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THE INFLUENCE OF THE INITIAL AND CATALYST CONCENTRATIONS ON THE DEHYDRATION OF D-FRUCTOSE*

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ABSTRACT

The dehydration at 95° of D-fructose (0.25M–1.0M) to 5-hydroxymethyl-2-furaldehyde (HMF) and the rehydration of HMF (0.25–1.0M) to levulinic and formic acids in 0.5–2M HCl has been studied. The conversion rate of D-fructose was proportional to the Hammett acidity. The acidity had a smaller influence on the conversion rate of HMF, although it was not proportional to the catalyst concentration. The rehydration of HMF was faster in the presence of D-fructose. The yield of levulinic acid was independent of the catalyst concentration, but was lower at higher initial concentrations of D-fructose and HMF, and a kinetic model has been derived. The formation of humin was of an overall order 1.3 in an intermediate between D-fructose and HMF, and of an order 1.7 in an intermediate between HMF and levulinic acid.

INTRODUCTION

The main products of the acid-catalysed dehydration of monosaccharides are 5-hydroxymethyl-2-furaldehyde (HMF) and levulinic acid (4-oxopentanoic acid), which are versatile materials[2-6]. The dehydration rate of D-glucose is ~40 times lower than that of D-fructose[4,7], and the product yield from D-glucose is much lower, probably due to the concurrent formation of reversion products[8,9].

We therefore limited our investigations to reactions with D-fructose, much progress has been made in the manufacture of D-fructose from the cheaper D-glucose[10].

EXPERIMENTAL

Aliquots (4 ml) of reaction mixtures variously containing 0.25, 0.5, and M D-fructose and HMF in 0.5, 1, 1.5, and 2M HCl were sealed in ampoules, quickly brought to 95° in a stream of hot air (Fig. 1), and then kept at 95° ±0.2°. During the heating period, the excess air in the ampoule could escape through a hollow needle temporarily inserted in the septum. At appropriate intervals, ampoules were cooled,

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*The Dehydration of D-Fructose (Formation of 5-Hydroxymethyl-2-furaldehyde and Levulinic Acid) Part II[1] and the contents were analysed[1] for D-fructose, HMF, levulinic acid, and humin Replacement of the air in the ampoules by nitrogen did not alter the experimental results

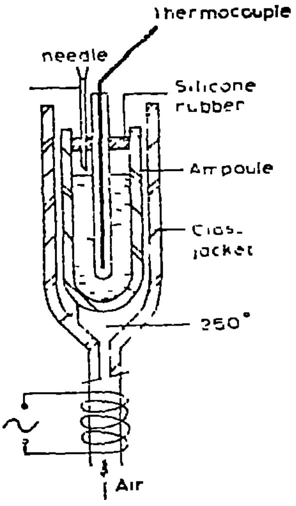

Fig 1 Ampoule in the preheating jacket.

The results are given in Tables I and II The amount of D-fructose and HMF converted into humin is calculated from the weight and the composition of the latter When mass balances were made, a deficit (X') was found, which is attributed to soluble humin-precursors

TABLE I

DEHYDRATION OF D-FRUCTOSE[a]

Time (min)	*F* (M)	*HMF* (M)	*LA* (M)	*HUM* (M)	*X'* (M)
*0.5*M D-*Fructose/0.5*M *HCl*					
20	0.46	0.03			
40	0.42	0.04	0.01		0.03
60	0.38	0.06	0.02		0.04
80	0.35	0.07			
120	0.30	0.10	0.04	0.01	0.05
160	0.27	0.11		0.02	
190	0.22	0.12	0.08	0.02	0.06
220	0.20	0.12	0.09	0.03	0.06
300	0.13	0.13	0.13	0.04	0.07
360	0.11	0.12	0.16	0.05	0.06
480	0.08	0.11	0.21	0.06	0.04
640	0.06	0.09		0.07	
700	0.04	0.08	0.27	0.08	0.03
1000	0.02	0.04	0.31	0.10	0.03
48 h			0.35	0.12	0.03

