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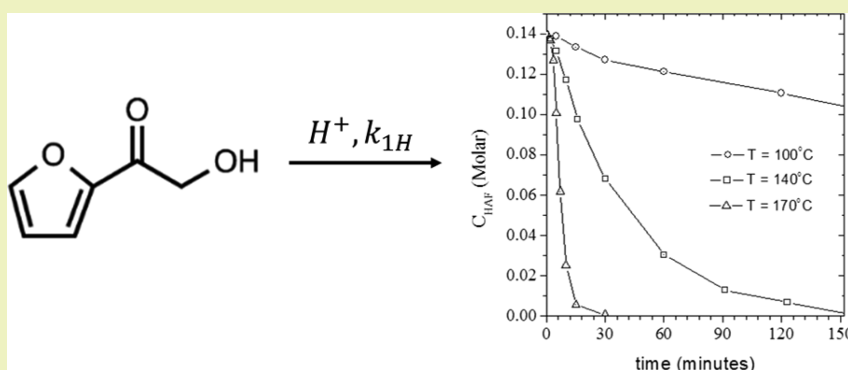
Biobased Furanics: Kinetic Studies on the Acid Catalyzed Decomposition of 2-Hydroxyacetyl Furan in Water Using Brönsted Acid Catalysts

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Supporting Information



ABSTRACT: Biobased furanics like 5-hydroxymethylfurfural (5-HMF) are interesting platform chemicals for the synthesis of biofuel additives and polymer precursors. 5-HMF is typically prepared from C6 ketoses like fructose, psicose, sorbose and tagatose. A known byproduct is 2-hydroxyacetyl furan (2-HAF), particularly when using sorbose and psicose as the reactants. We here report an experimental and kinetic modeling study on the rate of decomposition of 2-HAF in a typical reaction medium for 5-HMF synthesis (water, Brönsted acid), with the incentive to gain insights in the stability of 2-HAF. A total of 12 experiments were performed (batch setup) in water with sulfuric acid as the catalyst (100–170 °C, C_{H₂SO₄} ranging between 0.033 and 1.37 M and an initial 2-HAF concentration between 0.04 and 0.26 M). Analysis of the reaction mixtures showed a multitude of products, of which levulinic acid (LA) and formic acid (FA) were the most prominent (Y_{max,FA} = 24 mol %, Y_{max,LA} = 10 mol %) when using HCl. In contrast, both LA and FA were formed in minor amounts when using H₂SO₄ as the catalyst. The decomposition reaction of 2-HAF using sulfuric acid was successfully modeled (R² = 0.9957) using a first-order approach in 2-HAF and acid. The activation energy was found to be 98.7 (±2.2) kJ mol⁻¹.

KEYWORDS: Platform chemicals, Hydroxyacetyl furan, Kinetic modeling, Acid catalysis, Levulinic acid, Formic acid

INTRODUCTION

Biobased furanics like 5-hydroxymethylfurfural (5-HMF) are interesting platform chemicals for the synthesis of biofuel additives and polymer precursors like 2,5-furandicarboxylic acid and derivatives.¹ 5-HMF is typically prepared from C6-sugars, with a high preference for D-fructose. We have recently performed extensive experimental studies on the use of other C6-ketoses (fructose, psicose, sorbose and tagatose) for 5-HMF formation^{2–5} in water using sulfuric acid as the catalyst and it was shown that particularly sorbose is also a good source for 5-HMF synthesis (Scheme 1).

Besides the target component 5-HMF, considerable amounts of 2-hydroxyacetyl furan (2-HAF) or 2-furoylcarbinol were formed, the exact amount being a function of the ketose used. When using D-sorbose, the amount of 2-HAF was up to 10 mol %.³ 2-HAF is potentially an interesting biobased furanic compound with a high derivatization potential and activities to increase the 2-HAF yields from ketoses are in progress.

2-HAF was already reported as the side product of sucrose dehydration in acidic conditions in the 1950s.^{6,7} Later studies showed that it is also formed during the dehydration of the monomeric aldoses like glucose^{6,8–10} and mannose¹¹ and ketoses like fructose.^{11,12} A number of studies have been performed to elucidate the mechanism of 2-HAF formation from C6 sugars.^{8,9,12–15} It is postulated that 2-HAF is formed from D-fructose by an acyclic 2,3-enolization, which though is less favorable than the direct dehydration after an 1,2 enolization to form 5-HMF (Scheme 2).

