Carbohydrate Research, 217 (1991) 71–85
Elsevier Science Publishers B.V., Amsterdam

Mechanism of formation of 2-furaldehyde from D-xylose*

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(Received June 26th, 1990; accepted for publication in revised form December 15th, 1990)

ABSTRACT

The literature records two alternative hypotheses for the mechanism of dehydration of xylose to 2-furaldehyde (furfural), namely (*1*) a succession of reactions proceeding mainly via open-chain intermediates, and (*2*) an acid-catalyzed sequence proceeding through a 2,5-anhydride intermediate. The existing evidence for hypotheses (*1*) and (*2*) is reviewed and found to favor (*2*). The major products from xylose in water at 250° (with and without acid catalysis) have been investigated on a time-resolved basis. A kinetic model based on the second hypothesis is found to be consistent with the experimental data; whereas kinetic models based on the first hypothesis do not fit the data.

INTRODUCTION

In the U.S.A. over 60 000 000 kg of 2-furaldehyde are produced annually[1]. Although interest in improving the chemical technology employed in its production remains high[1,2], much of the key experimental work concerning the chemistry of furfural formation was reported over thirty years ago[3–7]. Another indication of the stasis besetting research in this commercially important area is the chronology of review articles on furfural formation: the two most recent reviews[8,9] are over 25 years old, and the remainder[3,10,11] are over 35 years old. Typical conditions which offer high yields of furfural from D-xylose include temperatures of 160° to 280°, sulfuric acid concentrations of 0.003 to 0.4 M, and reaction times of a few min or less[5,7]. Other products which may accompany furfural formation are listed in Table I. In Table I the co-product of formaldehyde, which should be a tetrose, has not been reported. Glycolaldehyde is the expected co-product of glyceraldehyde from the reverse aldol reaction of a pentose. Formic acid has been stated to be a co-product of resin formation[5], but in our experience this acid is produced in significant yield under relatively mild conditions in the absence of detectable resin formation[12]. 1,3-Dihydroxy-2-propanone ("dihydroxyacetone") could be an isomerization product of glyceraldehyde, or alternatively a reverse-aldol reaction coproduct with glycolaldehyde, derived from a ketopentose intermediate. Lactic acid forms from glyceraldehyde via pyruvaldehyde. The previously reported[15]

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* Part 3 of the series Kinetic studies of the Reactions of Ketoses and Aldoses in Water at High Temperature.

TABLE I

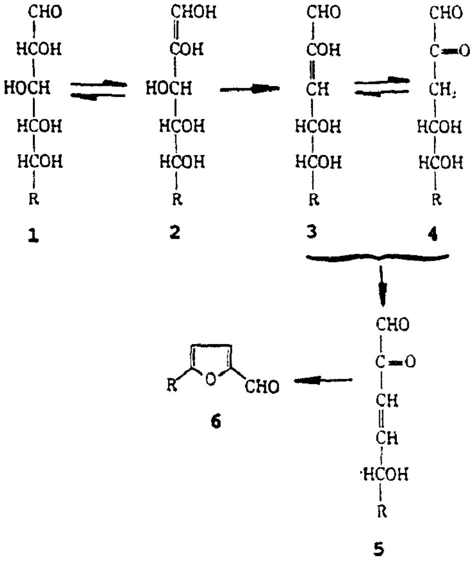
Reported products of xylose decomposition in water at elevated temperatures

Isomerization	*Dehydration*	*Fragmentation*	*Condensation*
Lyxose[b,c]	2-Furaldehyde[b]	Formaldehyde[15,a]	resin[5,a]
	Reductic acid[14,a]	Formic acid[5,b]	
		Acetaldehyde[15,a]	
		Crotonaldehyde[15,a]	
		Lactic acid[b,c]	
		Dihydroxyacetone[b,c]	
		Glyceraldehyde[b,c]	
		Pyruvaldehyde[b,c]	
		Acetol[b,c]	
		Glycolaldehyde[b,c]	

[a] Minor product. [b] Major product (generally > 1% absolute yield). [c] Identified for the first time in this work.

acetaldehyde is difficult to explain, and has not been detected in the present work. If present, an aldol condensation of acetaldehyde followed by a dehydration would account for the formation of crotonaldehyde. No convincing hypothesis has yet been advanced to account for the formation of either formic acid or acetol.

With the exception of furfural, few studies have been reported concerning the mechanism of formation of the products listed in Table I. Kinetic studies[5-7] suggested the role of a prior intermediate(s) in furfural formation, but its identity is unknown. These studies also indicated a second-order, secondary reaction between product furfural and the intermediate, resulting in the formation of destruction product (resin). Xylose



Scheme I (from ref. 18).

disappearance was reported to be first order[7], but the method of determination was not rigorous. The apparent first-order rate constant for xylose disappearance was shown to be directly proportional to the initial acid catalyst concentration[5,7]. Considering the limited availability and power of computers in 1959, the mathematical correlations developed by Root, Saeman, Harris and Neill[7], which described the time- and temperature-dependence of the formation of furfural, resin, and several intermediates from xylose using a complex reaction network, are quite remarkable.

