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THE INFLUENCE OF pH AND WEAK-ACID ANIONS ON THE DEHYDRATION OF D-FRUCTOSE*

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ABSTRACT

The influence of the pH (1–6) on the rates and yields in the dehydration of D-fructose to 5-hydroxymethyl-2-furaldehyde (HMF) and the rehydration of HMF to levulinic and formic acids at 175° has been studied by using a stirred tank-reactor. The conversion rate of D-fructose passes through a minimum at pH 3.1, whereas at pH >3.9 no formation of HMF occurred and at pH >2.7 no formation of levulinic acid occurred. Isomerisation to D-glucose is observed at pH >4.5. When a weak-acid anion, which functions as a base catalyst, is present at pH 3, the yield of HMF is lowered and isomerisation occurs.

INTRODUCTION

As previously shown[1-3], 98% of the reaction products of D-fructose in acid media consist of 5-hydroxymethyl-2-furaldehyde (HMF), levulinic (4-oxopentanoic) and formic acids, and humin. In alkaline solution, lactic and saccharinic acids are formed from sugars[4]. It has not yet been determined at what pH or degree of acidity the change in reaction type occurs. Reactions were therefore studied in the range pH 1–6. From explorative experiments and literature data[5,6], it appeared necessary to increase the reaction temperature to 160–190° in order to obtain rates comparable with those observed[1-3] at high acidity. Consequently, high-pressure apparatus was necessary. Owing to the formation of acidic products, autocatalysis may occur[7,8], and therefore the pH of the reaction mixtures was controlled by the addition of 4M KOH. Experiments without pH control and with the addition of salts were carried out in order to study the effect of anions and cations.

EXPERIMENTAL

In the apparatus shown in Fig. 1, the reaction liquid was circulated, and cooled and depressurised to 60° and 1 atmos. in order to measure the pH. Although this pH differs from that in the reactor, all data refer to the former conditions. A series of batch experiments was carried out at 175 ±0.5° and at 50 atmos. The initial con-

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*The Dehydration of D-Fructose (Formation of 5-Hydroxymethyl-2-furaldehyde and Levulinic Acid). Part IV[1-3].

centration of D-fructose was kept low at 0 25M, in order to avoid problems with the formation of humin The reaction was started by pumping, within 1 min, 4M D-fructose into the reactor. Samples were taken at 2-300 min and analysed[1] for fructose, HMF, and levulinic acid; humin could not be quantitated. Where appropriate, glucose was also determined. The concentrations were corrected for the dilution with alkali, and the effective reaction time was only 14/15 of the real time, because only 1.4 l of the total liquid volume of 1.5 l was contained in the reactor at high temperature.

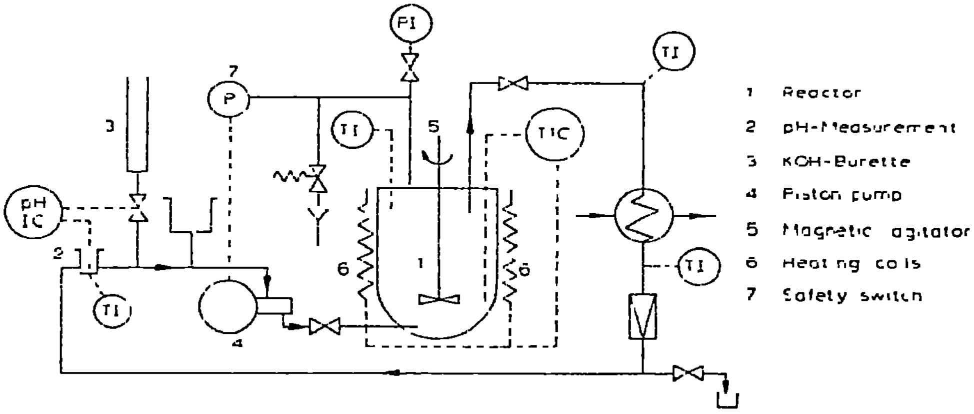


Fig. 1. Batch reactor with external pH control.

In the experiments with pH control, the initial pH was adjusted with formic acid to 1.0–1 1, 2 0, 2.7, 3 0, 3.3, 3.7, 4 0, 4.1–4 3, and 4.5–6 0. At pH >4, the system was not capable of maintaining a constant pH, the pH fluctuated between the values given. During the experiment, starting at pH 1 0, the pH rose to 1.1, probably owing to a slight decomposition of formic acid[5].

