



*Dedicated to Professor Valer Farcasan
on the occasion of his 95th anniversary*

MECHANISTIC INVESTIGATION OF GLYCEROL HYDROGENOLYSIS

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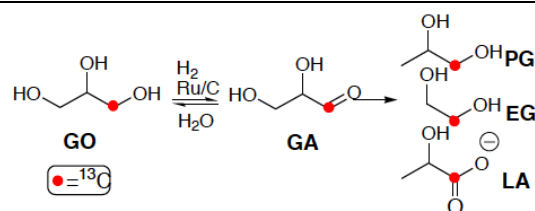
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Mechanistic pathways for catalytic hydrogenolysis of glycerol to propylene glycol, ethylene glycol, and lactic acid over supported metal catalyst are proposed and substantiated by conversion studies, isotopic labeling, reaction studies of proposed intermediates, and computational molecular modeling. Contrary to the naïve expectation of hydrogenolysis as the simple replacement of –OH by –H, the first step of reaction is the dehydrogenation of glycerol to glyceraldehyde. This aldotriose then reacts further via one of two paths: (1) retroaldol cleavage to the enediol of hydroxyacetaldehyde, which, with or without tautomerization, is reduced to ethylene glycol, or (2) keto-enol tautomerization to the enediol, which then dehydrates and tautomerizes to pyruvaldehyde. Subsequent hydrogenation or water addition and rearrangement leads to propylene glycol or lactic acid, respectively. The presence of base promotes both pathways but favors enolization and dehydration of the glyceraldehyde, which leads to propylene glycol and lactate formation.



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INTRODUCTION

Increasing interest in bio-based chemicals, particularly regarding conversion of carbohydrate monomers into valuable commodities,¹ has directed our attention to the hydrogenolysis of glycerol (**GO**). A commercial product itself, **GO** can be catalytically converted to propylene glycol (**PG**), ethylene glycol (**EG**), and lactic acid (**LA**), all major commodity chemicals, in the aqueous phase at relatively mild conditions. As the market expands for fat- and oil-based products, especially biodiesel, an

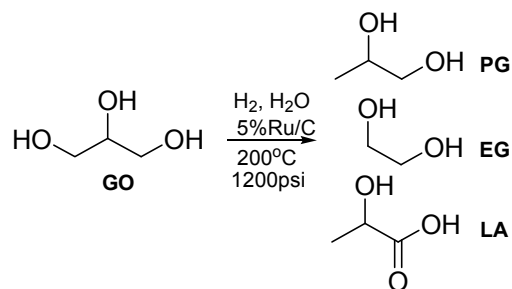
opportunity has emerged to exploit the nontoxic polyfunctional **GO** byproduct as a low cost feedstock.

Our goal is to gain understanding of the individual reaction pathways in Scheme 1 in order to enable practice of the more desirable **GO** conversion to the C3 products **PG** and **LA**. Additionally, we study glycerol to develop a general mechanistic understanding of polyol hydrogenolysis reaction path under heterogeneous catalytic conditions in water. With its three hydroxyl groups and two kinds of carbon centers, **GO** is a model compound for

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studying competitions between C-O and C-C bond cleavage and between primary and secondary HC-OH to C=O dehydrogenation, suggested as the first step in polyol hydrogenolysis.² Understanding and controlling these site preferences is critical to development of selective hydrogenolysis processes for larger bio-derived sugars or polyols such as sorbitol and xylitol.

