Supplementary Information

Kinetics of Homogeneous Brønsted Acid- Catalyzed Fructose Dehydration and HMF Rehydration: A Combined Experimental and Computational Study

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Buffer solution composition

Table S1. Composition of buffer solutions used for carrying out dehydration experiments.

	Volume of HCl 1N, ml	Volume of KCl 0.2 M, ml
Buffer pH = 0.7	35	50
Buffer pH = 1.1	26.8	50
Buffer pH = 1.6	1.56	50

Parameter Fitting

The parameters were determined by minimizing the error with respect to the carbon fraction, as shown in Equation 1, where *N* is the total number of experiments, N_C^i is the number of compounds in experiment *i*, N_t^i is the number of time points in experiment *i*, y_{ijk} is the moles of component *j* divided by the initial moles of reactants (equivalent to the yield for products) at time *k* in experiment *i*, y_j^{Mod} is the model predicted moles of component *j* divided by the initial moles of reactants at temperature T and pH of experiment *i* at time $t = t_k$.

$$F = \sum_{i}^{N} \sum_{j}^{N_C^i} \sum_{k}^{N_t^i} \left[y_{ijk} - y_j^{Mod} \left(T = T_i, pH = pH_i, t = t_k \right) \right]^2 \quad \text{S-1}$$

For each reaction, two parameters were fit independently. These are shown in Equation S-2 where k_i is the rate constant of reaction *i,* p_1^i is natural log of the reaction rate at the mean temperature of all reactions (108 °C in this case), p_2^i is the activation energy of reaction *i*, *R* is the ideal gas constant, and *T* is the temperature of the reaction. Five reactions were considered for a total of 10 fitted parameters.

$$k_i(T) = \exp\left[p_1^i - \frac{p_2^i}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \quad \text{S-2}$$

The quality of fit to each component was determined using the normalized root mean square error (NRMSE) given by Equation S-3.

$$NRMSE_i = 100\% \times \left(1 - \frac{\left\| y_j - y_j^{Mod} \right\|}{\left\| y_j - \hat{y}_j \right\|}\right) \quad \text{S-3}$$

van't Hoff equation:

$$K^{Eq}(T) = K^{Eq}(303K)\exp\left(\frac{-\Delta H}{RT}\right) \quad \text{S-4}$$

Levulinic Acid Reactivity

The reactivity of levulinic acid was determined by measuring the LA concentration (initial concentration of 2.5 %w/v) in HCl solution (pH = 1.1) at elevated temperature (T=110 °C) as a function of time. No reaction was observed.