The results are summarised in Table I and include the amount of alkali added to maintain constant pH, and the total amount of acids as determined by titration to pH 8; increases were proportional to the D-fructose conversion (Fig. 2). Foaming of the reaction mixture, probably due to the decarboxylation of saccharinic and formic acids, was observed at pH 3 3–6.0.

The results of experiments where pH was not controlled are given in Table II. Starting at pH 7, the pH quickly changed to <3 5 and a good yield of HMF was obtained. At the beginning of the reaction, a small amount of glucose was formed. When the initial pH was adjusted to 3.6 or 3 0 with formic acid, the pH subsequently changed to 3.1 or 2 9, respectively, and there was little difference in products in comparison with experiments at a constant pH of 3 3 or 3 0. The addition of sodium formate (0 25 mol/l) at pH 3 (adjusted with formic acid) profoundly changed the quantitative results, whereas there was little effect in a similar experiment using NaCl and HCl

TABLE I

CONCENTRATIONS (M) MEASURED FOR EXPERIMENTS WITH pH CONTROL

pH→	*1.0–1.1*			*2.0*			*2.7*		*3.0*		*3.3*		*3.7*		*4.0*	*4.1–4.3*	*4.5–6.0*	
Time (min)	*F*	*HMF*	*LA*	*F*	*HMF*	*LA*	*F*	*HMF*	*F*	*HMF*	*F*	*HMF*	*F*	*HMF*	*F*	*F*	*F*	*G*
2	0.10	0.07		0.22	0.02				0.24								0.15	0.03
5	0.02	0.10		0.17	0.06						0.22				0.21	0.20	0.08	0.02
10		0.10	0.01	0.12	0.10		0.21	0.04	0.22	0.02	0.21	0.03	0.20	0.01	0.18	0.15	0.05	0.01
20		0.07	0.02	0.07	0.12			0.08	0.19	0.04	0.18	0.06	0.17	0.02	0.14	0.10	0.02	
30		0.05	0.03	0.03			0.14	0.12		0.07		0.08	0.12	0.03	0.10	0.07		
45		0.03	0.04		0.12		0.11	0.14	0.14	0.10	0.13	0.09	0.09	0.05	0.07	0.05		
60		0.02			0.10	0.01	0.08	0.14		0.11		0.10	0.07	0.06	0.05	0.03		
90		0.01	0.05			0.02	0.05	0.13	0.08	0.13	0.07	0.11		0.06	0.03			
120			0.06		0.06	0.03		0.12		0.12		0.10		0.06				
180					0.03	0.04		0.12		0.11		0.09		0.05				
240					0.02			0.11						0.05				
300					0.01	0.05		0.10						0.04				
A[a]	—			—			0.004		0.008		0.015		0.045		0.085	0.11	0.20	
T[b] t = 0	6.04			0.46			0.025		0.007		0.002		<0.001		—	—	—	
t = 180	6.10			0.54			0.055		0.051		0.050		0.060		0.100	0.12	0.21	
foam	none			none			none		none		little		much		much	much	little	

[a] A = added alkali (equiv./l). [b] T = total acids (equiv./l)

TABLE II

CONCENTRATIONS MEASURED FOR EXPERIMENTS WITH CHANGING pH

pH→ *Catalyst* *Time (min)*	*7→3.2* None				*3.5→3.1* FA			*3.0→2.9* FA		*3.0* FA + 0.25M HCO$_2$Na			*3.0→2.9* FA + 0.25M NaCl		*3.0→2.9* HCl	
	pH	*F*	*G*	*HMF*	*pH*	*F*	*HMF*	*F*	*HMF*	*F*	*G*	*HMF*	*F*	*HMF*	*F*	*HMF*
5	4.0	0.20	0.03							0.16	0.01	0.01				
10	3.5	0.17	0.01	0.01	3.3	0.21	0.01			0.10	0.02	0.02	0.21	0.02		
20	3.2	0.15	0.01	0.02	3.2	0.18	0.03	0.19	0.04	0.05	0.02	0.03	0.18	0.05	0.20	0.03
30		0.12		0.05	3.1	0.16	0.04	0.17	0.07	0.03	0.01	0.04	0.15	0.07	0.18	0.05
45						0.12	0.06									
60		0.10		0.07		0.10	0.09	0.13	0.10	0.01		0.05	0.11	0.11	0.15	0.09
90		0.07		0.14		0.06	0.10	0.09	0.11			0.05	0.06	0.12	0.10	0.10
120		0.03		0.14		0.04	0.10	0.06	0.11			0.04	0.04	0.11	0.08	0.11
180	3.2			0.12	3.1	0.02	0.09	0.02	0.10			0.03	0.01	0.09	0.03	0.10
T[a] t = 0	—				—			0.007		1.39			0.009		—	
t = 180	0.057				0.055			0.051		0.68			0.060		0.072	