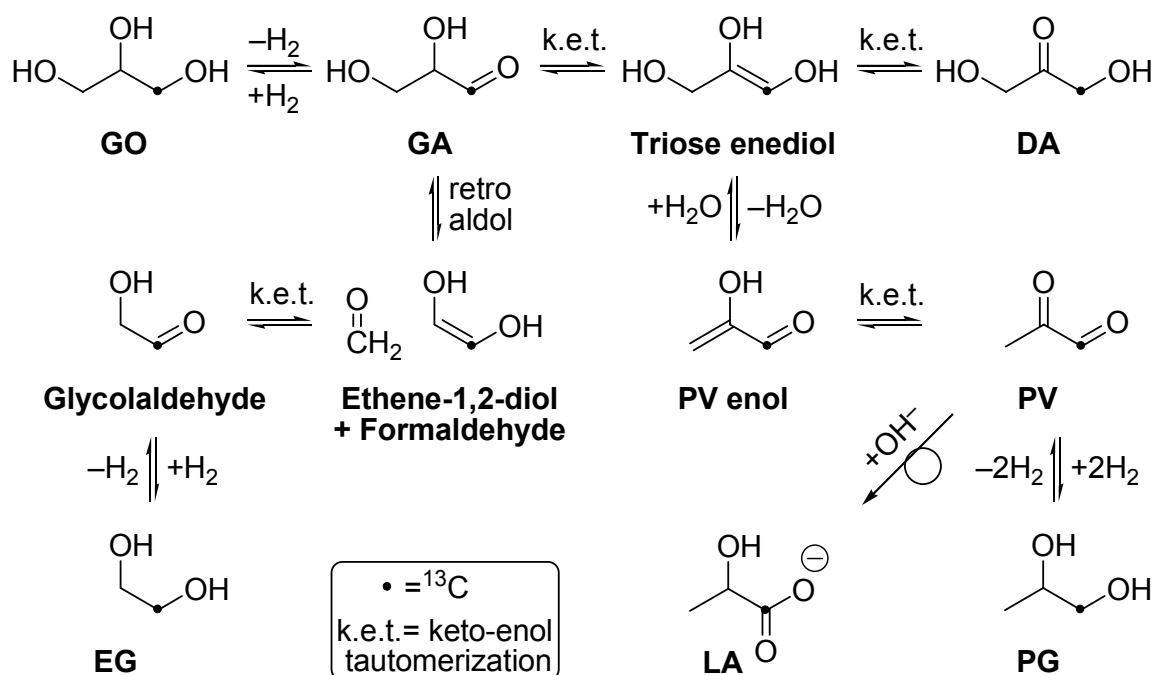
In this report we examine hydrogenolysis of **GO** over carbon-supported ruthenium catalysts at different reaction conditions, using HPLC and GC-MS to monitor catalyst activity and selectivity to the products presented in Scheme 1. The reaction mechanism is probed via deuterium labeling coupled with ¹³C-NMR spectroscopy, focusing on **GO** and its unsaturated congeners glyceraldehyde (**GA**), dihydroxyacetone (**DA**), and pyruvaldehyde (**PA**). We apply these tools here to characterize the reactivity of **GO**, but with the broader intent to extend their use to a range of hydrogenolysis reactions in water. The detailed labeling, thermochemical, and spectroscopic analysis of reaction paths and proposed reaction intermediates described herein complement a recent elegant kinetic study of this reaction presented by Shanks (ref 2).



Scheme 1 – Glycerol (**GO**) Hydrogenolysis.

MATERIALS AND PROCEDURES

Reactions were run in a Parr stirred autoclave (Model 4561) at 1200 psi (8.3 Mpa) H₂ or D₂ and 150–230 °C for 4 to 6 hours. One gram of the catalyst, 5 wt% Ru metal on activated carbon support,³ was first introduced into the reactor and reduced at 150 °C for two hours under 200 psi (1.4 Mpa) H₂ or D₂. A 100 g charge of feed solution (0.5 to 1.6 M substrate in water or deuterated water) was then added to the reactor, with initial pH adjusted if desired via base (KOH) or acid (H₃PO₄) addition. Once the reaction temperature was reached, samples were taken at selected times and analyzed via HPLC, GC-MS, and ¹³C- and ¹H-NMR. Quantitative evaluation of feed conversion and product yields included in Table 1 were based on HPLC⁴ analyses after 4 h reaction time at 200 °C and 1200 psi H₂.



