

Understanding Ketone Hydrodeoxygenation for the Production of Fuels and Feedstocks From Biomass

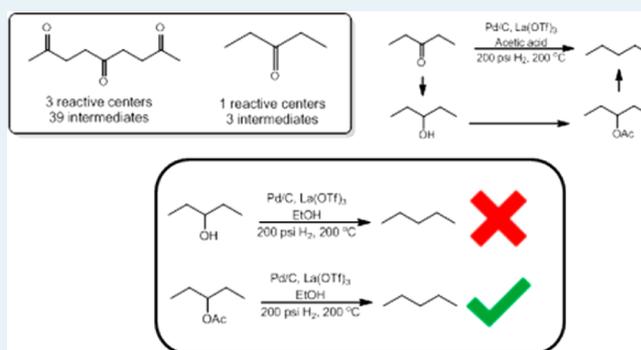
Amanda E. King,[†] Ty J. Brooks,[†] Yong-Hui Tian,^{‡,§} Enrique R. Batista,[‡] and Andrew D. Sutton^{*,†}

[†]Chemistry Division (C-IIAC; Inorganic, Isotope and Actinide Chemistry), [‡]Theoretical Division (T-1; Physics and Chemistry of Materials), Los Alamos National Laboratory, Los Alamos, New Mexico 87544, United States

Supporting Information

ABSTRACT: Although we can efficiently convert bioderived furans into linear alkanes, the most energy-intensive step in this approach is the hydrodeoxygenation of the intermediate polyketone. To fully understand this process, we have examined the hydrodeoxygenation of a model compound, 3-pentanone, which allows us to follow this process stepwise using Pd/C, H₂ (200 psi), and La(OTf)₃ in acetic acid to remove the oxygen atom at temperatures between 25 and 200 °C. We have found that ketone reduction to an alcohol is followed by acetoxylation, which provides a more facile route to C–O bond cleavage relative to the parent alcohol.

KEYWORDS: hydrodeoxygenation, biomass, ketone reduction, dehydration, mechanism



Non-food-based carbohydrates are attractive renewable starting materials for conversion into fuels and feedstocks.¹ Glucose and xylose, as the main building blocks of lignocellulosic biomass, are the most abundant monosaccharides on the planet, and their use as precursors for these applications is a worthwhile target.² Conversion of these sugars into platform chemicals such as furfural or 5-hydroxymethylfurfural (HMF) provides useful precursor molecules for further chain extension or derivatization to add value or energy density.^{3–8} For these molecules to be converted into direct drop-in fuel replacements, the abundant functional groups associated with carbohydrates (i.e., oxygen atoms) need to be removed. Recently, we developed a route for selective chain extension of furan aldehydes (furfural and HMF) to produce isolable higher-order furfuraldehydes containing between 8 and 16 carbon atoms. These can then be selectively converted into linear alkanes in excellent yields using a standard set of catalysts and reaction conditions.⁹ The chain-extended furfuraldehydes are converted into polyketones via hydrogenation of their exocyclic double bond, followed by subsequent acid-catalyzed ring opening.¹⁰ However, the following hydrodeoxygenation (HDO) reaction to convert the polyketones into hydrocarbons requires more forcing conditions (200 °C and 200 psi H₂). Reducing the energy required for this final step (i.e., via lower temperatures and pressures) should allow for a more economically viable process for potential commercialization. Studying this reaction and understanding the stepwise mechanism would allow us to improve the HDO reaction by specifically addressing the highest energy transformations. Herein, we report the use of a simple model system to probe a stepwise HDO reaction applicable to bioderived molecules.