TABLE I (*continued*)

Time (*min*)	*F* (M)	*HMF* (M)	*LA* (M)	*HUM* (M)	*X'* (M)
M D-*Fructose*/M *HCl*					
15		0.10			
30	0.66	0.19	0.04	0.03	0.08
60	0.45	0.24	0.11	0.06	0.14
90	0.32			0.08	
120	0.23	0.25	0.28	0.11	0.13
180	0.11	0.19	0.42	0.15	0.13
240		0.14	0.49	0.20	
300	0.03	0.09	0.53	0.23	0.12
24 h			0.65	0.34	0.01
*0.5*M D-*Fructose*/M *HCl*					
6	0.46				
12	0.43	0.03	0.01		0.03
20	0.39	0.06			
30	0.33	0.08	0.03		
50	0.28	0.11	0.05	0.02	0.04
60	0.23	0.12			
75	0.20		0.09		
90	0.16	0.13	0.11	0.03	0.07
120	0.12	0.13	0.15	0.04	0.06
150	0.09	0.12	0.20	0.05	0.04
180	0.07	0.11		0.06	
240	0.04	0.08	0.27	0.08	0.03
300	0.02	0.05		0.09	
360		0.04	0.30	0.10	
24 h			0.35	0.13	0.02
*0.25*M D-*Fructose*/M *HCl*					
15		0.02			
24	0.20	0.03	0.01		0.01
30	0.19		0.02		
36	0.16	0.04			
45	0.15	0.05	0.03		0.02
60	0.13	0.06	0.04		0.02
90	0.09	0.07	0.06	0.01	0.02
120	0.07	0.07	0.09		0.01
150	0.05	0.06	0.11	0.02	0.01
24 h			0.20	0.04	0.01
*0.5*M D-*Fructose*/*1.5*M *HCl*					
6	0.44				
12	0.38	0.07	0.02		0.03
15	0.35	0.09			
20	0.32	0.11	0.03		0.04
30	0.25	0.13	0.06	0.01	0.05
40	0.19	0.14	0.08	0.02	0.07
60	0.12	0.13	0.14	0.03	0.08
90	0.07	0.10	0.21	0.05	0.07
120	0.03	0.08	0.26	0.08	0.05
150	0.01	0.05	0.29	0.10	0.05

(*Table continued on p. 168*).

TABLE I (*continued*)

Time (*min*)	*F* (M)	*HMF* (M)	*LA* (M)	*HUM* (M)	*X′* (M)
*0.5*M D-*Fructose/1.5*M *HCl*					
250		0.02	0.32	0.11	
360			0.34	0.12	
24 h			0.35	0.14	0.01
M D-*Fructose/2*M *HCl*					
4	0.85	0.10			
5	0.82	0.13			
8	0.67	0.18	0.05	0.02	0.08
12	0.60	0.22			
15	0.55	0.26	0.08	0.05	0.06
24	0.37	0.31	0.15		
30	0.27	0.28	0.22	0.10	0.13
36	0.24	0.26	0.29		
45	0.14	0.24	0.35	0.16	0.11
60	0.09	0.16	0.45	0.21	0.09
72	0.05		0.54		
90	0.03	0.08	0.58	0.27	0.04
96	0.02				
120	0.01	0.03	0.62	0.30	0.04
24 h			0.65	0.34	0.01
*0.5*M D-*Fructose/2*M *HCl*					
5	0.43	0.06			
8	0.37	0.07			
11	0.33	0.10			
16	0.27	0.13	0.04		0.06
20	0.23	0.14			
24	0.19	0.15	0.07	0.03	0.06
32	0.15	0.15			
36	0.12	0.14	0.12	0.05	0.07
45	0.09	0.13	0.17	0.06	0.05
60	0.05	0.08	0.23	0.08	0.06
72	0.02	0.07	0.26	0.09	0.06
96	0.01	0.04	0.31	0.11	0.03
24 h			0.35	0.14	0.01
*0.25*M D-*Fructose/2*M *HCl*					
5	0.21	0.02			
8	0.20				
10	0.18	0.04	0.01		0.02
12	0.16	0.05			
16	0.15	0.06	0.02	0.01	0.01
24	0.10	0.08			
30	0.08	0.08	0.04	0.02	0.03
45	0.06	0.07		0.02	
60	0.03	0.05	0.10	0.03	0.04
72	0.02		0.12		
96	0.01	0.03	0.15	0.04	0.02
120		0.02	0.17	0.04	
24 h			0.20	0.05	0.00