Scheme 2 – Proposed sequence of steps for **GO** hydrogenolysis to **EG**, **PG** and **LA**.

Table 1
Summary of Reaction Conversions and Yields

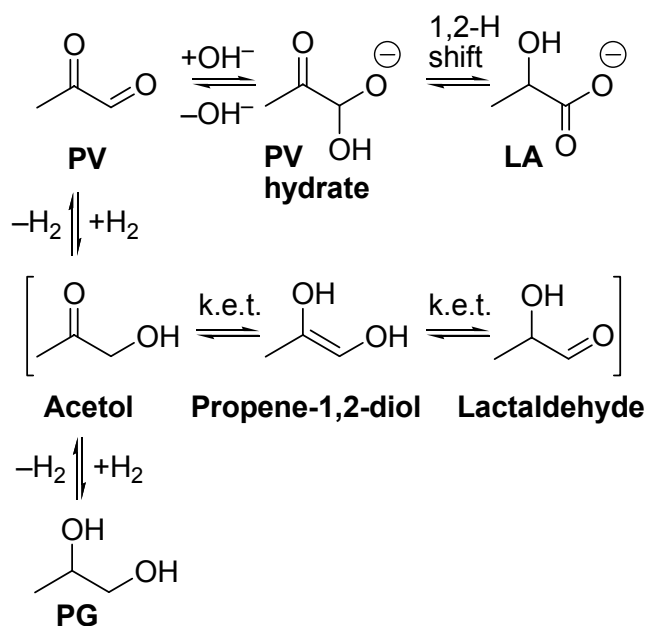
| Feed (M) | Conversion (%) | Product yield* (mol/mol feed) | | | | | | | |
|--|----------------|-------------------------------|--------|-------|-------|-------|--------|--------|--------|
| | | GO | 1,2-PG | EG | LA | GA | 1,3-PG | Acetol | Unacc. |
| GO (1.08M) + KOH (0.26 M) | 76 | - | 0.28 | 0.18 | 0.15 | 0.005 | 0 | 0 | 0.15 |
| GO (1.58M) | 49 | - | 0.08 | 0.06 | 0 | 0.06 | 0 | 0 | 0.29 |
| GO (1.63M) + H ₃ PO ₄ (0.002M) | 59 | - | 0.04 | 0.13 | 0.004 | 0.006 | 0.01 | 0 | 0.40 |
| GA (0.54M) + KOH (0.27M) | 98 | 0.14 | 0.52 | 0.21 | 0.12 | - | 0 | 0 | <0.02 |
| GA (0.54M) | 97 | 0.56 | 0.03 | 0.012 | 0 | - | 0 | 0 | 0.36 |
| DA (1.66M) + KOH (0.26M) | 100 | | 0.32 | 0.03 | 0.20 | 0 | 0 | 0 | 0.44 |
| | | 0.005 | | | | | | | |
| DA (0.56M) | 50 | 0.22 | 0.06 | 0.16 | 0 | 0 | 0 | 0 | 0.06 |
| PV (1.94M) | 100 | 0.08 | 0.13 | 0.02 | 0.18 | 0 | 0 | 0.06 | 0.53 |

* all values listed are HPLC determined, after 4h at 1200 psi H₂ and 200°C, with 1g Ru/C catalyst.

The extent of deuterium incorporation into unconverted **GO** and in products was determined via ¹³C-NMR and GC-MS.⁵ The use of ¹H- or ²H-NMR for quantitative analysis is encumbered by the overlap of ¹H signals corresponding to the three symmetry distinct H-C bonds and the broadening of signals via splitting by the deuterium atoms. In contrast, ¹³C-NMR analysis can take advantage of isotope shifts and peak splitting when D replaces H in H-C bonds.⁶ In order to compare the extent of deuterium incorporation in the starting material and the product, relaxation times for deuterium- and protium-bearing carbons were measured on a 500 MHz Varian NMR spectrometer using D-labeled **GO** and **PG**. Use of the longest relaxation time found (that for the fully-deuterated compounds) allowed quantitative analysis of product solutions via ¹³C NMR peak integration. This method was calibrated using different

concentrations of perdeuterated **GO** in unlabeled **GO** as standards.

