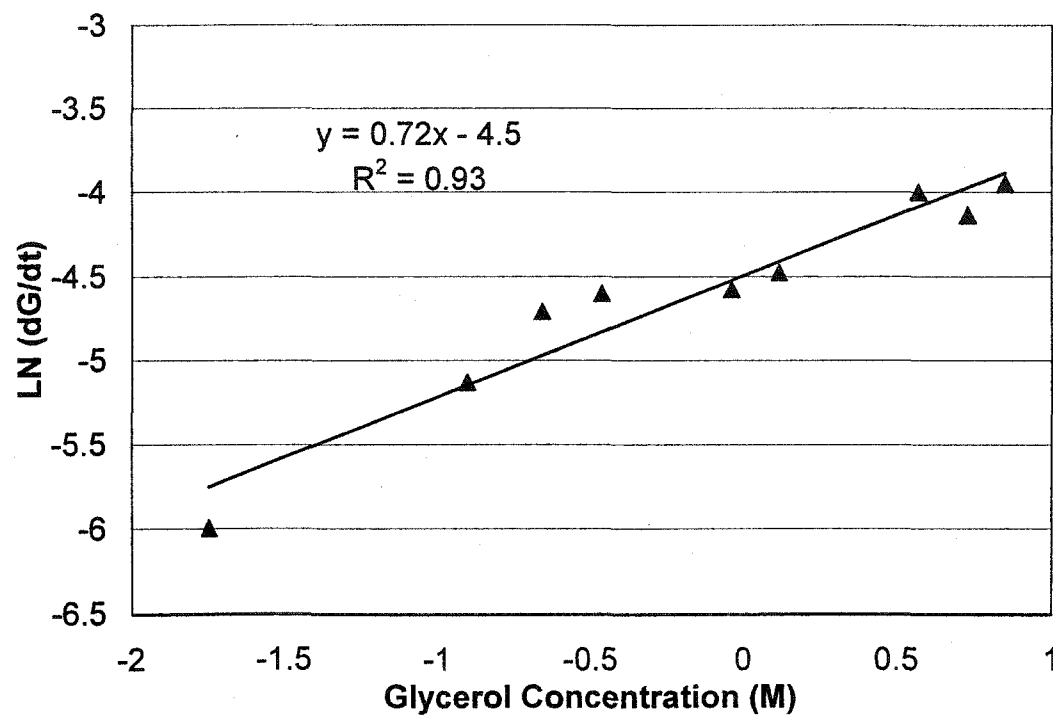


Figure 2.5: Determination of the reaction order for the glycerol reaction.

Reaction Order	k_G (L/mol)	k'_G (L ^{3/2} /(min*kgcat*mol ^{1/2}))	R^2
1	11	0.15	0.86
1.5	50	0.57	0.88

Table 2.3: Regression results for the glycerol rate constants at high pH conditions.

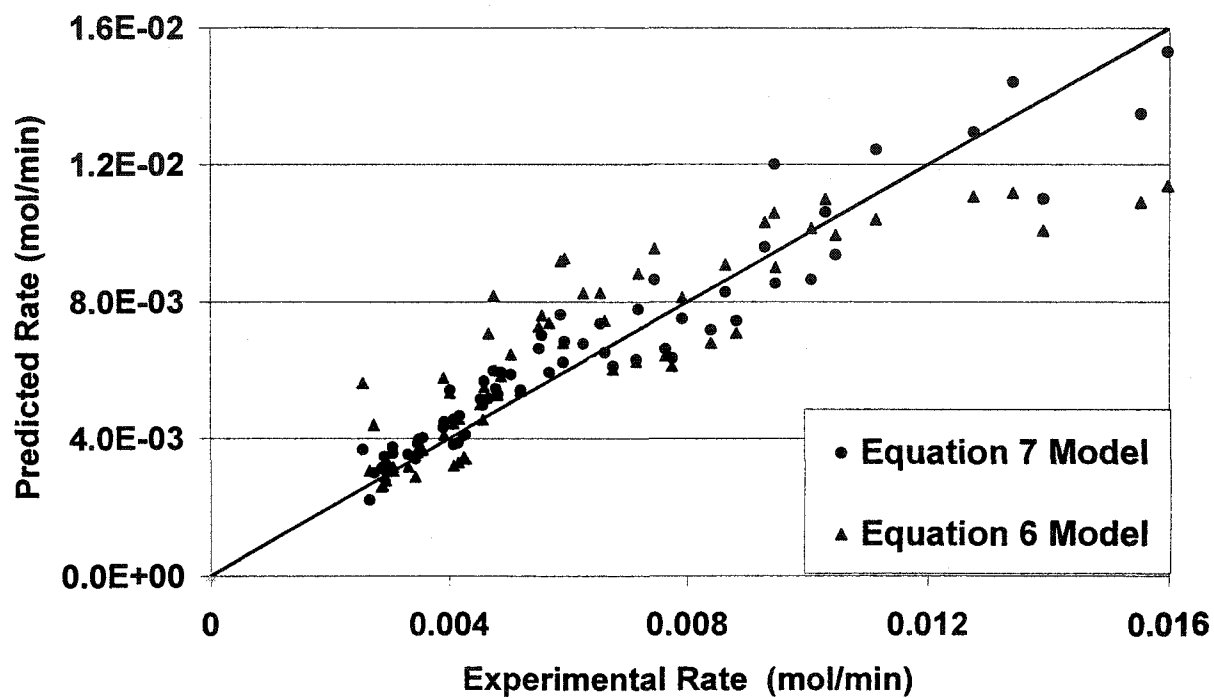


Figure 2.6: Comparisons of the parity plots for Equations 6 and 7.

Base Used	k_G (L/mol)	k_{EG} (L/mol)	k_{PG} (L/mol)	s_{EG}	s_{PG}
CaO	50	22	4	0.09	0.19
CaCO ₃	50	22	4	0.26	0.19
	k'_G (L ^{3/2} /(min*kgcat*mol ^{1/2}))	k'_{EG} (L/min*kgcat)	k'_{PG} (L/min*kgcat)	R^2	
CaO	39000	6700	1800	0.89	
CaCO ₃	7400	4600	800	0.77	

Table 2.4: Kinetic constants determined by regression for the glycerol and glycol reactions.

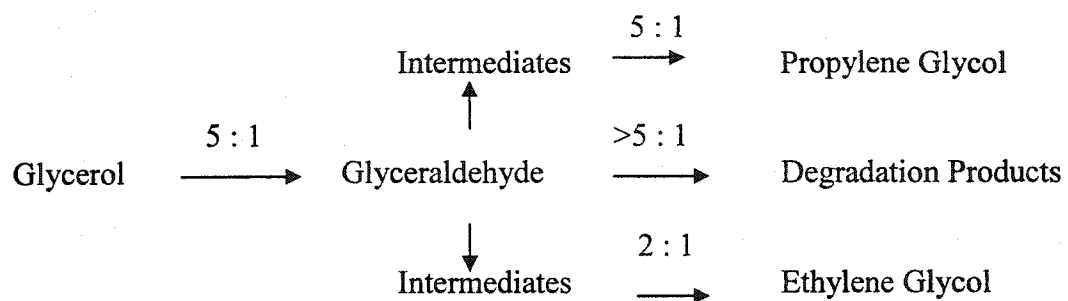


Figure 2.7: Flux maps showing the dependence of the reaction rates on pH.

CHAPTER 3

Effect of Sulfur and Temperature on Ruthenium Catalyzed Glycerol Hydrogenolysis to Glycols

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Daniel G. Lahr and Brent H. Shanks*

Department of Chemical Engineering*

Iowa State University

Ames, IA 50011, USA

Email: bshanks@iastate.edu

Abstract

The hydrogenolysis of glycerol to ethylene glycol and propylene glycol represents an initial system for developing an improved mechanistic understanding of the conversion of the more complex higher polyhydric alcohols. Previous work in our lab demonstrated the effects that pH, product degradation, and competitive adsorption have on the reaction system. This work is an extension that studies the effects of temperature and sulfur loading. Batch reactor studies with ruthenium on carbon catalysts were performed at a temperature range of 205 to 240°C and sulfur loading range of 0-1.0 mol S/Ru. Previous Langmuir-Hinshelwood type models were extended to include the data. Apparent activation energies for the glycerol reaction and the glycol degradation were determined. Previous studies for this system have focused on the aqueous phase scission reactions and metal catalyzed (de)hydrogenation reactions. Analyzing the reaction flux map with and without sulfur; however, leads to the conclusion that catalytic dehydration must also be occurring on the solid catalyst.

Keywords: Hydrogenolysis, Glycerol Reaction, Propylene Glycol Selectivity, Sulfur Modified Ruthenium

Introduction

While the hydrogenolysis of sorbitol to propylene glycol and ethylene glycol has been examined for over twenty years,^[1-7] the majority of the studies have been empirical in nature, focusing on varying catalyst compositions and operating conditions. The practical goal of these studies was to optimize both glycol production rates and selectivities. Although either goal could be independently achieved, gains in production rate inevitably gave a loss in selectivity and vice versa. The highest combined selectivity toward the two glycols with a reasonable production rate was 65%,^[1-5] which is not sufficient to be economically viable. Therefore, achieving the necessary improvement in glycol selectivity with a reasonable reaction rate requires a deeper understanding of the reaction mechanism, with the goal that a mechanistic understanding of the reaction will bring about a more rational approach to the development of improved catalyst systems.

The hydrogenolysis of higher polyols, such as sorbitol, xylitol, or glycerol, to form ethylene glycol and propylene glycol involves multiple steps.^[8] In the prevailing literature mechanism, the polyol is first reversibly adsorbed and dehydrogenated by the catalyst, leading to a desorbed aldehyde or ketone species. The product of the dehydrogenation reaction then can undergo a C-C scission via either the retro-aldol mechanism and/or oxidation followed by decarboxylation or a C-O scission by dehydration. While passing through reaction intermediates, both of these scissions are proposed to occur in the aqueous phase by base catalysis. The product(s) of either of these scission mechanisms contain a total of two unsaturated bonds; the dehydrated species contains two such bonds while the two species following the C-C scission contain one each. The unsaturated bonds are subsequently hydrogenated by the metal catalyst. The metal catalyst serves both

hydrogenating and dehydrogenating functions; therefore, the initial formation of the aldehydes and ketones is reversible. It has not been reported previously that the solid catalyst performs other functions.

To develop a better understanding of this complex reaction sequence, efforts need to be directed towards understanding the mechanism of the hydrogenolysis reaction as well as the interactions between the reactants, products, and catalysts. From the proposed overall model, two types of reactions occur, metal catalyzed dehydrogenation/hydrogenation and hydroxyl catalyzed C-C and C-O scissions. Previous work has examined the effect of pH, the degradation of products, and the competitive adsorption of products on the reaction rate of glycerol and selectivity toward the glycols.^[9] The pH of the system affected many of the intermediate reactions that occur within the hydrogenolysis reaction network and thus the product distribution. Product degradation was demonstrated to be important due to its impact on the overall selectivity to the glycols. Competitive adsorption of the products inhibited the reaction rate of glycerol. Due to the complexity of the hydrogenolysis system with higher polyols, these initial reaction studies were performed using glycerol, propylene glycol and ethylene glycol.

While the study gave insight into the reaction mechanism, further mechanistic development must necessarily consider the important role of sulfur modification on the ruthenium catalyst during the production of glycols from glycerol. Many groups have reported two primary effects that sulfur modification of the ruthenium has on the reaction.^[2,7,10] The first effect is the reduction in the overall reaction rate as sulfur is a well-known metal catalyst poison. However, in the case of the polyol products, a second effect occurs: the selectivity toward specific products increases. For example, the selectivity

toward propylene glycol increases dramatically as sulfur loadings increase. Montassier et al. reported an increase in selectivity toward propylene glycol from 10% without sulfur to 80% with one mole of sulfur per mole of ruthenium.^[5] The work was performed at pH 6, which lowered the overall glycerol reaction rate.

The goal of the current work was to continue development of a more detailed model for the portion of the hydrogenolysis process beginning with glycerol to ultimately help maximize yields to the desired glycols from higher polyols. The effect sulfur has on the reaction system and insights derived from these effects will be discussed. The work presented will discuss causality for the increased selectivity toward propylene glycol from glycerol when the sulfur loading increases and the catalyst requirements for commercial application of this process.

Experimental

Glycerol, ethylene glycol, 1,2-propylene glycol (all 99%+), calcium oxide (96%), and sodium sulfide hydrate (60%) were purchased from Acros Organics. High-purity hydrogen (99.992%) was used to pressurize the reactor. The catalyst, from Activated Metals & Chemicals, Inc., was 5 wt% ruthenium supported on activated carbon. The catalyst was received in a reduced state with a metal dispersion of approximately 30% and was handled as a wet powder with water content of about 50 wt%.

All reactions were performed in a 100-ml batch reactor (Autoclave Engineers) equipped with a stirrer, electric temperature controller, and sample port for liquid samples. For a typical reaction, 0.4-1.5 M solutions of glycerol, ethylene glycol, and/or propylene glycol were added with a 5 wt% Ru/C catalyst, 0-1.0 mol of sodium sulfide per mole

ruthenium, and a base for maintaining a constant pH. The predominant base used was 0.4 M CaO. The *ex situ* pH was measured after the reaction samples were stored at room temperature (20°C) for two hours to reduce the variance in pH measurements due to temperature. Using CaO in the 205°C experiments resulted in an average pH in the cooled samples of 11.7 while in the 240°C experiments the average measured pH was 11.2. Measurements on the samples taken throughout a reaction study showed that the measured *ex situ* pH did not vary significantly with time.

Initially, the reaction vessel was flushed consecutively with low-pressure nitrogen and low-pressure hydrogen. The system was then pressurized with 50 bar H₂ and heated to reaction temperature, which ranged from 205°C to 240°C. Two initial samples were taken and the hydrogen pressure was subsequently increased to 100 bar. The stirring speed was set to 500 rpm. Experiments at higher mixing speed showed no change in reaction performance; therefore, there were no external mass transfer limitations. The temperature, pressure, and mixing speed were held constant during the reaction.

Samples were taken in 15-min intervals for 75 min. The samples were cooled to less than 40°C as they were taken through a cooling loop. After the pH was measured, the samples were diluted with 60 wt% acetonitrile in water to a final value of 40 wt% acetonitrile. The samples were then analyzed with a Hewlett-Packard HC-75 HPLC using a Ca²⁺ cation exchange column from Hamilton with an RI detector. The column was run using a mobile phase of 40 wt% acetonitrile in water.

Effect of Temperature and Sulfur on Ethylene Glycol and Propylene Glycol Degradation

A previous glycerol hydrogenolysis study, which was performed under isothermal conditions, demonstrated that knowledge of the kinetics of the ethylene glycol and propylene glycol degradation kinetics was a necessary step in understanding the overall glycerol hydrogenolysis reaction.^[9] Therefore, further extension of the model required kinetic characterization of temperature and sulfur effects in the degradation of these products. The evaluation of the apparent activation energies and variation in competitive adsorption as a function of temperature for the product degradation reactions as determined from temperature studies allowed for the subsequent elucidation of the role of sulfur on the kinetics.

Experiments were first performed in which the temperature was varied with no sulfur introduction. When individually reacted, the degradation rate for both ethylene glycol and propylene glycol remained constant throughout the concentration range at each temperature level. Therefore, the zero-order reaction rate found for degradation of these compounds previously at 205°C existed throughout the temperature range. The apparent activation energies measured for the degradation of the two glycols across the 205-240°C temperature range were 62 kJ/mol for ethylene glycol and 45 kJ/mol for propylene glycol. The rate data from the two pure-component systems are shown in Table 3.1 as well as their relative pure-component degradation rate.

The degradation rate for the two glycols when both are present depends on the pure component intrinsic rates and their relative adsorption behavior. Therefore, degradation rate data were also obtained for an equimolar mixture (0.75 M) each of the glycols. The results

for the relative degradation rates of an equimolar glycol mixture are given in the last column in Table 3.1.

The Langmuir-Hinshelwood model developed previously at the base case conditions of 205°C^[9] was extended to the nonisothermal conditions. The degradation reactions for the two glycols was modeled as a set of two equations:

$$-r_{iG} = \frac{k'_{iG}(iG)}{k_{EG}EG + k_{PG}PG + 1} \quad (1)$$

where r_{iG} is the degradation rate for the glycol ($i = E$ for ethylene glycol and P for propylene glycol), k'_{iG} is the degradation rate coefficient for each glycol, with iG representing the respective concentrations of the glycols, and k_{EG} and k_{PG} are the respective adsorption constants for the glycols. The two glycol equations have eight parameters resulting from expressing each of the two degradation rate coefficients and the two adsorption coefficients in the Arrhenius form. Rather than fitting all of the experiment data with a multiple parameter regression, several constraining relationships were invoked.

Since the pure component degradation rates were zero order, two relationships were used to describe the limiting case of a single adsorbing glycol species and by assuming complete saturation of the glycol adsorption sites as shown in Equation 2 and 3:

$$k'_{PG} = k_{PG} \cdot r_{PG} \quad (2)$$

$$k'_{EG} = k_{EG} \cdot r_{EG} \quad (3)$$

where k'_{iG} are the degradation rate coefficients for the two glycols, k_{iG} are the inhibition constants for the two glycols, and r_{iG} are the degradation zero-order rates for each glycol as a function of temperature. In addition, the constant relative degradation rate for the glycols

added one more constraint. Dividing the rate equations for the two glycols, which have the functional form given in Equation 1, gave the competitive degradation ratio as shown in Equation 4:

$$k_r = \frac{k'_{EG} EG}{k'_{PG} PG} \quad (4)$$

where k_r is the competitive degradation ratio, which was found to be 4.1 from the equimolar reactions.

