Applied Catalysis A: General xxx (2012) xxx-xxx



Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Kinetics of monosaccharide conversion in the presence of homogeneous Bronsted acids

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A R T I C L E I N F O

Article history: Received 12 July 2012 Received in revised form 8 October 2012 Accepted 21 October 2012 Available online xxx

Keywords: Glucose Carbohydrates Dehydration Acid catalysis Sugar degradation

ABSTRACT

For the utilization of biomass in the fuel and polymer industry, a wide variety of catalysts have been studied for their activity either on the dehydration reaction in particular or on the monosaccharide degradations in general. Yet, systematic data outlining the effects of acidic features is not available and a common framework for catalytic activity comparison is missing that is needed for rational catalyst design. The current work aimed to provide insight about the effect of the nature of the acid and initial acidity on degradation kinetics of C_5 and C_6 carbohydrates and thereby built a platform allowing activity comparison. Mineral and organic acids ranging in acidic strength, hydrochloric, sulfuric, phosphoric, maleic, and propane sulfonic acid, were tested for their activity in the degradation of xylose, fructose and glucose at two different pH values; 1.5 and 3.6. In the presence of weak homogeneous acids, glucose undergoes degradation with drastically different activation energies at pH of 1.5 than at pH 3.6. Such a difference does not occur in the presence of strong homogenous acids. On the other hand, xylose and fructose undergo degradation with similar activation energies of approximately 140 kJ/mol regardless of the pH or nature of the homogeneous acid. A common framework that compiles the catalytic activities and outlines the differences potentially related to underlying mechanism changes provides the basis required for rational heterogeneous catalyst design.

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1. Introduction

Dehydration of monosaccharides to furanic compounds has regained considerable interest in the past decade either as a reaction that could provide valuable products for the renewable polymer and fuel industry or as one of the degradation reactions accompanying polysaccharide hydrolysis [1]. Studies considering dehydration as a side reaction during saccharification focus on how to minimize its occurrence. In contrast, dehydration reaction studies have the opposite focus of how to achieve higher furanic yields at high monosaccharide conversions. In relation to both objectives a wide variety of catalysts ranging from traditional strong mineral acids to novel ionic liquids immobilized on silica supports have been examined [2,3]. However, few studies report systematic data that compare catalytic performance using a common framework, in which parameters like the acid strength, catalyst concentration, and reaction temperature are systematically varied in order to explore more general information about the intrinsic kinetics and possible mechanisms for the reaction system. In this regard, using both mineral and organic acids of varying strength at different

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0926-860X/\$ – see front matter © 2012 Published by Elsevier B.V. http://dx.doi.org/10.1016/j.apcata.2012.10.013

pH levels, the possible effect of different acidic group features can be investigated for the hydrothermal degradation of glucose and xylose, which are the most common products of biomass hydrolysis. Additional knowledge can be gained by comparing their kinetics to the well-understood fructose degradation kinetics. These results can be used to build a common framework for catalytic activity comparison for different acidic moieties.

Saccharification, the hydrolysis of polysaccharides into monosaccharides, is a key first step for the valorization of agricultural lignocellulosic waste products [4,5]. While cellulose is composed of only glucose, the hydrolysis of hemicellulosic materials also produces xylose and arabinose as well as C₆ sugars, e.g., glucose, galactose and mannose. Utilization of traditional mineral acids, such as hydrochloric and sulfuric acids, readily causes degradation of the monosaccharides under hydrolysis conditions, among the degradation reactions is the dehydration of C₅ and C₆ sugars into furfural and 5-hydroxymethylfurfural (HMF). Additional degradation reactions occurring in conjunction with the dehydration reaction are condensation, fragmentation and polymerization reactions that result in, but are not limited to glyceraldehyde, glycolaldehyde, pyruvaldehyde, formaldehyde, levoglucosan, levulinic acid, acetic acid and formic acid [6]. Side reactions accompanying cellulose hydrolysis and glucose dehydration are summarized in Scheme 1.

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Scheme 1. Reaction scheme for cellulose hydrolysis and glucose degradation reactions.