Thermodynamic evaluation of the proposed mechanisms was performed using experimental and calculated heats of formation. For the species where no experimental data are available, heats of formation were calculated using the G3 composite ab initio method⁷ as implemented in the Gaussian 98 code.⁸ A 32-processor SGI Origin 3400 supercomputer was employed for all the calculations. The energetic consequences of solvation in water were approximated by using the Polarized Continuum Model (CPCM), calculated at the B3LYP/6-311+G(d,p)//MP2/6-31G* level.⁹ Although such continuum treatments are known to be imperfect for hydrogen bonding solvents and solutes, our intent in the solvation calculations was primarily to look for significant medium-induced shifts in the reaction thermochemistry.



Scheme 3 – Detailed conversion of PV into PG and LA.

RESULTS AND DISCUSSION

Hydrogenolysis of **GO** produces **PG**, **EG** and **LA** in varying quantities depending on the initial pH of the solution mixture (Table 1). Control experiments show that both catalyst and hydrogen are required for conversion to proceed at any pH. Conversion of **GO** and selectivity toward **PG** is generally higher when base is added.² However, the presence of base also leads to more lactic acid, as lactate, which is unreactive to further hydrogenolysis.¹⁰ In neutral or acidic conditions, only a small quantity of lactic acid is detected in the reaction mixture, as expected from our work on lactic acid hydrogenation to **PG**.¹⁰ With H_3PO_4 added, **EG** becomes the dominant product, and traces of 1,3-propanediol are also detected via HPLC. Though the latter product is of interest, control experiments have shown that it breaks down rapidly under the typical hydrogenation conditions and is thus not practically accessible from **GO**, under the conditions used here. At temperatures as low as 150 °C, under neutral conditions, the formation of a small amount (~2-6% of initial **GO**) of glyceraldehyde, **GA**, is observed.

The pattern of deuterium incorporation into **GO** and products as well as studies with ^{13}C labeled **GA** suggests a sequence of steps through which **GO** is hydrogenolyzed to **PG**, **EG** and **LA**, as shown in Schemes 2 and 3. A detailed thermodynamic of this hydrogenation/ hydrogenolysis pathway is presented in Table 2 and Scheme 4. Overall, it shows that formation of **LA** and **PG** is substantially exothermic, while **EG** formation via retro aldol condensation is endothermic. The remainder of this section describes experiments and computations to evaluate the proposed mechanistic sequence of steps.

Noting similar processes in related catalytic systems,¹¹ we have observed that H/D scrambling occurs between D_2O and H_2 gas in the presence of our Ru/C catalyst starting at temperatures as low as 35°C. Complete scrambling is achieved within 3 hr at 50°C and at shorter times at higher temperatures.¹² Cross experiments with H_2O - D_2 gave similar results; no exchange was observed without catalyst present. While this exchange prevents differentiation between the roles of H_2 and H_2O as sources of H in reaction products, it conveniently enables the use of D_2O with H_2 as the labeling mixture. It also reveals the fact that the catalyst is activating both H_2 and H_2O ; we have explored this process in some detail, and will present these results in a later publication.