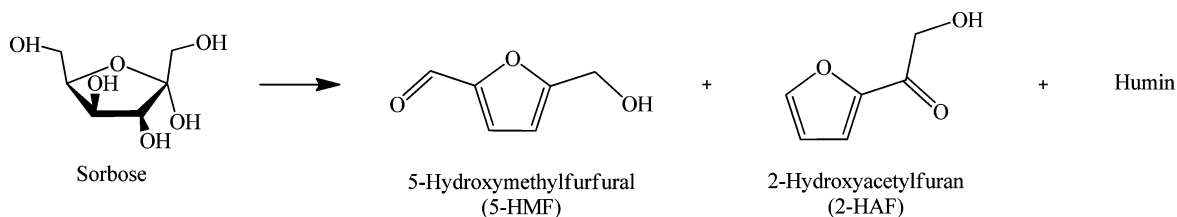
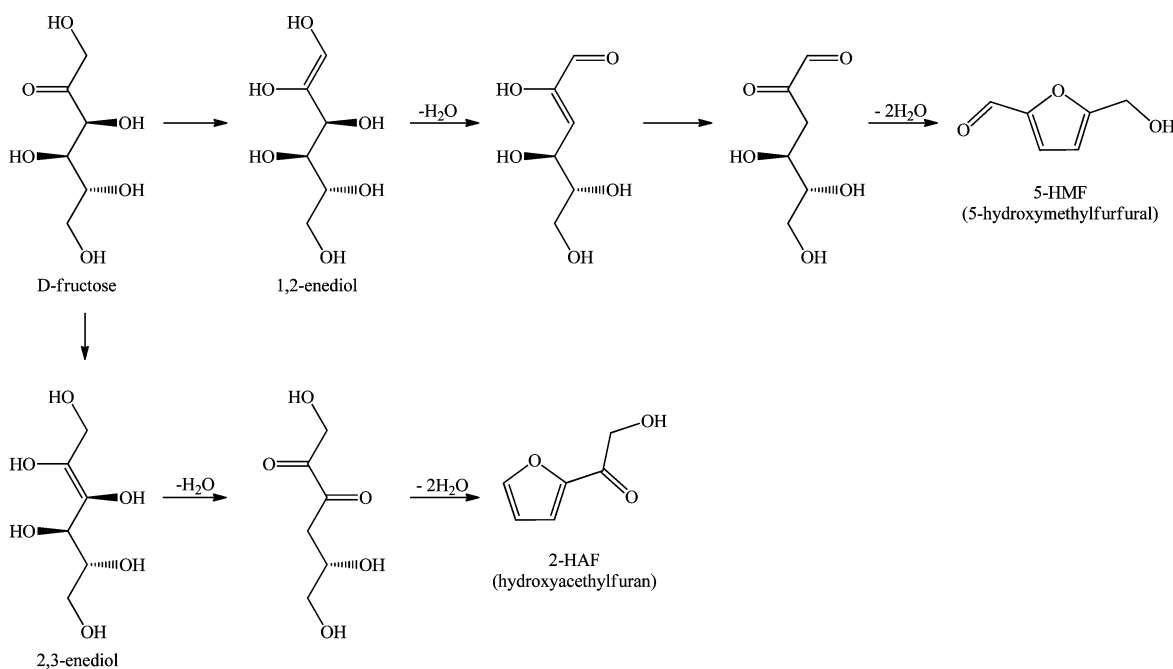
To optimize the synthesis of 2-HAF from C6 sugars, it is essential to gain insights in the stability of 2-HAF in the reaction medium and to obtain information about the reaction products, both qualitatively and quantitatively. We here describe

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Scheme 1. Reaction Scheme for the Acid Catalysed Hydrolysis of Sorbose in Aqueous Solutions

Scheme 2. Proposed, Simplified Mechanism for the Acid Catalyzed Reaction of D-Fructose to 5-HMF and 2-HAF^{8,9,12,14,15}

an experimental study on the conversion of 2-HAF in water using sulfuric acid as the catalyst at conditions of relevance (100–170 °C, $C_{H_2SO_4}$ ranging between 0.033 and 1.37 M, $C_{HAF,0}$ between 0.04 and 0.26 M). The reaction mixtures were analyzed with HPLC and GC/MS-FID for product identification. A kinetic model was developed and the kinetic parameters were determined. To investigate possible Brønsted catalyst effects, a number of experiments with HCl were performed as well. With this information, the rate of decomposition of 2-HAF can be determined as a function of process conditions and provide input in the research aimed to optimize 2-HAF yields from various sugars.

METHODS AND ANALYSIS

Experimental Procedures. All chemicals were used as received without further purification. Concentrated sulfuric acid (95–97 wt %) and formic acid (98% purity) were purchased from Merck KGaA (Darmstadt, Germany). 2-hydroxyacetyl-furan (2-HAF) with a purity $\geq 95\%$ was acquired from Otava Chemicals Ltd. (Ontario, Canada). Glucose ($\geq 99.5\%$ purity), 5-hydroxymethylfurfural (99% purity) and levulinic acid (98% purity) were obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Deionized water was applied to prepare all solutions.

The reactions were carried out in glass ampules with an internal diameter of 3 mm, a wall thickness of 1.5 mm, and a length of 15 cm. The ampules were filled at room temperature with a solution (0.5 cm³) of 2-HAF and sulfuric acid in the predetermined amounts and subsequently sealed with a torch. A series of ampules was placed in a rack and subsequently positioned in a constant temperature oven (± 0.1 °C)

that was preset at the desired reaction temperature. At different reaction times, an ampule was taken from the oven and directly cooled in an ice-water bath to quench the reaction. The liquid content was then filtered using a PTFE syringe filter (0.45 mm, VWR, The Netherlands). The particle free aliquot was diluted 7–8 times with water prior to analysis.

Methods of Analysis. The composition of the liquid phase was determined using an Agilent 1200 HPLC, consisting of a Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87H) and an RID detector. The mobile phase consists of an aqueous sulfuric acid solution (5 mM) at a flow rate of 0.55 cm³ per min. The column was operated at 60 °C. Sample analysis was complete within 60 min. A typical chromatogram is shown in Figure 1. The concentrations of 2-HAF, LA and FA in the product mixture were determined using calibration curves obtained by analyzing a number of standard solutions of known concentrations.

GC–MS analysis was performed using a HP6890 GC equipped with a HP1 column (dimethylpolysiloxane; length, 25 m; inside diameter, 0.25 mm; film thickness, 0.25 μ m) in combination with a HP5973 mass selective detector. Peak identification was done using the NIST05a mass spectral library. The injection and detection temperatures were set at 280 °C. The oven temperature was increased linearly over time from 30 to 280 °C with an increment of 5 °C/min.

Determination of the Heat Transfer Coefficient in the Oven.