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[a] Key F, D-fructose, HMF, 5-hydroxymethyl-2-furaldehyde, LA, levulinic acid, HUM, humin; X′, soluble humin-precursors

TABLE II

REHYDRATION OF HMF[a]

Time (*min*)	*HMF* (M)	*LA* (M)	*HUM* (M)	*X* (M)
*0.5*M *HMF/0.5*M *HCl*				
30	0.43	0.04		0.03
60	0.39	0.09	0.01	0.01
120	0.31	0.15		0.03
180	0.23	0.22	0.02	0.03
240	0.18			
360	0.12			
480	0.06	0.37	0.04	0.03
600	0.04	0.39	0.05	0.02
24 h		0.42	0.06	0.02
M *HMF/*M *HCl*				
15	0.87	0.09	0.02	0.02
30	0.76	0.16	0.03	0.05
60	0.56	0.32	0.08	0.04
90	0.44	0.43	0.10	0.05
135	0.31	0.54	0.13	0.02
180	0.20	0.60	0.15	0.05
240	0.12	0.68	0.16	0.04
300	0.06	0.70	0.18	0.06
24 h		0.76	0.20	0.04
*0.5*M *HMF/*M *HCl*				
15	0.43	0.05	0.01	0.01
30	0.37	0.09	0.02	0.02
60	0.27	0.18	0.03	0.02
120	0.15	0.29	0.04	0.02
180	0.10	0.35	0.05	0.00
240	0.06	0.39		
300	0.03	0.40	0.05	0.02
350	0.02	0.41		
24 h		0.42	0.06	0.02
*0.25*M *HMF/*M *HCl*				
15	0.22	0.03		
35	0.17	0.06	0.01	0.01
60	0.13	0.10		
120	0.07	0.15		
180	0.04	0.18	0.02	0.01
240	0.02	0.20		
310	0.01	0.22		
24 h		0.22	0.02	0.01
*0.5*M *HMF/1.5*M *HCl*				
15	0.39	0.09	0.01	0.01
30	0.32	0.16	0.02	0.00
45	0.24	0.21	0.03	0.02
70	0.14	0.29	0.04	0.03
120	0.07	0.35	0.05	0.03
240	0.02	0.40	0.06	0.02
24 h		0.42	0.07	0.01

(*Table continued on p. 170*)

TABLE II (*continued*)

Time (*min*)	*HMF* (M)	*LA* (M)	*HUM* (M)	*X'* (M)
*0.5*M *HMF/2*M *HCl*				
15	0.36	0.12	0.02	0.00
30	0.24	0.21	0.03	0.02
50	0.16	0.29	0.04	0.01
65	0.11	0.33	0.05	0.01
120	0.03	0.38		
240		0.41	0.06	
24 h		0.42	0.07	0.01

[a]For key, see footnote to Table I

DISCUSSION

The mechanism of the dehydration of D-fructose, which involves the enol forms of 3-deoxyhexosuloses and further dehydrated species, has been described[11-13]. The formation of the enediol from the D-fructose anomeric equilibrium mixture will be the rate-determining step[14]; sucrose, which gives D-fructofuranose after rapid hydrolysis, yields HMF at the same rate as D-fructose, which is mainly in the pyranoid form[4,15]. The formation of 2-(2-hydroxyacetyl)furan parallel to HMF will mainly contribute to the formation of humin[16].