Between the degradation rate equations for the two glycols and the constraining Equations 2-4, a set of five equations existed for fitting the eight kinetic parameters. With the available rate data, a statistically significant unique set of parameters could not be determined for the parameter set. The parameter estimation was insensitive to combinations of the pre-exponential and activation energy for the two glycol inhibition constants. From the previous isothermal experiments, k_{PG} equaled 4, so a further constraint imposed in the parameter estimation was setting k_{PG} to this constant value. This did not affect the quality of fit. Setting either k_{PG} or k_{EG} to a constant value while letting the other to be fit did not affect the quality of the overall parameter fit. The selection of k_{PG} as the parameter to remain constant rather than k_{EG} was arbitrary. The values obtained from fitting the pre-exponential constants and the apparent activation energies for the ethylene glycol and propylene glycol degradation reactions are given in Table 3.2. The R^2 value resulting from fitting the 19 reaction points used in the estimation was 0.94.

Since the degradation rate for ethylene glycol increased with temperature relative to the propylene glycol, the model suggested that the relative adsorption coverage of ethylene glycol on the catalyst must have decreased to account for the lack of change in the

competitive degradation ratio. The less reactive propylene glycol then occupied more active sites as the temperature increased, negating the higher relative reaction rate of ethylene glycol. Therefore, the glycol degradation reaction was a relatively simple system. The glycols adsorbed on the same sites and more sites were covered with propylene glycol as the temperature increased due to the lower relative reactivity of propylene glycol. Despite its reduced coverage, the higher reaction rate for ethylene glycol caused the relative degradation rate to remain constant. Therefore, the glycols were independent of each other on the catalyst.

Glycol degradation experiments were then performed in the presence of sulfur with sulfur/ruthenium molar (S/Ru) ratios of 0-0.8. Within the experimental temperature range the rate of degradation for the glycols became immeasurable for S/Ru ratios of greater than 0.5. For both glycols at a sulfur loading of 0.4, the reaction rate decreased to less than 15% of the original sulfur-free reaction rate. Shown in Figures 3.1 and 3.2 are the apparent activation energies found for the pure component studies with ethylene glycol and propylene glycol, respectively. As can be seen from the figures, the apparent activation energies for the degradation reactions appeared to be independent of the S/Ru ratio used. When equimolar initial glycol concentrations were used, the relative degradation rate for the glycols was also independent of the S/Ru ratio. Therefore, Equation 1 was modified by a linear sulfur factor as follows:

$$-r_{iG} = \frac{k'_{iG} (iG)^* (1 - 2S)}{k_{EG} EG + k_{PG} PG + 1} \quad (5)$$

where S is the molar ratio of sulfur to ruthenium. This equation, which fit the degradation data without further adjustment to the sulfur-free parameters given in Table 3.2, was only

valid to a ratio of 0.5 as higher ratios led to no glycol degradation. Figure 3.3 shows a parity plot of the observed ethylene glycol degradation rate versus the predicted rate, which confirms the independence of the apparent activation energy from the S/Ru ratio. A parity plot for propylene glycol degradation rates gave a similar result.

Since the apparent activation energies and relative rates for glycol degradation remained constant as sulfur was added, sulfur was not affecting the reaction chemistry but was merely acting to block reaction sites for the glycol dehydrogenation reactions. If sulfur had a broader affect on the reaction such as interacting with the glycols or changing the surface chemistry of the catalyst, the apparent activation energy of the degradation reaction would have changed. Once the glycol degradation reactions were thoroughly characterized, the hydrogenolysis reaction behavior of glycerol was determined.

Effect of Temperature and Sulfur on the Glycerol Reaction

In similar fashion to the glycols, the glycerol was reacted at a range of temperatures and sulfur loadings at an initial molar concentration range of 2.5-10 wt% (0.3-1.1 M) under mixing with no external mass transfer limitation. Unlike the glycols, the glycerol reaction was not zero order. The reaction order at 240°C as determined from initial rate data was 0.5, which was consistent with that reported previously at 205°C.^[9] The reaction order remained constant with all sulfur loadings as well. The relative inhibition effect of the glycols on the glycerol reaction at 240°C is shown in Figure 3.4. The effect shown in this figure is very similar to what was found previously at 205°C. In both cases, ethylene glycol affected the reaction rate of glycerol in proportion to the amount of ethylene glycol added. In contrast, the addition of propylene glycol had minimal effect on the reaction rate of the glycerol.

Analogous to the development of Equation 1, parameters for the glycerol reaction as given by Equation 6 were found:

$$-r_G = \frac{k'_G G^{1.5}}{k_G G + k_{EG} EG + k_{PG} PG + 1} \quad (6)$$

where r_G is the glycerol reaction rate, k'_G is the glycerol reaction rate coefficient, and k_G is the adsorption constant for glycerol. As seen for ethylene glycol and propylene glycol degradation, the relative rates for glycerol reaction and glycol degradation did not vary with temperature. Since the apparent activation energy for the glycerol reaction was lower than for the degradation of glycols, the fraction of adsorbed glycerol compared with that of the glycols increased with temperature.

The values for the glycerol reaction rate and adsorption constants, which are given in Table 3.2, were found from fitting Equation 6 to glycerol reaction data. In this fitting procedure, the ethylene glycol and propylene glycol adsorption constants were held fixed at the values determined from the pure component degradation reactions. The resulting fit of 80 glycerol reaction data points gave an R^2 of 0.94 using the parameter set given in Table 3.2. In a separate parameter estimation, the values in Table 3.2 were taken as initial guesses and the glycerol reaction data were refit while allowing all of the parameters to float. The resulting regressed parameters were not significantly different from those given in Table 3.2 and gave an R^2 of 0.94 that was identical.

Equation 1 gave the rate equations for the degradation of the glycols. The overall rate expressions used to determine the glycol selectivities must also include a generation term resulting from glycerol conversion. It was shown previously that a form of Equation 6 suitable for the glycols was as follows:

$$-r_{iG} = \frac{k_{iG}iG - s_{iG}k'_G G^{1.5}}{k_G G + k_{EG}EG + k_{PG}PG + 1} \quad (7)$$

where the iG concentrations correspond to $i = E$ for ethylene glycol and P for propylene glycol and the s_{iG} factors are the respective selectivity factors.^[9] The selectivity factors were defined simply as the fraction of the glycerol converted into either ethylene glycol or propylene glycol. Since glycerol could also react to form chemical species other than the desired glycols, the selectivity factors for the glycols will not necessarily sum to a value of one. The only glycerol reaction products that were measured were the two glycols. The selectivity factors represent the fraction of glycerol that forms each glycol, separate from the degradation of the glycols. Within the scatter of the data, no change in the selectivity factors was observed over the course of a reaction.

A regression fit of the selectivity factor at the each of the three temperatures studied are given in Table 3.3. As can be seen the selectivity to propylene glycol increased as the temperature increased, while the ethylene glycol selectivity was essentially constant. At 205°C, the selectivity toward propylene glycol was 0.19 and, at 240°C, it was 0.34. In contrast, the selectivity to ethylene glycol remained at about 0.09 across the temperature range.

The glycerol reaction was also characterized upon sulfur addition to the reaction system. Unlike with the glycol degradation reactions, sulfur affected the apparent activation energy for the glycerol reaction; the apparent activation energy increased with sulfur concentration, as shown in Figure 3.5. The Weisz-Prater number was estimated to be 1.4 at the highest reaction rate, which would correspond to the transition to internal diffusion limitation. However, a concomitant decrease in the observed reaction order from 0.5 to 0

was not observed indicating the kinetic control. Similar to glycol degradation, the glycerol reaction rate decreased with increasing sulfur. However, the glycerol reaction rate was not diminished to the extent that was found for glycol degradation. At a sulfur level of 0.4 S/Ru, the glycerol reaction rate was about 50% relative to the sulfur-free base case and about 30% at a S/Ru of 1.0. While the sulfur effect on glycol degradation could be explained by sulfur only blocking active sites, sulfur played a more complex role in the glycerol reaction. Due to the change in apparent activation energy, there was either a reaction step where sulfur affected the active intermediate or there were multiple reaction pathways of which sulfur preferentially limits one.

The propylene glycol selectivity was significantly impacted by sulfur loading, but the selectivity to ethylene glycol was not. The initial selectivity toward propylene glycol as a function of sulfur loading at 205°C is shown in Figure 3.6. The reaction rate at 205°C with a sulfur loading of 1.0 S/Ru was too small to produce a measurable selectivity value. The glycol selectivities were determined 15 min after initiation of a reaction, thereby limiting the effect degradation or competitive adsorption had on the results. For all three temperatures studied, the selectivity toward propylene glycol increased with sulfur loading. The slope and intercept of the lines for propylene glycol selectivity as a function of sulfur loading are given in Table 3.4. For the experimental temperature range, the change in propylene glycol selectivity with sulfur addition was attenuated as the reaction temperature was increased. In a previous study at a low pH of 6, the selectivity toward ethylene glycol decreased with increasing sulfur loading.^[5] Since the selectivity toward ethylene glycol decreases with increasing pH and is at a low value under the high pH conditions,^[9] a significant change in ethylene glycol selectivity as a function of sulfur loading was not found in the current study.

While the selectivity to propylene glycol increased with the S/Ru ratio, the overall flux toward propylene glycol decreased due to the decreasing glycerol reaction rate. At a S/Ru of 1.0, the flux toward propylene glycol was 60% of its value without sulfur. The higher selectivity to propylene glycol meant that the rest of the products, which were mostly degradation products with some ethylene glycol, had a flux of only 30% of the sulfur-free flux.

Mechanism Discussion

The overall reaction model that has been proposed for the glycerol hydrogenolysis reaction is shown in Figure 3.7. Glycerol is first adsorbed and dehydrogenated reversibly on the metal catalyst to form glyceraldehyde. The glyceraldehyde then desorbs from the catalyst and can react through four different paths in the basic media: the retro-aldol mechanism to form the precursor of ethylene glycol (glycol aldehyde), oxidation and subsequent decarboxylation to also form glycol aldehyde, dehydration to the precursor of propylene glycol (2-hydroxypropionaldehyde), or degradation to unwanted side products. The two glycol precursors could potentially also degrade to unwanted side products. Finally, the respective glycol precursors are hydrogenated by the metal function to the product glycols.

Previous studies have demonstrated that sulfur-modified ruthenium yields higher selectivity to propylene glycol and that sulfur interacts with metal catalysts such as ruthenium when operating at high pH. Yet, the previously postulated mechanism would suggest that changes in the relative selectivity to the two glycols would be dictated by solution phase reactions, since it is unlikely that sulfur modification of ruthenium would lead to changes in the relative adsorption and reduction selectivity of 2-hydroxypropionaldehyde

compared to glycolaldehyde. However, the relative degradation rates of the two glycols did not change with sulfur concentration and the sulfur did not affect the liquid phase reactions since the pH of the solution did not change when adding sulfur. The molar ratio of calcium oxide to sulfur in the reaction system at high sulfur levels is 25:1 and the solubility of calcium oxide gave a pH 1 unit higher than the molarity of the sodium sulfide added. Therefore, the postulated model must be missing a key reaction mechanism feature and this feature must be associated with the solid catalyst.

As manifest by the decreased glycerol reaction rate with increasing sulfur loading, sulfur appeared to block sites that led to the reaction of glycerol to glyceraldehydes, which subsequently desorbed and reacted further. However, the change in apparent activation for the glycerol reaction could not be explained merely by site blockage. There are two ways in which the sulfur could be interacting with the catalyst to produce this result. First, there may be two catalytic pathways that produced propylene glycol of which one was preferentially blocked by sulfur, the one being blocked having the lower activation energy. Second, sulfur could affect the active intermediate in the catalytic step that produces propylene glycol. Since sulfur is electronegative, it may attract the carbon atoms enough to weaken the carbon-oxygen bond allowing for an easier dehydration.

The previously postulated glycerol hydrogenolysis mechanism had glyceraldehyde as a common reaction intermediate for either propylene glycol or ethylene glycol. Therefore, if sulfur interaction with the Ru was changing the energetics of the adsorbed intermediate, the selectivity of both glycols would have been affected. The fact that increased sulfur loading only increased the selectivity toward propylene glycol led to the introduction of a proposed alternative dehydration reaction pathway on the catalyst. This added speculative reaction

pathway would be represented by direct dehydration of the adsorbed glyceraldehyde as shown by the arrow with asterisk in Figure 3.7.

Using this modified reaction network, the relative carbon selectivity through the desorbed glyceraldehyde path and the surface dehydration path could be determined. For this analysis, the end products were placed in three groups: (a) propylene glycol produced through surface dehydration, (b) propylene glycol produced through reaction of desorbed glyceraldehyde in solution, and (c) all other reactions that occur in solution, one of which is the reaction to produce glycolaldehyde and eventually ethylene glycol from glyceraldehyde. The total carbon selectivity of these three pathways sum to unity:

$$a + b + c = a' + b' + c' = 1 \quad (8)$$

where a , b , and c represent the relative selectivities to the three groups discussed above without sulfur present and a' , b' , and c' would represent these selectivities with sulfur present. Equation 8 can be rearranged to separate the propylene glycol producing reactions from the remaining reactions:

$$\frac{1 - a' - b'}{1 - a - b} = \frac{c'}{c} = x \quad (9)$$

where x is the carbon selectivity to non-propylene glycol products with sulfur relative to the selectivity without sulfur present.

At 205°C and a sulfur loading of 1.0 S/Ru, x was 0.64. At this sulfur loading, the selectivity toward the non-propylene glycol producing reactions, which are presumed to progress through a common solution-phase glyceraldehyde intermediate were decreased by 36%. For route (b), propylene glycol would also proceed through the solution-phase glyceraldehydes, so the carbon flow through this path would also be expected to be

attenuated by 36%. At higher temperatures with the same sulfur loading, this value was 0.74.

Assuming the Figure 3.7 flux map is accurate, propylene glycol could be produced from either a purely catalytic route (*a*) or through a liquid-phase route (*b*) or a combination of the two. Determining the relative fluxes through these pathways would be useful for catalyst design. While higher sulfur loadings caused the relative selectivity through path (*a*) to increase, the value of the absolute selectivity through each path is important. Both the dehydration and retro-aldol mechanisms are known to convert solution-phase glyceraldehyde to the two glycol intermediates under reaction conditions; therefore, there is likely to be at least some flux through (*b*).

In previous work, the selectivity toward ethylene glycol was found to vary as a function of pH.^[9] At a moderate pH of 8, the instantaneous selectivity toward ethylene glycol was 0.26; at a pH of 11, the selectivity dropped to 0.09. Glycolaldehyde, an intermediate in the production of ethylene glycol as shown in the Figure 3.8 reaction sequence, has two labile protons on the hydroxyl carbon that are prone to deprotonation. Even though the rates of glycolaldehyde production and reduction toward ethylene glycol are increased at higher pH, the rate of degradation increased more. The degradation reaction is likely more dependent on pH than the production reaction or the catalytic adsorption, because of these labile hydrogen atoms.

The pH dependence on selectivity was not found for propylene glycol.^[9] The instantaneous selectivity modeled for both pH levels was constant at 0.19 with a standard deviation of 0.06. The hydrogenolysis reaction selectivity toward propylene glycol did not vary with pH through the pH range of 5-11 (as determined using five bases) at either 205°C

or 240°C. The degradation of the propylene glycol intermediate would likely be pH-dependant; however, this was not found in the regression model since the selectivity did not change. Thus, two possibilities exist in which there may be little flux toward 2-hydroxypropionaldehyde or most of the flux that passes through this intermediate also degrades even at moderate pH. If the second situation occurred, it would be difficult to detect a pH dependence on the selectivity toward propylene glycol because the ratio of degradation versus reduction of 2-hydroxypropionaldehyde would be high even at moderate pH values. Under either situation, the majority of the flux to propylene glycol even without sulfur present must come via dehydration on the catalyst instead of in solution or else a noticeable difference in selectivity would exist as a function of pH.

Given the preponderance of propylene glycol production through the proposed catalytic dehydration pathway, the increased selectivity toward propylene glycol on sulfur-modified ruthenium should focus on the absorbed species. At ambient temperatures, the diffusion of hydrogen on a ruthenium catalyst surface was found to decrease by a factor of 30 upon addition of sulfur.^[10] This effect was caused by both geometric blocking and other long range electronic effects. Polyols adsorb onto ruthenium through oxygen and for dehydrogenation to occur two hydrogen atoms must diffuse away from the adsorbed polyol. The adsorbed sulfur may slow such diffusion allowing the more activated dehydration process to occur preferentially. The limiting step in the catalytic dehydrogenation of polyols was the surface reaction, while the adsorption and desorption steps were fast,^[9] so diffusion of hydrogen away from the polyol is required for the catalytic reaction to occur. Although sulfur would decrease the recombination of hydrogen atoms due to a lower diffusion rate and

occupation of recombination sites, the desorption of H_2 from ruthenium is not affected by sulfur.^[11]

The postulate that glycerol can react to form propylene glycol but not ethylene glycol on the catalyst is reasonable given that different mechanisms are used to convert glycerol into the two glycols. Ethylene glycol can be produced through either a retro-aldol or decarboxylation reaction, the first step of which involves a deprotonation on the hydroxyl group on the β -carbon in relation to aldehyde carbon. Propylene glycol can be produced via dehydration, the first step of which involves a deprotonation of the labile hydrogen for the carbon α from the aldehyde. Whether the catalyst converts an adsorbed glyceraldehyde into propylene glycol through the same mechanism is not known, but it is commonly known that dehydrogenating catalysts can also function as dehydration catalysts.

