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THE INFLUENCE OF WATER CONCENTRATION ON THE DEHYDRATION OF D-FRUCTOSE*

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ABSTRACT

The influence of water concentration on the rates and yields in the dehydration of D-fructose to 5-hydroxymethyl-2-furaldehyde (HMF) and in the rehydration of HMF to levulinic and formic acids at 95° has been studied by the addition of polyethylene glycol-600 (PG-600) to the reaction mixtures. Decrease of the water concentration highly increased the conversion rate of D-fructose, whereas that of HMF was slightly decreased, resulting in higher maximum concentrations of HMF from D-fructose. As compared with reactions in water, yields of levulinic acid were only slightly decreased at 40 vol. % PG-600 and halved at 70% PG-600.

INTRODUCTION

In the acid-catalysed dehydration of D-fructose to 5-hydroxymethyl-2-furaldehyde (HMF) and in the rehydration of HMF to levulinic (4-oxopentanoic) and formic acids, the conversion rate of D-fructose and of HMF is slightly influenced by the initial concentration, although the conversion of both can be described as a first-order process[1,2]. We now report on the effect of water concentration. Because the yields of HMF and levulinic acid are lower at higher initial concentrations of D-fructose, the latter concentration was kept constant at 0.5M. The amount of water in the reaction mixture was reduced by the addition of polyethyleneglycol-600 (PG-600) up to 70 vol. %. PG-600 was chosen because it can also be used as a liquefier in the vacuum-film distillation of HMF. The beneficial influence of organic solvents on the yields of HMF has been reported[3].

We have described[2] a kinetic model that accounted for the first-order conversion of D-fructose (F) into HMF, levulinic acid (LA), formic acid (FA), and humin (HUM), and for the fact that the yields of HMF and levulinic acid decreased at higher initial concentrations. Further, we showed that when reactions are carried out at only one initial concentration, the experimental data can be described as first-order

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

reactions, when the model reduces to

$$\begin{tikzcd}
F \arrow[r, "k_1"] \arrow[dr, "k_2"'] & HMF \arrow[r, "k_3"] \arrow[dr, "k_4"'] & LA+FA \\
 & HUM & HUM
\end{tikzcd}$$

with: $k_F = k_1 + k_2$ and $k_H = k_3 + k_4$

From this model, equations *1–5* can be derived

$$[HMF] = [HMF]_0 \exp(-k_H t) \tag{1}$$

$$[LA] = k_3/k_H [HMF]_0 [1 - \exp(-k_H t)] \tag{2}$$

$$[F] = [F]_0 \exp(-k_F t) \tag{3}$$

$$[HMF] = k_1 [F]_0/(k_F - k_H) [\exp(-k_H t) - \exp(-k_F t)] \tag{4}$$

$$[LA] = k_1 k_3 [F]_0/(k_F k_H) [1 - k_F/(k_F - k_H) \exp(-k_H t) + k_H/(k_F - k_H) \exp(-k_F t)] \tag{5}$$

The rate constants were evaluated by minimising the sum of the squares of the differences between calculated and experimental concentrations.

EXPERIMENTAL AND RESULTS

Using the apparatus and experimental procedures previously[1,2] described, batch experiments at 95° in glass ampoules were carried out with M HCl containing D-fructose (0.5 mol/l) and 10, 20, 40, and 70 vol. % PG-600, and with a solution containing HMF (0.5 mol/l) and 40 vol. % of PG-600. The results are shown in Table I and in Figs. 1 and 2.

Humin could not be determined gravimetrically since, in the presence of PG-600, the humin is more soluble. In 70% PG-600, no precipitation of humin occurs, but the mass balance was >100% when the polymers were precipitated by adding water and quantitated. The hydrogen content of the humin was also increased from 4.3 to 5.7%, indicating inclusion of an appreciable amount of PG-600. Moreover, at a higher PG-600 content, there was a growing discrepancy between the HMF concentrations determined by u.v. and g.l.c. methods, possibly because of the formation of HMF-PG-600 ethers[4], which are not detected in g.l.c.