Including dehydration, the monosaccharide conversion reactions can all be acid catalyzed and have very similar activation energies [7]. This fact further creates a challenge for selective monosaccharide dehydration and has prevented economically viable HMF production from glucose. In the pursuit for sustainable chemicals, HMF and furfural production from biorenewable resources has regained interest, because they are classified as potentially important building blocks for the polymer industry [1,8]. A wide range of novel catalysts have been recently reported that is attempting to achieve high yields of furanic compounds [9-11]. Also, a considerable amount of past literature investigated monosaccharide conversion, in particular dehydration, but few links have been established between the more recent studies with heterogeneous catalysts to these prior studies with homogeneous acids [3,6,8,12]. The use of different reaction conditions and lack of evaluation of intrinsic kinetic values such as activation energies and turnover numbers accounts for the absence of such links. Therefore, a more systematic evaluation of the reaction system will provide valuable insight about how acidic features affect the reaction results.

Parameters thought to play a key role in the dehydration reaction performance are temperature, nature of the solvent, and the type and concentration of the acid [4,13–16]. The effect of different acids on dehydration has been demonstrated by Dumesic and coworkers where they examined HMF formation from fructose in the presence of different mineral acids [16]. In experiments at pH 1.5 in a DMSO–water mixture with an extracting phase, phosphoric acid gave the highest selectivity at 170 °C followed by hydrochloric acid. Sulfuric acid yielded the lowest selectivity under their conditions. Accordingly, it was concluded that selectivity was affected by the choice of the acid. As these selectivity values were reported at different conversions there might have been a convolution between the conversion and the effect of the acid itself.

Another study comparing the effect of acid catalyst choice on monosaccharide degradation examined organic acids, including dicarboxylic acids, and compared their performance to that of sulfuric acid [5]. In that study, which explored cellobiose hydrolysis and degradation of the resulting glucose, maleic acid was active for hydrolysis and acetic acid was not under the reaction conditions employed. The maleic acid activity was postulated to be related to its being a diacid. Interestingly, maleic acid did not show any appreciable glucose degradation activity under the hydrolysis conditions employed, so it was a catalyst with higher selectivity for glycosidic bond hydrolysis relative to sulfuric acid. The ability to selectively hydrolyze cellulosic compounds without degradation has not been proposed with any other homogeneous acid. In fact, in many studies [8,12,14,15] both hydrolysis and the accompanying monosaccharide degradation reaction were reported to be directly proportional to the number of available protons regardless of the type of acid used. Glucose conversion with the dicarboxylic organic acids resulted in rates that were independent of the pH, but in the presence of sulfuric acid there was a direct relationship between the measured reaction rate and pH. Similarly, Bobleter et al. [14] reported pH-dependent reaction regimes for glucose degradation when sulfuric acid was used, but in the presence of acetic acid such dependency was not observed. Difference in the rates due to the choice of catalyst was also reflected in the activation energies and this difference in activation energies has been attributed to different mechanisms, although details about the mechanism change were not provided [5]. Similar studies with xylose also resulted in different activation energies for sulfuric acid and maleic acid [17].

Several mechanisms have been proposed for glucose dehydration and degradation. According to one hypothesis, glucose dehydration occurs from the acyclic form via a 1,2-enediol intermediate, which is also the intermediate in the fructose dehydration [18]. The slower dehydration rates of glucose relative to fructose have been explained by the lower concentration of the open-chain form for glucose due to its higher ring stability. Another hypothesis suggests that glucose isomerizes to fructose first via hydride shift and subsequently follows the same degradation mechanism as with fructose. Donald et al. [19] suggested hydrogen transfer from C₂ to C₁ during the conversion of aldoses to furfural derivatives which can account for 28% of the reaction proceeding via the ketose. The active forms for dehydration were proposed to be the furanose structure for C₆ sugars and pyranose structure for the C₅. The higher ratio of the xylopyranose form was used to explain the slower reaction for glucose relative to xylose, but proposed mechanism does not predict any change in the relative rates according to type of the acid catalyst used.

The discrepancy in the relative rates can be extended further. While comparable HMF yields were obtained from glucose and fructose at 175–390 °C in the presence of 10^{-2} M mineral acids with or without an organic extracting phase, a high yield of HMF was only obtained from fructose at 85–90 °C in the presence of >0.25 M strong mineral acids [3]. Under these conditions, the HMF yields from glucose or other aldohexoses were found to be very small. Whether it is the high temperatures and (or) low proton concentration that caused the change in the relative rate trends remained unresolved.