Conclusions

Despite significant interest in hydrogenolysis of higher polyols to glycols little information is available in the literature for the reaction system due to its complexity. Previous work on the effect of pH on glycerol hydrogenolysis and the degradation of the product glycols was extended to include the effects of temperature and sulfur. Empirical Langmuir-Hinshelwood type models were developed to characterize the reaction system for improving the understanding of this complex system. Due to competitive adsorption, the relative degradation rates of the glycols were independent of temperature. Sulfur modification of the ruthenium catalysts did not change the activation energy of the degradation reactions, but did dramatically suppress the reactions. Sulfur did affect the apparent activation energy of the glycerol reaction, which led to the postulate that

dehydration to propylene glycol may be occurring on the catalyst and not just in solution. Previous models for the reaction systems could not reconcile the results. It is unknown if the retro-aldol mechanism is occurring on the catalyst as well as in solution. The selectivity toward propylene glycol increased with sulfur loading due to this catalytic reaction. The results suggest that selectivity to propylene glycol relative to ethylene glycol and degradation products can be enhanced in the glycerol hydrogenolysis reaction if the catalyst is active for dehydration.

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individual glycol reaction				equimolar reaction
Temp (°C)	ethylene glycol degradation rate (mmol/min)	propylene glycol degradation rate (mmol/min)	relative individual degradation rate EG/PG	relative degradation rate EG/PG
205	2.5	3.0	0.8	4.2
220	4.0	4.3	0.9	4.1
240	7.2	6.6	1.1	4.1

Table 3.1: Relative glycol degradation rates.

parameter	Preexponential Factor	Units of PF	Apparent Activation Energy (kJ/mol)
k'_G	25000	$(L^{3/2}/min.mol^{1/2})$	45
k'_{EG}	4000	(L/min)	45
k'_{PG}	1000	(L/min)	45
k_G	230	(L/mol)	1
k_{EG}	0.27	(L/mol)	-17
k_{PG}	4	(L/mol)	0

Table 3.2: Calculated rate constants for the glycol degradation and glycerol reactions.

	Temperature (°C)	Selectivity	Data Points	R ²
Propylene Glycol	205	0.19	120	0.79
	220	0.27	27	0.92
	240	0.34	37	0.79
Ethylene Glycol	205	0.09	120	0.74
	220	0.11	27	0.67
	240	0.07	37	0.79

Table 3.3: Calculated selectivities of propylene and ethylene glycol.

Temperature (°C)	Slope	Intercept	R ²
205	0.27	0.21	0.86
220	0.22	0.26	0.85
240	0.18	0.30	0.70

Table 3.4: Calculated linear effect of sulfur on propylene glycol selectivity.

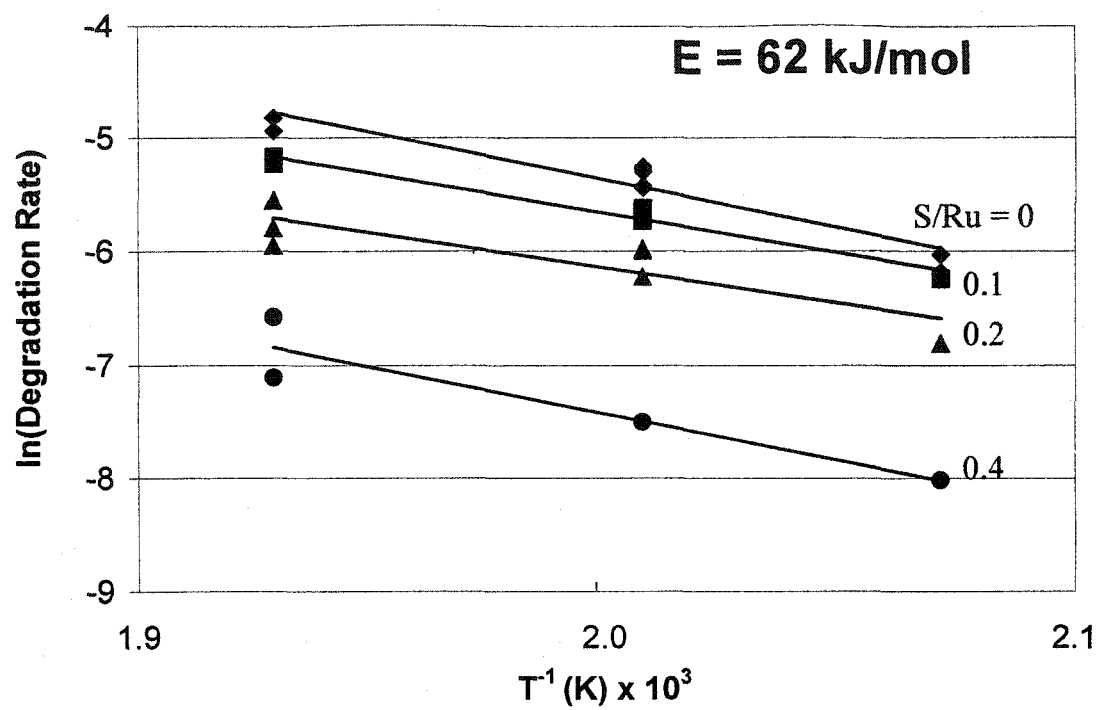


Figure 3.1: Effect of sulfur loading on the apparent activation energy of ethylene glycol degradation.

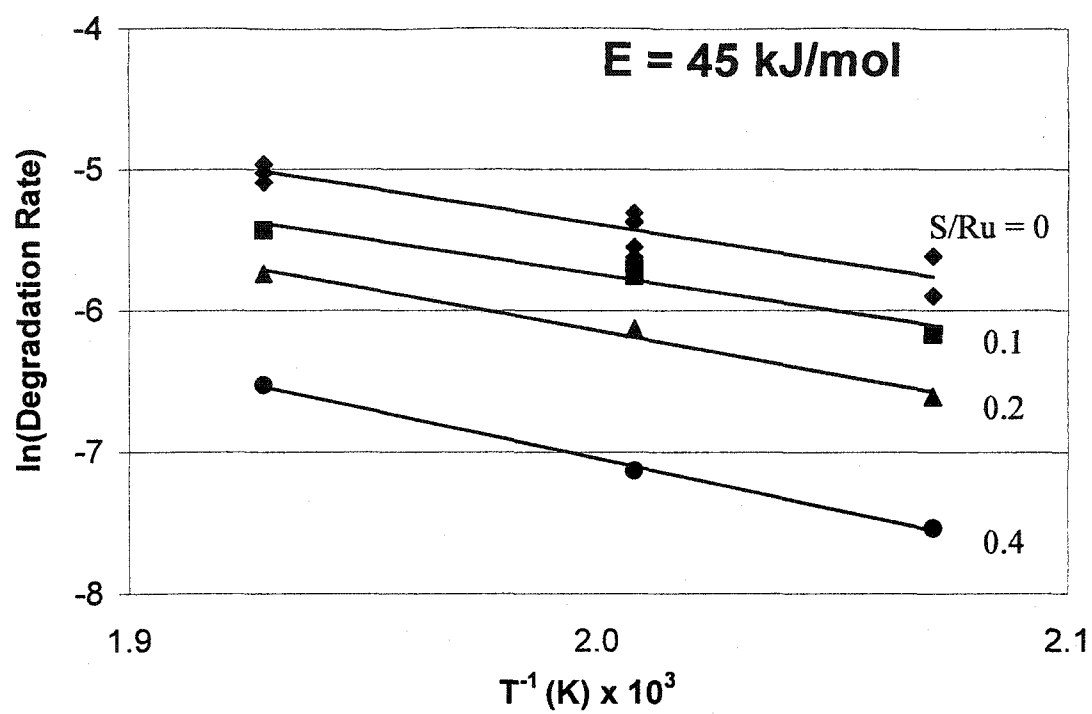


Figure 3.2: Effect of sulfur loading on the apparent activation energy of propylene glycol degradation.

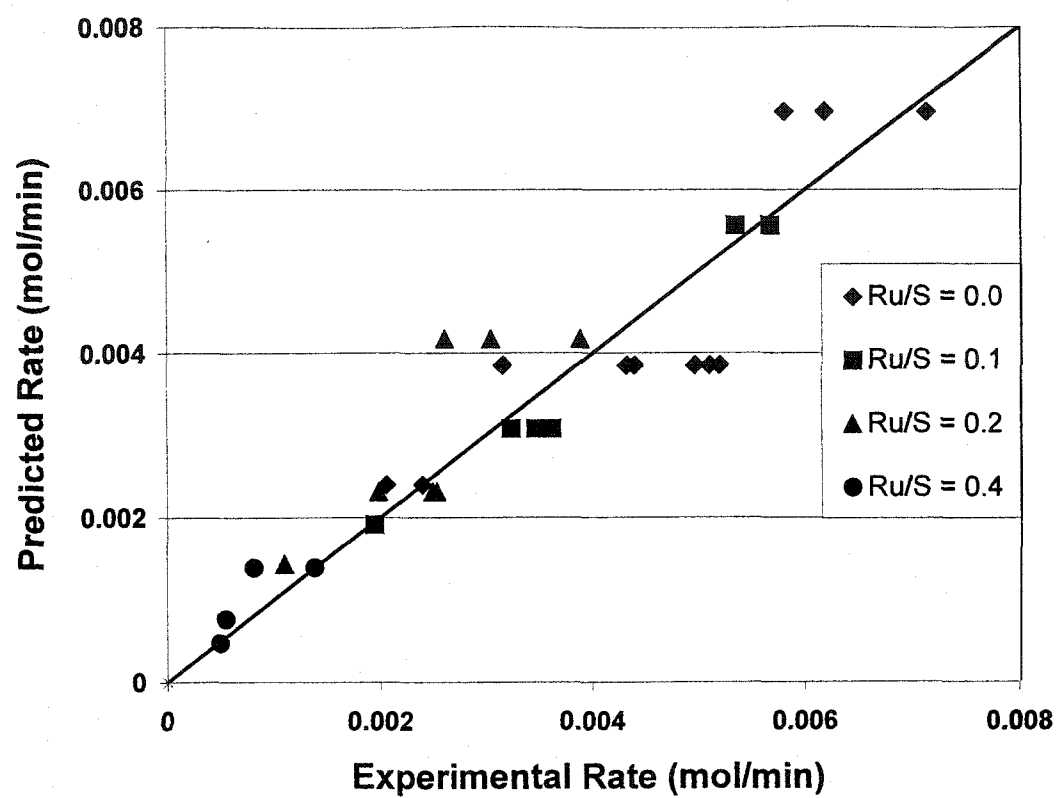


Figure 3.3: Parity plot for the ethylene glycol degradation reaction.

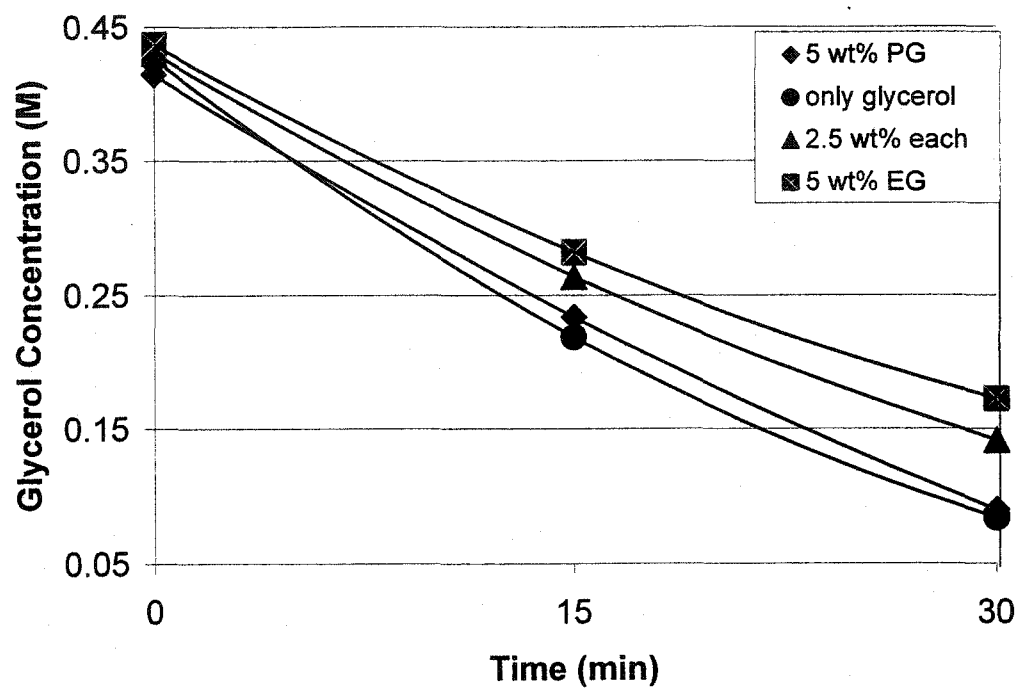


Figure 3.4: Glycerol reactivity as a function of glycol concentration at 240°C.

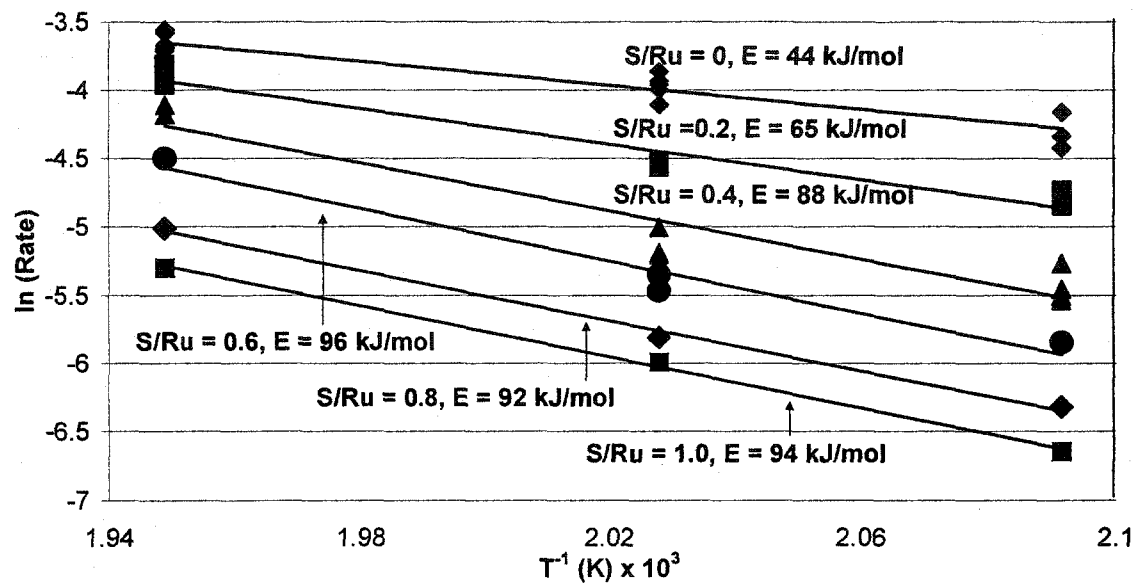


Figure 3.5: Apparent activation energy of the glycerol reaction as a function of sulfur loading.

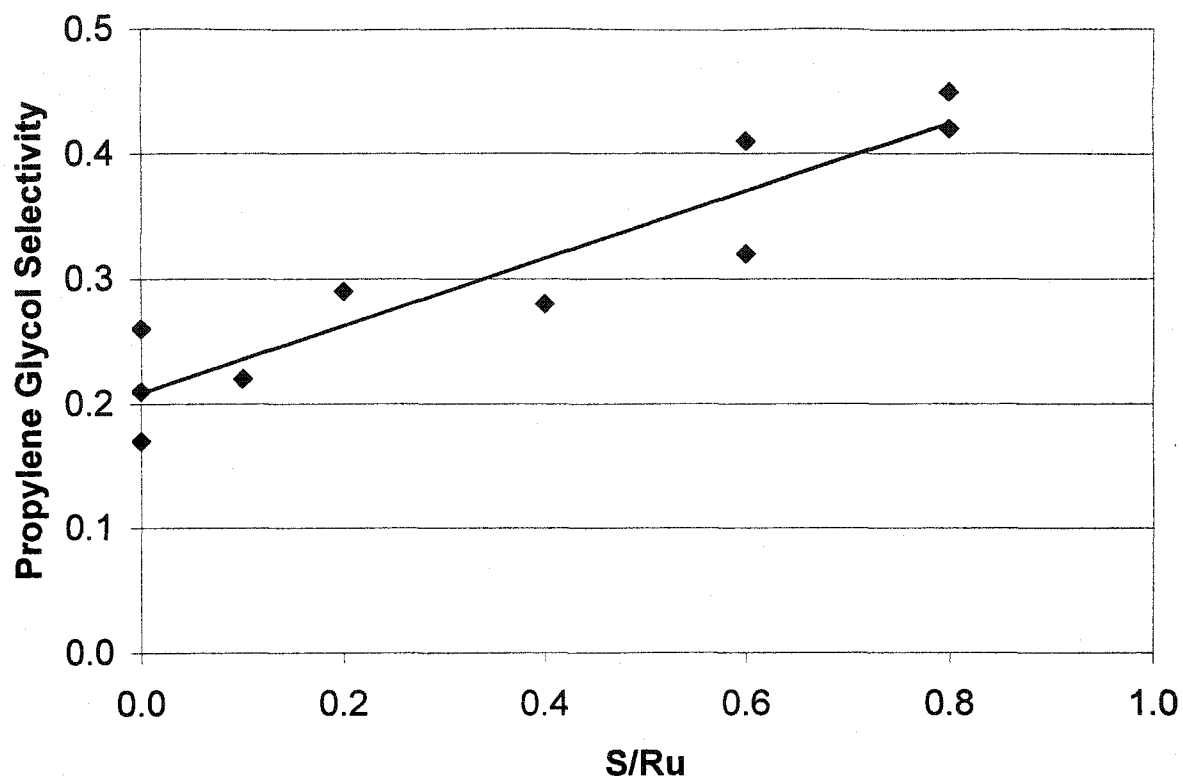


Figure 3.6: Effect of sulfur loading on propylene glycol selectivity at 205°C.