D-Fructose is dehydrated faster and HMF is rehydrated more slowly when the PG-600 concentration is higher (*i.e.*, the water concentration is lower), which results in a higher, maximum concentration of HMF. The levulinic acid yield is only slightly affected at <40% PG-600, but is appreciably diminished at 70%. This finding accords with the results of Teunissen[illegible], who decreased the water concentration by the addition of methanol and ethanol.

TABLE I

CONCENTRATION (M) MEASURED FOR DEHYDRATION AND REHYDRATION EXPERIMENTS WITH 0.50M SOLUTIONS OF D-FRUCTOSE AND HMF IN M HCl AT 95°

PG-600	*10%*			*20%*				*10%*				*70%*				*40%*		
Time (min)	*F*	*HMF*	*LA*	*F*	*HMF*		*LA*	*F*	*HMF*		*LA*	*F*	*HMF*		*LA*	*HMF*		*LA*
					Glc	*Ur*			*Glc*	*Ur*			*Glc.*	*Ur*		*Glc*	*Ur*	
15	0.40	0.06		0.39	0.08	0.08		0.28	0.13	0.13		0.07	0.32	0.36		0.45	0.45	0.04
30	0.31	0.09	0.02	0.30	0.13	0.13	0.02	0.18	0.21	0.22	0.02	0.02	0.33	0.35	0.02	0.41	0.42	0.07
60	0.23	0.14	0.04	0.21	0.18	0.18	0.03	0.07	0.26	0.28	0.06	0.01	0.28	0.32	0.04	0.34	0.36	0.12
120	0.11	0.15	0.13	0.09	0.18	0.19	0.13		0.20	0.24	0.14		0.20	0.25	0.09	0.23	0.26	0.21
180	0.06	0.12	0.19	0.04	0.14	0.15	0.18		0.13	0.18	0.19		0.14	0.20	0.12	0.16	0.20	0.26
240	0.03	0.08	0.23	0.02	0.09	0.11	0.23		0.10	0.16	0.23		0.10	0.15	0.14	0.12	0.16	0.30
300	0.02	0.06	0.27		0.06	0.09	0.26		0.08	0.15	0.26		0.07	0.12	0.14	0.09	0.14	0.33
24 h			0.34				0.34				0.32			0.02	0.17		0.03	0.40

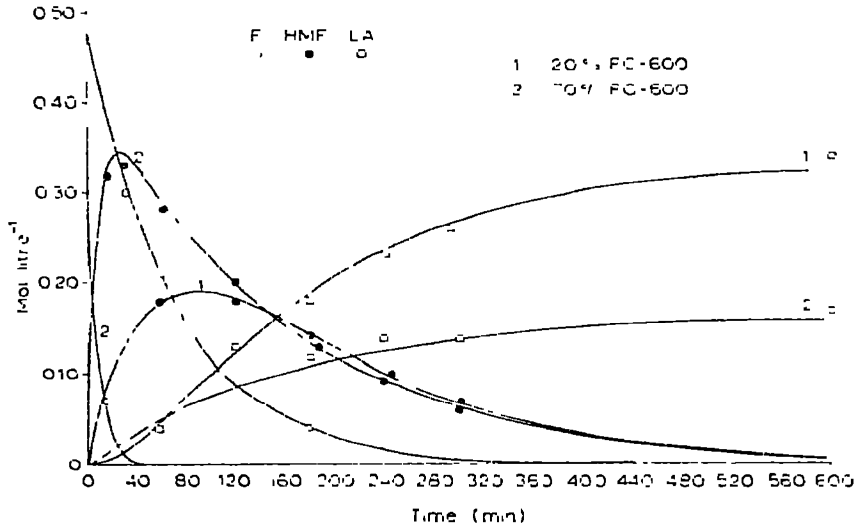


Fig 1. The dehydration of D-fructose M HCl, 95° Curves are computer-plotted using the first-order model