In this study, the effect of the nature of the acid and initial pH value on degradation kinetics were explored by examining organic and mineral acids of different strength for their activity on glucose, fructose and xylose at two different proton concentrations, pH 1.5 and 3.6. Sulfuric acid and hydrochloric acid were chosen as the strong mineral acids, phosphoric acid as the weak mineral acid, and maleic acid and 1-propylsulfonic acid as the weak organic acids. By studying the effects of these acids under the same conditions the effect of proton concentration was deconvoluted from the effect of acidic strength. Furthermore, by calculating the activation energies for a temperature range of 145–175 °C, the observed activities could be related to the proposed mechanisms.

2. Experimental

Hydrochloric acid (12 N, Fisher Chemicals), sulfuric acid (18 N, Fisher Chemicals), phosphoric acid (85%, Fisher Chemicals), maleic acid (99%, Acros), and 1-propanesulfonic acid (99%, Acros) were used as purchased. The reactants, D-fructose (Fisher Chemicals), D-xylose (Acros) and α -D-glucose (99%, Acros), were also used as

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purchased without further purification. For the kinetic experiments aqueous solutions of hydrochloric acid, sulfuric acid, phosphoric acid, maleic acid, or 1-propanesulfonic acid at two different pH values, 1.5 and 3.6 were prepared. The pH values of the solutions were measured at ambient temperature using a combined glass electrode (6.0233.100, Metrohm) attached to a Metrohm 798 MPT Titrino automatic titrator. Before each measurement the electrode was calibrated using three standard buffers at 4.00, 7.00 and 10.00.

The kinetic experiments were performed at 145, 160 and 175 °C in a 250 ml stirred batch reactor (Parr Instruments) equipped with a glass liner. Temperature control was maintained with a PID controller attached to a heating jacket and cooling coil. The corresponding sugar was added to the acidic solution in the amount needed for a final concentration of 0.11 M before the solution was charged to the reaction vessel. Time zero for the reaction was taken as the time when the desired reaction temperature was reached. As some sugar conversion occurred during the heating procedure, the reactor was sampled at this zero time and the resulting conversion was determined relative to this "starting" concentration. The reactor was pressurized with 300 psig nitrogen to ensure a condensed phase. A stirring rate was determined and selected to be sufficiently high to overcome mass transfer limitation. Samples collected during the kinetic runs were filtered through a 0.2 µm nylon filter (Cobert Assoc.) and pH was back-adjusted to 6-7 by addition of 4.0 M NaOH prior to HPLC analysis.

The samples were analyzed with a Hi-Plex H⁺ column (Polymer Lab.) at 65 °C on a Waters HPLC system equipped with a Waters 2414 Refractive Index detector (RID) and Waters 996 Photoiodide Array Detector (PAD). The mobile phase was a 10 mM sulfuric acid aqueous solution flowing at 0.6 ml/min. The RID peak areas and intensities were used to estimate the sugar concentrations to avoid peak convolutions in the presence of weak acids, dehydration product concentrations were determined using both the PAD peak area at 280 nm (conc. <0.2 wt%) and the RID peak areas (conc. >0.2 wt%) to maintain a linear relationship of the peak area or intensity with the concentration. The glucose concentrations in the samples were also confirmed with a Biorad Glucose Analyzer.

3. Results and discussion

When using Bronsted acids, the rates of dehydration and degradation for monosaccharides are generally proportional to the number of available protons (or hydronium ions). Therefore, the performance of different acids can best be achieved by measuring their catalytic activities at equal proton concentrations. As such the current study compared the activities of the various acids, hydrochloric, sulfuric, phosphoric, maleic and 1-propanesulfuric acid, at the same pH values rather than at the same molar acid amounts. The pH or available proton concentration at elevated temperature for the studied acids were calculated and the results are summarized in the supplemental material. Using a pH of 3.6 at room temperature as an example, the predicted pH values at 160 °C are 3.66 and 3.87 for sulfuric acid and phosphoric acid, respectively. And as such its potential effect on the rates was found to be within the experimental error margin for the reaction results. Therefore the change in the pH of the solution due to the increase of the pKa or activity coefficient was neglected and the results were interpreted as if the final proton concentrations in the experimental runs at the different temperatures were essentially equal to their ambient temperature values.