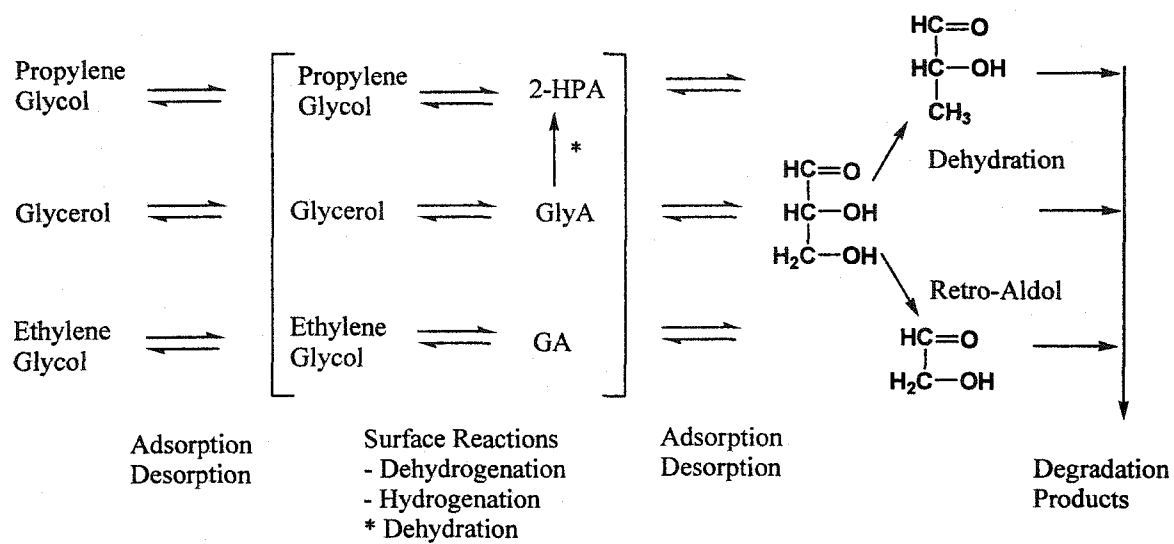


Figure 3.7: Overall reaction pathway for the production of glycols from glycerol.

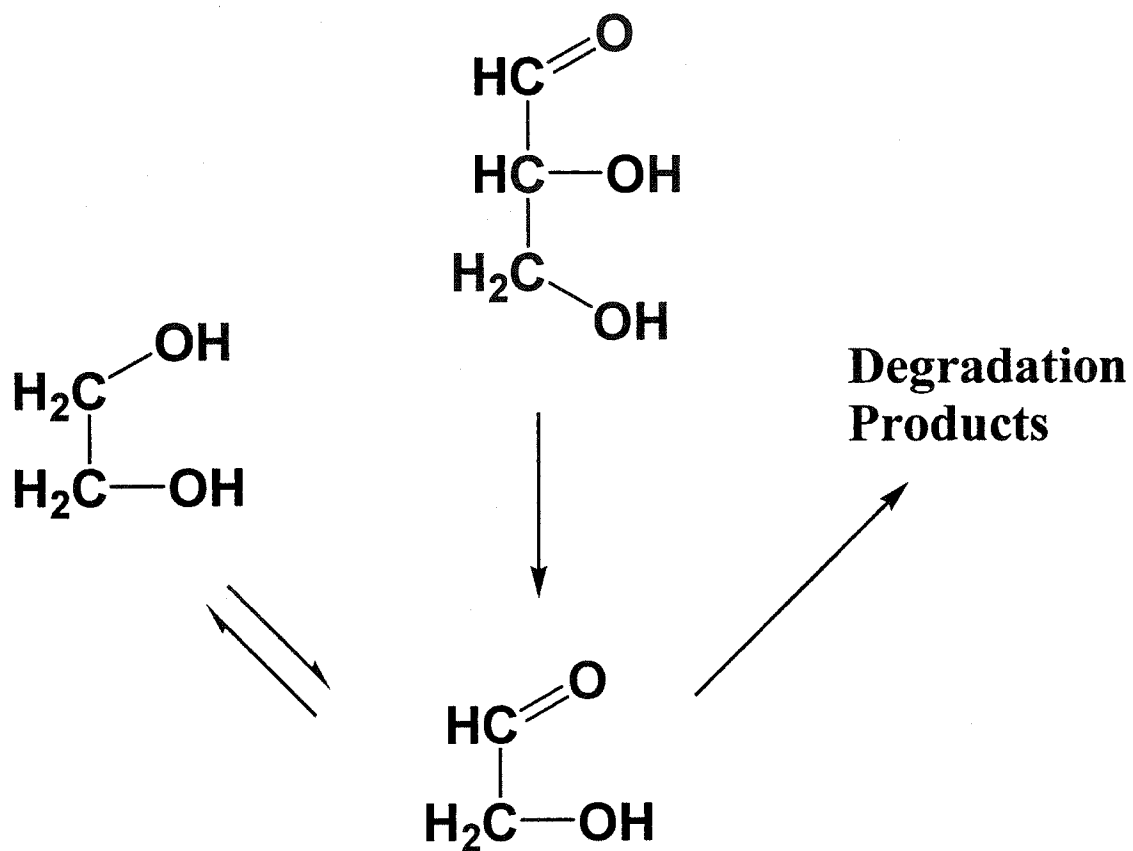


Figure 3.8: Glycolaldehyde production and reaction.

CHAPTER 4

Configuration Effects in the Hydrogenolysis of Higher Polyols

Daniel G. Lahr and Brent H. Shanks*
Department of Chemical Engineering*
Iowa State University
Ames, IA 50011, USA
Email: bshanks@iastate.edu

Abstract

The production of ethylene glycol and propylene glycol from biorenewable resources has been empirically studied numerous times. The goal of the previous work was to parametrically determine the best operating conditions for producing glycols. However, little work has been done to analyze the reaction mechanism. An improved understanding of the reaction mechanism will lead to improved catalyst systems. Nine polyols ranging from three to six carbons in length are reacted under hydrogenolysis conditions (205-240°C, 100 bar H₂). The reaction rates of the polyols depend on the configuration of the polyols. Polyols with all alcohol groups on the same side such as ribitol react faster than those with alcohol groups on both sides. Since the limiting step in this reaction is catalytic, insight into the adsorbed conformation of the polyol can be determined. The adsorbed conformation of polyols involves multiple hydroxyl groups. Also, the reaction rate of a polyol is a function of the number of consecutive hydroxyl groups facing the same direction when the carbon backbone is in a circular conformation leading to the proposal that this is the adsorbed conformation of the polyol.

Keywords: Adsorption, Configuration, Polyols, Conformation

Introduction

The hydrogenolysis of sorbitol to produce lower polyols such as glycerol, propylene glycol and ethylene glycol has been examined for over twenty years.¹⁻⁴ The majority of these studies have been empirical in nature, focusing on varying catalysts and operating conditions. The goal of these studies was to improve the selectivity toward glycols at a high reaction rate. Achieving either goal is feasible, a gain in the production rate gives a loss in selectivity and vice versa; the highest selectivity toward the two glycols with a high production rate is 65%.¹⁻³ Unfortunately, this selectivity is not sufficient to be economically viable. Achieving the necessary improvement in the glycol selectivities requires a deeper understanding of the reaction mechanism. An enhanced mechanistic understanding will bring about a rational development of improved catalyst systems to reach the desired product yields.

The hydrogenolysis of higher polyols such as sorbitol or xylitol to form ethylene glycol and propylene glycol has multiple steps.⁵ The polyol is first reversibly adsorbed and dehydrogenated by the catalyst leading to a desorbed oxidized species, either an aldehyde or ketone depending on which alcohol groups is dehydrogenated. Previous work discussing the hydrogenolysis of polyols has suggested that the product of dehydrogenation undergoes a C-C scission via the retro-aldol mechanism or a C-O scission by dehydration. The product(s) of these mechanisms contain olefinic bonds; the dehydrated species contains two such bonds, each species following the retro-aldol C-C scission contains one such bond. The olefinic bonds are subsequently hydrogenated by the metal catalyst. The metal catalyst serves as both a hydrogenating and dehydrogenating catalyst; therefore, the initial formation of the aldehydes and ketones is reversible.

For improved understanding to occur, efforts need to be directed towards the mechanism of the hydrogenolysis reaction. Due to the complexity of the hydrogenolysis reaction system, initial mechanistic studies were performed using glycerol, propylene glycol and ethylene glycol. The reaction rate of glycerol was found to be a function of the product concentration (ethylene glycol and propylene glycol). Also, the products were also found to degrade under reaction conditions.⁶ These results demonstrate the need to study initial reaction rate data when analyzing the hydrogenolysis mechanism. Many groups have reported an interesting effect on the reaction when adding sulfur to ruthenium; the selectivity toward propylene glycol increases.^{1,5} The limiting step of the reaction was found to be the catalytic dehydrogenation reaction, more specifically the diffusion of hydrogen adatoms away from the adsorbed polyol.⁷

Higher polyols are more complex than lower polyols for two reasons, the larger size and the different configurations possible due to the interior chiral carbons. While glycerol has an interior carbon, it is not chiral due to the same exterior functional groups. As CHOH groups can be added to D-glyceraldehyde in between the aldehyde group and neighboring alcohol group in two unique ways, CHOH groups can be added between the primary and secondary carbons of polyols. The configuration of all the higher polyols are shown in Figure 4.1. Two tetrutols, four pentitols, and eight hexitols can be drawn using this procedure. However, due to polyols having the same primary functional groups, some of these polyols are mirror images of each other, lowering the number of pentitols and hexitols to 3 and 6 respectively. Also, like glycerol, other symmetric higher polyols do not have a mirror image with a different configuration. Thus a few of these higher polyols do not have

the D-L nomenclature. Erythritol, ribitol, xylitol, allitol, and dulcitol have either a point or plane of symmetry; thus their mirror image will have the same configuration as the original.

The reaction rates of polyols are limited by the catalytic reaction rate. However, this does not guarantee that all polyols react at the same rate. Due to the different configurations of the stereoisomers, each polyol may have a different strength of adsorption. If a polyol has fewer steric hindrances, it can more strongly adsorb onto the catalyst increasing its reaction rate. The adsorption of sugars onto hydrous zirconium and hydrous iron oxide has shown that sugars with certain configurations have a stronger adsorption potential.⁸ Cyclic sugars which have the 2nd through 4th hydroxyl groups in the axial, equatorial, and axial positions respectively will have a higher adsorption potential. Also, polyols complexes with Ca(II) have been studied.⁹ Polyols which have more alcohol groups switching sides in the Haworth projection are more likely to form complexes. For example, xylitol at the first chiral carbon has the alcohol group on the right side, the second alcohol group on the left side, and the final alcohol group back on the right side. Ribitol has all alcohol groups on the same side. Xylitol thus has two inversions while ribitol has zero inversions causing xylitol to form better complexes with Ca (II) than ribitol. The differing reactions rates of polyols will lead to an increased understanding of how the polyols adsorb onto the catalyst surface.

Previous work developed an understanding of the hydrogenolysis of lower polyols; glycerol, ethylene glycol, and propylene glycol. The goal of the current work was to continue development of a mechanistic model for the hydrogenolysis of higher polyols. The relative reaction rates give rise to information about the adsorption behavior of polyols. This information will help in the rational design of catalysts in this system.

Experimental

Sorbitol (97%), mannitol (98%), dulcitol (galactical), xylitol, erythritol, glycerol, ethylene glycol, 1,2-propylene glycol, (all others 99%+), calcium oxide (96%), and sodium sulfide hydrate (60%) were purchased from Acros Organics. Arabitol (98%), adonitol (ribitol) (99%), and threitol (97%) were purchased from Sigma. High-purity hydrogen (99.992%) was used to pressurize the autoclave reactor. The catalyst purchased from Activated Metals & Chemicals, Inc. was 5 wt% ruthenium supported on activated carbon. The catalyst was handled as a wet powder with water content of about 50 wt%. The methodology of performing and analyzing reactions has been discussed earlier for lower polyols.

Hydrogenolysis of Higher Polyols

Figure 4.1 shows the configurations of all the possible higher polyols. With the exception of allitol, iditol, and talitol, all of these polyols were reacted under hydrogenolysis conditions; 205°C and 240°C, 100 bar H₂ with initial concentration of 0.5M to determine initial reaction rates and activation energies. As shown earlier, the reaction rate of a polyol is a function of the product concentration due to competitive adsorption.⁶ Thus, longer reaction times lead to systematic errors in measuring the reaction rate and selectivities and thus can give less accurate results. The initial reaction rates at 240°C and 205°C without sulfur of a variety of polyols is given in Table 4.1.

The reaction rates for these compounds vary by a factor of three, even though the reaction mechanisms for these compounds, are similar if not identical. The reaction rate does

not correlate with the length of the molecule. For example, at 240°C, the five-carbon molecules have reaction rates that rank 1st, 4th, and 7th among the nine molecules tested.

There is a correlation between reaction rate and polyol configuration. Those polyols which have fewer inversions have a higher reaction rate compared to those that do have inversions. For example, ribitol, arabitol, and xylitol have zero, one, and two inversions and a reaction rate in mmol/min of 11.0, 9.5, and 6.4 respectively. This contradicts what is expected from the complexation results. Polyols with more flips complex better with Ca (II), which is also shown in the calcium ion exchange HPLC column used to analyze the reaction samples; polyols with more flips take longer to elude from the column. If the complexation and HPLC results were to correlate with the reaction rate results, xylitol would have the highest reaction rate of the three pentitols instead of the lowest. An explanation for this deviation from expectation is the conformation of the polyol. As shown in Figure 4.2, if the carbons in the polyol form a zig-zag conformation, all of the hydroxyl groups of xylitol lie in the same direction. It has been shown through NMR that under ambient conditions polyols have zig-zag conformations in an aqueous solution. However, the adsorbed conformation of polyols on the catalyst at more extreme conditions is not necessarily a zig-zag conformation. If the adsorbed polyol conformation is cyclical, all of the hydroxyl groups of ribitol lie in the same direction. This is also shown in Figure 4.2. If more hydroxyl groups lie in the same direction, the adsorption potential of the polyol is increased. Thus it is proposed that the conformation of polyols on ruthenium is cyclical.

There is a correlation between reaction rate and ability for the compound to adsorb onto the catalyst. Assuming that the most stable conformation of the polyols is ring-like as opposed to a staggered chain; ribitol, with all three hydroxyl facing the same side, is able to

absorb all five oxygen atoms onto a surface. However xylitol, which has the interior hydroxyl group on the opposite side of the other two chiral hydroxyl groups, due to its conformation is sterically unable to absorb all five oxygen atoms onto a surface. It may absorb onto the catalyst in a number of ways, two of which are shown in Figure 4.3. Xylitol can have up to three or four oxygen molecules adsorb onto the catalyst. Arabitol also can have up to four oxygen molecules adsorb on the catalyst.

Even though both xylitol and arabitol can have four hydroxyl groups adsorbed onto the catalyst, they have differing reaction rates. This is also evident in the hexitols; both dulcitol and mannitol can have four of the six hydroxyl groups adsorbed when the carbon backbone is circular. However, they too have different reaction rates. Sorbitol, which could have 5 hydroxyl groups adsorbed, has the same reaction rate as mannitol. Thus the correlation between reaction rate and configuration is not as simple as number of inversions or number of hydroxyl groups facing the same direction. By defining the maximum number of consecutive oxygen atoms that can be adsorbed, a correlation is found. This is shown in Figure 4.4. Xylitol, for example, has three consecutive oxygen atoms that can be adsorbed out of the five available or a 0.6 adsorption fraction. The reaction of a polyol is plotted against its adsorption fraction in Figure 4.4. As shown in the figure, those polyols with a larger adsorption fraction have a higher reaction rate. Since this gives the best correlation with the data, it is proposed that the adsorbed conformation of the polyol is circular, with the number of consecutive hydroxyl groups impacting the reaction rate. One reason for this correlation is that the branch not adsorbed may aid in the desorption via physical forces acting on this branch.

The hydrogenolysis rate of polyols decreases with the addition of sulfur. However, the relative decrease is not the same for each polyol. Table 4.2 lists each polyol and the relative reaction rates of the polyols with sulfur vs. without sulfur. The values for the glycols and glycerol were determined earlier. Not surprisingly, all of these values are under 1. However, these values are very different and depend on the size of the polyol. The two four-carbon polyols show little effect with sulfur coverage, with the reaction rate dropping by about 5%. However, the reaction rates of the three and six-carbon molecules drop by 60%. This sulfur effect occurred at both 205°C and 240°C.

Conclusions

The hydrogenolysis rates of a variety of polyols have been found and correlated to the configuration of the polyol. Polyols with alcohol groups on the same side in the Hayworth projection have the highest reaction rates. The decarboxylation reaction is shown to be significant in explaining the product distribution of higher polyols. A selectivity map was used to analyze the products and predict the relative dehydrogenation rates of the different alcohol groups on higher polyols. The addition of sulfur lowered the dehydrogenation selectivity of the primary alcohol group.

