

2003

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## 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 glycol 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

catalysts, ethylene glycol, propylene glycol, hydrolysis, kinetics

## Disciplines

Chemical Engineering

## Comments

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

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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 glycol 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.

## Introduction

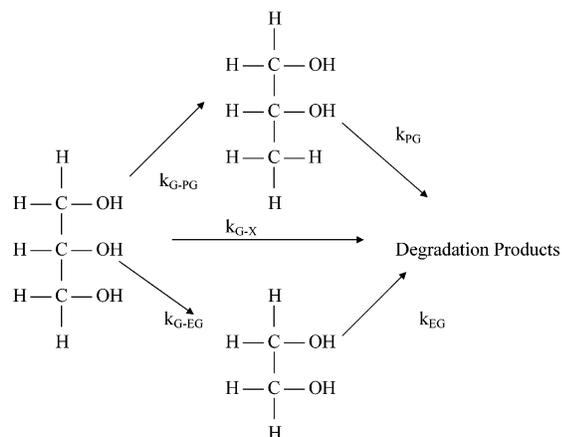
The catalytic production of ethylene glycol and propylene glycol from higher polyols such as sorbitol and xylitol has been studied over the past decades.<sup>1–7</sup> The goal of this research was largely to optimize empirically the production of glycerol, ethylene glycol, and propylene glycol. The highest selectivities reported for the reaction of sorbitol with ethylene glycol and propylene glycol are approximately 65%, which is not high enough to be commercially viable.<sup>1–5</sup> Past work has focused on catalyst modifications, types of base cocatalyst, 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 the pH value, has been discussed.<sup>7,8</sup> In addition, a mechanistic understanding 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.<sup>9</sup> However, other than the reaction of sorbitol, all other steps are modeled as elementary first-order noncatalytic 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.<sup>10</sup> 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, is affected by base catalysis and goes through a number of intermediates. The product(s) of either mechanism contain(s) two olefinic bonds, which are subsequently hydrogenated by the metal catalyst. The metal catalyst is both a hydrogenating and a 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 and 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.

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**Figure 1.** Schematic of the modeled reaction pathways.

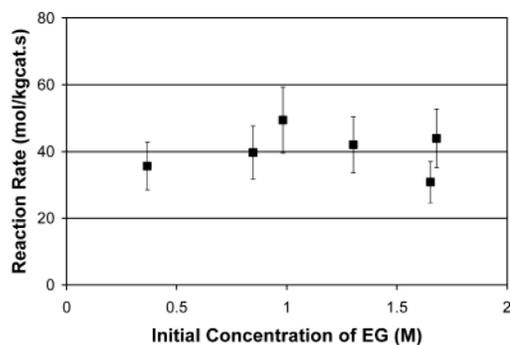
The goal of this work was to develop a mechanistic model for the glycerol reaction portion of the hydrogenolysis process to ultimately help maximize yields to the desired glycols. A schematic of the model framework is shown in Figure 1. Discussions of the pH and competitive adsorption effects on this reaction system are included. The model presented here discusses the production of ethylene glycol and propylene glycol from glycerol.

## Experimental Section

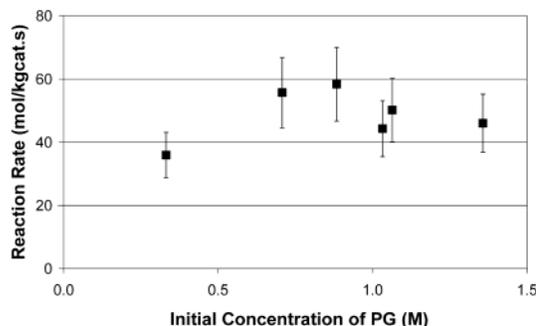
Glycerol, ethylene glycol, and 1,2-propylene glycol (all 99%+) were purchased from Acros Organics and diluted with deionized water for these experiments. Hydrogen (99.992% purity) as well as two bases, calcium oxide (96%) and calcium carbonate (99%), both of which came from Acros Organics, was used.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

All reactions were performed in a 100-mL 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 0.4 M CaO held the pH at 11.7, while CaCO<sub>3</sub> held the pH near 8.0. Measurements of each sample taken throughout the reaction showed that the 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 of H<sub>2</sub> and heated to the 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-min intervals for 75 min. 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<sup>2+</sup> cation-exchange column from Hamilton with a refractive index



**Figure 2.** Ethylene glycol reaction rate as a function of the initial ethylene glycol concentration.



**Figure 3.** Propylene glycol reaction rate as a function of the initial propylene glycol concentration.

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 to 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 the 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 and 3 are the degradation rates for the ethylene glycol and propylene glycol, respectively, as a function of the initial concentration of the glycol. Because the reaction rate was independent of the 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 and 50 mol/(kg of catalyst)·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