Fig 2 contains log-plots of the D-fructose and HMF conversion data. Although the straight lines are not parallel (see below), the first-order conversion is in good agreement with the experimental results, and accords with literature data[4,7,17-19]. From the data in Tables I and II, it appears that the final yield of levulinic acid decreases, and the amount of humin formed increases, at higher initial concentrations of D-fructose and HMF. Because several of the intermediates in the proposed

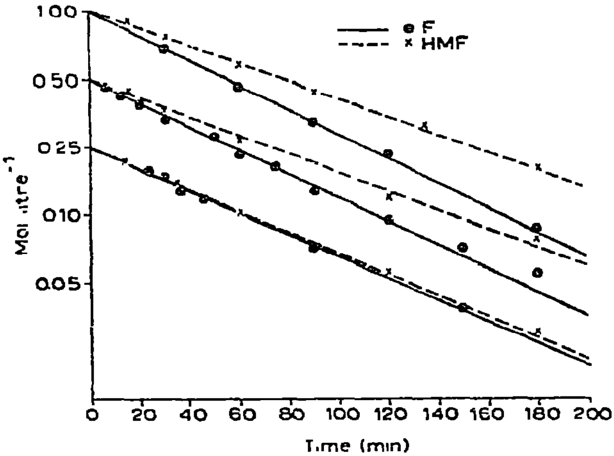
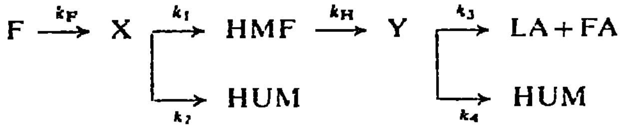


Fig 2 Log plots of F and HMF data M HCl, 95°

mechanisms[11,12] can be expected to polymerize, this trend can be explained by assuming that D-fructose (F) is converted by a first-order reaction into an intermediate (X) from which humin (HUM) is formed by a reaction of an order (n_x) that is higher than unity, and from which HMF is formed by a first-order reaction. In the same way, HMF is rehydrated to give levulinic (LA) and formic acids (FA) *via* an intermediate (Y) from which humin can also be formed by a reaction with an order (n_y) higher than unity. This situation can be expressed by the following model:



The following differential equations can be derived:

$$d[\mathrm{F}]/dt = -k_F[\mathrm{F}] \qquad 1$$

$$d[\mathrm{X}]/dt = k_F[\mathrm{F}]-k_1[\mathrm{X}]-k_2[\mathrm{X}]\uparrow n_X \qquad 2$$

$$d[\mathrm{HMF}]/dt = k_1[\mathrm{X}]-k_H[\mathrm{HMF}] \qquad 3$$

$$d[\mathrm{Y}]/dt = k_H\,[\mathrm{HMF}]-k_3[\mathrm{Y}]-k_4[\mathrm{Y}]\uparrow n_Y \qquad 4$$

$$d[\mathrm{LA}]/dt = k_3[\mathrm{Y}] \qquad 5$$

From the analyses[1], it appeared that no significant amount of intermediates ($<2\%$ of the initial concentration) is present, which is in accordance with the high rates of dehydration of these compounds[20]. From computer calculations with the model, it appeared from the D-fructose, HMF, and levulinic acid data that the concentrations of intermediates were in the range 0–5% of the initial concentration for X, and 0–1% for Y.

Due to the unknown concentrations of X and Y, k_1 to k_4 cannot be ascertained separately. However, because these concentrations are very low, the steady-state concept can be used to derive new model parameters, k_X and k_Y, which can be solved from the experimental data. Thus, equations *2* and *4* reduce to equations *6* and *7*,

$$k_F[\mathrm{F}] = k_1[\mathrm{X}]+k_2[\mathrm{X}]\uparrow n_X \qquad 6$$

$$k_H[\mathrm{HMF}] = k_3[\mathrm{Y}]+k_4[\mathrm{Y}]\uparrow n_Y \qquad 7$$

and s_X, the fraction of D-fructose reacting to HMF, and s_Y, the fraction of HMF reacting to levulinic acid, are defined in equations *8* and *9*

$$s_X = -d[\mathrm{HMF}]/d[\mathrm{F}] = k_1[\mathrm{X}]/k_F[\mathrm{F}] \qquad 8$$

$$s_Y = -d[\mathrm{LA}]/d[\mathrm{HMF}] = k_3[\mathrm{Y}]/k_H[\mathrm{HMF}] \qquad 9$$