At the initial phase of the reaction, the reaction takes place non-isothermally due to heating of the contents of the ampule from room temperature to the oven temperature. To gain insight in the time required to heat up the reaction mixture and to compensate for this effect in the kinetic modeling studies, the temperature inside the ampules as a function of time during the heat up process was determined experimentally. For this purpose, an ampule equipped with a thermocouple was filled with glycerine. The ampule was subsequently

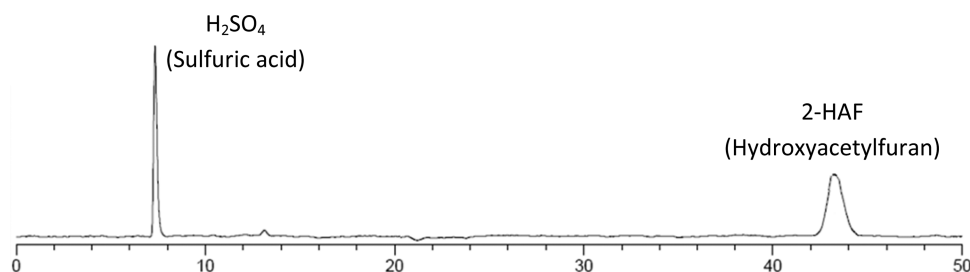


Figure 1. Typical chromatogram for a reaction mixture (HPX-87H Biorad Aminex organic acid column, RI detector).

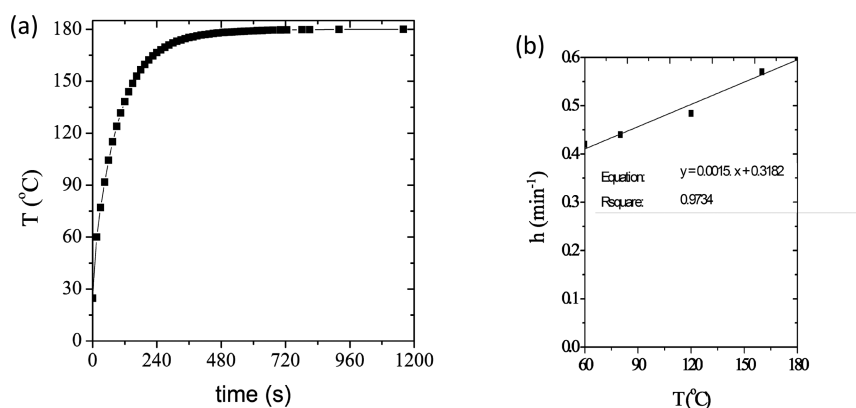


Figure 2. (a) Heating profile of the reaction mixture at $T_{\text{oven}} = 180\text{ }^{\circ}\text{C}$ (■, experimental data; solid curve, modeled profile according to eq 3). (b) h value versus the oven temperature.

placed in the oven and the temperature versus time profile was recorded. A typical profile is given in Figure 2. This procedure was repeated for a number of oven temperatures. The experimental profiles at different temperatures were modeled using a heat balance for the contents in an ampule:

$$\frac{d(MC_p T)}{dt} = U \cdot A_t \cdot (T_{\text{oven}} - T) \quad (1)$$

Here M is the mass of the solution, C_p is the heat capacity and A_t is the contact surface area.

When assuming that the heat capacity of the reaction mixture is constant and not a function of temperature, rearrangement of eq 1 gives:

$$\frac{d(T)}{dt} = \frac{U \cdot A_t}{M \cdot C_p} \cdot (T_{\text{oven}} - T) = h \cdot (T_{\text{oven}} - T) \quad (2)$$

Solving the ordinary differential eq 2 with the initial value $t = 0$, $T = T_i$ leads to

$$T = T_{\text{oven}} - (T_{\text{oven}} - T_i) \exp^{-ht} \quad (3)$$

Equation 3 was incorporated in the kinetic model to describe the nonisothermal behavior of the system at the start of the reaction. The value of h was determined by fitting the temperature–time profile for an experiment using a nonlinear regression method. A representative example with the experimental values and the model line is given in Figure 2. The h value is a function of the temperature and varied from 0.4147 min^{-1} ($T_{\text{oven}} = 60\text{ }^{\circ}\text{C}$) to 0.5985 min^{-1} ($T_{\text{oven}} = 180\text{ }^{\circ}\text{C}$). The temperature dependence of the h value was found to be essential linear, see Figure 2 right for details.

Definitions. The conversion of 2-HAF and the yield of LA are defined in eqs 4 and 5 and are mol % based.

$$X_{\text{HAF}} = \frac{(C_{\text{HAF},0} - C_{\text{HAF}})}{C_{\text{HAF},0}} \quad (4)$$

$$Y_{\text{LA}} = \frac{(C_{\text{LA}} - C_{\text{LA},0})}{C_{\text{HAF},0}} \quad (5)$$

Determination of the Kinetic Parameters. The kinetic parameters were determined using a maximum likelihood approach, which is based on minimization of the errors between the experimental data and the kinetic model. Details about this procedure can be found in the literature.^{16,17} Error minimization to determine the best estimate of the kinetic parameters was performed using the MATLAB function *lsqnonlin*, a nonlinear least-squares method that is based on Trust-Region-Reflective algorithm.

RESULTS AND DISCUSSION

2-HAF Reactivity in Water Using H_2SO_4 as the Catalyst. Screening Studies. In the first stage of this study, the effect of process conditions on the conversion of 2-HAF in water using sulfuric acid as the catalyst was investigated in a batch setup. A total of 12 experiments was performed in a temperature window of $100\text{--}170\text{ }^{\circ}\text{C}$, $C_{\text{H}_2\text{SO}_4}$ ranging between 0.033 and 1.37 M, and an initial 2-HAF concentration ($C_{\text{HAF},0}$) between 0.04 and 0.26 M. A typical concentration–time profile for an experiment is shown in Figure 3.