Acknowledgements

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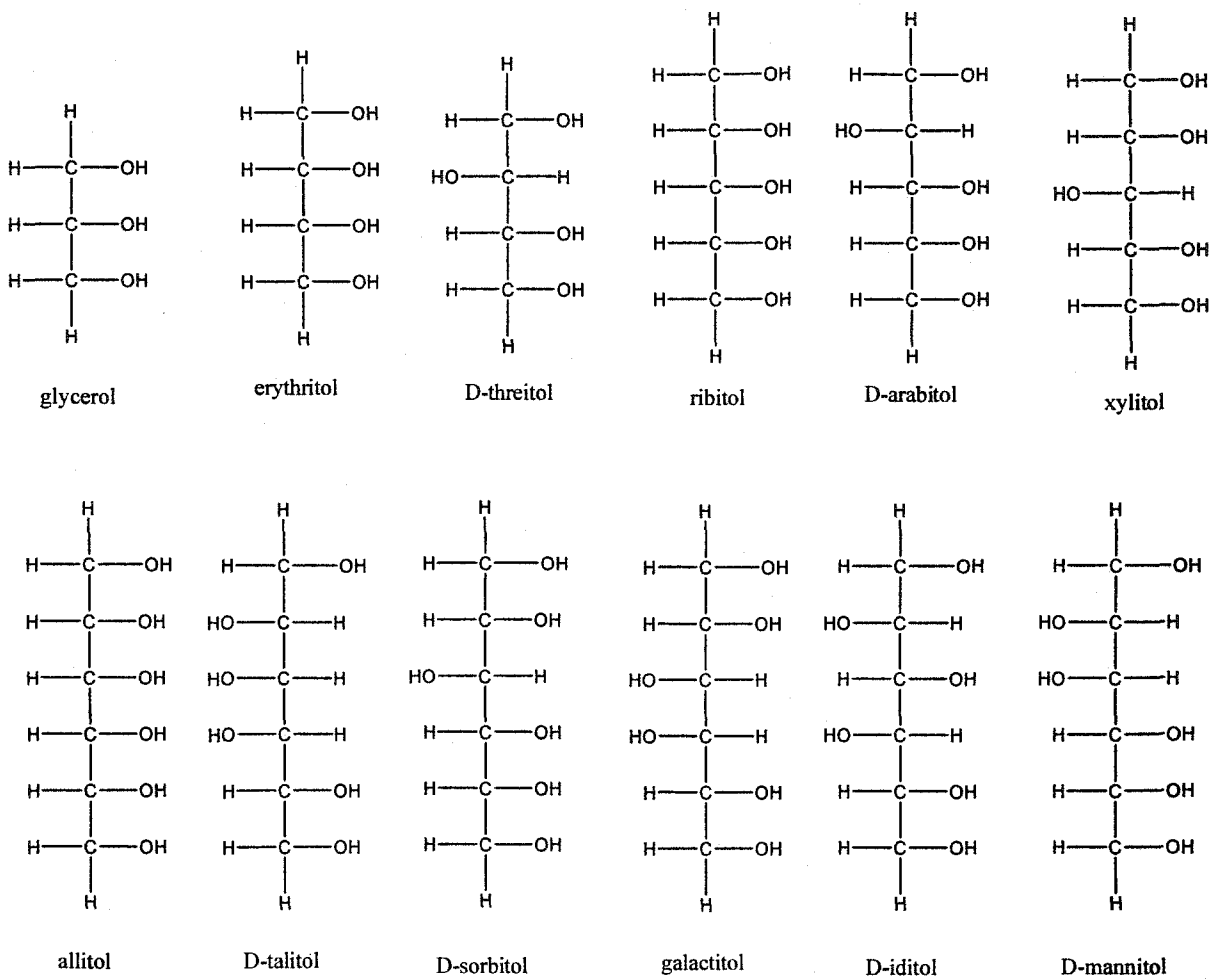


Figure 4.1: Structure and Names of Higher Polyols

Compound	Reaction Rate at 205°C mmol/min	Reaction Rate at 240°C mmol/min	Maximum Consecutive Oxygen Atoms	Adsorption Potential
Glycerol	3.9	10.3	3	1.00
Erythritol	3.4	10.1	4	1.00
Threitol	2.0	5.0	3	0.75
Ribitol	3.3	11.0	5	1.00
Arabitol	3.0	9.5	4	0.80
Xylitol	2.5	6.4	3	0.60
Mannitol	2.8	7.8	4	0.67
Sorbitol	2.5	6.7	4	0.67
Galactical	N/A	3.5	3	0.50

Table 4.1: Reaction Rates and Adsorption Ratio for a Variety of Polyols

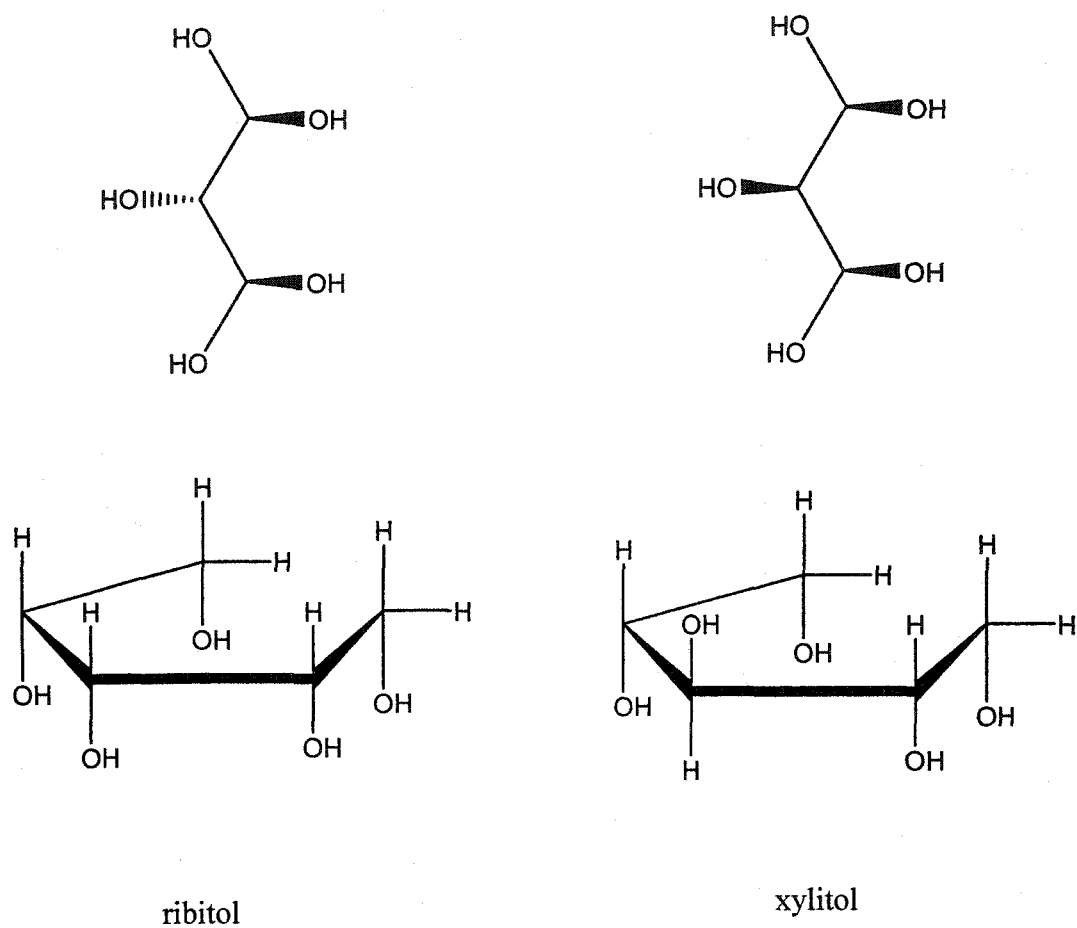


Figure 4.2: Staggered and Circular Conformations of Ribitol and Xylitol

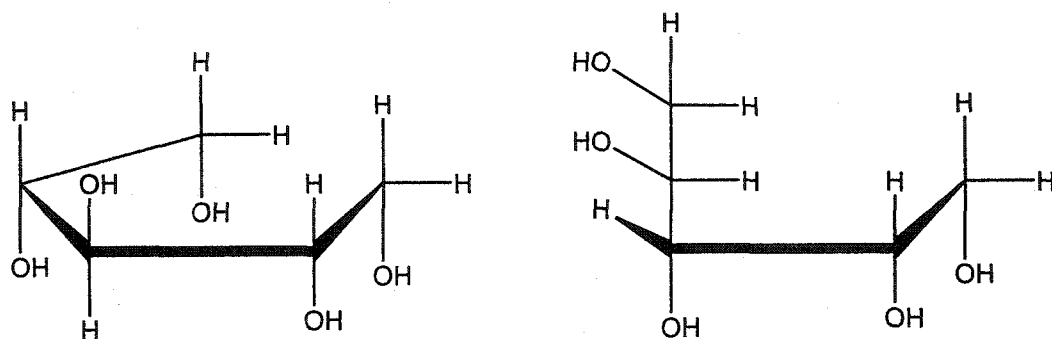


Figure 4.3: Two Possible Adsorption Conformations of Xylitol

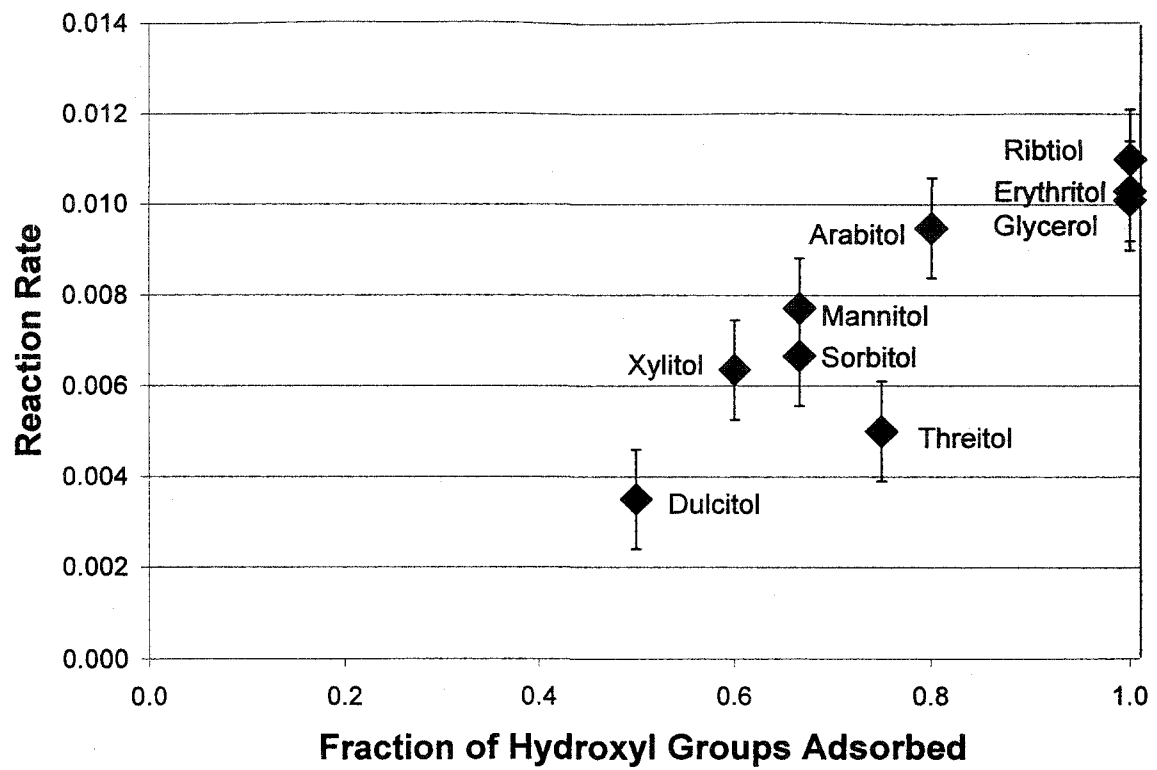


Figure 4.4: Reaction Rate vs. Adsorption Fraction of Higher Polyols

Compound	Reaction Rate Fraction With Sulfur
	1.0 mol S / mol Ru
Glycerol	0.41
Erythritol	0.92
Threitol	0.95
Ribitol	0.78
Arabitol	0.77
Xylitol	0.71
Mannitol	0.46
Sorbitol	0.37

Table 4.2: The Fraction Reaction Rate of Polyols with the Addition of Sulfur

CHAPTER 5

Modifying and Mapping the Hydrogenolysis Mechanism of Higher Polyols

Daniel G. Lahr and Brent H. Shanks*
Department of Chemical Engineering*
Iowa State University
Ames, IA 50011, USA
Email: bshanks@iastate.edu

Abstract

The production of ethylene glycol and propylene glycol from biorenewable resources has been empirically studied numerous times. The results of these studies have not produced an economically feasible process. An improved mechanistic understanding of the reaction system will lead to an industrial application of the process. Nine polyols ranging from three to six carbons in length are reacted under hydrogenolysis conditions (205-240°C, 100 bar H₂, 0.0-1.0 mol S/mol Ru). Previous work has described the retro-aldol mechanism as the main pathway leading to C-C scission. However, the retro-aldol mechanism is shown to be insufficient in explaining the production of tetritols from pentitols while the decarboxylation mechanism explains this selectivity well. Information about the relative dehydrogenation rates is gained leading to a selectivity map describing the carbon flux from higher polyols to lower polyols. The relative dehydrogenation rates of alcohol groups changes as sulfur is added. The primary alcohol group is dehydrogenated 50% of the time without sulfur and only 20% of the time at a sulfur loading of 1.0 mol S/mol Ru independent of the original polyol length.

Keywords: Polyols, Retro-aldol, Decarboxylation, Selectivity Map, Dehydrogenation

Introduction

The hydrogenolysis of sorbitol to produce lower polyols such as glycerol, propylene glycol and ethylene glycol has been examined for over twenty years.¹⁻⁴ The majority of these studies have been empirical in nature, focusing on varying catalysts and operating conditions. The goal of these studies was to improve the selectivity toward glycols at a high reaction rate. Achieving either goal is feasible, a gain in the production rate gives a loss in selectivity and vice versa; the highest selectivity toward the two glycols with a high production rate is 65%.¹⁻³ Unfortunately, this selectivity is not sufficient to be economically viable. Achieving the necessary improvement in the glycol selectivities requires a deeper understanding of the reaction mechanism. An enhanced mechanistic understanding will bring about a rational development of improved catalyst systems to reach the desired product yields.

The hydrogenolysis of higher polyols such as sorbitol or xylitol to form ethylene glycol and propylene glycol has multiple steps.⁵ The polyol is first reversibly adsorbed and dehydrogenated by the catalyst leading to a desorbed oxidized species, either an aldehyde or ketone depending on which alcohol groups is dehydrogenated. Previous work discussing the hydrogenolysis of polyols has suggested that the product of dehydrogenation undergoes a C-C scission via the retro-aldol mechanism or a C-O scission by dehydration. The product(s) of these mechanisms contain unsaturated bonds; the dehydrated species contains two such bonds, each species following the retro-aldol C-C scission contains one such bond. The olefinic bonds are subsequently hydrogenated by the metal catalyst. The metal catalyst serves as both a hydrogenating and dehydrogenating catalyst; therefore, the initial formation of the aldehydes and ketones is reversible.

One mechanistic study focused on the elimination of two suspect mechanisms; the retro-Claisen and retro-Michael mechanisms as potential pathways leading to C-C scission. In this study, all and only products expected from the retro-aldol mechanism were found. However, many of the molecules tested in this study could react via another mechanism, producing the same reaction products as the retro-aldol mechanism produces.⁶ At high temperatures and basic conditions aldehydes can also react via the decarboxylation reaction leading to a carbon-carbon bond breaking. The two mechanisms leading to C-C scissions are shown in Figure 5.1. As Figure 5.1 shows, if the initial reactant is glyceraldehyde, which is the dehydrogenation product of glycerol, both the retro-aldol and decarboxylation reactions lead to the same product, glycol aldehyde which can be reduced to glycerol. The molecules in this mechanistic study are similar to glycerol because they are 1,3 diols. Larger aldehydes will produce different products from these mechanisms.

For improved understanding to occur, efforts need to be directed towards the mechanism of the hydrogenolysis reaction. Due to the complexity of the hydrogenolysis reaction system, initial mechanistic studies were performed using glycerol, propylene glycol and ethylene glycol. The reaction rate of glycerol was found to be a function of the product concentration (ethylene glycol and propylene glycol). Also, the products were also found to degrade under reaction conditions.⁷ These results demonstrate the need to study initial reaction rate data when analyzing the hydrogenolysis mechanism. Many groups have reported an interesting effect on the reaction when adding sulfur to ruthenium; the selectivity toward propylene glycol increases.^{1,5} The limiting step of the reaction was found to be the catalytic dehydrogenation reaction, more specifically the diffusion of hydrogen adatoms away from the adsorbed polyol.⁸

Sorbitol has six alcohol groups that can be dehydrogenated to form either an aldehyde or ketone. When the oxidized species desorbs into the solution, it can react via the retro-aldol or decarboxylation reaction. Depending on which alcohol group is oxidized, a variety of different products can be produced. Figure 5.2 shows the six oxidized species that can form followed by the products that can be produced. For example, if the top primary alcohol group of D-sorbitol is oxidized, D-glucose can form. The oxidation and subsequent decarboxylation of D-glucose leads to D-arabinose. The retro-aldol mechanism splits D-glucose into D-erythrose and glycol aldehyde. These intermediates can both react further or be reduced to arabitol, erythritol, and ethylene glycol respectively. Oxidation of the other primary alcohol group followed by a similar sequence can lead to xylitol, threitol, and ethylene glycol. The oxidation of the secondary alcohols groups leads to fructose or sorbose. These hexuloses can react via retro-aldol to form the three molecules classically defined as the smallest carbohydrates, dihydroxyacetone and (D or L) glyceraldehyde. These can all be reduced to glycerol. The ketones formed via the interior alcohol groups can react via retro-aldol in two ways. The retro-aldol mechanism splits the beta carbon-carbon bond from the ketol group. These interior ketones have two such bonds. Also, in both cases one product is another ketone. The reduction of a ketone can lead to two different polyols due to the chirality of the interior carbon. Thus the oxidation of either interior hydroxyl group can lead to both tetritols, all three pentitols, and ethylene glycol. In Figure 5.2, the decarboxylation reactions are labeled, while the remaining cleavage reactions are via the retro-aldol reaction. Based on specific pentitols or tetritols formed, a determination of which alcohol groups are dehydrogenated will result.