Despite the absence of experimental evidence supporting the role of 3-deoxyglycosulose intermediates in the formation of furfural, various reviewers[8,9] posit their importance (see Scheme I) apparently without reservation, depending largely on the analogy of the observed formation of a trace amount of the deoxyglycosulose from fructose in aqueous acid. It is ironic therefore that much evidence exists which implies the non-involvement of these deoxyglycosuloses in furfural formation. The conditions under which the deoxyglycosulose forms from fructose are dramatically different (milder) than those used to produce furfural from xylose[12]. Consequently, it is not surprising that no 3-deoxyglycosulose has been detected in experiments designed to study furfural formation from xylose. More importantly, the key investigation by Feather and coworkers[16,18] of furfural formation from D-xylose in D_2O revealed no incorporation of deuterium into the furfural. Feather explained this finding by assuming a lack of equilibrium between intermediates 3 and 4 in Scheme I. But the concurrent formation of lyxose with furfural from xylose (see Table I) indicates that the rates of enolization and de-enolization are significant under conditions which actually produce furfural from xylose. Consequently, the presumption that intermediate 3 does not equilibrate with 4 seems to be untenable. A more logical explanation for Feather's findings is that the 3-deoxypentosuloses are simply not involved in the formation of furfural from D-xylose. A particularly disturbing aspect of the mechanism given in

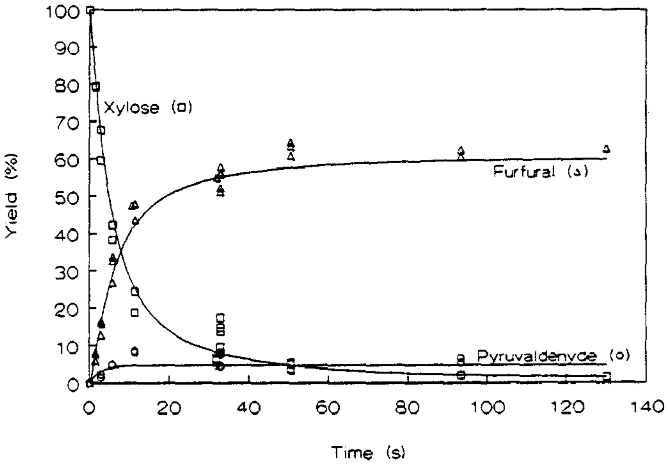


Fig. 1. Absolute yields of reactant and products from 0.05M D-xylose in water at 250° with 20mM H_2SO_4 catalyst as a function of residence time.

Scheme I is its inability to explain the role of acid as a catalyst in the formation of furfural from xylose. The fact that the 3-deoxyglycosuloses are important intermediates in the low temperature, base-catalyzed reaction chemistry of sugars is no reason to suppose that they play a role in the high temperature, acid-catalyzed regime. Similarly, Scheme I bears no obvious relationship to the high temperature, acid-catalyzed reaction chemistry of closely related model compounds[13]. For these reasons we are led to seek an alternative mechanism for the acid-catalyzed formation of furfural from xylose.

Recently Antal and Mok[19] concluded that the acid-catalyzed formation of a 2,5-anhydride intermediate is the first step in the main reaction channel which forms 2-furaldehydes from aldoses. The subsequent development of conjugation by acid-catalyzed elimination of water completes the mechanism of furfural formation from D-xylose. The potentially important role of intramolecular etherification reactions in the formation of furfural from D-xylose was recognized over 50 years ago by Hurd and Isenhour, and confirmed in a recent study of model compounds[13]. More importantly, this mechanism predicts the non-incorporation of deuterium into furfural formed from xylose in D_2O. In his review of the 2,5-anhydrides of sugars, Defaye[20] notes that the 2,5-anhydroaldose more closely resembles the 2-furaldehyde than the aldose, and that

TABLE II

Some major products from xylose in water at 250° as analyzed by h.p.l.c.[a]

Compound	*Retention Time (min)*	*Comment*
Xylose	13.2	(*i*) These five species were all quantified by r.i. Species were identified primarily by retention time. U.v. spectra of all of these product peaks were identical with the relevant authentic compounds.
Lyxose	13.8	
Other pentose	14.8	
Glyceraldehyde	15.4	
Pyruvaldehyde	16.4	
Glycolaldehyde	16.8	Depending on their relative concentration, these two species were often not separated and not quantified.
Lactic acid	17.0	
Dihydroxyacetone	18.0	Species not separated. However, because dihydroxyacetone absorbs negligibly (when compared to formic acid) in the u.v. at 214 nm, the peak is quantified by u.v. as formic acid (except when an interference is detected by an adjacent unknown which also absorbs at 214 nm).
Formic acid	18.2	
Acetol	22.7	Same as (*i*)
Furfural	57.4	Quantified by both r.i. and u.v.; identity confirmed by u.v. spectra.