**Table 1. Competitive Adsorption between Ethylene Glycol and Propylene Glycol**

reaction no.	ethylene glycol (wt %)	propylene glycol (wt %)	fractional turnover for EG	fractional turnover for 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

glycol were introduced to the reactor at varying weight ratios from 1:3 to 3:1. The same temperature, pressure, and catalyst amount as those in the pure-component degradation experiments were used. The degradation rate was subsequently determined from the slope of the concentration versus time plot. Because 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 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 the catalyst in the reaction system. The total turnover of each reaction from Table 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 1, the fractional turnover for ethylene glycol was significantly higher than that for 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 because these calculations did not include the degradation of glycols.

Previous work has indicated that either polyol will adsorb to ruthenium through oxygen.<sup>11</sup> Therefore, one could speculate that the presence of the nonoxygenated 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.

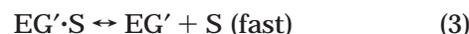
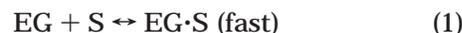
The catalytic degradation of the glycols may proceed through the conversion of a hydroxyl group into a ketyl or aldehyde group, depending on if an interior or exterior oxygen is dehydrogenated, as has been implicated in the production of glycols via hydrogenolysis.<sup>5,10</sup> The electron density 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

**Table 2. Regression Results for the Glycol Degradation Equations**

	high pH	low pH
$K_{EG}$ [L/min·(kg of catalyst)]	6300	3700
$K_{PG}$ [L/min·(kg of catalyst)]	1800	750
$k_{EG}$ (L/mol)	21	21
$k_{PG}$ (L/mol)	4.0	4.0
$R^2$	0.84	0.82

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.<sup>10</sup> Other reaction pathways are also likely to be pH dependent. 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 high-performance liquid chromatograph. In addition, the initial concentration of glycol did not affect the degradation rate. These two facts lead to the conclusion that eq 2 represents the limiting step. Furthermore, because 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

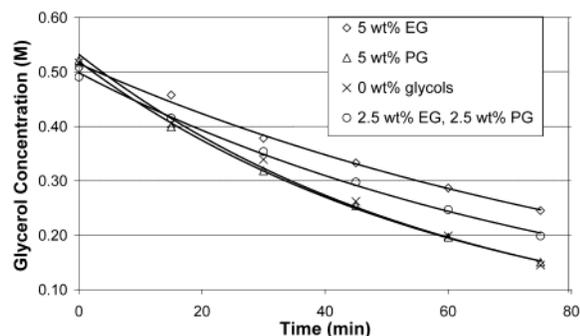


where EG is ethylene glycol, S is the catalytic site, EG' is the aldehyde formed by dehydrogenation of ethylene glycol, and X represents the degradation products. The degradation products were not measured or identified. However, these species do not affect the mechanism because the limiting step occurs prior to production 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 eq 5, where  $r_{iG}$  is the degradation rate for the glycol ( $i$

$$-r_{iG} = \frac{K_{iG}(iG)}{K_{EG}EG + K_{PG}PG + 1} \quad (5)$$

= E for ethylene glycol and P for propylene glycol),  $K_{iG}$  is the degradation rate constant,  $iG$  is the respective concentrations of the glycols, and  $k_{EG}$  and  $k_{PG}$  are the respective adsorption constants for the glycols. The constants found in eq 5 were obtained by a regression fit to the degradation data. Shown in Table 2 are the values for the rate constants determined from fitting the model given in eq 5 to degradation data at each pH



**Figure 4.** Glycerol reaction as a function of the glycol concentration.

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 eqs 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 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 a 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.

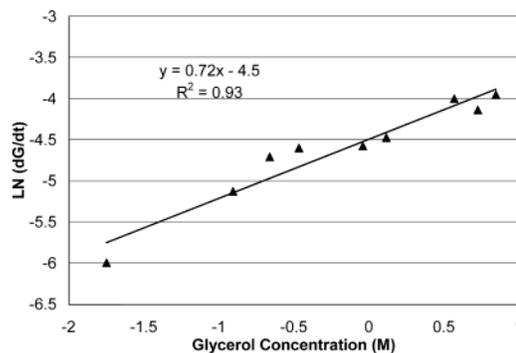
The reaction pathway was assumed to be similar for glycerol to that used for the glycols above, in which the glycerol was first dehydrogenated to an aldehyde or ketone. In this case, the oxidized species can react via a C–C or C–O cleavage from the retro-aldol or dehydration reaction, respectively, which would be expected to be pH dependent. The pH-dependent 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 were 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 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.