The two different proton concentrations, pH 1.5 and 3.6, were chosen to cover most of the pH range used in the literature. Commonly, kinetic and mechanistic studies regarding the



Fig. 1. Sugar (glucose (a), xylose (b), fructose (c)) conversions at 175 °C, pH 3.6 in the presence of HCl (\blacktriangle), H₂SO₄ (\blacksquare), H₃PO₄ (×), maleic acid (*) and 1-propane sulfonic acid (\blacklozenge).

monosaccharide degradation or dehydration reactions were conducted in the presence of strong mineral acids with the highest molarity being 50 mM, which for sulfuric acid corresponds to a pH value of approximately 1.5. In contrast, more recent studies with heterogeneous catalysts were performed at higher pH values. Unfortunately, the exact proton concentrations in the presence of heterogeneous catalysts such as ion-exchangers and zeolites were typically not reported. The pH values were reported for organic acid functionalized mesoporous silica when used for cellobiose hydrolysis and they range from a pH of 3.0 to 4.5 [20]. Therefore, studying the proton activity at pH values of 1.5 and 3.6 bracketed a significant portion of the literature and enabled a bridge between the results using either homogeneous acids or heterogeneous acids. Values of the pH of less than 1.5 were not explored due to the difficulty of achieving those values with the weak acids.

A similar objective was followed when choosing the temperature range to investigate. Although some mechanistic studies were carried out at much higher temperatures such as 390 °C [21], the bulk of the studies were performed within the range of 145–175 °C. Particularly in the case of glucose, reaction rates at 145 °C are rather difficult to determine as the error bars become large relative to the change in reaction rates if not very carefully analyzed. Also at the lower rates of reaction, the kinetics can be modified by the formation of acids during the reaction. These acids will self-catalyze the reaction and cause higher rates. At higher temperatures, and hence higher decomposition rates, the formation of these acids was reported to be insignificant [12]. Overall, comparing the activation energies is a more reliable way for understanding the effect of acidity rather than comparing the relative rates at a single reaction temperature.

Shown in Figs. 1 and 2 are the rates of monosaccharide conversion at 175 °C and 160 °C, respectively, when using an initial pH of 3.6. As discussed in the Section 2, the conversion values were adjusted to zero corresponding to time zero, which was the time that the desired reaction temperature was reached. This adjustment allowed a more direct comparison of the conversion rates amongst the different monosaccharides. In reality, the reactants were charged to the reactor initially and some conversion occurred during the heat-up period. This initial loss was determined to be less than 10% and was insignificant compared to the total conversion during the time of the reaction run at the designated reaction temperature. For all of the runs, significant amounts of soluble and

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Fig. 2. Glucose conversions at 160 °C and pH 3.6 in the presence of HCl (\blacktriangle), H₂SO₄ (\blacksquare), H₃PO₄ (×), maleic acid (*) and 1-propane sulfonic acid (\blacklozenge).

insoluble humin formation were observed, but their production rate was not quantified. The formation of the insoluble humins precluded performing closed carbon balances on the samples. The only reaction product that was quantified was the yield of the furanic compounds.

As can be seen in Fig. 1 no differences in conversion rates were observed amongst the homogeneous acids at pH 3.6 and 175 °C. However, when the temperature was 160 °C at pH 3.6 the strong acids gave significantly higher conversion rates than the weak acids. A similar trend was also observed when the reaction temperature was 145 °C and the pH value 3.6 with the conversions in the presence of maleic acid, phosphoric acid and 1-propanesulfonic acid being similar to each other, whereas the conversions when using hydrochloric acid or sulfuric acid were the same and at a higher level. The results for pH 1.5 are not shown as no significant difference was observed in the sugar conversion rates for any of the acids examined. This result at pH 1.5 was in agreement with the chemistry of the monosaccharide conversion being performed via hydronium ions such that no effect of the dissociated anions could be observed.