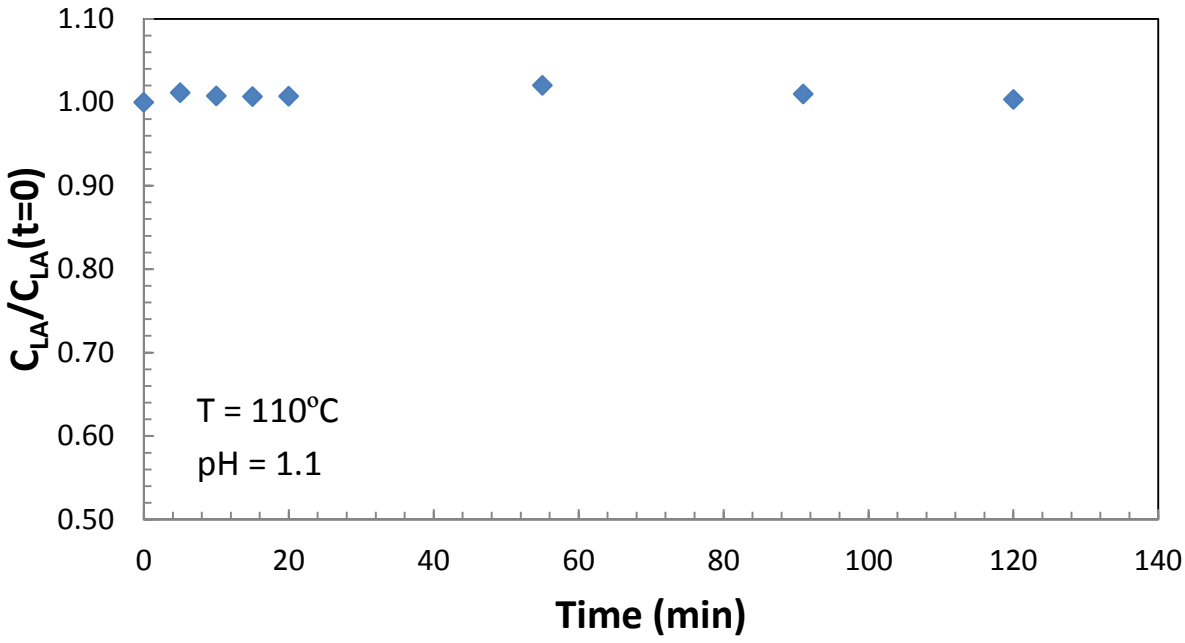

Figure S1. Fraction of initial levulinic acid concentration remaining in solution as a function of time for 2.5 wt% LA, pH = 1.1 (HCl), and T = 110 °C. After two hours, no reaction of levulinic acid is observed.