After reaction, the solution was slightly yellowish, and in case of the experiments at more severe conditions, also contained some brown solids (humins). The main detectable soluble component was LA, though the amount was always less than 4 mol %. HPLC revealed the presence of numerous other peaks with small intensities, of which none could be assigned unequivocally (see Supporting Information, Figure S1)

When analyzing the reaction mixture with GC–MS, a peak at a retention time of about 11 min was assigned by the GC–MS library as butyrolactone (73% probability). However, spiking of a representative HPLC sample with butyrolactone, showed that the latter was detected at a retention time of 26.1 min. The initial HPLC sample did not show this peak, a clear indication that butyrolactone is not formed during reaction.

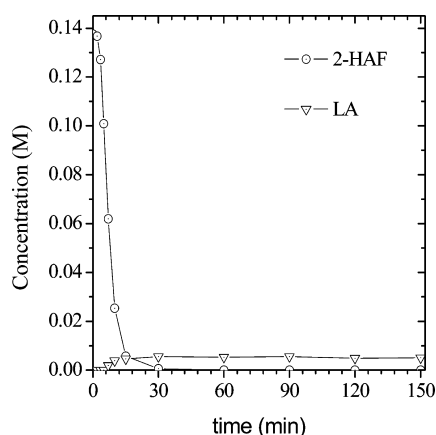


Figure 3. Typical reaction profile for the acid-catalyzed decomposition of 2-HAF at $T = 170\text{ }^{\circ}\text{C}$, $C_{\text{H}_2\text{SO}_4} = 1.37\text{ M}$, $C_{\text{HAF},0} = 0.14\text{ M}$.

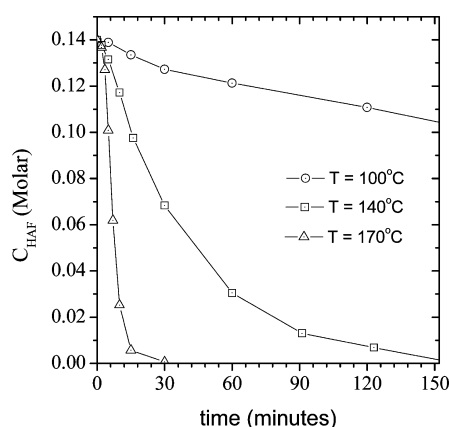


Figure 4. Concentration of 2-HAF versus time at different temperatures ($C_{\text{HAF},0} = 0.14\text{ M}$, $C_{\text{H}_2\text{SO}_4} = 1.37\text{ M}$).

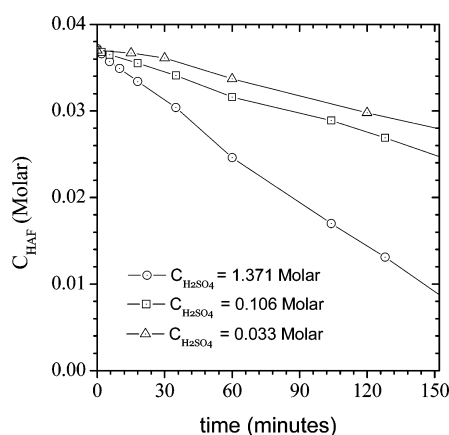


Figure 5. Concentration of 2-HAF versus time at different sulfuric acid concentration ($C_{\text{HAF},0} = 0.04\text{ M}$, $T = 120\text{ }^{\circ}\text{C}$).

In conclusion, the results indicate that 2-HAF is not stable under the conditions employed during its synthesis from C6-ketoses. As such, 2-HAF is an intermediate product and optimum reaction conditions need to be employed to maximize its yield. In this respect, there are strong resemblances with the synthesis of furfural from C5-sugars in water using Brønsted acids as the catalyst. Here furfural is also prone to decompose to complex mixture of products and selection of proper reaction conditions to reduce the rate of furfural decomposition is of

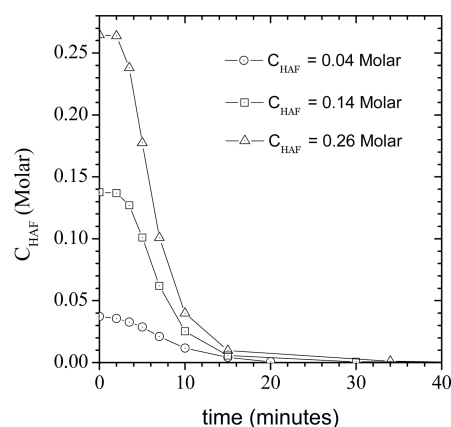


Figure 6. Concentration of 2-HAF versus time at different initial 2-HAF concentration ($C_{\text{H}_2\text{SO}_4} = 1.37\text{ M}$, $T = 170\text{ }^{\circ}\text{C}$).

Scheme 3. Simplified Reaction Scheme for the Acid Catalyzed Decomposition of 2-HAF

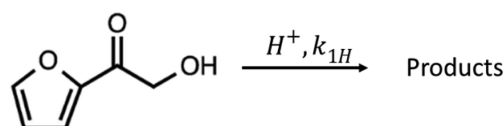


Table 1. Kinetic Parameter Estimation for Decomposition of 2-HAF using H_2SO_4 as the Acid Catalyst

Parameter	Value
R^2	0.9957
E_{IX} (kJ mol^{-1})	98.7 ± 2.2
k_{IRX} ($\text{M}^{-1} \text{min}^{-1}$) ^a	0.032 ± 0.001

^aThe values were determined at a reference temperature (T_{R}) of $140\text{ }^{\circ}\text{C}$

prime importance to obtain high furfural yields. In addition, it is clear that 2-HAF is not easily converted to LA and as such, is not a major source of LA when converting C6 sugars like for instance sorbose to 5-HMF.