Interestingly, the different acids when tested at 160 °C and pH 1.5 were found to give different selectivity toward dehydration products for each of the sugars as shown in Fig. 3. For glucose and



Fig. 3. HMF/furfural selectivity after 30 min at 160 °C in the presence of different acids at pH 1.5 for xylose (\Box), glucose (\Box), fructose (\Box) and at pH 3.6 for glucose (\blacksquare).

Table 1

Apparent activation energies for glucose, fructose and xylose.

Glucose	E_a (kJ/mol)		Literature values	E _a (kJ/mol)
	pH 1.5	pH 3.6		
Hydrochloric acid	138	137	1.5 M sulfuric acid [4]	137
Sulfuric acid	142	138	50 mM sulfuric acid [8]	118
Phosphoric acid	145	82	50 mM maleic acid [5]	73
Maleic acid	138	78	20% SBA-15-BuCOOH [20]	79
Propanesulfonic acid	148	83	15% SBA-SO ₃ H [20]	75
Fructose				
Hydrochloric acid	132	136	50 mM sulfuric acid [4]	138
Sulfuric acid	139	128	1.5 M sulfuric acid [8]	136
Phosphoric acid	146	144		
Maleic acid	138	142		
Xylose				
Hydrochloric acid	133	136	50 mM sulfuric acid [4]	134
Sulfuric acid	135	138	1.5 M sulfuric acid [8]	134
Phosphoric acid	128	126	Hydrothermolysis [3]	137
Maleic acid	138	150	50 mM maleic acid [8]	204
Propanesulfonic acid	150	127	15% SBA-SO ₃ H [20]	150

fructose, the selectivity followed the decreasing order of H_3PO_4 , H₂SO₄ and HCl, which also follows the trend of the basic strength of the anion. Therefore, it could be speculated that complexion of the dissociated anions with an intermediate leading to dehydration products might have occurred. Such a complex formation of HMF or its intermediate with the Cl⁻ or SO₄²⁻ was proposed previously when the glucose dehydration was examined in the presence of magnesium and aluminum salts [22]. In that study, saturated solutions of the salts were used in the absence of acidic protons and the different activity of chloride and sulfate ions were explained by the sulfates and chlorides constituting classes of salts, which could exert different effects on glucose reactivity. Dehydration to HMF was proposed to proceed via participation of aquo- and hydroxyl-complexes leading to an extensively hydrogen-bonded species intermediate in the presence of sulfate ions, whereas an exocyclic –CH₂OH elimination originating from so called "anions guiding rail" was responsible for the furan ring formation in the presence of chloride ions [23]. The conditions used in this study, e.g., much lower concentration of anions and the presence of acidic protons, did not lead to a discernable glucose conversion difference between HCl and H₂SO₄. Solutions of sulfuric acid contain predominantly bisulfate ions rather than the sulfate ions and these bisulphate ions are less strong complexation agents. Therefore, a better explanation for the higher selectivity with H₂SO₄ than HCl is the complexation of Cl⁻ anions with the HMF product itself causing its further conversion and thereby decreasing the vield [23].

In the Bronsted acid catalyzed conversion of monosaccharides, first order reaction kinetics based on the sugar concentration has been widely used in modeling studies [5,8]. Shown in Table 1 is the apparent activation energies calculated for the acids using initial reaction rate data and the Arrhenius relationship (Eq. (1)) while assuming a first order reaction rate expression.

$$k = A * \exp\left(\frac{-E_a}{RT}\right) \tag{1}$$

As shown in Table 1, the apparent activation energy values were found to be quite similar for all of the acids with the exception of the weaker acids under pH 3.6 conditions. For this case, the apparent activation energy for glucose was found to be significantly lower than the commonly reported values for strong mineral acids. A similar low apparent activation energy value was reported in the presence of organic acid functionalized mesoporous silica previously [20] as well as with maleic acid [5]. In the later study, it was proposed that dehydration using maleic acid led to a different dehydration mechanism, which was attributed to

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Pre-exponential rate constants for glucose.