The addition of sulfur has been shown to change the product distribution in the sorbitol hydrogenolysis reaction. It appears that the reason for this selectivity change is the relative dehydrogenation rates of the alcohol groups. For example, if the secondary alcohol groups are dehydrogenated at an increased selectivity, a higher selectivity toward three-carbon molecules will result.

Previous work developed an understanding of the hydrogenolysis of lower polyols; glycerol, ethylene glycol, and propylene glycol. The goal of the current work was to continue development of a mechanistic model for the hydrogenolysis of higher polyols. Analysis of the products leads to a selectivity map which describes the relative carbon fluxes through the many pathways in this complex system. Both sets of information will help in the rational design of catalysts in this system.

Experimental

Sorbitol (97%), mannitol (98%), dulcitol (galactical), xylitol, erythritol, glycerol, ethylene glycol, 1,2-propylene glycol, (all others 99%+), calcium oxide (96%), and sodium sulfide hydrate (60%) were purchased from Acros Organics. Arabitol (98%), adonitol (ribitol) (99%), and threitol (97%) were purchased from Sigma. High-purity hydrogen (99.992%) was used to pressurize the autoclave reactor. The catalyst purchased from Activated Metals & Chemicals, Inc. was 5 wt% ruthenium supported on activated carbon. The catalyst was handled as a wet powder with water content of about 50 wt%. The methodology of performing and analyzing reactions has been discussed earlier for lower polyols.

Product Distribution

The reaction of higher polyols has historically been performed to produce ethylene glycol and propylene glycol. However, other polyols can be formed as well. As shown in Figure 5.2, sorbitol can react to form many compounds besides the glycols. If the third hydroxyl group (counting from the top) is dehydrogenated and this molecule is desorbed into solution, a sequence of the retro-aldol reaction plus catalytic reduction produces either arabitol or ribitol. If the fourth hydroxyl group is dehydrogenated and the molecule follows the same sequence, either arabitol or xylitol can be formed. The dehydrogenation of the 1st, 3rd, 4th, or 6th hydroxyl group can also lead to either erythritol or threitol. If the 2nd and 5th hydroxyl groups are dehydrogenated followed by the retro-aldol and reduction, two molecules of glycerol are formed. This is the ideal carbon-carbon cleavage because the maximum amount of three-carbon molecules can be formed from this pathway. Ethylene glycol is produced from the reduction of the two-carbon fragment left over in the retro-aldol production of the four-carbon molecules. Propylene glycol is formed via dehydration of glycerol. Along with these products, epimers of sorbitol can form. A dehydrogenation and rehydrogenation of a chiral hydroxyl group leads to epimers. Starting from the 2nd hydroxyl group and moving toward the 5th hydroxyl group, the following epimers of sorbitol can be formed: mannitol, allitol, dulcitol, and iditol. The remaining epimer, talitol, requires two hydroxyl groups to switch sides. Symmetric compounds such as mannitol and dulcitol will form fewer compounds. For example, the dehydrogenation of either tertiary hydroxyl group of mannitol gives rise to the same intermediate – 3-keto mannitol. Also, the dehydrogenation of either primary hydroxyl group of mannitol leads to mannose. The dehydrogenation and

subsequent retro-aldol scission of any hexitol's secondary hydroxyl groups gives rise to the same intermediates.

Table 5.1 lists the carbon selectivities toward a variety of product for the four to six carbon epimers at 240°C with and without sulfur. The addition of sulfur increased the selectivity toward propylene glycol slightly while the selectivity toward ethylene glycol does not change measurably with sulfur. Sulfur decreased the formation of intermediate polyols, polyols in between the reactant and the glycols. The addition of sulfur also increased the selectivity toward molecules which are stereoisomers of the reactant. However, the overall rate of epimerization of the pentitols and hexitols does not change with the addition of sulfur.

As shown in Table 5.1, not all epimers or intermediates are produced in the hydrogenolysis reaction. The products depend on the initial reactant. For example, threitol is the only four-carbon polyol formed from xylitol, erythritol is the only four-carbon polyol formed from ribitol, and both are formed from arabitol. The distribution of products leads to insights about the mechanistic pathway followed. Previous literature has discussed the main path toward carbon-carbon cleavage is the retro-aldol mechanism. Figure 5.3 shows the only way the retro-aldol mechanism can be used to produce a four-carbon polyol from xylitol, a five-carbon polyol. The initial dehydrogenation of xylitol is of the interior hydroxyl group leading to 3-keto xylitol. According to the retro-aldol mechanism, the carbon-carbon cleavage occurs on the beta carbon-carbon bond. If the 1st or 2nd hydroxyl groups were dehydrogenated, the carbon-carbon cleavage that would result gives rise to a three carbon/two carbon split. Only by oxidizing the interior hydroxyl group can the top or bottom carbon-carbon bond break leaving (D or L) erythrulose. Breaking the top bond produces D-erythrulose, while breaking the bottom bond produces the mirror image L-erythrulose. There

is no reason to suspect that one molecule adsorbs onto the catalyst differently from the other. Thus, any compounds produced that are mirror images should behave equally. It is possible, without other information, to speculate that the ruthenium catalyst selectively reduces all erythrulose into threitol. However, a similar molecule can be used as a raw material and reduced. Fructose, also a ketone, at 40°C, 100 bar H₂, with the same catalyst was reduced to mannitol and sorbitol in a 2:1 ratio. The study of the other pentitols will confirm that the threitol produced via xylitol hydrogenolysis did not pass through an erythrose intermediate.

The conversion of ribitol into four-carbon polyols shows a similar and different result compared to xylitol. If the interior hydroxyl group of ribitol is dehydrogenated, the same intermediate, 3-keto xylitol is produced. Unlike xylitol, the hydrogenolysis of ribitol leads to the production of erythritol, not threitol. The hydrogenolysis of arabitol gives more insight. Even though the dehydrogenation of arabitol leads a different keto polyol, the subsequent carbon-carbon cleavage leads to D-erythrulose, the same intermediate found for the other two five-carbon stereoisomers. The retro-aldol mechanism for the three five-carbon polyols is shown in Figure 5.4. Thus, the production of four-carbon polyols via retro-aldol cleavage from a five-carbon polyol goes through the same intermediate for each of the three epimers. However, as stated earlier, the four-carbon polyol distributions of the three epimers are distinctly different. Thus, the retro-aldol mechanism is not sufficient in describing the production of tetritols from pentitols.

Instead, the likely mechanism is the decarboxylation of an aldehyde. An aldehyde is formed when a primary hydroxyl group of a polyol is dehydrogenated. This molecule could follow the retro-aldol pathway and split into a three-carbon and two-carbon molecules. An aldehyde can also be oxidized in a high pH environment to form an acid. Further basic

oxidation on the second carbon can lead to the removal of the acid group in the form of carbon dioxide. The product is another aldehyde, which could repeat the same cycle. If a five-carbon polyol progresses through a decarboxylation cycle once and is subsequently reduced, a four-carbon polyol is formed in which its two chiral carbons will have the same configuration as the third and fourth carbons of the original five-carbon polyol. Since xylitol and ribitol both have a plane of symmetry, the primary dehydrogenation and subsequent decarboxylation and reduction produce one four-carbon polyol for each polyol: threitol from xylitol and erythritol from ribitol. Arabitol is not symmetric and this pathway can lead to either epimer. The predicted decarboxylation product distribution of the five-carbon epimers matches the experimental data exceptionally well as the predicted retro-aldol product distribution does not.

This behavior is shown in the six-carbon polyols as well. If the third (or by symmetry the fourth) hydroxyl group of dulcitol is dehydrogenated and is followed by a retro-aldol reaction leading to a 5:1 split, xylulose is formed. Xylulose is also formed via dehydrogenation of the fourth hydroxyl group of sorbitol followed by the 5:1 retro-aldol reaction. Xylulose can be reduced to xylitol or arabitol. The hydrogenolysis of dulcitol only produces arabitol, which would come from the decarboxylation of galactose. To parallel the argument developed from the five-carbon discussion, the hydrogenolysis of iditol would need to be studied. The dehydrogenation of an interior hydroxyl group followed by a 5:1 retro-aldol split also produces xylulose. The decarboxylation of idose would give xylitol. Even though the study of iditol is not economically feasible, the hydrogenolysis of dulcitol to pentitols shows the same pattern as the hydrogenolysis of pentitols. As with dulcitol and iditol, mannitol and allitol both produce only ribulose after a tertiary dehydrogenation and a

5-1 retro-aldol split. Sorbitol and talitol can produce both pentuloses via the same sequence. As with the first pair of hexitols, each of the following pairs has one expensive polyol. Thus a detailed proof of decarboxylation was not performed.

However, if any of the six-carbon polyols has a tertiary hydroxyl group dehydrogenated followed by a 4-2 retro-aldol cleavage, erythrulose is formed. Thus, as with the five-carbon polyols, the relative production rates of the two four-carbon polyols should be the same for each six-carbon epimer. As shown in Table 5.1, this is not the case. The tetritol distribution again corresponds to the original configuration of the hexitol. From the previous model and current adaptation, there are two possible mechanisms to produce the described tetritol distribution. These are shown in Figure 5.5. Mannitol can undergo a primary dehydrogenation followed by either two decarboxylation cascades or a single retro-aldol scission leaving erythrose which is reduced to erythritol.

A second conclusion can be deduced from this data. There is either little dehydrogenation of the tertiary hydroxyl groups or the retro-aldol scission rate is smaller for 3-keto sugars. If either there was a significant amount of dehydrogenation on the tertiary hydroxyl groups compared to the primary and secondary hydroxyl groups or the 3-keto sugars had a competitive retro-aldol scission rate, it would manifest itself in the four-carbon polyol selectivities. Irregardless of the polyol distribution from the hydrogenation of erythrulose, either erythritol would be produced from xylitol and dulcitol or threitol produced from ribitol and mannitol. Since neither occurs, either the dehydrogenation of the tertiary hydroxyl groups is small compared to the dehydrogenation of the other hydroxyl groups or the retro-aldol scission of 3-keto sugars is smaller than the other two oxidized species.

Epimers are also not equally produced. Epimers are produced by the catalytic dehydrogenation of a hydroxyl group, subsequent desorption, followed by a rehydrogenation that switches the configuration of the hydroxyl group. Each five-carbon polyol can form its two epimers by switching the configuration of one hydroxyl group. This is shown in Figure 5.6. The selectivity of epimerization is xylitol > arabitol > ribitol, which is the opposite of the reaction rates of the epimers. Arabitol is preferentially produced from xylitol, while xylitol is preferentially produced from ribitol and arabitol. The production of 3-epimers is evidence for the postulation that the retro-aldol scission of 3-keto sugars is relatively low. As shown by Doraiswamy⁹, the reduction of glucose with Raney Ni occurred with aqueous glucose reacting with adsorbed hydrogen resulting in an adsorbed sorbitol molecule. The ketone, 3-keto xylitol may also react in the same manner, being reduced to either epimer. The newly formed polyol would likely be adsorbed via multiple hydroxyl groups. Less ribitol is formed from xylitol then vice versa, because the adsorbed ribitol is more likely to react than the adsorbed xylitol.

Flux Analysis

The selectivity data for the polyols studied can be used to probe the details of the mechanism. It is critical that selectivity data for all polyol sizes are used. For example, if only sorbitol (or only six-carbon polyols) is used, it would be difficult to model how the intermediates in this reaction behave. The hydrogenolysis pathway of smaller polyols contains common intermediates with the hexitols allowing for fewer equations. Also, if only these intermediate polyols are used, four-carbon and five-carbon polyols, then it would be difficult to separate the dehydrogenation selectivities of the hydroxyl groups. This is shown

in Figure 5.7. For example, a five-carbon polyol can split into a three-carbon and two-carbon molecules via initial dehydrogenation of either the primary or secondary hydroxyl groups. From the discussion earlier, one can correlate the dehydrogenation rate of the top carbon by the production rate of four-carbon polyols. However, an aldehyde that can react via the decarboxylation sequence to form a four-carbon aldehyde can also produce glyceraldehyde via the retro-aldol mechanism. The selectivity of retro-aldol vs. decarboxylation can not be determined without the six-carbon polyols. If one assumes that there is relatively little dehydrogenation of the third and fourth hydroxyl groups in six-carbon polyols or little retro-aldol scission of these ketones, and that the decarboxylation vs. retro-aldol selectivities of all aldehydes are the same, then the relative dehydrogenation rates of all polyols can be found.

The molecules involved in the flux analysis are shown in Figure 5.8. There is no distinction of stereoisomers in Figure 5.8; all stereoisomers are assumed to behave the same. The molecules in Figure 5.8 are labeled with two numbers. The first is the number of carbons in the molecule; the second is the hydroxyl group that is dehydrogenated. Molecules that are fully reduced have a zero as the second number. The reactions modeled are the catalytic oxidation and reduction of the hydroxyl groups, the retro-aldol reaction, and the decarboxylation reaction. These are listed in Figure 5.9 with the labeling system found in Figure 5.8.

This analysis was performed at four conditions. The temperature ($^{\circ}\text{C}$) and sulfur loading (mol S/mol Ru) of the four conditions are as follows: (205,0), (205,1), (240,0), and (240,1). The relative hydroxyl groups' dehydrogenation and subsequent reaction rates are assumed to vary with polyol length and with operating conditions. The relative rates of

decarboxylation and retro aldol mechanisms are assumed to be constant with polyol size. Any ketone with at least four carbons that is formed is assumed to split only via the retro-aldol mechanism. Also, the fraction of any intermediate that is reduced to a polyol is assumed to be constant. This analysis also assumes that when any saturated polyol is formed and desorbed into solution that it does not react further. Thus initial selectivities are used instead of final selectivities to avoid the need to account for product degradation. A flux map describing the carbon flux is shown in Figure 5.10. Equations for the molar rates based on one mole of reactant toward each polyol length based on Figure 5.10 are given as follows:

$$C5:C6 = \alpha\eta \quad (1)$$

$$C4:C6 = \alpha(\eta\gamma + \mu) \quad (2)$$

$$C3:C6 = 2\beta + \alpha(\mu\delta + \eta\sigma + \eta\gamma\delta) \quad (3)$$

$$C2:C6 = \alpha(\mu + 2\theta(\mu + \nu\delta) + \eta\sigma) \quad (4)$$

$$C4:C5 = \pi\gamma \quad (5)$$

$$C3:C5 = \tau + \pi(\sigma + \gamma\delta) \quad (6)$$

$$C2:C5 = \tau + \sigma\pi + 2\pi\gamma\delta \quad (7)$$

$$C3:C4 = \phi\delta + \xi \quad (8)$$

$$C2:C4 = 2\phi\theta \quad (9)$$

where the first number represents the length of the product and the second number represents the length of the reactant. The molar rates include the final production of a new polyol and all intermediates formed with that polyol length. Since the flux through a polyol size is

assumed to correlate with the flux stopping at a polyol size, the total molar flow can be determined.

Results from this analysis are shown in Table 5.2. The results represent the fraction of the dehydrogenated hydroxyl groups that were in the primary position. The rest of the hydroxyl groups dehydrogenated are assumed to be in the secondary position. There are three different variables that could affect the relative dehydrogenation rate; temperature, original polyol length, and sulfur loading. There is little variation with temperature. The fit predicts a higher primary dehydrogenation fraction for the 4-carbon polyols, but inserting the lower numbers from the other polyols does not significantly change the quality of fit. Increasing the sulfur loading from 0.0 to 1.0 mol S/mol Ru lowers this dehydrogenation fraction by an average of 27%. Using the non-sulfur results drastically changes the quality of fit, thus there is a significant effect on the relative dehydrogenation rate due to sulfur loading. This effect has been assumed previously because of the increased selectivity toward propylene glycol with the addition of sulfur. When the secondary hydroxyl group of sorbitol is dehydrogenated, decarboxylation does not occur and the resulting split via retro-aldol is to two three-carbon molecules, maximizing the amount of glycerol or propylene glycol that can be produced.

The second result from the flux analysis is determination of the fraction of aldehydes that react via decarboxylation or retro-aldol. This result is 56% of aldehydes react via decarboxylation while the remaining 44% react via the retro-aldol mechanism. This is important in designing potential catalysts for this system. While it was already known that aldehydes are generally not wanted for the lower potential of three-carbon molecules produced, glucose could still produce three ethylene glycol molecules via two retro-aldol

steps and reduction of the products. However if 56% of aldehydes react via decarboxylation, removing one carbon from the molecule, there is even less of a benefit. This is only a loss of potential product. The knowledge of decarboxylation occurring in the solution phase further emphasizes the need for catalysts to selectively dehydrogenate the secondary hydroxyl group.

Conclusions

The decarboxylation reaction is shown to be significant in explaining the product distribution of higher polyols. The study of multiple stereoisomers gives insight into the relative dehydrogenation and subsequent retro-aldol scission rates. A selectivity map was used to analyze the products and predict the relative dehydrogenation rates of the different alcohol groups on higher polyols. The addition of sulfur lowered the dehydrogenation selectivity of the primary alcohol group.