[a] *Chromatographic conditions*: column–Interaction ION-300 at 65°. mobile phase–0.5 mL/min of 2mM H_2SO_4 in otherwise deionized water; detector–r.i. and u.v.-vis diode array.

the oxolane ring is particularly stable to attack by hydrolytic agents. Furthermore, these anhydride rings are not rendered more sensitive to acid hydrolysis by the presence of an aldehyde group α to the oxygen atom of the heterocycle[20]. Moreover, the formation of 2-furaldehyde by the action of 0.1 M acid on 2,5-anhydro-L-arabinose has been observed by several researchers[20–23]. Defaye[20] discusses the possibility that 2,5-anhydro sugars may be the key intermediates in the formation of furaldehydes from pentoses and hexoses, but he concluded that the etherification pathway plays only a minor role in their formation.

EXPERIMENTAL

The apparatus and procedures employed in this work have been fully described in earlier papers[12,13,19]. All substrates and reference compounds were used as received, in the purest commercially available grades.

Analysis of products was accomplished primarily by h.p.l.c. as described in ref. 12. The recent addition of a u.v.-vis diode array detector (Hewlett–Packard Model 1040A) assisted in confirming the identity of eluting compounds and distinguishing species in merged peaks (see Table II).

RESULTS AND DISCUSSION

The effects of residence time (with and without sulfuric acid catalyst), acid concentration, and reactant xylose concentration (with acid catalyst) on absolute product yields in water at 250° and 34.5 MPa are displayed in Figs. 1–4 and summarized in Table III. As the saturation pressure of water at 250° is 3.97 MPa, it is obvious that we could have obtained liquid water conditions for this work with a pressure as low as 4.0 MPa. However, our studies have spanned a broad range of temperatures, emphasizing reaction chemistry in liquid water. At 275° the required (saturation) pressure is 5.94 MPa; whereas at 370° the pressure is 21.0 MPa. Early in our work we decided to employ the high-pressure limit of our system (34.5 MPa) as the baseline condition, which enables us to achieve liquid-water chemistry ($K_W \geq 10^{-14}$) to temperatures[24,25] somewhat in excess of 400°. Thus, the high pressure employed in this work was selected to retain liquid-water chemistry at all temperatures of interest, and to facilitate intercomparison of data obtained at different temperatures. Nevertheless, we note that because liquid water is almost incompressible, we found that a decrease in pressure from 34.5 to 6.3 MPa has no significant effect on the acid-catalyzed reaction chemistry[26] of xylose in water at 250°. Consequently, the data and models we present are relevant to liquid-phase reaction conditions involving much lower pressures.

A striking aspect of Fig. 1 is the changing rate of disappearance of xylose. During the first stage of reaction almost 80% of the xylose disappears within 10 s, leaving residual xylose whose concentration slowly decays during the next 40 s to ~4% of the initial concentration. This residual xylose suffers little further degradation out to a residence time of 130 s. The factors leading to this arcane behavior are discussed later.

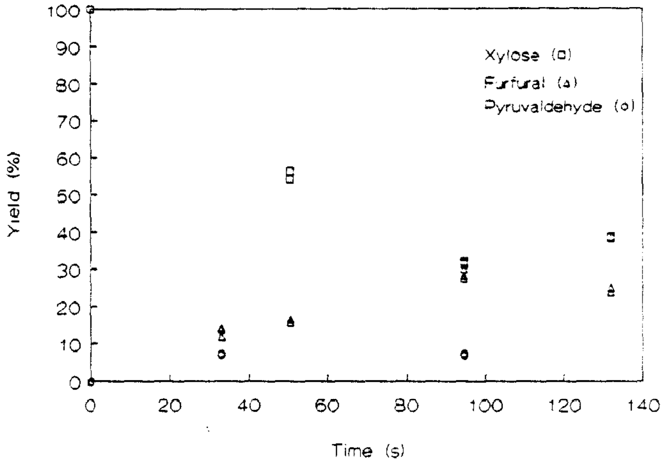


Fig. 2. Absolute yields of reactant and products from 0.05M D-xylose in water at 250° without catalyst as a function of residence time.