Initial mechanistic studies utilizing polyketone substrates were complicated by the presence of multiple reactive centers within the substrates. For example, 2,5,8-nonanetriene could potentially yield 39 possible intermediates. To overcome this complication, 3-pentanone was chosen as a model substrate containing a single functional group that was anticipated to proceed through a pathway that included 3-pentanol and 2-pentene. This allows for rapid and easy identification of intermediates and gives us a model system in which we can effectively screen catalysts and reaction conditions to elicit the desired transformations. To test this hypothesis, we subjected each of these compounds to our typical HDO conditions (Pd/C, La(OTf)₃, acetic acid, 200 psi H₂, 200 °C, 15 h) and observed pentane formation in all cases. We also obtained ethyl acetate as a side product from acetic acid reduction under these conditions.¹¹

To observe the intermediates, we performed the HDO reaction of each substrate as a function of temperature. Our standard reactions involved combining the reactants in a stainless steel reactor and heating for 15 h at temperatures between 25 and 200 °C (with 200 psi H₂ if required). Following cooling of the reactor, the crude reaction mixtures were filtered and yields were obtained by ¹H NMR relative to an internal standard. For the HDO reactions of 3-pentanone, 3-pentanol, and 2-pentene, the product distributions are shown in Figure 1.

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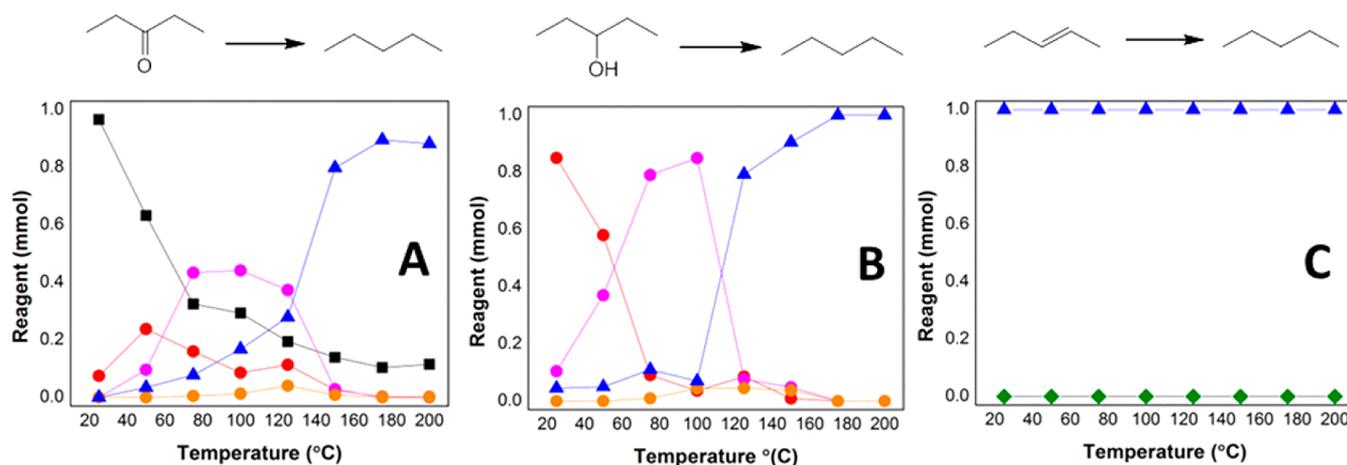


Figure 1. Temperature-dependent product distributions observed when 3-pentanone (A), 3-pentanol (B), and 2-pentene (C) are subjected to standard HDO conditions for 15 h ([substrate] = 400 mM, [La(OTf)₃] = 60 mM, 10 wt % Pd/C relative to substrate, 2.5 mL acetic acid, 200 psi H₂). Substrate key: 3-pentanone = ■, 3-pentanol = red solid circle, 3-acetoxypentane = magenta solid circle, 2-acetoxypentane = orange solid circle, 2-pentene = green diamond, pentane = blue triangle.

At temperatures above 175 °C, 3-pentanone forms pentane as the sole product at up to 85% yield. At temperatures below 175 °C, 3-pentanol and the intermediates 2- and 3-acetoxypentane are observed (Figure 1A). The acetoxypentanes prove to be important intermediates in our process, and their importance will be discussed later. Decreasing the temperature results in lower conversions of 3-pentanone, and the expected 2-pentene intermediate is not observed under these conditions.

