The Dehydration of D-Fructose to 5-Hydroxymethyl-2-furaldehyde

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Synopsis. The continuous dehydration of D-fructose is carried out under mild conditions, using the strongly acidic ion-exchange resin with a low divinylbenzene content as the catalyst and dimethyl sulfoxide as the solvent, to give 5-hydroxymethyl-2-furaldehyde in a high yield.

Because of its potential versatility as a starting material for industrial chemicals and polymers,[1] 5-hydroxymethyl-2-furaldehyde (HMF) has been expected to be a staple chemical derived from such renewable raw materials as farm and wood products. The present authors have now investigated the procedure for obtaining HMF from D-fructose, since marked progress in the production of D-fructose from D-glucose is being made.[2]

Bonner *et al.* obtained HMF in a 71 mol% yield (based on the fructose portion) by the iodine-catalyzed dehydration of sucrose in *N,N*-dimethylformamide.[3] On the other hand, HMF has been reported to be obtained in an 80 mol% yield by the acid-catalyzed dehydration of D-fructose in tetrahydrofurfuryl alcohol, but about 40% of the HMF thus formed was found as the ether of the solvent.[4] Recently, the continuous dehydration of D-fructose catalyzed by such homogeneous acids as hydrochloric acid and phosphoric acid has been reported.[5,6] However, a continuous dehydration using a solid catalyst has never been reported.

The dehydration of D-fructose catalyzed by a strongly acidic ion-exchange resin in dimethyl sulfoxide (DMSO) was found to give HMF in a high yield under mild conditions.

TABLE 1. DEHYDRATION OF D-FRUCTOSE CATALYZED BY DIAION PK-216
Fructose, 0.5 M; catalyst, 10 meq.; solvent, DMSO; reaction mixture, 50 ml; 80 °C.

Reaction time / min	Yield of HMF (mol%)
40	30
100	57
200	81
300	89
500	90

The results of the batch-by-batch dehydration of D-fructose with Diaion PK-216 in DMSO are shown in Table 1. As shown in Table 1, HMF is obtained in a 90 mol% yield, based on the D-fructose, after 500 min.

Analyses of the reaction mixture by TLC[7] and GPC (Chromosorb 101, 1 m, 220 °C) showed that only a trace amount of by-products, such as bis(5-formylfurfuryl) ether and levulinic acid, were formed. The total amount of the acids formed during dehydration was found to be 0.34 mmol (1.4 mol% based on the D-fructose) by the titration of the reaction mixture. The dehydration product was identified as HMF by means of its IR and NMR spectra, and the dehydration of D-fructose catalyzed by the resin catalyst in DMSO is quite selective to HMF.

The effect of the divinylbenzene (DVB) content in various ion-exchange resins on the rate of the dehydration of D-fructose to HMF in DMSO was investigated. The rate of HMF formation can be given by;

$$\frac{d[HMF]}{dt} = k([F^\circ]-[HMF])$$

where [HMF], [F°], and k are the concentration of HMF, the initial concentration of D-fructose, and the rate constant, respectively.[8] A plot of the value of $\log [[F^\circ]/([F^\circ]-[HMF])]$ against t gave a straight line at an earlier stage of the reaction. The values of k for the batch-by-batch dehydration were obtained for various resins; they are shown in Table 2, which shows that the dehydration rate depends markedly on the DVB content in the resin used and that the porous resin is more effective than the gel-type ones when the DVB content in the resins is the same.

The apparent volume(V) of the resin containing 10 meq. of the sulfo group was measured after dipping overnight in DMSO. Then the values of k/V (activity per unit volume of the resin catalyst) were calculated; they are also shown in Table 2, with the values of V. Table 2 shows that even the value of k/V increases as the DVB content in the resin decreases.

The stability of the catalytic activity of the resin for the continuous dehydration of D-fructose to HMF in DMSO was examined using Amberlite IR-118 with

TABLE 2. EFFECT OF DVB CONTENT ON THE RATE CONSTANT, k, AND THE VALUE OF k/V
Solvent, DMSO; resin catalyst, 10 meq.[a]

	Resin	DVB content (%)	k (s^{-1})	V (ml)	k/V (s^{-1} ml^{-1})
Porous type	Diaion PK-208	4	3.01×10^{-4}	8.3	3.6×10^{-5}
	Diaion PK-216	8	1.46×10^{-4}	6.3	2.3×10^{-5}
	Diaion PK-228	14	0.17×10^{-4}	3.7	0.46×10^{-5}
Gel type	Amberlite IR-118	4	2.74×10^{-4}	8.9	3.1×10^{-5}
	Amberlite IR-120	8	0.58×10^{-4}	5.6	1.0×10^{-5}
	Lewatit SC-108	8	0.36×10^{-4}	5.2	0.68×10^{-5}

a) Other conditions as given in Table 1.