The effect of temperature, sulfuric acid concentration and initial 2-HAF concentration on the decomposition rate of 2-HAF were determined, and the results are given in Figures 4, 5 and 6. It is evident that higher temperatures and sulfuric acid concentrations result in higher decomposition rates of 2-HAF. In contrast, the conversion of 2-HAF is almost independent of the initial 2-HAF concentration (Figure 6), an indication that the reaction order in 2-HAF is close to 1 (*vide infra*).

LA was formed in detectable amounts only for the experiments performed at relatively severe conditions, i.e. the highest sulfuric acid concentration (1.37 M) and temperatures of $140\text{ }^{\circ}\text{C}$ and above. However, the yields of LA were always below 4 mol %, a clear confirmation that 2-HAF is not a major precursor for LA formation.

Development of a Kinetic Model. The conversion of 2-HAF was modeled based on the simplified reaction scheme given in Scheme 3.

The reaction rate was initially modeled using a power-law approach; see eq 6 for details.

$$R_{\text{1HAF}} = k_{\text{1H}}(C_{\text{HAF}})^{\alpha_1}(C_{\text{H}^+})^{\alpha_2} \quad (6)$$

The temperature dependency of the kinetic constant is defined in terms of a modified Arrhenius equation:

$$k_{\text{1H}} = k_{\text{1RH}} \exp\left[\frac{E_{\text{1H}}}{R} \left(\frac{T - T_{\text{R}}}{T_{\text{R}} T}\right)\right] \quad (7)$$

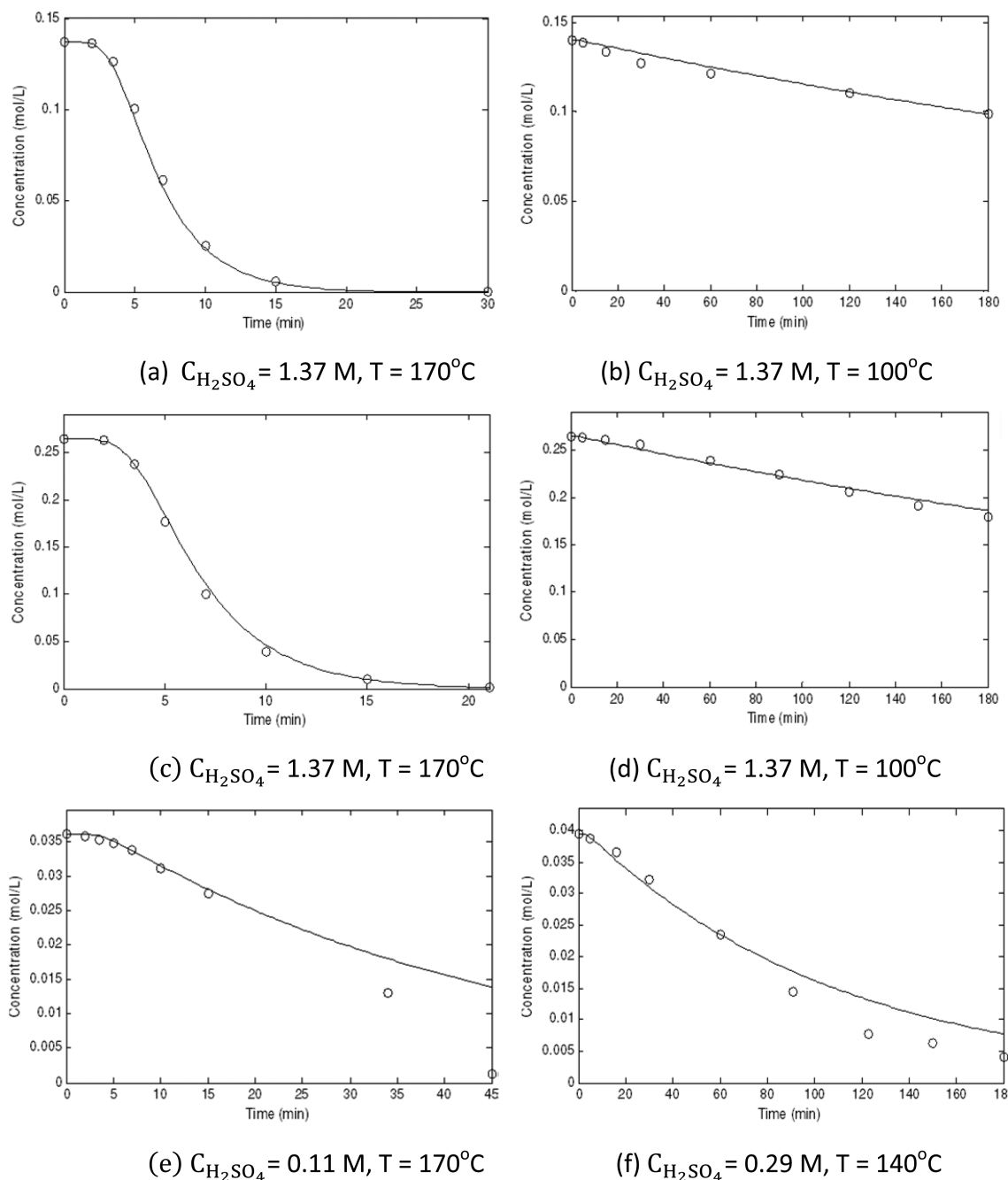


Figure 7. Comparison of experimental data (○) and kinetic model (solid lines) for different initial 2-HAF concentrations, temperature and acid catalyst concentrations.