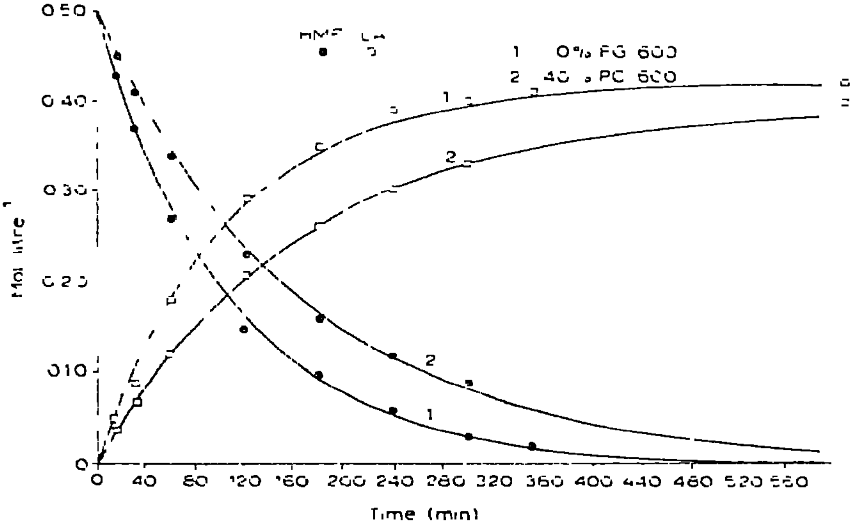


Fig 2 The rehydration of HMF M HCl, 95 Curves are computer-plotted using the first-order model

DISCUSSION

Values for k_1, k_F, k_3, and k_H were evaluated by using the kinetic model The experiments involving 0.5 mol/l concentrations of D-fructose and HMF in M HCl, without PG-600 addition[2], were also included The value for k_1/k_F could be fixed at 0.81 (±0.02), which accords with the value found previously[2] for k_x at $n_x = 1$ The results are given in Tables II and III The k_H values for the experiments starting with D-fructose appear to be higher than for those with HMF This effect has already been explained[2] A good data-fit was obtained, as shown in Figs 1 and 2

TABLE II

VALUES FOR k_H AND k_3/k_H FROM EXPERIMENTS STARTING WITH HMF

PG 600 (%)	100 k_H min^{-1}	k_3/k_H
0	0.94 ± 0.05	0.84 ± 0.03
40	0.61 ± 0.05	0.79 ± 0.04

TABLE III

VALUES FOR k_F, k_3/k_H, AND k_H FROM EXPERIMENTS STARTING WITH D-FRUCTOSE (k_1/k_F = 0.81 ±0.02, THE RANGE FOR k_3/k_H = ±0.04)

PG-600 (%)	100 k_F min^{-1}	k_3/k_H	100 k_H min^{-1}
0	1.18 ± 0.05	0.84	1.23 ± 0.11
10	1.25 ± 0.12	0.83	0.99 ± 0.10
20	1.45 ± 0.13	0.82	0.82 ± 0.06
40	3.43 ± 0.55	0.79	0.68 ± 0.04
70	12.7 ± 3.5	0.41	0.64 ± 0.04

The main effect of adding PG-600 is on the rate of the reaction, *i e* on k_F and k_H The activity of HCl changes very little[6], although the dielectric constant of the solution is lowered[7], it will have a negligible influence as compared to solvation effects[8] We have shown already that k_F followed the Hammett acidity. By analogy with the proposals of Bascombe and Bell[9], it was expected that $k_F = k_0$ [HCl] $[H_2O]^{-4}$, which is derived from the reaction $F + H^+ 4H_2O \rightleftharpoons FH^+ + 4H_2O$ if the formation of the enol from FH^+ is rate-determining However, from the effect of the addition of PG-600 at constant [HCl], it followed that the negative order in $[H_2O]$ was much lower, and, consequently, the order in [HCl] was higher than unity.

Fig 3 shows a log–log plot of k_F and k_H for M HCl against C_r, the relative water concentration $[H_2O]/55.6$; k_F is proportional to $C_r^{-1.7}$ and k_H to $C_r^{+0.75}$ A plot of $\log(k_F/C_r^{-1.7})$ and $\log(k_H/C_r^{+0.75})$ against $\log[\mathrm{HCl}]$ gave the exponents for [HCl] (Figs 4 and 5) The expressions *6* and *7* appear to hold approximately:

$$k_F = 0.0103[\mathrm{HCl}]^{1.6}\ C_r^{-1.7}\ \mathrm{min}^{-1}, \qquad (6)$$

$$k_H = 0.0100[\mathrm{HCl}]^{1.3}\ C_r^{-0.75}\ \mathrm{min}^{-1} \qquad (7)$$

The experimental and calculated values for k_F and k_H are shown in Table IV

The powers −1.7 and +0.75 reflect the hydration changes necessary in the formation of the transition states from D-fructose and HMF, and the proton. In accordance with published[10] mechanisms, the following interpretation can be given The abstraction of H-1 in the formation of the enediol from the protonated D-fructose molecule is difficult to accomplish and, therefore, desolvation of the proton is necessary. The electron displacement in the first step of the rehydration of HMF is so