Acknowledgements

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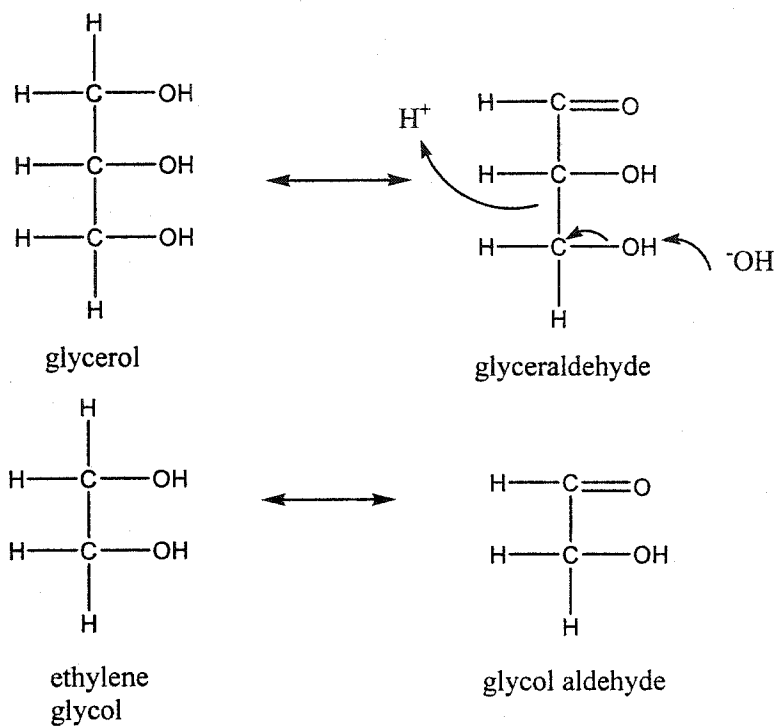


Figure 5.1A: Retro-aldol mechanism

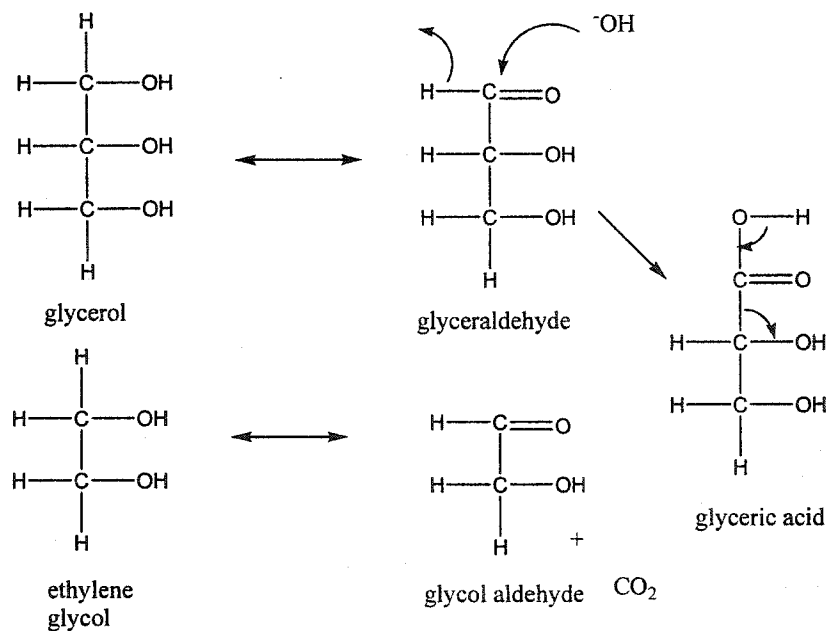


Figure 5.1B: Decarboxylation mechanism

Figure 5.1: Two C-C scission mechanisms; retro-aldol and decarboxylation

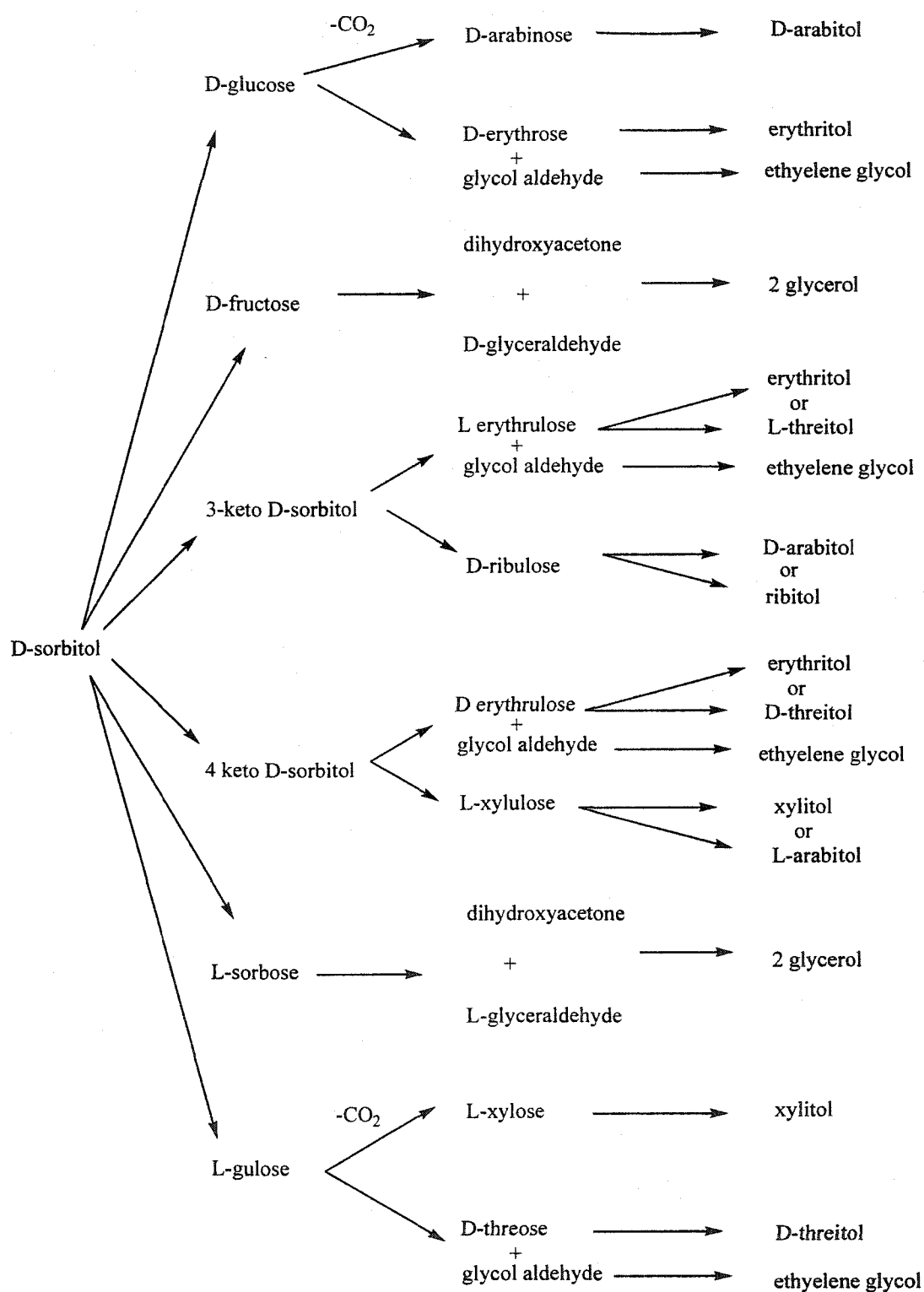


Figure 5.2: Potential Products Produced from Sorbitol via Retro-Aldol or Decarboxylation Reactions after an initial Dehydrogenation Step

Polyol	Temperature (°C)	sulfur loading	Ethylene Glycol			Propylene Glycol			Glycerol		Erythritol		Threitol		Arabitol		Ribitol		Xylitol		Tallitol	Mannitol	Sorbitol	Dulcitol	Allitol	Iditol	Total
Erythritol	240	0	0.24	0.21	0.02	0.07																					0.54
Erythritol	240	1	0.17	0.22	0.01	0.14																					0.54
Threitol	240	0	0.28	0.23	0.01	0.15																					0.67
Threitol	240	1	0.23	0.28	0.02	0.18																					0.71
Xylitol	240	0	0.23	0.20	0.06	0.04																					0.60
Xylitol	240	1	0.32	0.24	0.02	0.00																					0.76
Ribitol	240	0	0.25	0.19	0.08	0.00																					0.65
Ribitol	240	1	0.26	0.19	0.00	0.00																					0.55
Arabitol	240	0	0.25	0.18	0.10	0.01																					0.71
Arabitol	240	1	0.28	0.18	0.02	0.00																					0.60
Sorbitol	240	0	0.09	0.22	0.02	0.00																					0.48
Sorbitol	240	1	0.13	0.28	0.06	0.01																					0.63
Mannitol	240	0	0.11	0.23	0.10	0.08																					0.55
Mannitol	240	1	0.08	0.27	0.12	0.07																					0.61
Dulcitol	240	0	0.17	0.25	0.024	0.00																					0.51
Dulcitol	240	1	0.16	0.30	0.016	0.00																					0.64