[a] T = total acids (equiv/l)

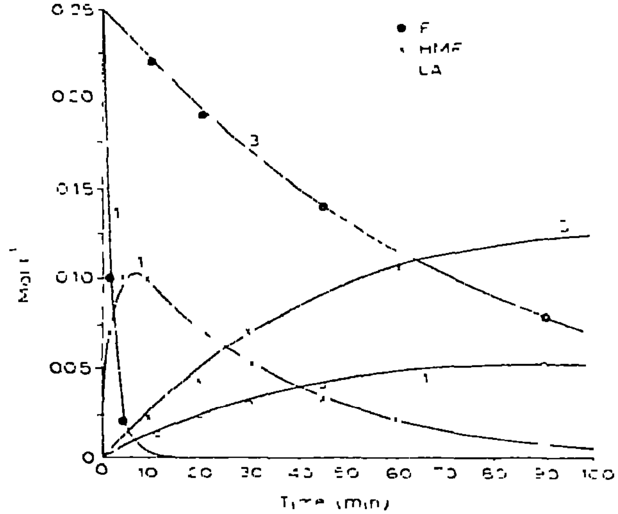


Fig 2 Dehydration of D-fructose 175 pH 1 and 3 Curves are computer-plotted using the first-order model

DISCUSSION

Using the first-order model, previously described[3], the values of k_F were determined from the fructose data, k_1/k_F and k_H from the HMF data, and k_3/k_H from the levulinic acid data The results are given in Tables III and IV There is a good fit of the model with the experimental results, except for experiments at pH >4 where deviations are caused by the isomerisation to glucose, and by the fluctuations in pH

For acid-base catalysis, the rate constant, k, can be described as. $k = k_0 + k_{H^+}[H^+] + k_{HO^-}[HO^-] + k_A[A] + k_B[B]$, where A is an acid or proton donor, and B a base or proton acceptor; k_0 represents the catalytic influence of water, which functions both as an acid and as a base From the titration data in Tables I and II, an average content of A, undissociated weak acids, and B, weak-acid anions, were

TABLE III

VALUES FOR k_F, k_1/k_F, k_H, AND k_3/k_H FROM EXPERIMENTS WITH pH CONTROL

pH	*100* k_F *min*$^{-1}$	k_1/k_F	*100* k_H *min*$^{-1}$	k_3/k_H
1 0 1 1	48 ± 26	0 50 ±0 05	3 2 ±0 3	0 44 ±0 08
2 0	7 0 ± 0 7	0 74 ±0 06	1 1 ±0 1	0 25 ±0 06
2 7	1 9 ± 0 1	1 00 ±0 10	0 6 ±0 2	0
3 0	1 3 ± 0 1	0 92 ±0 08	0 5 ±0 2	0
3.3	1 5 ± 0 2	0 80 ±0 07	0 5 ±0 1	0
3 7	2 2 ± 0 2	0 32 ±0 05	0 3 ±0 1	0
4 0	2 8 ± 0 3	0	?	
4 1 4 3	4 3 ± 0 7	0	?	
4 5 6 0	20	0	?	

TABLE IV

VALUES FOR k_F, k_1/k_F, k_H, AND k_3/k_H FROM EXPERIMENTS WITH CHANGING pH

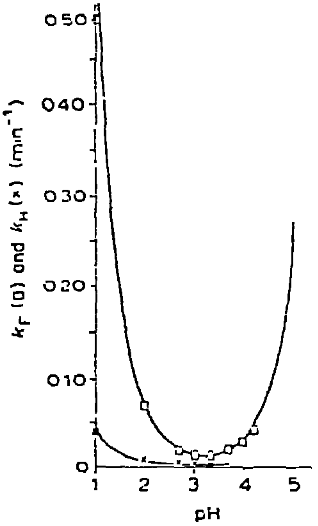
pH	*Catalyst*	*100* k_F *min*$^{-1}$	k_1/k_F	*100* k_H *min*$^{-1}$
7 3 2	None	1 8	0 50	0 0
3 6 3 1	FA	1 6 ±0 1	0 50 ±0 06	0 2 ±0 1
3 0 2 9	FA	1 2 ±0 1	0 92 ±0 08	0.7 ±0 1
3 0	FA + HCO_2Na	8 2 ±1 3	0 17 ±0 05	0 1 ±0 2
3 0 2 9	FA + NaCl	1.6 ±0 1	0 81 ±0 09	0 6 ±0 1
3 0 2.9	HCl	1.0 ±0 2	0 90 ±0 15	0 5 ±0 1

determined. These values include the formic acid and sodium formate added and also the weak acids (formic, levulinic, lactic, and saccharinic acids) that are formed during the reaction. Expressions *1* and *2* appear to hold approximately.

