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QUANTITATIVE FORMATION OF FURFURAL AND METHYLFURFURAL FROM PENTOSES AND METHYLPENTOSES

By Elizabeth E. Hughes and S. F. Acree

ABSTRACT

A procedure, previously reported, which gave quantitative production of furfural from xylose, was applied to arabinose and rhamnose. It consisted in rapid steam distillation of the pentose in 12-percent hydrochloric acid saturated with sodium chloride. Although the conversion of arabinose and rhamnose is slower than that of xylose, theoretical yields of furfural and methylfurfural, respectively, were obtained.

The effects of several salts in the distilling medium were also studied. The rates of production of furfural from xylose or arabinose in the presence of these salts and of methylfurfural from rhamnose in the presence of sodium chloride were obtained. Salts which caused the distillation temperature to go above 112° C increased the initial rate of formation of furfural but lowered the yields.

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I. INTRODUCTION

In a previous paper [1]¹ it was shown that conversion of xylose into quantitative yields of furfural may be accomplished by employing as the distilling medium a 12-percent solution of hydrochloric acid saturated with sodium chloride and by removing the aldehyde quickly from the solution with a rapid stream of steam. Since it was believed that this procedure might prove to yield quantitative amounts of furfural and methylfurfural when applied to other pentoses and methylpentoses, the study was extended to include arabinose and rhamnose.

The three pentoses derived from the pentosans xylan, araban, and rhamnosan are the sugars most commonly encountered in fibers and natural products. The pentoses are not determined as such, but are estimated from the amounts of furfural and methylfurfural obtained when the fibers are distilled with hydrochloric acid. As theoretical

¹ Figures in brackets indicate the literature references at the end of this paper.

yields of the aldehydes have not been obtained in the usual methods of distilling pentoses, empirical values have been adopted for the calculation of the pentosan content when these procedures are used.

The variations in yield of furfural obtained from xylose, depending upon the type of distillation employed (from 88 percent by the standard distillation procedure to 100 percent by our procedure), were discussed fully in the previous paper [1]. The conversion of arabinose is slower than that of xylose, with about 74 percent of the theoretical yield of furfural in the standard procedure. As stated in the earlier paper [1], the yields of furfural from xylose and arabinose and methylfurfural from rhamnose reported by Jolles [2] and Pervier and Gortner [3], which were practically theoretical, have not been duplicated by other workers, perhaps because of inaccuracies found later in the methods used for determining the aldehydes. Kullgren and Tyden [4], who saturated the hydrochloric acid with sodium chloride to give constant conditions for distillation, secured about the same yields as other workers obtain with the standard method.

It was the purpose of this investigation to obtain, if possible, theoretical yields of furfural and methylfurfural from the three pentoses and to adapt the procedure to the practical determination of pentosans. In an attempt to shorten the distillation period, the effects of some salts and of other reagents in the distilling medium were studied with xylose and arabinose. Xylose, the most easily converted sugar, was used chiefly for the experimentation. During this study the rates of production of furfural and methylfurfural from the three pentoses mentioned above were also obtained.

II. EXPERIMENTAL PROCEDURE

The distillation procedure was fully described in the paper on the quantitative formation of furfural from xylose [1]. It consisted essentially in distilling the pentose in a solution of 12-percent hydrochloric acid to which sodium chloride had been added and in using a rapid stream of steam to remove the aldehyde as soon as possible. A means of collecting the distillate without loss of furfural by volatilization was provided. This comprised an especially constructed apparatus having ground-glass joints, a diagram of which also was given in the earlier paper. By the use of an electrically controlled heater the distillation proceeded at 110° C at a rate of 200 ml of distillate every 30 minutes. More acid was added to the distillation flask through a separatory funnel as needed. The acidity of the distillate was adjusted to about 1 *N*, and the furfural and methylfurfural determinations were made by the bromine method at 0° C [5].

III. EXPERIMENTAL RESULTS AND DISCUSSION

1. STEAM DISTILLATION OF ARABINOSE

Samples of l-arabinose varying in amount from 0.05 to 0.2 g were treated by the procedure given above. The results of the distillations are given in table 1. The rate of production of furfural is shown in figure 1. It is apparent that practically theoretical yields may be obtained by this procedure if the distillation is continued until

the reaction is completed. The amounts of furfural in the last fractions of distillate are very small, but the bromine method is sufficiently sensitive for their determination. The amounts in the several fractions are added, and the values in the last column of table 1 show the total percentages of the theoretical amounts of furfural obtained.