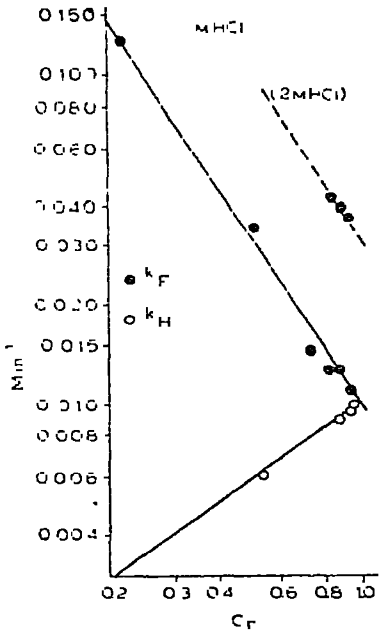
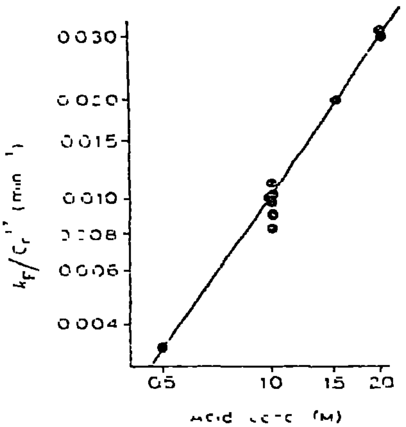


Fig 3 The dependence of k_F and k_H on the relative water concentration.



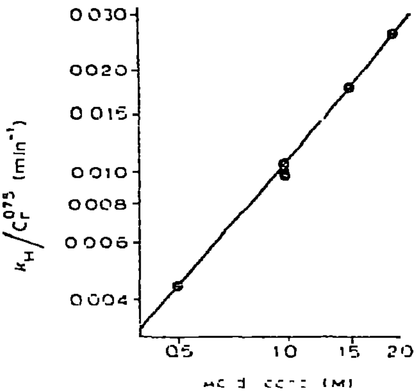


Fig 4 The dependence of k_F on the concentration of HCl

Fig 5. The dependence of k_H on the concentration of HCl easy to accomplish that no desolvation of the proton is necessary. This interpretation also reflects the greater dependence of k_F than of k_H on [HCl]

TABLE IV

EXPERIMENTAL AND CALCULATED (ACCORDING TO EQUATIONS 6 AND 7) VALUES FOR k_F AND k_H

HCl (M)	*F* (M)	*100* k_F		*HCl* (M)	*HMF* (M)	*100* k_H	
		Found	*Calc*			*Found*	*Calc*
0.5	0.50	0.40	0.38	0.5	0.50	0.42	0.39
1.0	1.00	1.25	1.30	1.0	1.00	0.90	0.91
1.0	0.50	1.18	1.18	1.0	0.50	0.94	0.95
1.0	0.25	1.09	1.12	1.0	0.25	0.99	0.96
1.5	0.50	2.33	2.32	1.5	0.50	1.66	1.60
2.0	1.00	4.17	4.12	2.0	0.50	2.33	2.30
2.0	0.50	3.90	3.74				
2.0	0.25	3.70	3.53	1.0	0.50		
1.0	0.50			*PG-600* (%)			
				40		0.61	0.62
PG-600 (%)							
10		1.25	1.44				
20		1.45	1.80				
40		3.43	3.14				
70		12.7	13.4				

Thus, the displacement of water by PG-600 (or other solvents) in the dehydration reaction is very beneficial to the formation of HMF because it accelerates its formation and retards its hydrolysis

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