The conversion of 3-pentanol into pentane goes to completion at temperatures above 175 °C, with both 2- and 3-acetoxypentane observed below this temperature. Below 100 °C, 3-acetoxypentane was the major observed product (Figure 1B), and as the reaction temperature is decreased, lower conversion of 3-pentanol is seen. The lack of observable 2-pentene indicates that the alkene intermediate is readily hydrogenated under these reaction conditions; accordingly, hydrogenation of 2-pentene proved to be facile at all temperatures investigated (Figure 1C).

Employing Pd/C and La(OTf)₃ independently rather than in tandem allowed us to isolate intermediates in the HDO process. Subjecting 3-pentanone to HDO conditions (200 °C) in the absence of La(OTf)₃ yields only 3-acetoxypentane (Figure 2), confirming that the role of La(OTf)₃ is to facilitate C–O bond cleavage. Following this reaction as a function of temperatures shows reduction to the alcohol at 100 °C, followed at higher temperatures by a conversion into the acetoxypentanes with nearly complete conversion at 180 °C. As expected, heating 3-pentanol in the presence of La(OTf)₃ in acetic acid results in efficient production of 3-acetoxypentane at 100 °C and 2-pentene at 150 °C; in addition, the 2-acetoxypentane intermediate is also observed at temperatures >100 °C (Figure 3).

The individual steps of the net dehydration reaction were also studied. The acetoxylation of 3-pentanol proceeds to completion at 100 °C in acetic acid, and heating 3-acetoxypentane with La(OTf)₃ results in nearly complete conversion into 2-pentene at temperatures >150 °C (Figure 4). The reverse reaction (i.e., the acetoxylation of 2-pentene) does not proceed at 150 °C in acetic acid alone, although a small amount of both 2- and 3-acetoxypentane are observed in the presence of La(OTf)₃ and prolonged heating. 2-Acetoxy-

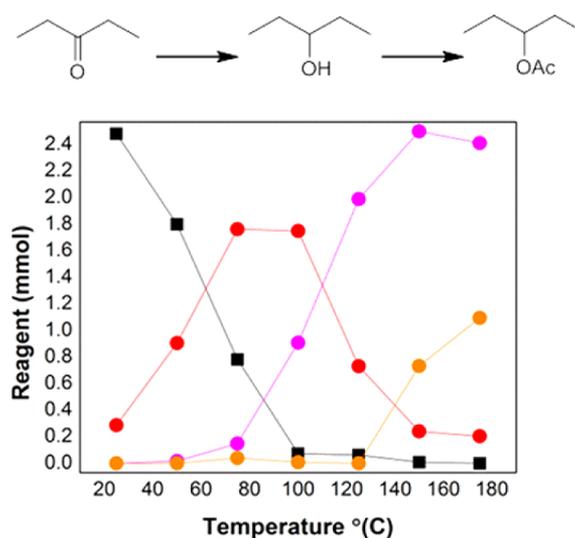


Figure 2. Temperature-dependent product distributions observed during the HDO reaction with La(OTf)₃ absent for 15 h ([substrate] = 1.2 M, 10 wt % Pd/C relative to substrate, 2.5 mL acetic acid, 200 psi H₂). Substrate key: 3-pentanone = ■, 3-pentanol = red solid circle, 3-acetoxypentane = magenta solid circle, 2-acetoxypentane = orange solid circle.

tane can be substituted for 3-acetoxypentane with no change in reactivity observed.

To determine the importance of acetoxypentane and whether this is a key intermediate that facilitates facile C–O cleavage, we attempted the dehydration of 3-pentanol and 3-acetoxypentane in sulfolane. In the presence of La(OTf)₃ excluding acetic acid, 3-pentanol did not undergo C–O cleavage reactions; however, subjecting 3-acetoxypentane to identical conditions yielded complete conversion into the alkene at 150 °C. This result indicates that the acetate moieties are important in enabling more facile C–O bond cleavage and subsequent alkene formation.