In $\text{D}_2/\text{D}_2\text{O}$, H/D exchange in **GO** begins at 150 °C at the terminal carbons (C1 and C3). Thus **GO** conversion appears to start with reversible dehydrogenation to form **GA**, its aldehyde congener.¹³ At higher temperature (200 °C), H/D exchange is also observed at the secondary carbon.¹⁴ Besides the obvious direct dehydrogenation/hydrogenation path, deuterium incorporation at C2 might also arise via the enol of **GA**, commonly termed the triose enediol. This species is familiar as an intermediate in the base-catalyzed isomerization of **GA** to dihydroxyacetone (**DA**).¹⁵ Significantly, small quantities of **GA** but no **DA** are observed by HPLC in the reaction mixtures. Our calculated energetics and available literature agree on an estimated $K = [\text{DA}]/[\text{GA}] = 7\text{-}10$, with **DA** thermodynamically more stable than **GA** (Table 2, Scheme 4); observable quantities of **DA** should thus be present if it were in tautomeric equilibrium with **GA**.^{16,17,18} Evidently this equilibration is not achieved; rather, dehydrogenation of **GO**'s primary CH_2OH sites and rehydrogenation of the $\text{C}=\text{O}$ bond in **GA** are both faster than tautomerization, making small quantities of **GA** available for chemistry that leads to product formation. Meanwhile, the absence of **DA** and of D-incorporation only at C2 in **GO** suggest that direct C2 dehydrogenation/rehydrogenation is not significant in the **GO** hydrogenolysis studied here.

To further explore its role as the first intermediate in **GO** hydrogenolysis, **GA** was used as feed in reactions run with and without base added. Without base, **GA** is hydrogenated mainly to **GO**, with **PG** and **EG** formed in the same ratio as found from **GO** fed without base (Table 1). With base added, **GA** is transformed primarily into **PG** and **LA** along with a smaller quantity of **EG** (Table 1). Also, small amounts of pyruvaldehyde (**PV**) are identified among the products. Thus base favors conversion to desired three-carbon products, at the expense of **EG** while promoting formation of **LA** as lactate anion, a species for which hydrogenation is distinctly contrathermodynamic (Table 2). We infer that base accelerates **GA** dehydration to form pyruvaldehyde enol, which then undergoes hydrogenation to produce **PG** or water addition and intramolecular rearrangement to form **LA** (see Schemes 2, 3). While dehydration of **GA** is thermoneutral both the subsequent hydrogenation and the hydration of the **PV** enol are highly exothermic, as seen from Scheme 4.

The claim that **GA** leads to **PG** via enolization, H_2O elimination, and subsequent hydrogenation

predicts that the CH₃ group in **PG** should arise from C3 in **GA** (Schemes 2 and 3), as easily tested by ¹³C isotopic labeling. With 1.1 M ¹³C=O labeled **GA** as feed at 200°C and 1200 psi H₂, the ¹³C label was found equally distributed between the two terminal carbons in the product **PG**. This finding confirms the notion that **GA** hydrogenation and subsequent desorption of **GO** from the catalyst are much faster than **GA** tautomerization; liberation of free ¹³C-OH labeled **GO** eliminates the identity of ¹³C label with the C=O of **GA**. To slow **GA** hydrogenation and thus enhance the effect of tautomerization, we reran the experiment with ¹³C-labeled **GA** at lower **GA** feed concentration (0.11 M), lower pressure (800 psig H₂) and lower temperature (150°C). The **PG** obtained under these conditions was 85% ¹³CH₂-OH labeled, confirming the postulated **PG** formation mechanism.