TABLE 1.—Yields of furfural from arabinose

Weight of arabinose	Volume of distillate collected	Amount of bromine consumed	Weight of furfural found	Theoretical weight of furfural	Yields of furfural
<i>g</i>	<i>Liters</i>	<i>M-eq</i>	<i>g</i>	<i>g</i>	<i>Percent</i>
0.0513.....	2.2	0.679	0.0326	0.0328	99.4
0.0682.....	2.6	.910	.0437	.0436	100.2
0.1015.....	2.9	1.359	.0653	.0650	100.5
0.1048.....	4.6	1.399	.0672	.0671	100.1
0.1581.....	5.4	2.104	.1011	.1012	99.9
0.2029.....	3.4	2.623	.1260	.1299	97.0

2. STEAM DISTILLATION OF RHAMNOSE

The amounts of *l*-rhamnose (hydrate) used were 0.05 to 0.2 g. In the procedure used for the conversion of xylose and arabinose, the heat was applied to the flask containing the distilling solution and the

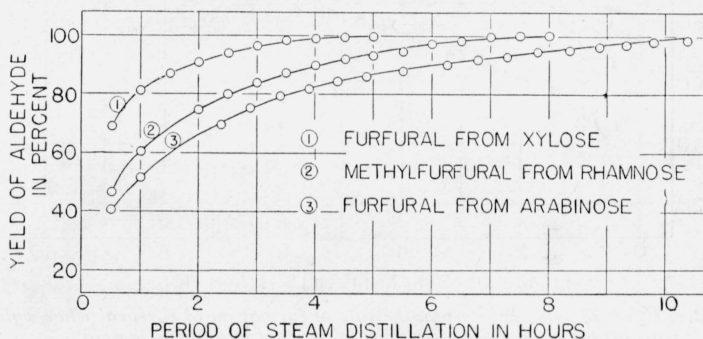


FIGURE 1.—Rate of formation of aldehydes from pentoses by steam distillation in 12-percent hydrochloric acid saturated with sodium chloride.

steam was not introduced until the temperature of the solution reached about 100° C. For rhamnose it was found necessary to modify this procedure slightly, as the first experiments gave yields 3 to 5 percent low, and the first fraction of distillate was very light pink, instead of being colorless. Since it seemed probable that some of the methylfurfural formed during the first period of heating had polymerized before being removed, the steam was introduced as soon as heat was applied to the solution. A colorless distillate was then obtained, and the sum of the fractions gave practically theoretical yields. The rate of production of methylfurfural by this method is shown with the other curves in figure 1, and the total yields of methylfurfural are given in table 2.

TABLE 2.—Yields of methylfurfural from rhamnose (hydrate)

Weight of rhamnose (hydrate)	Volume of distillate collected	Amount of bromine consumed	Weight of methylfurfural found	Theoretical weight of methylfurfural	Yields of methylfurfural
<i>g</i>	<i>Liters</i>	<i>M-eq</i>	<i>g</i>	<i>g</i>	<i>Percent</i>
0.0500.....	1.6	0.783	0.0308	0.0302	101.9
0.0733.....	2.2	1.111	.0437	.0443	98.6
0.0831.....	3.6	1.271	.0500	.0502	99.5
0.0980.....	3.2	1.528	.0601	.0592	101.4
0.1102.....	2.5	1.716	.0674	.0666	101.2
0.2020.....	3.2	3.058	.1202	.1221	98.4

3. EFFECTS OF SALTS AND OF OTHER REAGENTS UPON THE RATE OF FORMATION OF FURFURAL WHEN XYLOSE OR ARABINOSE IS STEAM-DISTILLED FROM 12 PERCENT HYDROCHLORIC ACID

Steam distillation of pentoses from 12 percent hydrochloric acid takes place at temperatures varying from 103° to 108° C. The addition of sufficient sodium chloride to saturate the acid solution increases

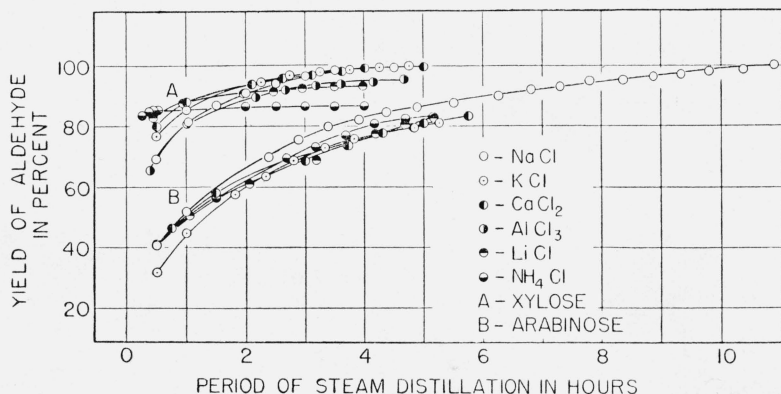


FIGURE 2.—Effect of some salts upon the rate of formation of furfural when xylose or arabinose is steam-distilled in 12 percent hydrochloric acid.

this temperature to 110° C. It was thought possible that salts which would give still higher temperatures would accelerate the formation of the furfural, which might be carried off by the steam before decomposition could take place. This would be especially desirable for the conversion of arabinose, which is much slower than that of xylose. For this purpose potassium, calcium, lithium, and ammonium chlorides were used. When it was found that no increases in yields were obtained in the first 2 liters of distillate, the distillations were not carried to completion.