Substituting *8* in *6*, and *9* in *7* gives equations *10* and *11*,

$$s_X\uparrow n_X/(1-s_X) = k_X[\mathrm{F}]\uparrow(1-n_X) \qquad 10$$

$$s_Y \uparrow n_Y/(1-s_Y) = k_Y[\mathrm{HMF}] \uparrow (1-n_Y) \qquad 11$$

where

$$k_X = k_F \uparrow (1-n_X)\ k_1 \uparrow n_X/k_2, \qquad 12$$

and $$k_Y = k_H \uparrow (1-n_Y)\ k_3 \uparrow n_Y/k_4 \qquad 13$$

This means that the kinetics are now fully determined by the model parameters k_F, k_X, n_X, k_H, k_Y, and n_Y Equations *1–5* were numerically integrated by using equation *8–11* The model parameters were evaluated by minimising the sum of squares of the difference between the calculated and experimental concentrations The differences were weighed by the corresponding analytical error[1] The differences between calculated and observed data is smaller than the analytical error.

Since the k_H values calculated from experiments with D-fructose are substantially higher than those calculated from experiments with HMF, the interaction of D-fructose and HMF was studied The concentrations of HMF and levulinic acid after 10 and 30 min at 95° were measured for molar solutions of HMF, D-fructose, and D-glucose, and of mixtures of HMF and D-fructose, and HMF and D-glucose, in 2M HCl The results are given in Table III The values of HMF and LA for the mixed solutions were not equal to the sum of the values for the separate experiments The conversion rate for HMF is accelerated 38% in the presence of D-fructose or D-glucose

TABLE III

REACTIONS OF M D-FRUCTOSE (F), D-GLUCOSE (G), AND HMF IN 2M HCl AT 95° AFTER 10 AND 30 MIN

	HMF (M)		*LA* (M)	
	10 min	*30 min*	*10 min*	*30 min*
HMF	0.79	0.49	0.16	0.39
F	0.20	0.29	0.04	0.20
G	—	0.01	—	—
F + HMF	0.92	0.66	0.24	0.66
G + HMF	0.72	0.38	0.21	0.47

TABLE IV

VALUES FOR k_F AND k_H

HCl (M)	F_0 (M)	*100* k_F *min*$^{-1}$	HMF_0 (M)	*100* k_H *min*$^{-1}$
0.5	0.50	0.40 ±0.03	0.50	0.42 ±0.02
1.0	1.00	1.25 ±0.02	1.00	0.90 ±0.02
1.0	0.50	1.18 ±0.04	0.50	0.94 ±0.05
1.0	0.25	1.09 ±0.05	0.25	1.09 ±0.06
1.5	0.50	2.33 ±0.07	0.50	1.66 ±0.15
2.0	1.00	4.17 ±0.12		
2.0	0.50	3.90 ±0.12	0.50	2.33 ±0.09
2.0	0.25	3.50 ±0.22		

Values for k_F and k_H, calculated from the conversion data for D-fructose and HMF, are given in Table IV. These values are slightly dependent on the initial concentration, since the reaction rate is also influenced by the water concentration at low concentrations of water, k_F is higher and k_H lower.

In Fig. 3, k_F and k_H (for 0.5M solutions) are plotted as a function of the concentration of hydrochloric acid. The values for k_F are proportional to the Hammett acidity[21,22] (h_0), whereas k_H is less influenced by the acidity but still increases more than proportionally with the catalyst concentration. The k_H values are in good agreement with the HMF conversion data given by Heimlich[19] and Teunissen[18]. For D-fructose conversion, no comparable data could be found in the literature.