In this equation, T is the reaction temperature and T_R is the reference temperature, which was set at 140°C for this study. The acid concentration is included in the reaction rates and calculated as follows

$$C_{\text{H}^+} = C_{\text{H}_2\text{SO}_4} + \frac{1}{2}(-K_{\text{a,HSO}_4^-} - C_{\text{H}_2\text{SO}_4} + \sqrt{(K_{\text{a,HSO}_4^-} + C_{\text{H}_2\text{SO}_4})^2 + 4C_{\text{H}_2\text{SO}_4}K_{\text{a,HSO}_4^-}}) \quad (8)$$

where $K_{\text{a,HSO}_4^-}$ is the dissociation constant of HSO_4^- , which was calculated using eq 9.

$$K_{\text{a,HSO}_4^-} = 10^{-p_{K_a}} \quad (9)$$

Here the p_{K_a} is calculated with eq 10 using a correction for the temperature of the mixture (T):

$$p_{K_a} = 0.0152T - 2.636 \quad (10)$$

For a batch reactor setup, the concentration of the 2-HAF as a function of time is represented by the following differential equation:

$$\frac{dC_{\text{HAF}}}{dt} = -R_{\text{1HAF}} \quad (11)$$

Modeling Results. A total of 12 experiments gave 122 experimental data points that consist of the concentrations of 2-HAF at different batch times. The best estimation of the kinetic parameters and their standard deviations were determined using

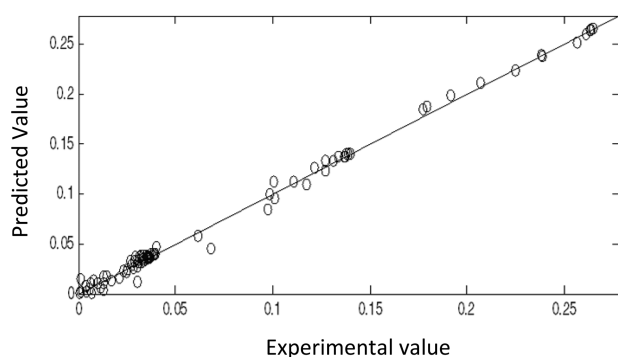


Figure 8. Parity plot with the experimental and corresponding model values (C_{HAF} , M).

a MATLAB optimization routine. The results when using the power-law model are given in the Supporting Information (Table S1). However, the values of the powers in the reactants (2-HAF and H^+) were close to 1 for the power-law model and as such the number of model parameters was reduced by taking orders of 1 for both 2-HAF and H^+ ($a_{\text{H}} = \alpha_{\text{HAF}} = 1$) in the model.

Good agreement between model and experimental values was observed. This is evident from the R^2 of 0.9957 (Table 1),

the experimental and model graphs (Figure 7) and a parity plot in Figure 8.

The activation energy for the reaction is 98.7 kJ/mol. A comparison with literature data is difficult as no studies have been reported for the decomposition reaction of 2-HAF. However, it is informative to compare the activation energy with those reported for the reaction of 5-HMF to either LA and/or humins. An overview is given in Figure 9 and detailed information is shown in Table 2.

The data reveal that the activation energy for the decomposition of 2-HAF is in the range as reported for that of 5-HMF to humins and within the range for 5-HMF to LA. However, a good comparison is difficult as the activation energies from 5-HMF cover a large range due to the use of various catalysts. When only considering the reactions with sulfuric acid (white bars in the Figure 9), it can be concluded that the activation energy for the decomposition of 2-HAF to humins is comparable with that for 5-HMF to humins.

For the optimization of the conversion of C6 sugars to either 2-HAF or 5-HMF, it is of interest to compare the relative stability of both compounds under reaction conditions. In Figure 10, the relative ratio of the reaction rates for the decomposition of 2-HAF ($R_{\text{I,HAF}}$), as presented in this study, and those for 5-HMF ($R_{\text{HMF,tot}}$) are provided. The data for 5-HMF were taken from an earlier publication of our group using sulfuric acid as the catalyst.²

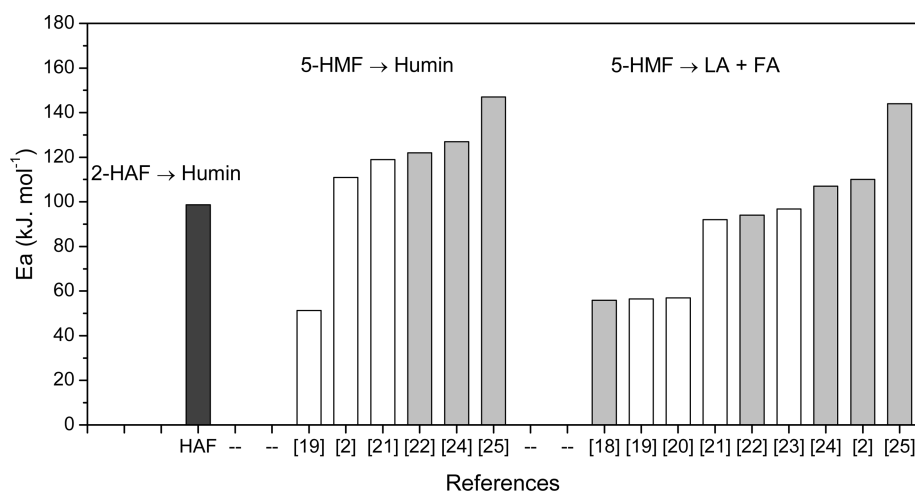


Figure 9. Activation energies for the conversion of 2-HAF (black bar) and 5-HMF (white bars: using H_2SO_4) and other homogeneous acid catalysts (gray bars).