This reaction pathway is summarized in Scheme 1; palladium reduces the ketone to the alcohol, which is converted to the acetoxypentane by acetic acid. The C–O bond cleavage is facilitated by the La(OTf)₃, resulting in the alkene, which is

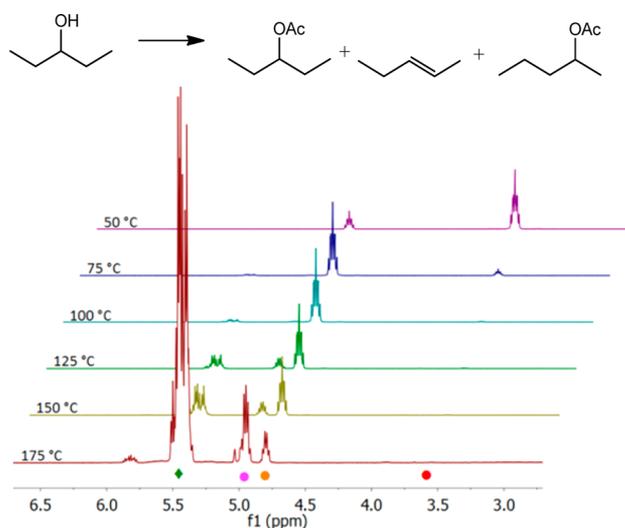


Figure 3. ^1H NMR following the $\text{La}(\text{OTf})_3$ catalyzed dehydration of 3-pentanol in acetic acid. Substrate key: 3-pentanol = red solid circle, 3-acetoxypentane = orange solid circle, 2-acetoxypentane = magenta circle, 2-pentene = green diamond.

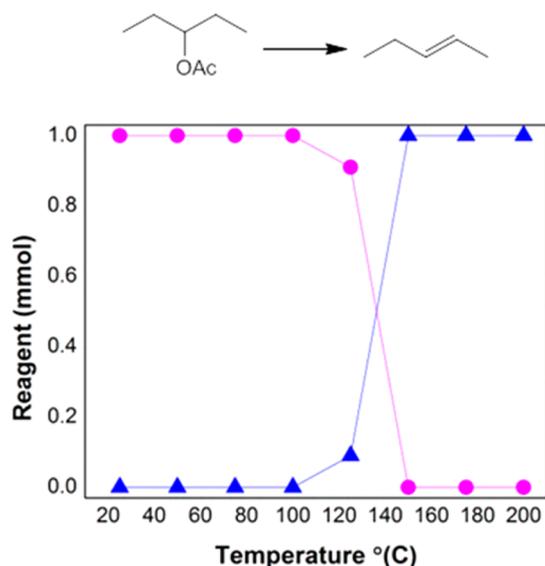


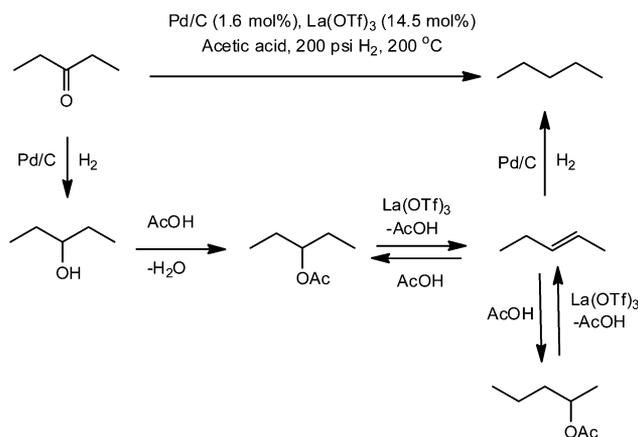
Figure 4. Temperature-dependent product distributions observed during the C–O bond cleavage reaction with $\text{La}(\text{OTf})_3$ in acetic acid; 15 hours ($[\text{substrate}] = 1.2 \text{ M}$, $[\text{La}(\text{OTf})_3] = 40 \text{ mM}$, 2.5 mL acetic acid). Substrate key: 3-acetoxypentane = magenta solid circle, pentane = blue triangle.

readily hydrogenated to the alkane. Using acetic acid as a solvent also has the benefit of being able to solubilize all the intermediates, which prevents precipitation and char formation upon heating.