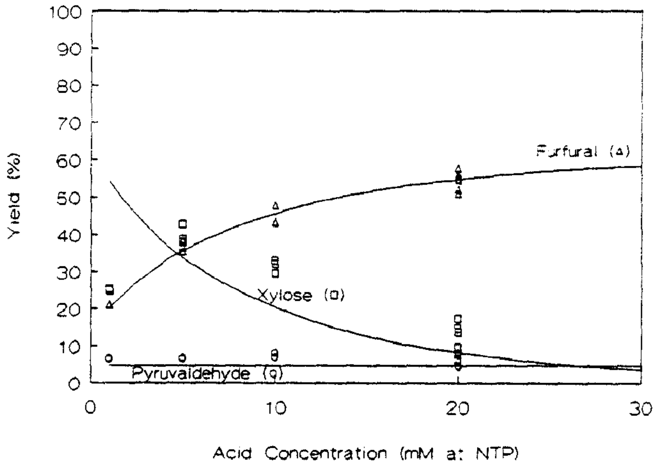


Fig. 3. Absolute yields of reactant and products from 0.05M D-xylose after 32 s in water at 250° as a function of H_2SO_4 concentration.

They appear to be largely, but not completely associated with product inhibition (decrease in concentration of H^+ resulting from protonation of furfural). In Fig. 3 the disappearance of xylose is strongly influenced by acid concentration; whereas initial reactant concentration (Fig. 4) has a lesser effect on the yield.

The behaviour of furfural displayed in Figs. 1–4 is less recondite. In the presence of acid, furfural forms without delay and steadily reaches a maximum yield of ~63% after 50 s. This yield is strongly influenced by the acid concentration (Fig. 3), and somewhat influenced by the initial reactant concentration (Fig. 4). The stability of furfural in the presence of acid (see Fig. 1) is not consistent with the model of Dunlop[5]

TABLE III

Results of acid-catalyzed dehydration of xylose in water at 250°, 34.5 MPa

			Yield (mol%)								
Xylose Conc. (mM)	*Acid* (mM)	*Time* (*s*)	*Xylose*	*Lyxose*	*Other Pentose*	*Glyceraldehyde*	*Pyruvaldehyde*	*Glycolaldehyde*	*Lactic Acid*[a]	*Acetol*	*Furfural*
50	1	32	25	8	2	1	6	11	7	4	21
50	5	33	40				7				37
50	10	33	32				7				45
50	20	1.5									8
50	20	1.5	79								6
50	20	2.8	64				2				15
50	20	2.9									16
50	20	5.7	40				5				27
50	20	5.7									33
50	20	11	22				8				46
50	20	33	15				8				57
50	20	33	9	1	1		4			5	52
50	20	33	6	2	0.5		5	5	4	2	55
50	20	50	4								64
50	20	50	5								62
50	20	93	2				6				62
50	20	130	2								63
20	20	32	7	3			5	6	3		55
20	20	33	7	0.3			4				53
100	20	33	11	4	2	1	4	8	5	4	45
5	40	33									56

[a] Estimated yield based on marginally separated h.p.l.c. peaks.

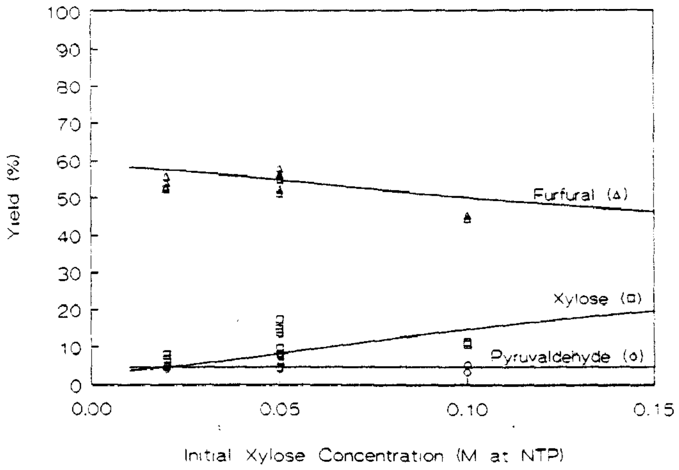


Fig. 4. Absolute yields of reactant and products from D-xylose after 32 s in water at 250° with 20mM H_2SO_4 catalyst as a function of D-xylose concentration.