Table 2. Overview of the Activation Energies for the Conversion of 2-HAF and 5-HMF Using Several Homogeneous Acid Catalysts in Water

#	Feed		Acid			E_a (kJ mol ⁻¹)		ref
	Name	C_{feed}	Name	Concentration	T (°C)	5-HMF or 2-HAF to LA	5-HMF or 2-HAF to humins	
1	Glucose	0.0057–0.333 M	Buffer: butyric acid/ H_3PO_4 and NaOH	pH 1–4	170–230	56	n.d.	18
2	Wheat	16:1 w/w water:wheat	H_2SO_4	1–5 w/w-%	190–230	56	51	19
3	5-HMF	5%-w/v	H_2SO_4	1–5 w/w-%	170–210	57	n.d.	20
4	5-HMF	0.1–1 M	H_2SO_4	0.005–1	140–180	92	119	21
5	5-HMF	n.d.	HCl, subcritical water	1.8	210–270	94	122	22
6	5-HMF	0.06–0.14 M	H_2SO_4	0.025–0.4 N	160–220	97	n.d.	23
7	Glucose	56–112 mM	CH_3COOH	5–20 w/w-%	180–220	107	127	24
8	5-HMF	0.1–1 M	H_2SO_4	0.05–1 M	98–181	110	111	2
9	Cellulose	49.8–149 mM	HCl	0.309–0.927 M	160–200	144	147	25
10	2-HAF	0.04–0.26 M	H_2SO_4	0.033–1.37 M	100–170	n.d.	99	This study

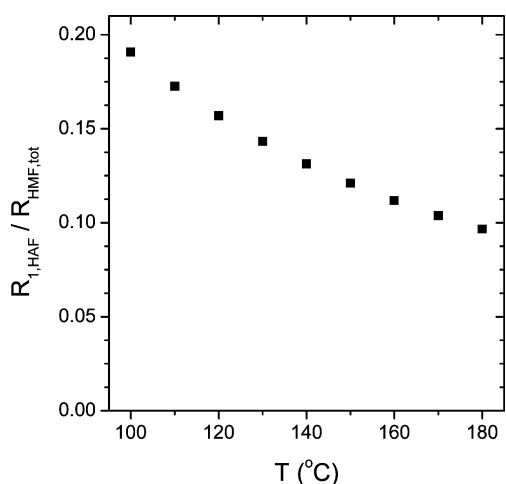


Figure 10. Ratio of reaction rates for 5-HMF and 2-HAF decomposition versus the temperature ($C_{acid} = 0.1$ M, $C_{HMF} = C_{HAF} = 0.25$ M).

For 5-HMF, the reaction rate was the sum of the rate of reactions ($R_{HMF,tot}$) to both LA ($R_{HMF,LA}$) and humin ($R_{HMF,humin}$).

On the basis of these data, we can conclude that 2-HAF is more stable under the given reaction conditions than 5-HMF. Moreover, this effect is more pronounced at higher temperatures, in line with the lower experimental activation energy found for the reaction of 2-HAF (99 kJ mol⁻¹) compared to 5-HMF (110 kJ mol⁻¹) when using sulfuric acid as the catalyst.

2-HAF Reactivity in Water Using HCl as the Catalyst. To gain insights in the role of the Brønsted acid catalyst, a number of exploratory experiments were carried out with HCl instead of sulfuric acid ($C_{HAF,0} = 0.14$ M, $C_{HCl} = 1.37$ M, $T = 170$ °C). The concentration time profiles for 2-HAF and LA for both inorganic acids are provided in Figure 11.

The conversion rate of 2-HAF was slightly higher when using HCl. The kinetic constant at 170 °C for HCl was calculated from the concentration time profile in Figure 11 using a first order approach in 2-HAF and H⁺ and found to be 0.23 M⁻¹ min⁻¹,

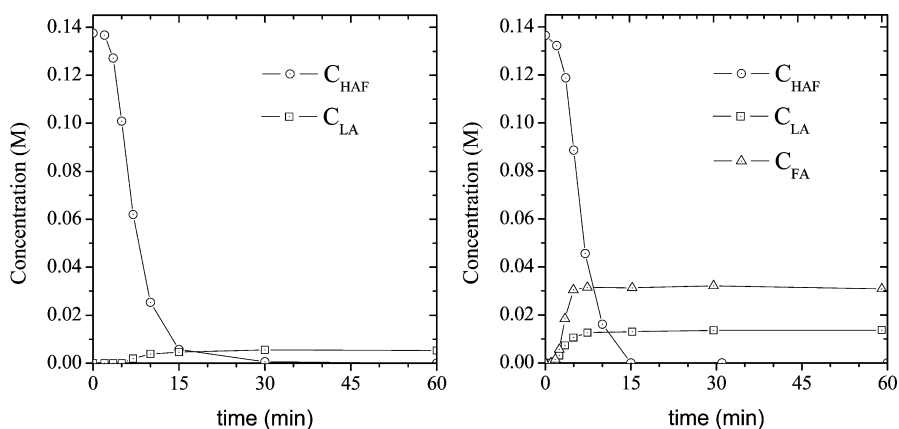


Figure 11. Comparison of the concentration–time profiles for the acid-catalyzed decomposition of 2-HAF in water at 170 °C, $C_{HAF,0} = 0.14$ M using $C_{H_2SO_4}$ (left) and C_{HCl} (right) at a concentration of 1.37 M.