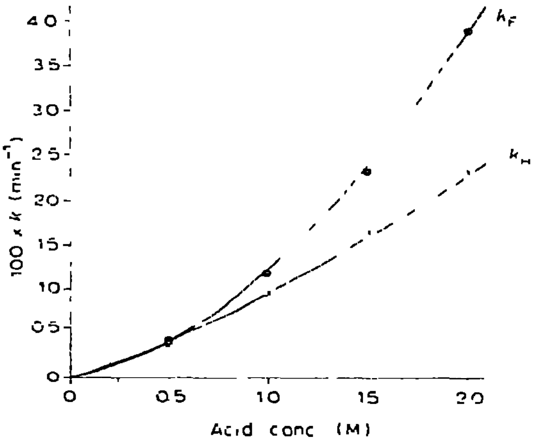


Fig. 3. Influence of the acid concentration on k_F and k_H

The next step in the evaluation of the kinetic model was the determination of k_X, n_X, k_Y, n_Y, and $k_{H,F}$. First, k_Y and n_Y were calculated from levulinic acid data for reactions starting with HMF. The known values for k_H did not need to be adjusted. Thereafter, k_X, n_X, and $k_{H,F}$ were calculated from HMF and levulinic acid data for reactions starting with D-fructose, using the values of k_Y and n_Y already obtained. The known values for k_F did not need to be adjusted. The results for k_Y and n_Y shown in Table V indicate that several combinations of k_Y and n_Y can be used equally well to describe the experimental results. However, for $n_Y = 1.7$, k_Y has a constant value of 1.7 for all experiments. Therefore, this combination is the most acceptable. It also follows from the data for $HMF_0 = 0.50$ mol/l that when experiments are carried out at only one initial concentration, separate values for k_Y and n_Y cannot be obtained and a simple first-order model with $n_Y = 1$ will describe the experimental results satisfactorily.

The results for k_X, n_X, and $k_{H,F}$, with k_Y and n_Y both fixed at 1.7, are given in Table VI. In the same way as described above, an average constant value of 2.1 for

TABLE V

THE EVALUATION OF k_Y AND n_Y

HCl (M)	*HMF*$_0$ (M)	k_Y		
		$n_Y = 1$	$n_Y = 1.7$	$n_Y = 2$
0.5	0.50	5.0	1.7	1.1
1.0	1.00	3.1	1.7	1.4
1.0	0.50	5.3	1.9	1.3
1.0	0.25	7.2	1.7	1.0
1.5	0.50	4.5	1.7	1.1
2.0	0.50	5.0	1.6	1.1

TABLE VI

THE EVALUATION OF k_X, n_X, AND $k_{H,F}$

HCl (M)	F_0	k_X			*100* $k_{H,F}$ *min*$^{-1}$
		$n_X = 1$	$n_X = 1.3$	$n_X = 2$	
0.5	0.50	4.0	2.1	1.4	0.44 ±0.04
1.0	1.00	3.6	2.1	2.2	1.15 ±0.16
1.0	0.50	4.3	2.1	1.4	1.25 ±0.09
1.0	0.25	9.9	2.3	1.0	1.35 ±0.15
1.5	0.50	3.5	2.0	1.4	2.28 ±0.14
2.0	1.00	3.5	2.1	1.8	4.12 ±0.22
2.0	0.50	4.3	2.2	1.1	3.68 ±0.30
2.0	0.25	10.3	1.9	0.8	3.05 ±0.25

k_X at $n_X = 1.3$ was found. Thus, for experiments with only one initial concentration of D-fructose, a simple first-order model is satisfactory.