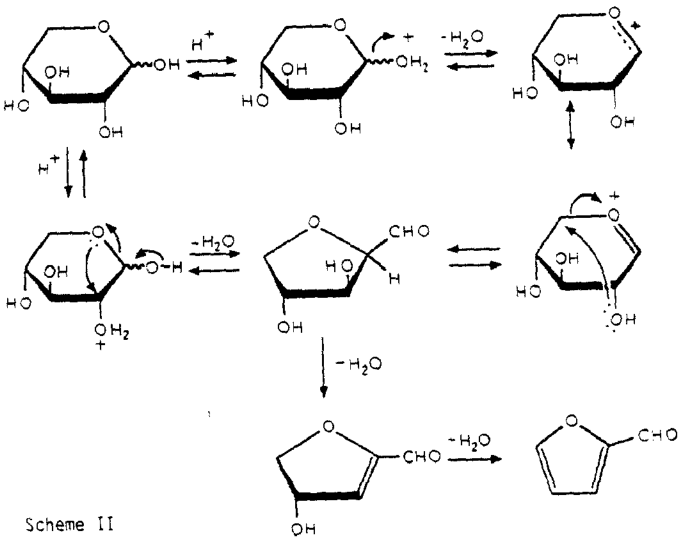
and Root *et al.*[7]. To explore this disagreement we executed several experiments, some of whose results are displayed in Table IV. An experiment using pure 0.05M furfural as the reactant with 20mM sulfuric acid catalyst evidenced no furfural disappearance after 32 s at 250°. A related experiment involving 0.05M furfural with 0.05M xylose without acid catalyst led to essentially complete recovery of the furfural accompanied by very high yields of fragmentation products. An experiment with 0.05M furfural and 0.05M xylose with 20mM sulfuric acid catalyst (see Table IV) evidenced a significantly decreased yield of furfural (131% instead of 152%) and high yields of fragmentation products. At first we interpreted this result to be consistent with the earlier work of Dunlop[5] and Root *et al.*[7] concerning the formation of "resins" from xylose and furfural, but after considerable modelling we realized that the results of this experiment more closely resemble the results of its non-catalyzed analogue, and an experiment in Table III involving 0.05M xylose with 0.001M H_2SO_4. Apparently the real role of furfural is that of a Brønsted base which reacts with H_3O^+ to form stable, protonated furfural; thereby decreasing the concentration of acid catalyst and causing the chemistry to more closely resemble the uncatalyzed situation.

Perhaps the most incisive observation contained in this paper concerns the evolution of pyruvaldehyde displayed in Fig. 1. After about 12 s the pyruvaldehyde yield reaches a maximum value of 4–8% and thereafter is relatively stable at 4–6% up to 93 s. This value is not significantly influenced by the presence or absence of acid catalysts (see Figs. 2 and 3), nor is it influenced by the initial reactant xylose concentration (see Fig. 4). This behavior contrasts markedly with that of furfural. The kinetic behavior of these two species (furfural and pyruvaldehyde) does not permit the possibility of a common intermediate being active in their formation. No imaginable kinetic model involving pathways which lead to pyruvaldehyde and furfural via acyclic xylose can be consistent with the data displayed in Figs. 1–4. It seems logical to insist that pyruvaldehyde and the other fragmentation products derive from acyclic xylose, leaving one of the ring forms to be the source of furfural. This explanation requires the rate of isomerization of the two ring forms via the open-chain intermediate to be relatively slow at 250°. If furfural forms from one of the ring isomers, and the fragmentation products derive from the open-chain form, and if the rates of ring opening and closure are slow, then the stable residual yield of xylose observed at residence times beyond 50 s is evidently the other ring form.

The behavior of lyxose given in Table III is consistent with the foregoing hypothesis. Lyxose appears to form rapidly from open-chain xylose, and disappears more slowly to produce furfural and other byproducts. Increasing acid concentration reduces the lyxose yield, presumably by increasing the rate of lyxose conversion into furfural. Data from an experiment involving 0.05M lyxose as a reactant with 5mM H_2SO_4 are displayed in Table IV. The very low yield of product xylose in this experiment is noteworthy, and consistent with the low yields of product lyxose obtained from reactant xylose. Evidently the rate of the Lobry de Bruyn–Alberda van Ekenstein rearrangement is slow at 250° in the presence of acid. This finding is consistent with an earlier paper in this series[12], which revealed the rate of the glucose–fructose isomerization to be slow in the presence of acid at 250°.

In order to obtain short residence-time data for Fig. 2 we attempted to employ the small, capillary-tube reactor (as in Fig. 1); however the xylose yield curve did not join smoothly with the data displayed in Fig. 2. Further work convinced us that this was an artifact of wall-catalyzed chemistry resulting from the very large surface-to-volume ratio of the capillary-tube reactor. Similar wall effects could not be detected in the presence of acid, nor were such effects detected in related work involving alcohols[24–27]. In spite of the compromising influence of these wall effects on our uncatalyzed results, we wish to note that without acid catalyst, furfural evidenced an accelerating rate of formation for residence times below 10 s. This behavior is consistent with an autocatalytic mechanism involving an acidic product of xylose decomposition. To examine the possibility of product formic acid acting as a catalyst for furfural formation, we executed back-to-back experiments involving 0.05M xylose reactant with and without formic acid catalyst. The absolute yield of furfural increased from 14% without acid to 17% in the presence of 20mM formic acid catalyst. This result is consistent with the possibility of furfural formation by an autocatalytic mechanism involving formic acid. We also note the presence of a similar lag phase in the rate of degradation of sucrose in melts as well as in concentrated aqueous solution, which has previously been shown[29] to be due to autocatalysis by acids formed in the early stages of the reaction.