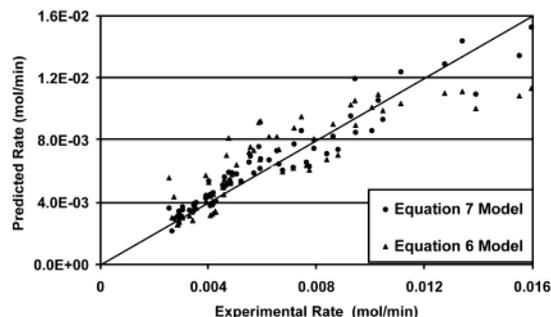
The glycerol reaction data were first fit by regression analysis to the model given by eq 6, where  $r_G$  is the

$$-r_G = \frac{K_{iG}G}{k_G G + k_{EG}EG + k_{PG}PG + 1} \quad (6)$$

glycerol reaction rate for the glycol,  $K_{iG}$  is the glycerol reaction rate constant, and  $k_G$  is the adsorption constant



**Figure 5.** Determination of the reaction order for the glycerol reaction.



**Figure 6.** Comparisons of the parity plots for eqs 6 and 7.

**Table 3. Regression Results for the Glycerol Rate Constants at High pH Conditions**

reaction order	$k_G$ (L/mol)	$K'_{iG}$ [ $L^{3/2}/min \cdot (kg \text{ of catalyst}) \cdot mol^{1/2}$ ]	$R^2$
1	11	0.15	0.86
1.5	50	0.57	0.88

for glycerol. The values used for  $k_{EG}$  and  $k_{PG}$  in the analysis were those given in Table 2 from the ethylene glycol 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  $R^2$  value of the resulting model. Using eq 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  $K'_{iG}$  with a 92% certainty that the value was significant compared to zero. Because 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  $K'_{iG}$  and  $k_G$  estimation. The resulting equation

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

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, eq 7 was consistent with the reaction order found from the initial rate data for glycerol conversion. The values of the model constants,  $K'_{iG}$  and  $k_G$ , as determined from regression analysis of the glycerol reaction data are given in Table 3 for the eqs 6 and 7 glycerol models. Shown in Figure 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 eq 6 gives clear curvature in the

**Table 4. Kinetic Constants Determined by Regression for the Glycerol and Glycol Reactions**

base used	$k_G$ (L/mol)	$k_{EG}$ (L/mol)	$k_{PG}$ (L/mol)	$s_{EG}$	$s_{PG}$	$K_G$ [L <sup>3/2</sup> /min·(kg of catalyst)·mol <sup>1/2</sup> ]	$K_{EG}$ [L/min·(kg of catalyst)]	$K_{PG}$ [L/min·(kg of catalyst)]	$R^2$
CaO	50	22	4.0	0.09	0.19	39000	6700	1800	0.89
CaCO <sub>3</sub>	50	22	4.0	0.26	0.19	7400	4600	800	0.77

parity plot at the higher reaction rates. In contrast, the eq 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 a form similar to eq 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 eq 8, where the  $iG$

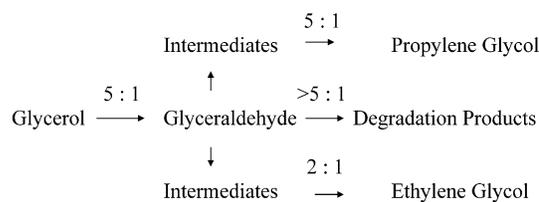
$$-r_{iG} = \frac{k_{iG}iG - s_{iG}K_G G^{1.5}}{k_G G + k_{EG}EG + k_{PG}PG + 1} \quad (8)$$

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. Because 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 1.

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 effects of pH on the 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 as well as the resulting  $R^2$  value between the model and experimental data are given in Table 4.

## 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 because of its high reactivity. The intermediate can be rehydrogenated or passed through a reaction cascade to form multiple molecules (e.g., ethylene glycol, propylene glycol, etc.). Because of the inability to measure the intermediate species concentration, the

**Figure 7.** Flux maps showing the dependence of the reaction rates on the pH.

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 because 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 to be 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  $4 \times 10^{-6}$  M. The saturated hydrogen concentration in the aqueous bulk phase has been determined at lower pressures.<sup>13</sup> 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, 4 orders or magnitude higher than that of 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.<sup>12,13</sup>

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 the 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 5 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, because of 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.<sup>12</sup> 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 because 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 will 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 the 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.

## Acknowledgment

This work was financially supported by the Iowa Energy Center and the USDA through the Iowa Biotechnology Byproducts Consortium. The catalyst was provided by Activated Metals & Chemicals, Inc.

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Received for review June 2, 2003

Revised manuscript received August 21, 2003

Accepted August 25, 2003

IE030468L