Supporting Information

Experimental and Theoretical Studies of the Acid-Catalyzed Conversion of Furfuryl Alcohol to Levulinic Acid in Aqueous Solution

Gretchen M. González Maldonado¹, Rajeev S. Assary²,³, James Dumesic*,¹, Larry A. Curtiss²,⁴

¹ Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, Wisconsin 53706, United States
² Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
³ Chemical & Biological Engineering, Northwestern University, Evanston, Illinois 60208
⁴ Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439,

*Corresponding author: dumesic@engr.wisc.edu

NMR Spectra
Figure S 1. $^1$H NMR spectra for intermediate A. This spectrum was referenced to diethyl ether that was part of the isolation process (2.2 – 3.0 ppm)
Figure S 2. $^1$H NMR spectra for intermediate A. This spectrum was referenced to diethyl ether that was part of the isolation process (3.9 – 5.0 ppm)
Figure S 3. Intermediate B $^1$H NMR (referenced to external DSS)
Figure S 4. FAL $^1$H NMR standard in D$_2$O (referenced to external DSS)

Water
Figure S 3. TOCSY NMR Spectrum of Intermediate A
Figure S 4. COSY NMR Spectrum of Intermediate A

The doublet labeled as D at 4.81 ppm in the previous figure was sacrificed when doing the solvent suppression for the COSY acquisition. Therefore no cross peak is seen between group D and group C.
Figure S 5. TOCSY NMR Spectrum of Intermediate B
Computational Studies

1. Protonation of Furfuryl alcohol.

Figure S 4. Computed free energy of protonation of various positions of furfuryl alcohol computed at the G4MP2 level of theory (298 K, in kcal/mol). The solvation free energy contributions were computed using SMD model at the B3LYP/6-31G(2df,p) level of theory. A value of -262.4 kcal/mol is taken into account for the proton solvation energy of aqueous solution.
2. Possible nucleophillic addition reactions with FAL cation

Figure S 5. Computed free energies of addition reactions of FAL cation with water at the B3LYP/6-31G(2df,p) level of theory. The solvation contributions to the free energy are calculated using the SMD model at the same level of theory.

I  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{O} \text{H} \text{C} \text{H} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{H}_3\text{C} \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \Delta G = -7.6 \text{ kcal/mol} \]

II  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
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\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{H}_3\text{C} \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \Delta G = -0.3 \text{ kcal/mol} \]

III  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
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\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{H}_3\text{C} \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \Delta G = +35.7 \text{ kcal/mol} \]

IV  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{O} \text{H} \text{C} \text{H} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{H}_3\text{C} \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \Delta G = +22.2 \text{ kcal/mol} \]

V  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{O} \text{H} \text{C} \text{H} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{H}_3\text{C} \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \Delta G = +0.6 \text{ kcal/mol} \]

VI  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{O} \text{H} \text{C} \text{H} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \text{H}_3\text{C} \text{C} \equiv \text{C} \text{H} \text{C} \equiv \text{CH} \text{C} \equiv \text{C} \text{H} \]  
\[ \Delta G = +6.4 \text{ kcal/mol} \]