Scheme II displays two possible mechanisms for furfural formation involving the xylopyranose isomers. We believe xylofuranose to be the relatively stable species which constitutes the residual xylose observed at long residence times (see Fig. 1). One of the pathways displayed in Scheme II, which involves the formation of the xylosyl cation by elimination of the C-1 hydroxyl group, followed by the substitution of O-2 at C-5 with simultaneous scission of the C-5–O-5 oxygen linkage, closely resembles an earlier proposal by Shafizadeh *et al.*[30] for the zinc chloride-catalyzed, pyrolytic mechanism of furfural formation from various substituted phenyl β-D-xylopyranosides at 500°.



Scheme II

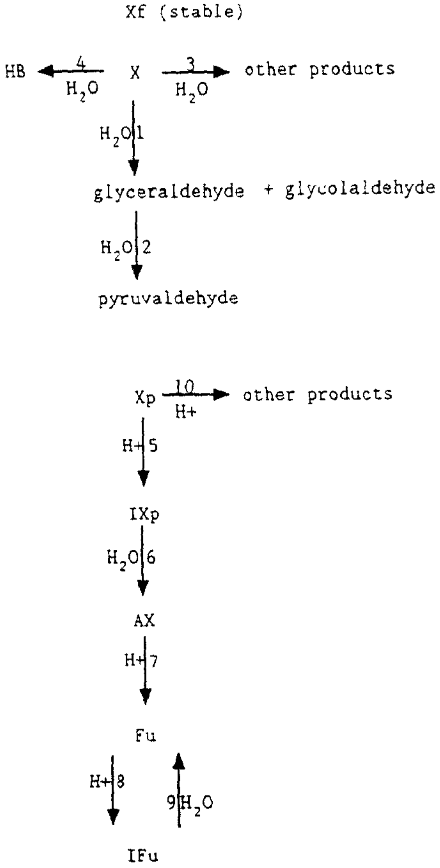


Fig. 5. Kinetic model of furfural formation.

The preceding discussion, combined with the mechanism given in Scheme II, motivates the kinetic model displayed in Fig. 5 for the reactions of xylose in water with sulfuric acid at high temperatures. In Fig. 5 the acyclic xylose isomer rapidly decomposes by three parallel pathways to glycoaldehyde and pyruvaldehyde (via glyceraldehyde), an unidentified acid, and other products (including lyxose, arabinose, lactic acid, glycolaldehyde, and acetol). The xylofuranose isomers are stable under the conditions studied in this work. The xylopyranose isomers form the 2,5-anhydride via a protonated intermediate according to the mechanism of Scheme II. The subsequent steps, which involve the irreversible development of conjugation, are incorporated into the model as a single, acid-catalyzed step. Alternatively, the xylopyranose isomers can suffer degradation to other minor products by the acid-catalyzed pathway *10* in Fig. 5.

The kinetic model displayed in Fig. 5 results in the following set of coupled, non-linear, ordinary differential equations (ODE's) governing the time evolution of products in the reactor:

$$\mathrm{d}[\mathrm{Xf}]/\mathrm{d}t = 0 \tag{1}$$

$$\mathrm{d}[\mathrm{X}]/\mathrm{d}t = -(k_1 + k_3 + k_4)\,[\mathrm{H_2O}][\mathrm{X}] \tag{2}$$

$$\mathrm{d}[\mathrm{GA}]/\mathrm{d}t = k_1[\mathrm{H_2O}][\mathrm{X}] - k_2[\mathrm{H_2O}][\mathrm{GA}] \tag{3}$$

$$\mathrm{d}[\mathrm{PA}]/\mathrm{d}t = k_2[\mathrm{H_2O}][\mathrm{GA}] \tag{4}$$

$$\mathrm{d}[\mathrm{HB}]/\mathrm{d}t = k_4[\mathrm{H_2O}][\mathrm{X}] \tag{5}$$

$$\mathrm{d}[\mathrm{Xp}]/\mathrm{d}t = -(k_5 + k_{10})[\mathrm{H^+}][\mathrm{Xp}] \tag{6}$$

$$\mathrm{d}[\mathrm{IXp}]/\mathrm{d}t = k_5[\mathrm{H^+}][\mathrm{Xp}] - k_6[\mathrm{H_2O}][\mathrm{IXp}] \tag{7}$$