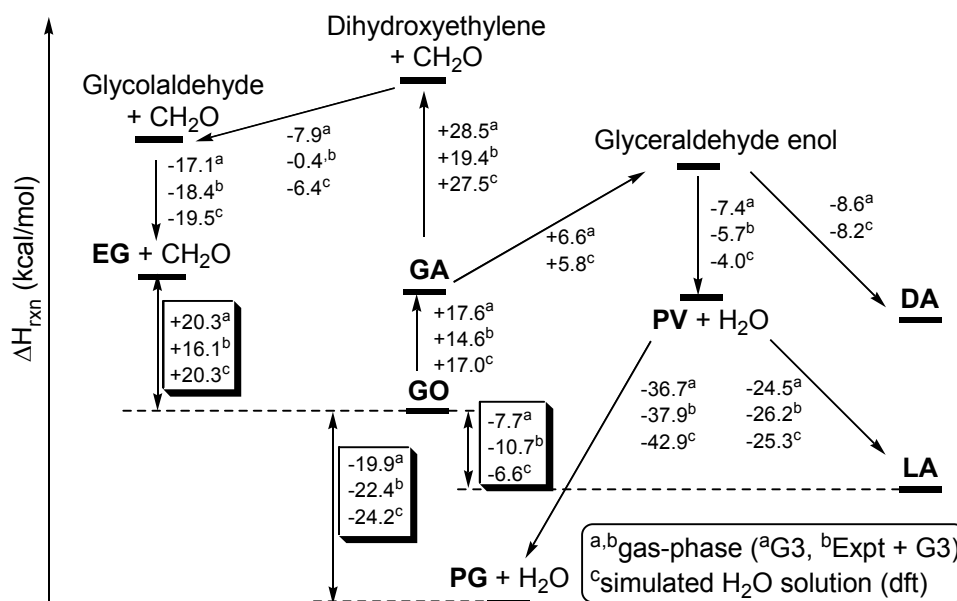
If ethylene glycol, **EG**, is produced via a retro-aldol cleavage of **GA** with formaldehyde as a byproduct, the **EG** formed from the ¹³C=O labeled **GA** should retain the ¹³C label (Scheme 2). The **PG**, **EG**, and **GO** from the lower concentration (0.11 M) **GA** feed were derivatized using an excess of acetic anhydride and pyridine and analyzed using GC-MS. The pronounced M+1 peak for the **EG** derivative confirm the presence of one ¹³C carbon atom in the majority of the **EG**, consistent with the starting compound **GA** reacting via the proposed retro aldol path to **EG**. Even though the retro aldol process is calculated to be 27.5 kcal/mol endothermic in solution (Scheme 4) the overall conversion of **GA** to **EG** is only 2.7 kcal/mol endothermic. The corresponding one-carbon byproducts formaldehyde or its hydrogenated congener, methanol, were not detected in the above-described mild conversion of ¹³C-labeled **GA**. Either adsorption and decomposition of CH₂O on the catalyst surface¹⁹ (similar to the decarbonylation process described in metal-catalyzed homogeneous systems²⁰) or rapid hydrogenation to methane may account for our failure to observe any of these C1 products.

In the **PG** obtained via **GO** hydrogenolysis, in D₂/D₂O at 200°C, all H sites are fully deuterated. Most strikingly, the methyl group is fully D substituted, presumably via both incorporation into the terminal positions of **GO** prior to reaction and rapid keto-enol tautomerization involving **PV**. Control experiments with **PG** as feed in D₂/D₂O at 150°C show complete D-incorporation in 2 hr at C1, partial exchange at C2, and negligible exchange at C3. However, at 200°C, all three C

sites in **PG** are fully deuterated, suggesting that the keto-enol tautomerization and resulting aldehyde-ketone isomerization become accessible with higher temperatures. Consistent with these ideas, dehydration of **GA** to **PV** is known to be only slightly faster than the dehydration of **DA** to **PV**, with the two corresponding rates being 1.9 x 10⁻¹ s⁻¹ and 1.7 x 10⁻¹ s⁻¹ at 300°C.¹⁵

To explore the keto-enol tautomerization of **GA** and its interconversion with **DA**, several reactions with **DA** as feed were performed. The dominant products of **DA** hydrogenolysis in base are **PG** and **LA** (Table 1). Only trace quantities of **GO** and very little **EG** are formed, whereas **GA** in base gives substantial **GO** and **EG** as products. Evidently, as shown in Scheme 2, **DA** undergoes base catalyzed keto-enol tautomerization to the triose enediol followed rapidly by the long-known dehydration to pyruvaldehyde.¹⁵ At neutral pH, **DA** hydrogenolysis forms substantial **EG** and **GO**, indicating that triose enediol dehydration to **PV** is slower without base but that direct hydrogenation or tautomerization to **GA** followed by hydrogenation to **GO** or retro-aldol cleavage to **EG** remain accessible. These findings are consistent with the H/D exchange studies of **GO**, which indicate that **DA** is not the first intermediate formed in **GO** conversion.