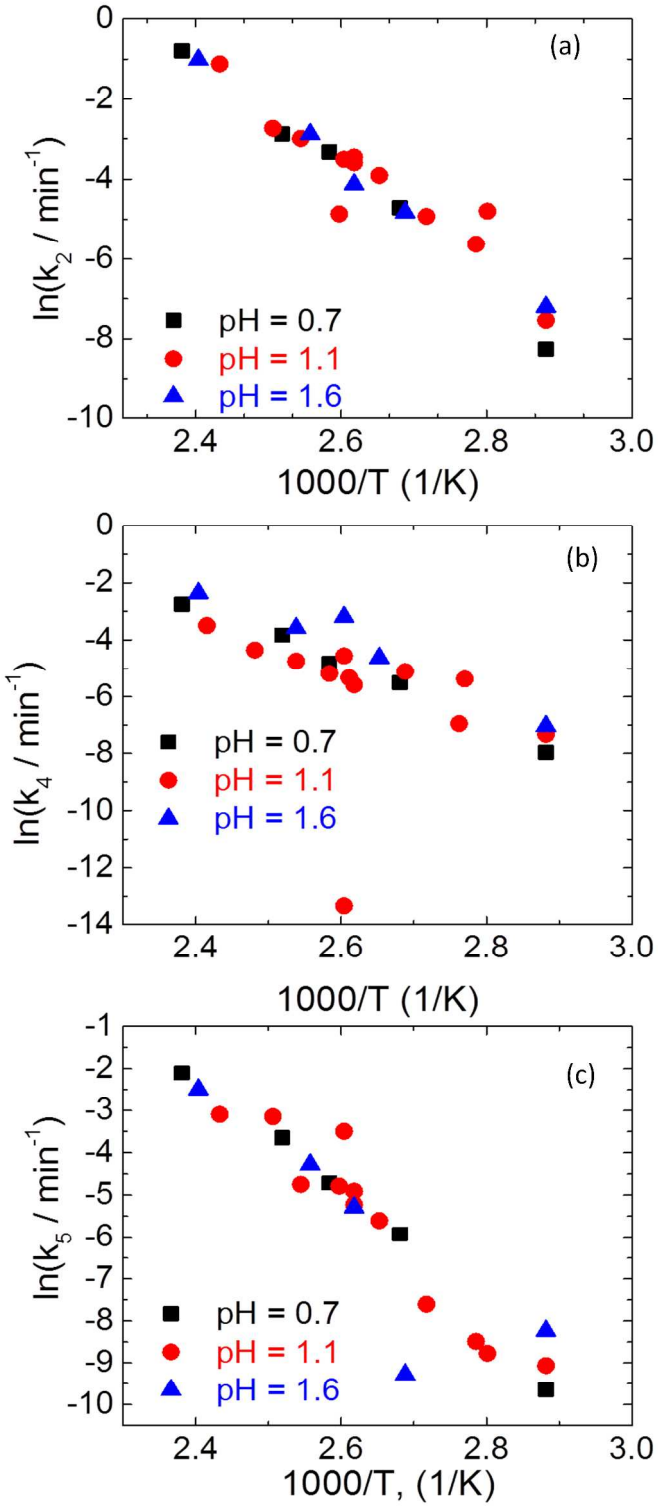

Figure S2. Arrhenius plots for fructose degradation to humins (a), and HMF degradation to humins (b), and fructose degradation to formic acid (c) at various values of pH.

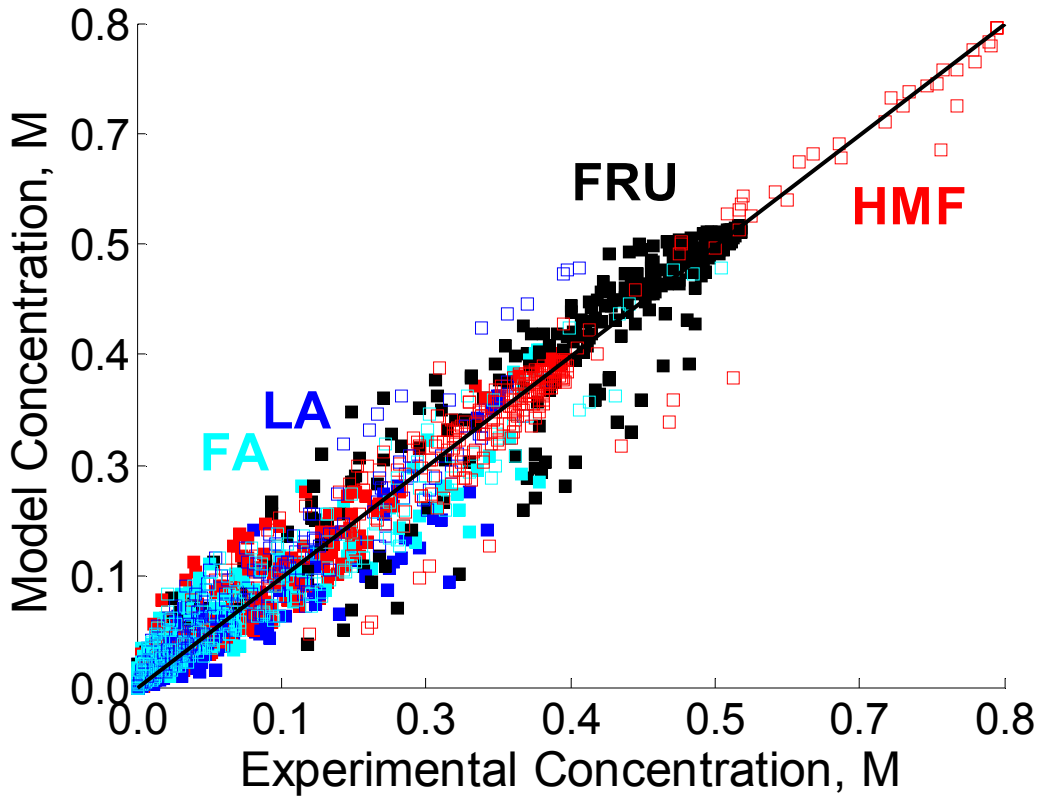

Figure S3. Parity plot of model predictions. Each symbol represents a concentration, with open points from experiments starting with HMF and closed symbols from experiments starting with fructose.