$$\mathrm{d}[\mathrm{AX}]/\mathrm{d}t = k_6[\mathrm{H_2O}][\mathrm{IXp}] - k_7[\mathrm{H^+}][\mathrm{AX}] \tag{8}$$

$$\mathrm{d}[\mathrm{Fu}]/\mathrm{d}t = k_7[\mathrm{H^+}][\mathrm{AX}] + k_9[\mathrm{H_2O}][\mathrm{IFu}] - k_8[\mathrm{H^+}][\mathrm{Fu}] \tag{9}$$

$$\mathrm{d}[\mathrm{IFu}]/\mathrm{d}t = k_8[\mathrm{H^+}][\mathrm{Fu}] - k_9[\mathrm{H_2O}][\mathrm{IFu}] \tag{10}$$

where [ ] = concentration at reaction temperature and pressure (RTP), Xf = xylofuranose, X = acyclic xylose, GA = glyceraldehyde, PA = pyruvaldehyde, HB = acidic product derived from X, Xp = xylopyranose, IXp = protonated xylopyranose intermediate, AX = 2,5-anhydroxylose, Fu = furfural, IFu = protonated furfural intermediate, and $[\mathrm{H^+}]$ is the time-dependent concentration of protons. We use the algebraic charge conservation relationship $[\mathrm{H^+}] = [\mathrm{H_2SO_4}]_0 + [\mathrm{HB}] - [\mathrm{IXp}] - [\mathrm{IFu}]$ to calculate the time-dependent concentration of protons, where $[\mathrm{H_2SO_4}]_0$ is the initial concentration of sulfuric acid at RTP. Also we assume that the xylose concentration measured by h.p.l.c. is given by [Xf] + [X] + [Xp] + [IXp] + [AX], and the measured furfural concentration is given by [Fu] + [IFu]. Earlier work[25–28] has shown that low concentrations of sulfuric acid complety dissociate to $\mathrm{H^+}$ and $\mathrm{HSO_4^-}$ at RTP, but that $\mathrm{HSO_4^-}$ does not dissociate to a significant extent at RTP. Because all the reactant and product mixtures employed in this work involve low concentrations of various solutes in water, we use the tabular equation of state of pure water[31] to convert concentrations measured at NTP to those used in the kinetic model at RTP.

The concentrations of the protonated intermediates IXp and IFu play a pivotal role in the kinetic model. As their concentrations increase, the concentration $[\mathrm{H^+}]$

TABLE IV

Results of selected experiments involving reactants furfural, lyxose, and xylose

Reactant(s)	*[H$_2$SO$_4$]* (mM)	*Molar yields (%) of products*								
		Xylose	*Lyxose*	*Other Pentose*	*Pyruv-aldehyde*	*Glycer-aldehyde*	*Glycol-aldehyde*	*Lactic Acid*	*Acetol*	*Furfural*
0.05M Furfural	20									98
0.05M Furfural + 0.05M Xylose	Nil	3.6	8.7	2.5	9.5	2.2	30.	25.		104
0.05M Furfural + 0.05M Xylose	20	7.6	5.2	2.0	4.6	1.6	17	8.5		131
0.05M Xylose	20	6.4	2.0	0.3	4.6		4.6	3.6	2.3	55
0.05M Lyxose	5	2.0	17.7	1.5	5.3	1.0			4.5	37

TABLE V

Best-fit values of the constants k_i and mole fractions f_x, f_{xp}, and f_{xl}[a]

Parameter	*Values of* i									
i	1	2	3	4	5	6	7	8	9	10
k_i/s^{-1}*(mol/dm^3)*$^{-1}$	2.13 E−3	1.00 E+5	4.13 E−3	1.82 E−3	5.58 E00	7.58 E+2	1.29 E+2	5.90 E00	4.83 E−4	1.94 E00

[a] f_x = 1.78 E−1; f_{xp} = 8.08 E−1; f_{xl} = 1.4 E−2.

decreases and the rate of conversion decreases. This feedback enables our model to avoid the use of rate constants which depend upon some power of $[H^+]$. Thus the rate equations *(6)*–*(10)* are linear in $[H^+]$, and the rate constants k_5, k_6, k_8, and k_9 may be viewed to be elementary rate constants.

The solutions to Equations *(1)*–*(9)* are dependent on the rate constants k_i, and the mol fractions f_X, f_{Xp}, f_{Xf} of the acyclic, pyranose, and furanose isomers at the entrance of the reactor (which define the initial conditions). The inverse problem in chemical kinetics is to find values of these parameters (rate constants and mol fractions) which result in a best fit of the solutions to the ODE's with the experimental data. If the fit is good, the kinetic model is said to be consistent with the experimental data. Because we have found that the steady-state idealization does not preserve the character of the actual solutions to ODE's such as Eqs. *(1)*–*(10)* above[27], we integrate Eqs. *(1)*–*(10)* numerically to obtain "exact" solutions. Algorithmic details of this approach are described in earlier papers[27,32,33]. The best-fit values of the k_i and f_X, f_{Xp}, f_{Xf} are given in Table V.