$$k_F = 0.005+5[H^+]+1.5\times 10^8[HO^-]+0.28[B] \text{ min}^{-1} \qquad 1$$

$$k_H = 0.005+0.35[H^+] \text{ min}^{-1} \qquad 2$$

No significant catalytic influence was found for the undissociated weak acids; k_{HO^-} and k_B could not be determined from the k_H values, because, below pH 4, $[HO^-]$ and [B] were too small In Fig 3, k_F and k_H are shown as functions of pH: the curves represent equations *1* and *2* D-Fructose is most stable at pH 3.1. Na^+ and Cl^- ions have no direct catalytic influence, but slightly accelerate the reaction by changing the activity of the species involved (salt effect).



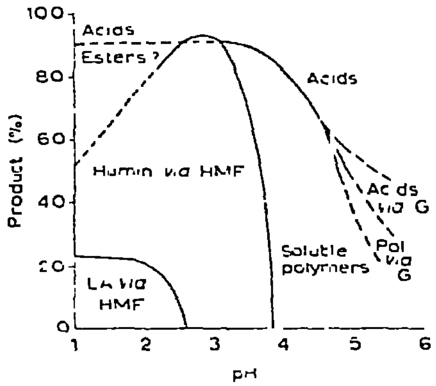


Fig 3. The dependence of k_F and k_H on pH

Fig 4 The product distribution as a function of pH. The percentage of D-fructose converted into the products mentioned is given

According to equations *1* and *2*, the rates of the dehydration and rehydration reactions are correlated with the acidity. For the more-concentrated acid solutions, the catalytic activity, or the acidity, is more than proportional to the acid concentration, whereas, at lower concentrations of acid, the acidity is proportional to $[H^+]$. The rate constants k_F and k_H are about equal at 95°, whereas at 175°, k_F is $>10k_H$. This finding is in accordance with the fact that the energy of activation [29 (Ref. 5) and 34 kcal/mol (Ref 9)] for k_F is higher than that [23 (Ref. 5) and 26 kcal/mol (Ref 10)] for k_H. The values for k_F are in good agreement with those found by Breen[6] and McKibbins[5] at 175°, and extrapolation of the values found by Dworschak[9] at 75–100° results in a value which is only 30% lower The values for k_H are in good agreement with those found by McKibbins[5] and Orsi[10].

A total picture of the reaction pathways of the experiments with pH control was derived from the reaction rate constants and is given in Fig 4 At pH >2 6, there was no formation of levulinic acid, and no formation of HMF occurred at pH >3.9 A small amount of fructose isomerised to glucose at pH >4 5, and the amount of acids formed increased with increasing pH.

The addition of formate at pH 3 accelerated the D-fructose conversion, caused isomerisation to D-glucose, and decreased the yield of HMF. Moreover, the u.v absorption was about twice the value expected from the concentration of HMF as determined[1] by g.l.c., indicating the formation of other furan compounds. The fact that HMF was not formed at pH >4 conflicts with the assertion made by Smith[11] that variation of pH in the range 1–10 is not important in the preparation of HMF.

Previous experiments[2] showed the yields of HMF and levulinic acid to be independent of the concentration of HCl above 0.5M. For formic acid catalysis, however, the yield of HMF decreased at pH <3, which may be due to the formation of formic esters from D-fructose or intermediate products since formic acid is present in large amounts at low pH. At pH >1, the yield of levulinic acid increases with decreasing pH, which is in accordance with the results of McKibbins[5]

Thus, the dehydration of D-fructose to HMF and the rehydration of HMF to levulinic and formic acids is catalysed by acids More-acidic conditions are needed for the formation of levulinic acid than for HMF. At lower acidities, concurrent, base-catalysed reactions occur which are most probably polymerisation, cleavage, and rearrangement reactions of the 3-deoxyhexosulose intermediates

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