Table 5.1: Product Distribution of the Hydrogenolysis Reaction of Higher Polyols

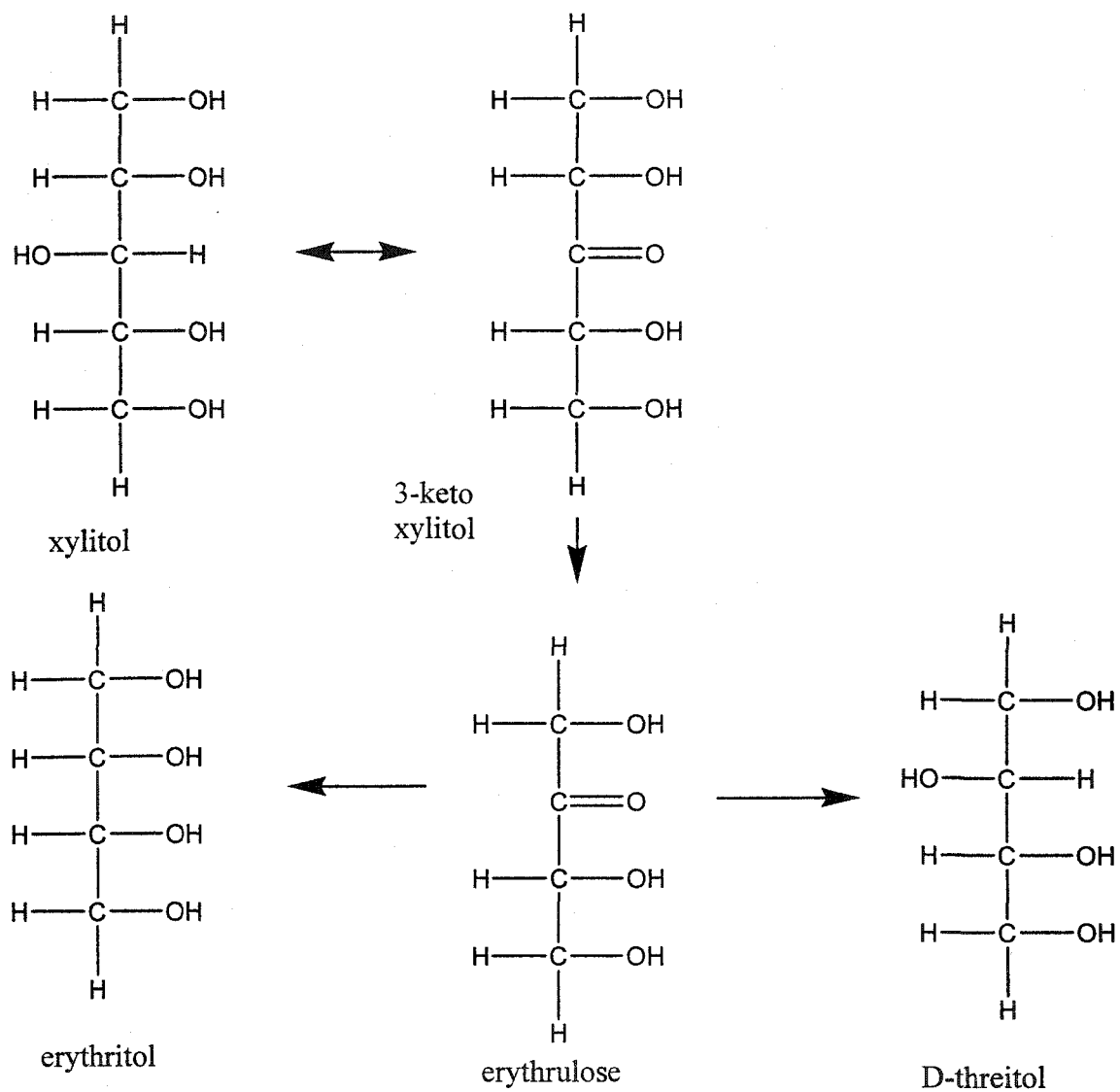


Figure 5.3: Production of Tetritols from Xylitol via Retro-Aldol Mechanism

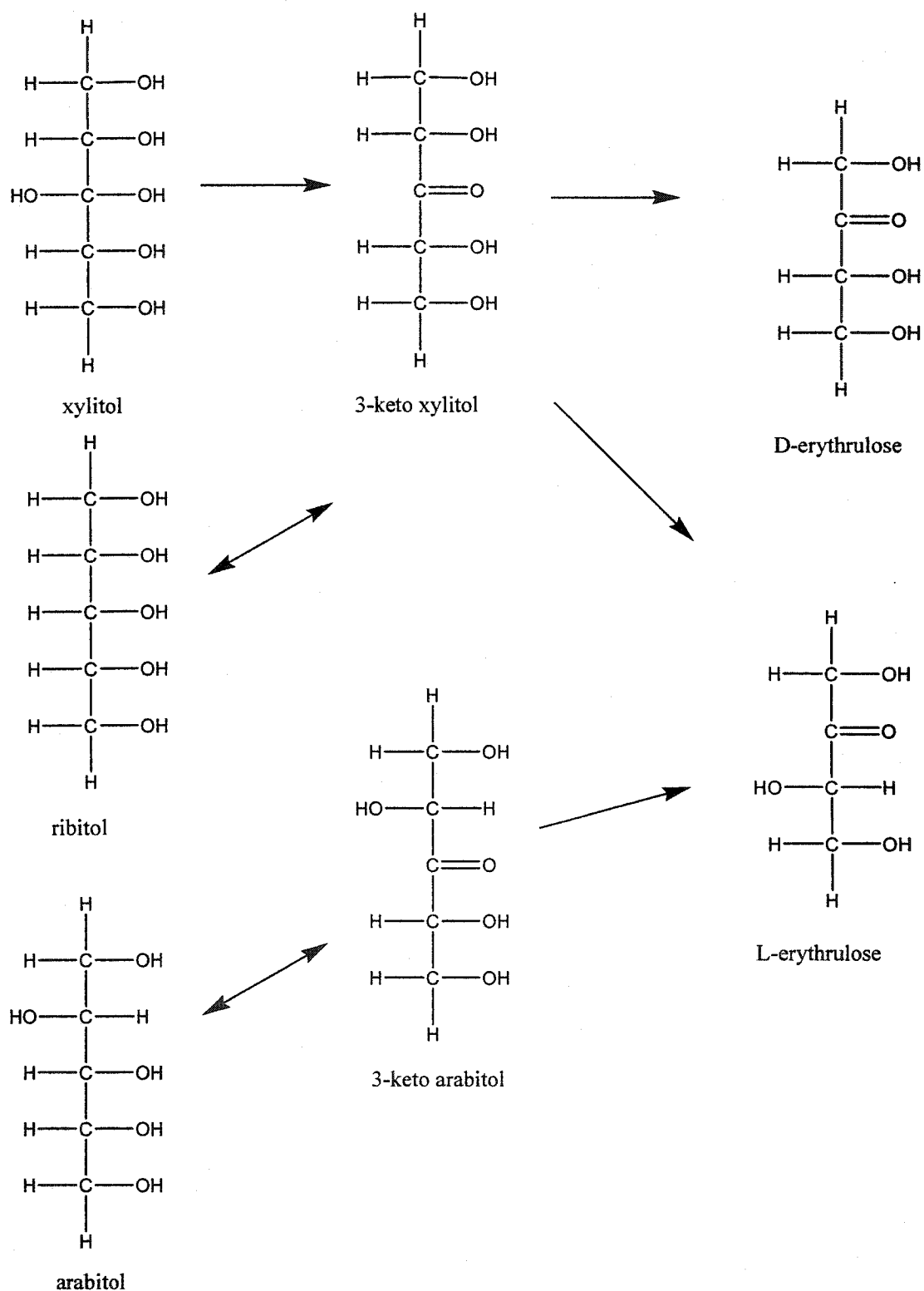


Figure 5.4: Common Intermediates in the Production of Tetrulose from Pentitols

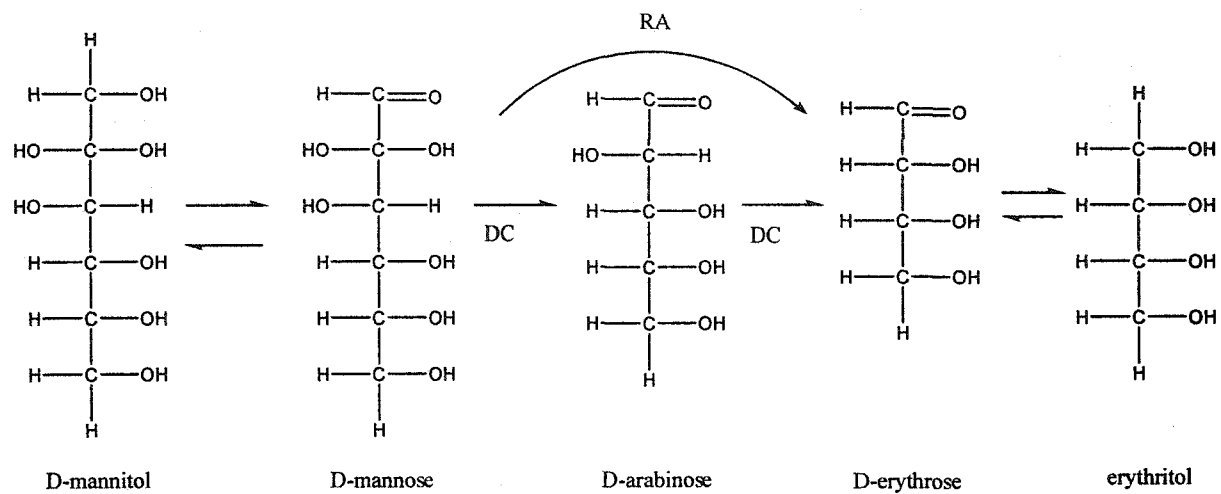


Figure 5.5: Two Possible Routes from Mannitol to Erythritol

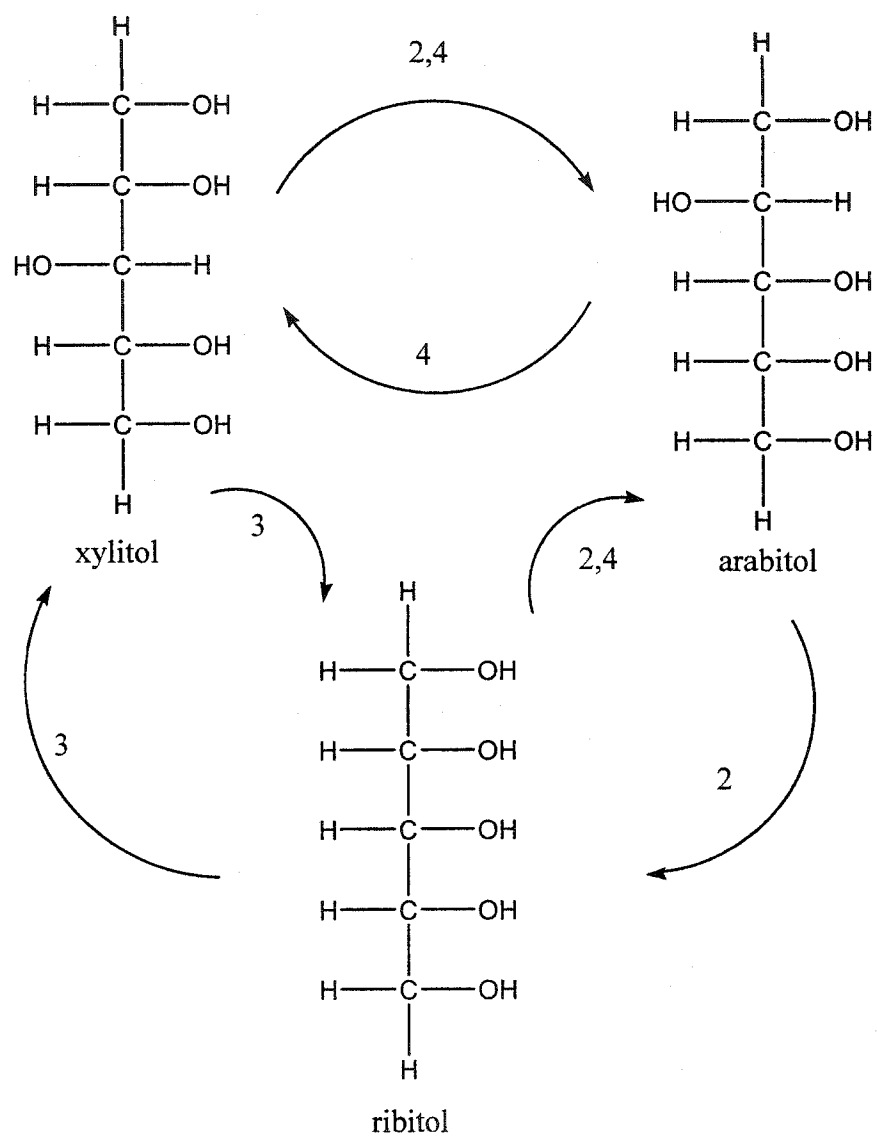


Figure 5.6: The Three Tetritols and Their Epimer Relationships

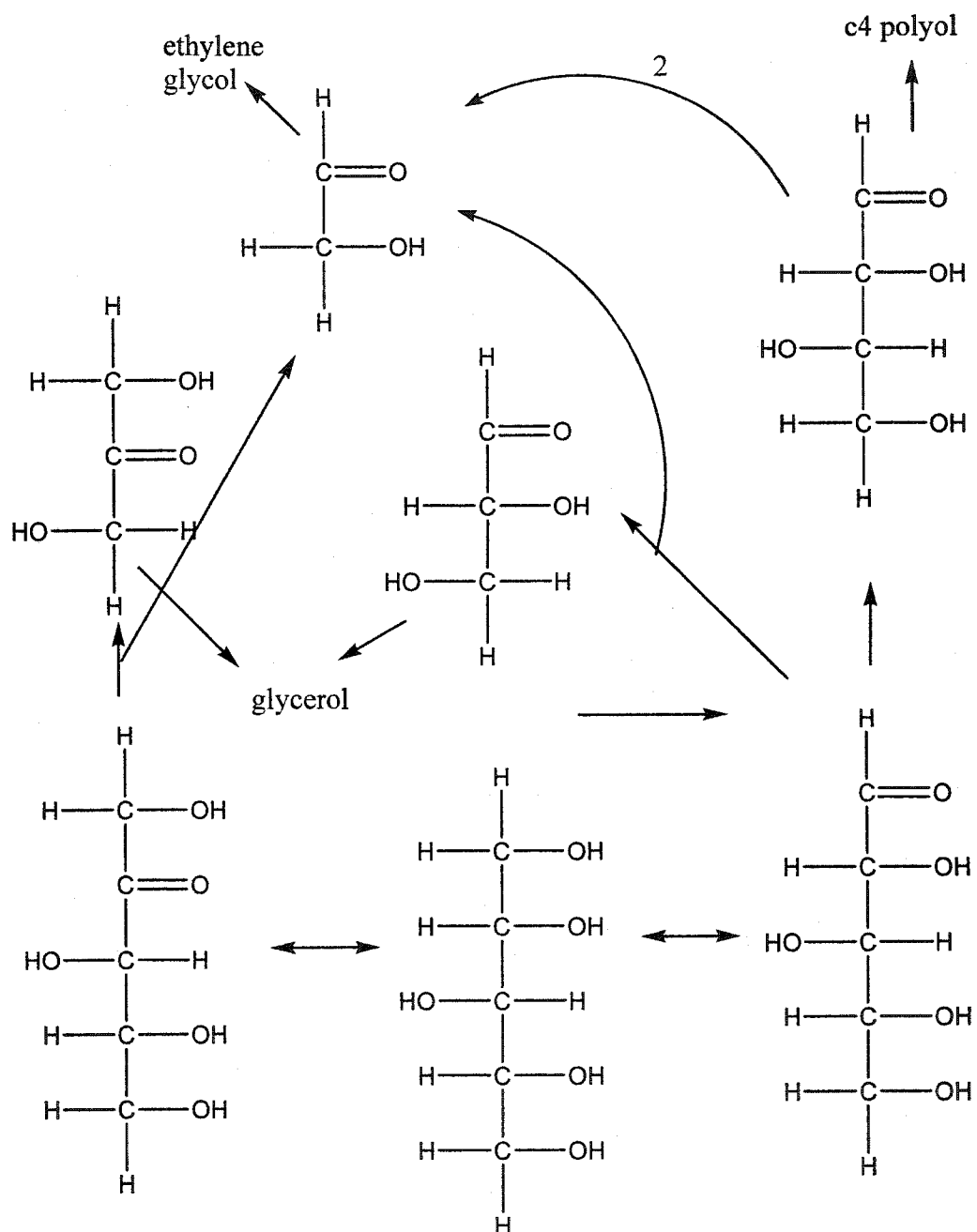


Figure 5.7: Potential Products and Pathways in Xylitol Hydrogenolysis Reaction

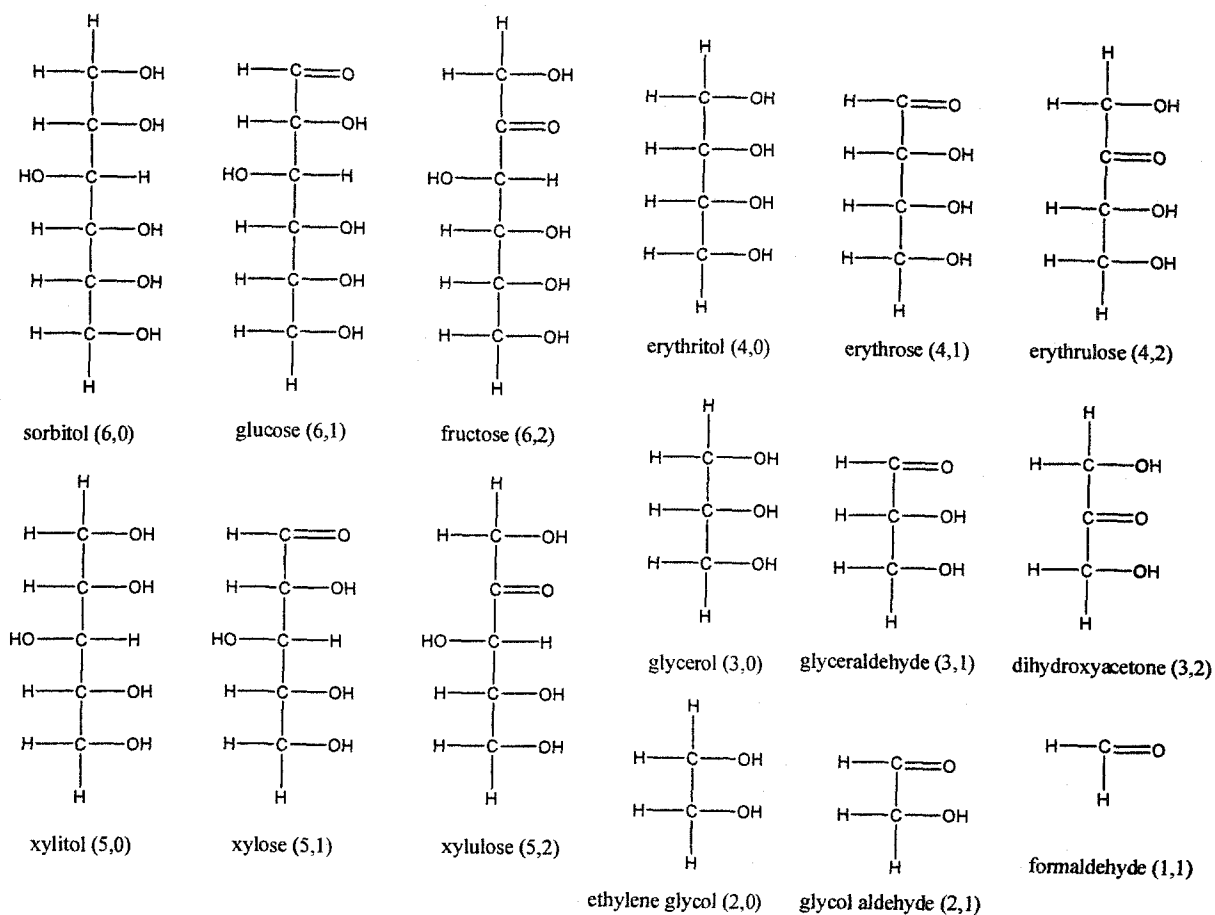


Figure 5.8: Compounds in the Flux Map with Nomenclature

60 \leftrightarrow 61
60 \leftrightarrow 62
60 \leftrightarrow 60 e
61 \rightarrow 51+11
61 \rightarrow 41+21
62 \rightarrow 31+32
50 \leftrightarrow 51
50 \leftrightarrow 52
50 \leftrightarrow 50 e
51 \rightarrow 41+11
51 \rightarrow 31+21
52 \rightarrow 32+21
40 \leftrightarrow 41
40 \leftrightarrow 42
40 \leftrightarrow 40 e
41 \rightarrow 31+11
41 \rightarrow 21+21
42 \rightarrow 31+11
30 \leftrightarrow 31
30 \leftrightarrow 32
31 \rightarrow 21+11
20 \leftrightarrow 21
21 \rightarrow 11+11

Figure 5.9: Reactions Modeled in Flux Map

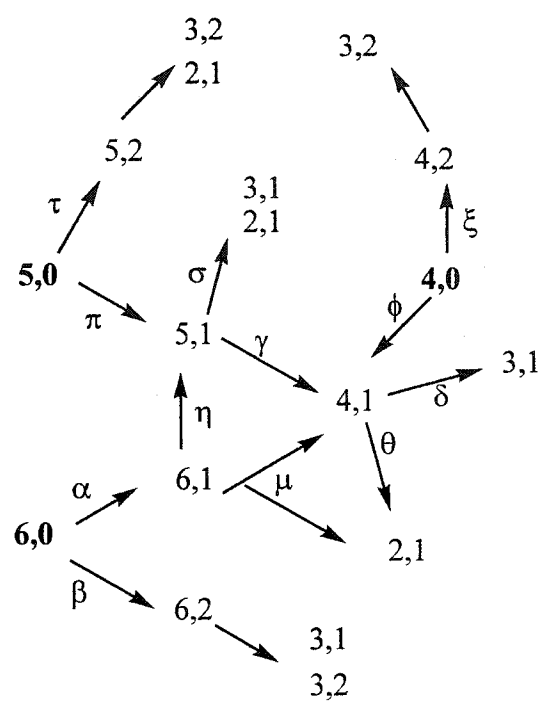


Figure 5.10: Flux Map of Higher Polyol Hydrogenolysis

Temp/(S/Ru)	original polyol length		
	6	5	4
205/0	0.44	0.46	0.52
205/1	0.20	0.15	0.25
240/0	0.44	0.37	0.59
240/1	0.21	0.07	0.32

Dehydrogenation fraction which occurs
on the primary hydroxyl group

Table 5.2: Dehydrogenation Fraction on Primary Alcohol Group

CHAPTER 6

General Conclusions and Future Work

6.1 General Conclusions

A mathematical model describing the glycerol to glycols reaction was developed that incorporates competitive adsorption of all three compounds, accounts for pH effects on the reaction rates, and predicts the instantaneous selectivity toward both glycols. The reaction rates of all three compounds increased with pH. The instantaneous selectivity to propylene glycol did not change with pH, unlike the selectivity to ethylene glycol. Propylene glycol had lower affinity for active sites on the metal catalyst compared to glycerol and ethylene glycol, which competed relatively equally for sites.

This model was then advanced to include effects of temperature and sulfur. The relative reaction rates of the three compounds when competing for active site does not change with temperature because the controlling feature is the adsorption potential of each compound and not the relative reaction rates. Sulfur affects the apparent activation energy of the glycerol reaction; thus, there is more than dehydrogenation occurring while glycerol is adsorbed. The selectivity toward propylene glycol increases with sulfur loading due to a catalytic dehydration reaction. Sulfur selectively blocks the process leading to reaction in the liquid phase, most of which is degradation, allowing the catalytic reaction to proceed. Also, the catalytic dehydration reaction is the cause of most propylene glycol produced as opposed to the liquid phase dehydration.

The hydrogenolysis rates of a variety of polyols have been found and correlated to the configuration of the polyol. Polyols with alcohol groups on the same side in the Hayworth projection have the highest reaction rates. The decarboxylation reaction is shown to be significant in explaining the product distribution of higher polyols. A selectivity map was used to analyze the products and predict the relative dehydrogenation rates of the different alcohol groups on higher polyols. The addition of sulfur lowered the dehydrogenation selectivity of the primary alcohol group.

6.2 Future Work

The use of glycerol in the earlier studies has a second advantage. Along with being used as a foundation for higher polyols, glycerol itself can be used to a raw material in the production of the glycols. While pure glycerol is more valuable than the glycols, impure glycerol could be used. In the production of biodiesel, crude glycerol is produced. This stream is up to 85% glycerol while the rest is mostly water with some methanol, basic catalyst, and other impurities. These impurities are found in the raw material in biodiesel production, which range from soybean oil to beef tallow. Even if all these impurities were removed, the purification of glycerol is energy intensive. If the crude glycerol instead was converted into propylene glycol and ethylene glycol, a pre-diluted antifreeze is produced. This bioantifreeze would increase the value of the biodiesel products, increasing the demand for renewable resources.

While the selectivity map can be used to predict the relative dehydrogenation rates, a second method to make this prediction is with proton NMR. Proton NMR can be used to

measure dehydrogenation of hydroxyl groups due to the deuteration of these hydroxyl groups. The reactions are run in the same manner, except under deuterium pressure and in deuterium oxide. Since the previous reactions are run under hydrogen pressure, ruthenium, due to the strong equilibrium toward rehydrogenation, will reduce any aldehyde produced with hydrogen obtained from the gas phase. When reactions are run with deuterium, the hydrogen removed is replaced with deuterium. By determining the number of hydrogen atoms lost in each alcohol position, a measurement of the relative production rates of specific dehydrogenated species is found. The selectivity map can also be determined for other catalysts, which can help in designing catalysts for this system.

There are a number of molecules that can also give insight into the hydrogenolysis of polyols. There include pentaerythritol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol and other unsaturated polyols. Pentaerythritol consists of a carbon with four $\text{-CH}_2\text{OH}$ groups attached. This molecule according to Hawley would not dehydrate because there are no α -hydrogen atoms relative to a dehydrogenated hydroxyl group. For the same reason, this molecule could not enter a decarboxylation cascade, but could only react via a retro-aldol scission and could be used to study the effects of sulfur on the retro-aldol reaction rate. The remaining molecules are simpler than saturated polyols because of the fewer active sites. By analyzing these simpler molecules insights in the hydrogenolysis reaction can be determined.