The values of f_X, f_{Xp} and f_{Xf} in Table V, constitute the "best fit values" of the kinetic model. The f values for neutral aqueous solutions of xylose under ambient conditions are respectively 0.0017, 0.995, and <0.01 (ref. 34), whereas our model requires corresponding values of 0.178, 0.81, and 0.01 at 250°. It is known that, in general, the proportions of aldehyde and furanose forms of glycoses are increased markedly at the expense of the pyranose forms as the temperature of neutral aqueous solutions is increased[35]. Therefore the high value of f_X indicated by the model is not surprising. The increase in content of furanose isomers on heating to 250° appears to be less dramatic. The presence of dilute acid is not expected to influence the isomeric composition of xylose, and the aldehydrol form is not expected[35] to be present in significant amount at 250°.

The large increase in the proportion of open-chain xylose must be achieved very rapidly during heating of the solution to 250°, yet our model requires that subsequent conversion of X to Xp must be relatively slow, since X and Xp yield different degradation products (namely, fragmentation products and furfural). This apparent paradox may be at least partly explained as follows. The interconversion of X, Xp, and Xf is the mutarotation process and the activation energy for this overall process is relatively low (16.8 kcal.mol^{-1})[34]. The activation energies for the xylose degradation processes such as furfural formation are likely to be much greater. Thus the activation energy for acid hydrolysis of the methyl xylopyranosides[36] is 34 kcal.mol^{-1} and in this reaction the rate-determining step is the formation of the same xylopyranosyl cation as that shown in Scheme II. On this basis we might anticipate that xylose interconversion reactions (mutarotation) would be much *less* accelerated by a major increase in temperature than the xylose degradation reactions. Hence the interconversions occur *relatively* slowly at 250°.

The solid lines given in Figs. 1, 3, and 4 display the fit of the model to the data using the rate constants given in Table IV. The model is not used to fit the uncatalyzed data in Fig. 2 because the exact nature of the autocatalytic reaction, including the identity and concentration *vs* time behavior of the autocatalytic acid product of xylose decomposition, is not known. The fit of the model to the time-dependent furfural yield is excellent, and its fit to the xylose and pyruvaldehyde yield is good. However, its fit to the xylose data with low acid ($[H_2SO_4]$ = 1mM) is not good. This reflects the fact that we have not succeeded in characterizing all the products (especially acidic products) of xylose decomposition in the low-acid regime. As more experimental data describing the time evolution of lyxose, lactic acid, acetol, formic acid, and other products become available, the model given in Fig. 5 can be refined to better describe the decomposition behavior of xylose. Over 40 models were investigated during the past three years in the course of this research. The earliest models emphasized the role of acyclic xylose in furfural formation. These models were grossly incapable of fitting the experimental data. Of all the models we have studied, the model displayed in Fig. 5 (based on Scheme II) is the only one which we found to be consistent with our experimental data.

We must emphasize that this study makes no attempt to maximize the yield of furfural from xylose. In order to identify the "optimal" conditions for manufacturing furfural from xylose, the temperature dependence of the rate constants displayed in Fig. 5 and Table V must be determined. This is a subject for future research.

CONCLUSIONS

Our experimental data and modeling results are consistent with the following conclusions. In liquid water at 250° in the presence of 0.001–0.02M sulfuric acid:

(*1*) the open-chain xylose isomer is initially present in relatively large amount (18% of total xylose) and quickly reacts to form glyceraldehyde, pyruvaldehyde, lactic acid, glycolaldehyde, formic acid, acetol, and other fragmentation products, as well as lyxose and arabinose;

(*2*) the furanose ring forms of xylose are initially present in small amounts and are relatively stable over a time period of 100 s or less;

(*3*) the xylopyranose ring-forms react to form the 2,5-anhydride of xylose, which develops conjugation by further dehydrations to form furfural;

(*4*) the rates of ring opening and closure, as well as the rate of the Lobry de Bruyn–Alberda van Ekenstein rearrangement are significant, but relatively slow under these conditions;

(*5*) further progress in detailing the commercially important, acid-catalyzed, high-temperature reaction chemistry of xylose in water must rest on more complete, quantitative analyses of the complex set of products born by these reactions, including the putative 2,5-anhydroxylose intermediate.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under grant no. CBT-8812954 (UH), the Coral Industries Endowment (UH), and by the University of Montana. The authors thank Dr. Ivan Simkovic for analyses of early experimental work not reported in this paper, and Mr. Sunil Sinha (UH) for assistance with the experiments.

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