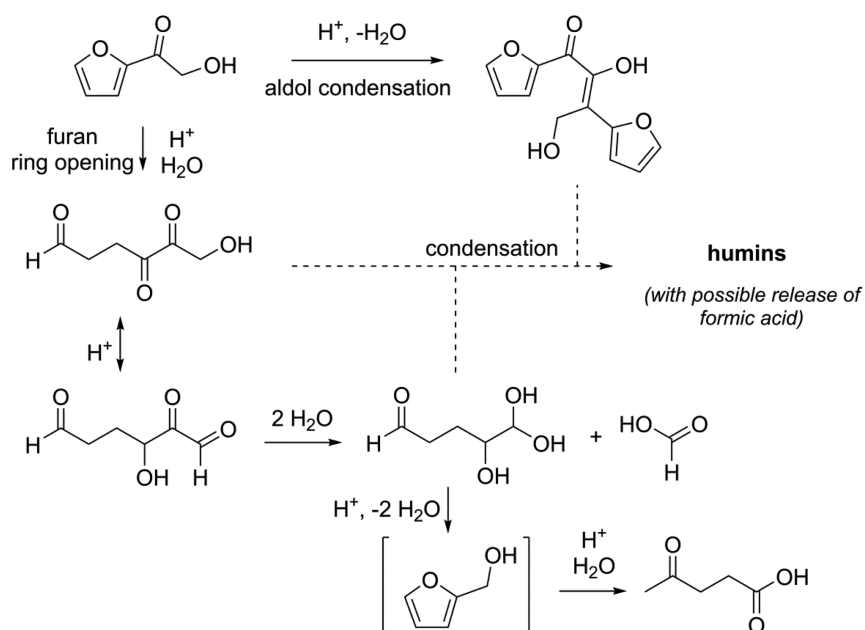


Figure 12. Proposed reaction network for 2-HAF decomposition in aqueous media using Brønsted acids.

which is slightly higher than for sulfuric acid ($0.16 \text{ M}^{-1} \text{ min}^{-1}$) at similar conditions. Of interest is the significantly higher concentration of LA and FA in the product mixture when using HCl as the catalyst. For this particular experiment, the yield of LA was 10 mol %, and the FA yield was up to 24 mol %, the remainder being unidentified soluble products and insoluble resinous compounds known as humins.

On the basis of the product composition, a tentative reaction network is proposed; see Figure 12 for details. It involves the formation of humins by acid-catalyzed (aldol) condensation reactions of the starting materials and subsequent reactions with intermediates. LA and formic acid may be formed from an intermediate α -hydroxy-keto-aldehyde, obtained by the ring opening of 2-HAF followed by an acid catalyzed rearrangement. However, detailed mechanistic studies, beyond the scope of this paper, will be required to strengthen this proposal.

The differences in reaction rate and product composition between HCl and sulfuric acid indicate that the outcome of the reaction is depending on the inorganic acid used as the catalyst for the reaction. Based on the fact that both acids are strong and as such the H^+ concentrations are about equal, the anion must play an important role. Such anion effects also have been reported for Brønsted acid catalyzed furfural decomposition reactions in water. The activation energy for HCl ($E_a = 48.1 \text{ kJ/mol}^{26}$) was reported to be about half of that when using H_2SO_4 ($E_a = 83.6 \text{ kJ/mol}^{27}$). The authors explained these results by assuming a difference in reaction mechanism for both acids due to anion effects, involving a ring opening mechanism when using Cl^- versus a direct dehydration mechanism when using sulfuric acid.^{28–31} Anion effects have also been reported for the conversion of 5-HMF, another example of a biobased furanic, to LA and formic acid. For instance, Yoshida et al.³² reported on the acid-catalyzed production of 5-HMF from D-fructose and the subsequent rehydration to LA in subcritical water using both sulfuric acid and HCl as the catalysts. Remarkable differences in the rate of reaction were observed between both acids at similar pH values, with HCl giving higher 5-HMF yields. In addition, the addition of salts like NaCl and Na_2SO_4 showed that Cl^- ions accelerate the conversion of fructose to 5-HMF and the subsequent reaction of 5-HMF to LA whereas sulfate ions have an inhibiting effect on the rehydration reaction to LA. However, to the best of our knowledge, detailed mechanistic studies to explain and rationalize these anion effects on the stability of biobased furanics like furfural and 5-HMF have not been reported to date.

CONCLUSIONS

2-HAF is a known side product from the acid catalyzed dehydration of C6 sugars to 5-HMF in water using Brønsted acid catalysts. For optimization of the 2-HAF yields from C6-sugars, information about the stability of 2-HAF in the reaction medium at relevant conditions is required. In this paper, the kinetics of 2-HAF decomposition using sulfuric acid as the catalyst in water have been determined. A good agreement between model and experimental data ($R^2 = 0.9957$) was obtained when using a first-order approach in both 2-HAF and H^+ . The activation energy was $98.7 \pm 2.2 \text{ kJ/mol}$. At $170 \text{ }^\circ\text{C}$, the reaction rate using HCl is slightly higher than for H_2SO_4 and combined with the differences in product portfolio suggests that the anion plays a major role. The reaction does not lead to the formation of a single reaction product; instead, a multitude of soluble non-identified products was observed (HPLC) and solids formation was also inevitable. The only exceptions are LA and FA, which were present in significant amounts when using HCl as the catalyst

($Y_{\text{LA}} = 10 \text{ mol } \%$ and $Y_{\text{FA}} = 24 \text{ mol } \%$). The findings described in this paper will be of relevance for the development of an efficient route for 2-HAF from C6 sugars and allow selection of optimum conditions to reduce the rate of 2-HAF decomposition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.6b03198](https://doi.org/10.1021/acssuschemeng.6b03198).

HPLC chromatograms for a typical reaction product using sulfuric acid as the catalyst and a description of the model discrimination approach (PDF)

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Notes

The authors declare no competing financial interest.

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