The mechanism shown in Schemes 2 and 3 involves pyruvaldehyde (**PV**) as an intermediate en route to **PG** and **LA**. Calculated heats of reaction indicate that conversion of **PV** is highly exothermic both to **LA** and to **PG**, as seen from Table 2 and Scheme 4. Because of its high intermolecular reactivity in basic solution, hydrogenation experiments with **PV** feed were run only at neutral pH, yielding **PG** and **LA** together with self-condensation byproducts. Surprisingly, **GO** and **EG** were also formed in these reactions. This finding implies Michael addition of water to the enol of **PV** to form the triose enediol and, from it, **GA** and/or **DA**. Though unexpected, this reversible dehydration is consistent with the reaction calculated thermoneutrality (Table 2, Scheme 4). Finally, the reaction of **PV** gives a small quantity of 1-hydroxy-2-propanone (hydroxyacetone or acetol), a hydrogenation intermediate on the path to **PG** (see Scheme 3). No 2-hydroxypropanal (lactaldehyde), the other partial hydrogenation product of **PV**, is seen, as expected from the relative kinetic and thermodynamic preference for hydrogenation of aldehydes over ketones (Table 2).



Scheme 4 – Thermodynamic analysis of GO hydrogenolysis pathways.

Table 2

Calculated and Experimental (Kcal/mol) Heats of Formation and Solvation (G3 Enthalpy in hartrees, all other Kcal/mol)

| Species | Gas Phase | | Solution | | |
|----------------------------------|-------------|-----------------|------------------|--------------------------|------------------------------|
| | G3 Enthalpy | G3 ΔH_f | Exp ΔH_f | ΔG_{CPCM} | Energies in H ₂ O |
| Dihydroxyacetone (DA) | -343.35280 | -124.6 | | -13.0 | -137.7 |
| Dihydroxyethylene ^a | -228.87815 | -68.2 | -75.5 | -9.6 | -77.9 |
| Ethylene glycol (EG) | -230.08194 | -93.6 | -94.3 | -10.7 | -104.2 |
| Formaldehyde (CH ₂ O) | -114.42724 | -26.7 | -27.7 | -1.5 | -28.2 |
| Glyceraldehyde (GA) | -343.34956 | -122.6 | | -12.7 | -135.3 |
| Glyceraldehyde enol ^b | -343.33902 | -116.0 | | -13.5 | -129.5 |
| Glycerol (GO) | -344.54160 | -140.6 | -138.1 | -12.1 | -152.7 |
| Glycolaldehyde | -228.89068 | -76.1 | | -8.2 | -84.2 |
| Hydrogen (H ₂) | -1.16407 | -0.5 | 0.0 | | |
| Hydroxyacetone | -268.17426 | -89.9 | | -8.1 | -97.9 |
| Lactic Acid (LA) | -343.38981 | -147.9 | | -11.0 | -158.8 |
| Lactic Acid Enol | -343.34788 | -121.5 | | -12.2 | -133.7 |
| Lactaldehyde hydrate | -344.55892 | -151.5 | | -12.0 | -163.5 |
| Lactaldehyde | -268.16685 | -85.3 | | -7.4 | -92.6 |
| Lactaldehyde enol ^c | -268.15725 | -79.2 | | -8.2 | -87.4 |
| Propylene glycol (PG) | -269.35912 | -103.4 | -102.7 | -9.9 | -113.3 |
| Pyruvaldehyde (PV) | -266.97252 | -65.8 | -64.8 | -3.7 | -69.5 |
| Pyruvaldehyde enol | -266.96766 | -62.8 | | -4.4 | -67.2 |
| Water (H ₂ O) | -76.37826 | -57.6 | -57.8 | -6.5 | -64.0 |

^a Ethene-1,2-diol in Scheme 2; ^b Triose enediol in Scheme 2; ^c Propene-1,2-diol in Scheme 3.