We also analyzed this reaction pathway via computational studies applied to reaction free energies for all the intermediate steps in Scheme 1. The computed free energy landscape indicates that once the first step (pentanone to pentanol) is accomplished, the rest of the reaction follows in an exergonic fashion (i.e., downhill).

Our calculations did not include the modeling of the Pd/C catalysis within ketone reduction; however, we find this reaction to be uphill by only $\Delta G = +0.4 \text{ kcal/mol}$. From the point of view of the accuracy of density functional theory, these

Scheme 1. Reaction Pathway and Intermediates Formed in Acetoxy-Mediated Hydrodeoxygenation



two species are isoenergetic (pentanone + H_2 and pentanol); however, Pd/C lowers the H_2 dissociation barrier, thus accelerating this reaction. Step 2 consists of the acetoxylation of pentanol. As in all the remaining steps, the reaction free energy can be affected by side reactions in solution; therefore, several possibilities were considered, as detailed in the Supporting Information. The formation of the acetoxypentane is favored by 0.31 kcal/mol. This step is followed by the release of HOAc and formation of pentene and is exergonic, releasing $\Delta G = 6.9 \text{ kcal/mol}$. Again, depending on the different models we studied for coordination of HOAc in solution, the reaction free energy can vary by 0.2 kcal/mol, and in the crudest model, by 2.6 kcal/mol; however, this does not change the conclusion of the favorability of this step. Finally, reaction with H_2 yields pentane in a highly exergonic reaction, with a $\Delta G = -17.5 \text{ kcal/mol}$, which supports the experimental data.

The results of this study have important implications for the design of catalysts for the HDO of biomass derived molecules into fuels, especially those that facilitate the removal of a ketone fragment. Our standard HDO reaction conditions permit both ketone reduction and C–O bond cleavage. The latter transformation is a multistep process that is aided by the formation of the corresponding acetoxy compound. Cleavage of the C–O bond in this intermediate requires lower temperatures than the parent alcohol under the conditions we employ.

Although a number of both precious and nonprecious metal catalysts for ketone hydrogenation at temperatures as low as 25 °C are known, to the best of our knowledge very few are stable under the acidic conditions employed in this study.^{12–17} To that end, we are currently developing more-effective ketone reduction approaches into our HDO process. By breaking down the HDO reaction into several reaction steps that are easy to study, we can rapidly screen catalysts and conditions to develop faster and lower energy routes to bioderived replacements for fuels and chemical feedstocks. In addition, by studying this reaction in depth, we have uncovered the importance of acetate esters as intermediates in the cleavage of C–O bonds within our HDO process. This can be applied to other routes that have also adopted our approach of utilizing acetic acid¹⁸ and could give insight into the mechanism involved in the use of other acid catalysts^{19,20} and the selection of acid used for this purpose. We have achieved this by using a simple commercially available surrogate for this reaction that can be easily and rapidly studied and can be used effectively to screen new catalysts and reaction conditions in the future. By

doing this, we have revealed an additional component of our initial HDO chemistry using acetic acid for us to consider as we strive to minimize required energy inputs for the conversion of biomass-derived substrates into drop-in fuels and feedstocks. Future work is focused on optimizing performance through the use of flow reactors to capitalize on the insight presented in this manuscript and applying this stepwise approach to polyketone substrates.

■ ASSOCIATED CONTENT

📄 Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501965w

Full experimental and computational details ([PDF](#))

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: adsutton@lanl.gov.

Present Address

[§](Yong-Hui Tian) College of Life Science, Sichuan University, Chengdu 610065, China.

Notes

The authors declare no competing financial interest.

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