Glucose	$A(\min^{-1})$		$A_0 ({ m min}^{-1})^{ m a}$	
	pH 1.5	pH 3.6	pH 1.5	pH 3.6
Hydrochloric acid Sulfuric acid Phosphoric acid Maleic acid Propapeculfonic acid	5.46E14 7.18E14 8.15E14 8.26E14 6.96E14	4.40E12 5.78E12 3.57E04 3.52E05 4.26E05	1.73E16 2.27E16 2.58E16 2.61E16 2.00E16	1.75E16 2.30E16 1.42E08 1.40E09 1.70E09

^a Modified Saeman equation constants with the assumption of m equal to 1.

maleic acid being a diacid. While more work is needed to decipher the exact reaction mechanism, the kinetic results in the current study may indirectly suggest that there is potentially a different dehydration mechanism associated with weaker acids when a pH value of 3.6 is used, but that this result was not correlated with whether a mono- or diacid was used. The possibility of different dehydration mechanisms was previously proposed by Antal et al. [3], but the reaction conditions causing the different mechanisms to become predominant were not systematically evaluated.

The change in the apparent activation energy was also manifested in the preexponential factors, which were determined from the Arrhenius plot and are shown for glucose in Table 2. Saeman [24] modified the classical Arrhenius equation to predict the effect of the proton concentration on cellulose hydrolysis and glucose degradation, where the acid concentration was expressed separately from the pre-exponential factor. This relationship has been widely accepted and was further generalized by replacing the acid concentration with the proton concentration to produce a modified Saeman equation (Eq. (2)) [5].

$$k = A_0 * \left[\mathrm{H}^+\right]^m * \exp\left(\frac{-E_a}{RT}\right)$$
⁽²⁾

In this equation the exponential term *m* was defined to account for the effects realized when different acid catalysts or reaction conditions were used. To be able to determine the constant *m*, the proton concentration at the reaction temperature has to be known. However, the pH value changes according to reaction temperature and, therefore, the y-intercept of the fitted Arrhenius plot includes an average effect of these temperature dependent pH values. As the determination of constant *m* was not the intent of the current study, the pre-exponential factors were determined using the conventional Arrhenius plot and not the modified Saeman equation and as such the proton concentration would be implicitly included in those pre-exponential values. This approach is reasonable for the current study as the different acids were compared under the same pH condition. As can be seen in Table 2, the values for the pre-exponential factors were quite similar for all of the acids at the pH 1.5 conditions. However, at pH 3.6 there was 5-6 orders of magnitude difference in the value between the weak acids and strong acids. To provide a rough comparison of the pre-exponential factors for different pH values, the pre-exponential factors were calculated assuming that the factor *m* in Saeman equation was equal to 1, which is a commonly used value [4]. These new pre-exponential factors based on the Saeman equation are also listed in Table 2. When the effect of proton concentration was deconvoluted from the pre-exponential rate constant, similar values were obtained at different pH values in the presence of strong acids. However, the values found for the weak acids still gave a large difference between those at pH 1.5 and pH 3.6.

In one of the proposed mechanisms for dehydration of glucose to HMF, the activated transition state for glucose conversion was suggested to involve an 1,2-enediol intermediate that then could dehydrate via further enolization and formation of hexosuloses as represented by acyclic route in Fig. S1 [3]. As the open-chain form of the sugar was responsible for the formation of the 1,2-enediol intermediate, the lower activity of glucose was explained as being due to the lower ratio of open-chain form than with fructose. For this mechanism, the rate-limiting step was proposed to be the protonation of the pyranose form and subsequent ring opening [3].

An alternative mechanism proposed that glucose first isomerized to fructose and then followed the same conversion pathway as fructose [12]. The rate-determining step for this mechanism was proposed to be the isomerization step, which would lead to the glucose conversion having a different apparent activation energy than fructose would. Glucose can be isomerized to fructose via base or acid/base catalysis with base catalysis being more effective for the isomerization. In the presence of both an acid and base, a concerted push-pull mechanism was suggested, that is first driven by the attack of the base [18]. In the presence of the base only, the isomerization appeared to occur via a hydride shift from C_2 to C_1 and as such the formation of an 1,2-enediol intermediate was not observed [18].