CONCLUSIONS

A solid mechanistic picture of GO conversion to PG, EG, and LA over Ru/C catalysts in water has emerged from our isotopic labeling, NMR and HPLC analyses, and modeling calculations. Schemes 2 and 3 summarize our model for the

conversion of GO to PG, EG, and LA. Scheme 4 follows the proposed reaction paths with the calculated heats of reaction both for gas phase and aqueous solution. No evidence is seen for direct catalytic C-O or C-C hydrogenolyses of GO. Were such processes important, PG and EG would be converted to methanol, ethanol, and the propanols,

none of which are seen under the present conditions. Instead, the first step en route to all three products is primary HC-OH dehydrogenation to form **GA**, as indicated by H/D exchange and direct detection of **GA**. This dehydrogenation is the most endothermic step in the reaction, as evidenced both by ab initio calculations and by the low **GA** concentration observed during **GO** conversion. Cleavage of C-O bonds takes place via slow enolization and rapid dehydration, while C-C rupture arises via retro aldol condensation. Reduction and rearrangement of the resulting unsaturated products yields the observed **PG**, **EG**, and **LA** products. Base accelerates the elimination and rearrangement processes, fostering **PG** formation at the expense of **EG**, but diverting substantial material to **LA** in the form of lactate. However, once acidified, **LA** is easily and cleanly hydrogenated to **PG**,¹⁰ promising an efficient overall conversion of **GO** to **PG**.

These results sharpen the mechanistic picture for glycerol hydrogenolysis; more generally, they provide chemical insights into a key class of “green” chemical pathways: the hydrogenolysis reactions of polyols and carbohydrates.

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12. For D₂O/H₂ exchange studies, the reactor was charged with 1g reduced catalyst, 100 ml deuterated water, and 8.3 MPa H₂. Samples from the gas phase were collected and analyzed via mass spectrometry (Ametek M100M Residual Gas Analyzer). The scrambled hydrogen pool contains H and D in a ratio of 1:10. We performed all our **GO** hydrogenolysis experiments with D₂ in D₂O in order to have the same available deuterium pool in each case analyzed.

13. Similar dehydrogenation behavior is suggested for primary alcohols in homogenous systems, where Rh complexes catalyze dehydrogenation followed by decarbonylation to complete C-C cleavage. See M. A. Andrews and S.A. Klaeren, *J. Am. Chem. Soc.*, **1989**, *11*, 4131; M. A. Andrews, *Organometallics*, **1989**, *8*, 2703
14. After 1h at 150°C, C1HD=45%, C1D2 10% C2D 0%; after 1h at 200°C, C1HD100%, C1D2 60%, C2D 40%; after 2h at 200°C the C1 and C3 are fully equilibrated with the H/D pool, while C2 remains only partially deuterated, C1DH100%, C1D2 80%, C2D 60%.
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16. Literature kinetic models of GA and DA reactions in sub- and supercritical water¹⁷ yield an equilibrium constant $K = \frac{[DA]}{[GA]} = \sim 7$ at 300-400°C and 25-40 MPa. Similarly, at 25 °C, a value of $K > 10$ has been reported.¹⁸ Since these values bracket our conditions (200°C and 8.5MPa), it is reasonable to expect $K = 7-10$ for the present work as well.
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19. Control experiments with formic acid as feed under the hydrogenolysis conditions described here were expected to lead to formaldehyde or methanol; however, the results indicated a fast reaction (formic acid conversion reached 100% in less than an hour) with complete lack of detectable products in the aqueous phase of the reaction mixture.
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