Table 3. Continuous dehydration of D-fructose using amberlite IR-118 as the catalyst
D-Fructose in feed, 0.5 M.

Elapsed time (h)	Concentration of HMF (M)
50	0.4
100	0.45
200	0.47
400	0.45
900	0.45

a low DVB content. After the feed solution had begun to be supplied into the column reactor containing the resin and DMSO, the concentration of HMF in the eluted solution was measured at varying times. As shown in Table 3, after about 100 h the concentration of HMF reached 0.45 M and stayed there even after 900 h.

The catalytic activity and acidity of the resin used for the continuous dehydration for 900 h were re-examined; no decrease was found in these catalytic properties.

Experimental

Preparation of Catalyst. The resins were washed with distilled water and conditioned by converting them to the sodium form and by then reconverting them to the hydrogen form. Samples were dried under a vacuum (1—2 mmHg) at 60 °C for about 6 h and used after dipping overnight in DMSO. The acidity of the resin was measured by titration.

Batch-by-batch Dehydration. A DMSO solution (50 ml) containing D-fructose (25 mmol) and the resin catalyst (10 meq. as the sulfo group) were added to a 200-ml glass flask, which was then immersed in a bath thermostated at 80±0.1 °C and the solution was stirred by a magnetic stirrer. The quantity of HMF formed was determined by means of UV absorption (λ=284 nm; Hitachi Spectrophotometer-124) after dilution (1×10^2—2×10^2 times) by distilled water. Samples (about 0.1 ml) were withdrawn at varying times.

Continuous Dehydration. Continuous dehydration was carried out using a glass column (inner diameter, 20 mm) packed with the catalyst (74 ml, 86.6 meq. as the sulfo group). The temperature of the column was kept at 60±0.1 °C by the use of a ribbon heater equipped with a thermoregulator. A DMSO solution containing D-fructose (0.5 M) and water (5 vol%)[9] was charged (mean rate=3.7 ml/h) continuously to the top of the column by means of a perista-pump (Atto Corp. SJ-1215), and the content of HMF in the eluted solution was measured as has been described above.

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References

1) For example, C. J. Moye, *Rev., Pure Appl. Chem.*, **14** 161 (1964); J. A. Moore and J. E. Kelley, *Macromolecules*, **11**, 568 (1978); J. M. Kimko, S. S. Moore, D. M. Walba, P. C. Hiberty, and D. J. Cram, *J. Am. Chem. Soc.*, **99**, 4209 (1977).

2) K. Yoritomi, "Denpun Kagaku Hand Book," ed by J. Nikuni, Asakura Shoten (1977), p. 476; Y. Fujii and B. Okamura, *Kagaku To Kogyo*, **31**, 537 (1978).

3) T. G. Bonner, E. J. Bourne, and M. Ruszkiewicz, *J. Chem. Soc.*, **1960**, 787.

4) C. J. Moye and R. J. Goldsack, *J. Appl. Chem.*, **16**, 206 (1966).

5) B. F. M. Kuster and H. J. C. Van der Steen, *Staerke*, **29**, 99 (1977).

6) B. F. M. Kuster and J. Laurens, *Staerke*, **29**, 172 (1977).

7) C. J. Moye, *Aust. J. Chem.*, **19**, 2317 (1966).

8) B. F. M. Kuster and Hessel S. van der Baan, *Carbohydr. Res.*, **54**, 165 (1977); B. F. M. Kuster, *ibid.*, **54**, 177 (1977).

9) Water was added to prevent the DMSO solution in the line from freezing. It has been found, by the batch-by-batch dehydration of D-fructose, that the addition of 5 vol% of water to the DMSO solution decreases the reaction rate ($k=2.4\times10^{-4}$ s^{-1}, for Diaion PK-208 under the reaction conditions given in Table 2), but scarcely interferes at all with the selectivity to HMF.