The data fit was checked by making plots using the calculated values for the model parameters. Two plots are given in Figs. 4 and 5. The deviations in Fig. 4 of the calculated curves from the experimental data for levulinic acid and HMF indicate that $k_{H,F}$ decreases somewhat during the reaction. This finding is in accordance with the fact that $k_{H,F}$ is dependent on the D-fructose concentration. The values for k_X, n_X, k_Y, and n_Y are independent of the catalyst concentration, which means that the selectivities s_X and s_Y, as can be seen from equations *10* and *11*, are not influenced by the acidity.

Some proposals for the kinetics of the dehydration reaction, which can be used as an extension of our model have been published, *e.g.*, the reaction X + HMF → HUM as suggested by McKibbins[17], and the reaction X → Y as suggested by Feather and Harris[13]. These extensions did not give any improvement of the data fit. Therefore, the foregoing kinetic model is the simplest that can describe the dehydration and rehydration reactions of D-fructose and HMF.

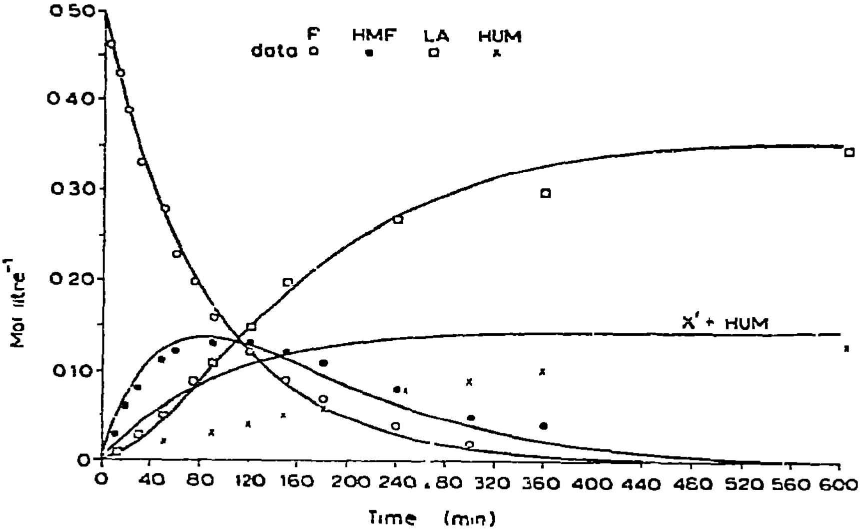


Fig 4 Dehydration of D-fructose M HCl, 95°. Curves are computer-plotted using the kinetic model

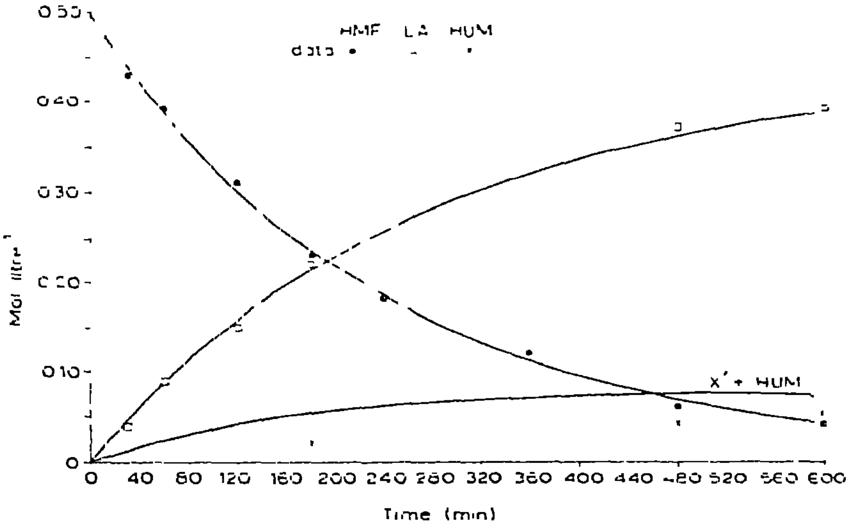


Fig 5 Rehydration of HMF 0.5M HCl, 95°. Curves are computer-plotted using the kinetic model

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