Simulation studies of the xylose and glucose degradation pathways [7,25,26] suggested that different mechanisms can dominate depending on the reaction conditions, such as the acidity, presence of co-solvents, or the temperature. However, for glucose the protonation of the glucose molecule was still found to be the rate limiting step. The strongest proton affinity was found for the C₂–OH group and only the protonation of this group led to the formation of HMF either in simulations corresponding to vacuum or with explicit water molecules. The simulations suggested that the protonation of the C₃–OH group might or might not take place depending on the acidity. At lower acidities, the proton at C₃ usually transferred back to the water molecule, while at higher acidities this protonation might lead to degradation [25]. For the latter case, ring opening was observed following protonation. In contrast, protonation at C_2 resulted in the formation of 2,5-anhydride ketose intermediates directly via a hydride shift [25]. Subsequent elimination of water from the 2,5-anhydride intermediate would then readily occur, which is similar to fructose degradation, as represented by the cyclic route shown in Fig. S1.

A mechanistic study of fructose dehydration to HMF at 250 °C with 50 mM sulfuric acid suggested that HMF formation occurred via a fructofuranosyl-cationic intermediate rather than a 3deoxyhexosulose intermediate resulting from an enediol reaction [6]. Only under weak acidic conditions was some formation of HMF from fructose observed via 3-deoxyhexuloses, but at rates relatively slower than with the fructofuranosyl-cationic intermediate mechanism. A fructofuranosyl-cationic intermediate mechanism, which is shown in Fig. S2, was originally proposed by Antal et al. [6] was further confirmed in later experimental studies at varying acidic conditions and temperatures. In our study, the observed apparent activation energy for fructose conversion was in good agreement with previously reported values and did not change according to pKa of the acid catalyst or the pH of the reaction solution. Therefore, the activation energy data from the current kinetics results do not conflict the proposed mechanism.

Further insight can be provided by the xylose degradation mechanisms, since xylose is an aldose like glucose but it has a higher ratio of the β -furanose form at equilibrium than with fructose. Mechanistic studies on furfural formation from xylose revealed that at high temperature in the acidic regime xylose is initially present in three different forms [27]. The open-chain form of xylose has been suggested to be responsible for fragmentation product formation and the xylopyranose form leads to furfural via 2,5-anhydride intermediates, while the furanose form is stable [3]. The ring-opening isomerization was reported to be relatively low at 250 °C in the presence of 10^{-3} to 10^{-2} M H₂SO₄ and 3-deoxyglycosuloses were 6

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important intermediates only at low temperatures during base catalyzed reactions. These different postulated pathways for xylose decomposition are summarized in Fig. S3. A mechanism change did not appear to be observed in our study either due to change in acidic strength or pH. Our values were consistent with most literature values. The exception is a report in which an apparent change in mechanism was observed for xylose degradation during hemicellulose hydrolysis in the presence of maleic acid [17]. It is possible that if we had explored broader pH and temperature regimes that we might have observed such a change.

The results for glucose conversion with the different acids and pH levels can be interpreted by considering the different proposed pathways for xylose and the apparent HMF formation mechanism from fructose. Within this context, it seems most likely that at lower pH values glucose first isomerizes to fructose and then decomposes like fructose. Whereas, at the pH 3.6 value in the presence of weak acids the glucose decomposes directly via the 1,2-enediol intermediate although it is also possible that the cyclic route (see Fig. S1) could be followed at the higher pH value.

4. Conclusions

Understanding the degradation pathways of monosaccharides and the effect of acidic properties on those pathways is of great importance for optimizing both polysaccharide hydrolysis and monosaccharide dehydration. Unfortunately, there is apparently conflicting results presented in the literature as the comparison between different acid catalysts is not performed in a systematic manner in which the effects of acid strength and number of acid sites is deconvoluted. The current study examined homogeneous acids with a range of acid strengths and compared their reactivity at fixed pH values. By comparing the apparent activation energies of model monosaccharides, it was found that sugars such as fructose and xylose displayed distinctly different dehydration reaction characteristics than glucose. For fructose and xylose, it was found that regardless of the nature of the acid, only the H⁺ activity was responsible for the degradation conversion rates, while the associated anions only led to some differences in selectivity toward HMF and furfural. In contrast, the strength of the acid did affect glucose degradation. In the presence of weak homogeneous acids, glucose underwent degradation at pH values of 1.5 and 3.6 with differences in both the apparent activation energies and the pre-exponential factors. Such a difference did not appear to occur in the presence of the strong homogenous acids.

Acknowledgement

This material is based upon work supported by the National Science Foundation under Award No. EEC-0813570.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.10.013.

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