The curves in figure 2 indicate that steam distillations from 12-percent solutions of hydrochloric acid containing sodium, potassium, or calcium chloride all give practically theoretical yields of furfural from xylose. Distillation takes place at 110° to 112° C, and the differences in the rates of formation of furfural are not significant. The use of lithium chloride with a higher temperature of distillation results in an increase in the initial rate of formation of furfural, but low yields are obtained. The first fraction of distillate is much more acid,

and this with the higher temperature favors polymerization, which probably accounts for the low yields of furfural. The addition of ammonium chloride causes the distillation to take place at 115° to 116° C, with the same resulting low yields. It has the added disadvantage that during steam distillation some material which reacts with bromine is obtained in the distillate. Steam distillations using 25 and 50 g of ammonium chloride in 12-percent hydrochloric acid produced material in 1 liter of distillate which consumed bromine corresponding to 0.4 ml and 0.8 ml of 0.1 *N* thiosulfate solution, respectively. A correction for this bromine consumption is necessary or false high values will be obtained. Stannous and zinc chlorides are distinctly disadvantageous, with yields of about 52 percent. A similar result was found by Kline and Acree [6] for stannous chloride.

TABLE 3.—*Effect of salts and other reagents upon the yields of furfural from xylose and arabinose*

Reagents added to 100 ml of 12-percent HCl	Approximate temperature of distilling solutions	Furfural obtained from 0.1 g of pentose		
		From xylose	From arabinose	
A. STANDARD DISTILLATION. RATE OF 180 ml/hr				
20 g of NaCl.....	110	88.2	73.4	
50 g of CaCl ₂ ·2H ₂ O.....	112	-----	72.5	
50 g of NH ₄ Cl.....	115	-----	58.7	
B. FAST STEAM DISTILLATION. RATE OF 400 ml/hr				
		Yield in 2 liters		Yield in total distillate
		Percent	Percent	Percent
20 g of NaCl.....	108 to 110	100.0	86.0	100.0
20 g of KCl.....	108 to 110	99.7	^a 80.5	-----
25 g of CaCl ₂ ·2H ₂ O.....	111 to 112	98.9	-----	-----
50 g of CaCl ₂ ·2H ₂ O.....	111 to 112	99.7	83.0	^a 95.0
20 g of LiCl.....	115 to 120	94.7	-----	-----
50 g of LiCl.....	115 to 126	-----	^a 82.0	-----
30 g of AlCl ₃	108 to 109	94.6	-----	-----
20 g of NH ₄ Cl.....	115 to 116	87.2 (corr.)	86.4 (corr.)	-----
50 g of NH ₄ Cl.....	115 to 116	86.2 (corr.)	-----	-----
38 g of SnCl ₂ ·2H ₂ O.....	108 to 109	51.9	-----	-----
23 g of ZnCl ₂	108 to 109	51.3	-----	-----
40 g of silica gel.....	103 to 108	94.9	-----	-----
20 g of silica gel and 30 g of KCl.....	109 to 110	100.5	80.5	100.1
20 g of NaCl and 0.02 g of iodine.....	110	-----	^a 87.0 (corr.)	-----
20 g of NaCl and 0.07 g of piperidine.....	110	-----	^a 70.5 (corr.)	-----
20 g of NaCl in 24-percent HCl.....	110	80.9	-----	-----

^a Distillations were not carried to completion as indicated by the presence of furfural in the last fraction of distillate.

Although some of the salts appear better than others in the initial rate of conversion of xylose, the experiments show that the rate of conversion of arabinose is only slightly influenced by the different salts. The addition of very small amounts of iodine and piperidine, for which corrections also had to be made for bromine consumption by products in the distillate other than furfural, did not accelerate the rate of formation of furfural. The addition of silica gel instead of a soluble salt to give the effect of increased surface upon the rate of reaction without an increase in temperature offered no advantage.

When silica gel was used in conjunction with potassium chloride, there was no increase in rate of formation of furfural and practically the same yields were obtained as those found with potassium chloride alone.

As most of the determinations of the rate of production of furfural and methylfurfural required 10 or more steps in the titrations, it is not surprising that the final percentages show an error of 1 or 2 percent. Even though extreme caution was used to maintain a temperature of exactly 0° C for the titrations and a period of reaction with bromine of exactly 5 minutes, the uncertainty was greater in the determinations of methylfurfural than in the determinations of furfural.

The experiments show that the conversion of the smaller amounts of pentose is completed sooner than that of the larger quantities. For this reason, in applying this procedure, it is considered desirable to use amounts of pentose not in excess of 0.1 g.

IV. REFERENCES

- [1] E. E. Hughes and S. F. Acree, *J. Research NBS* **21**, 327 (1938)RP1132.
- [2] A. Jolles, Sitzber. Akad. Wiss. Wien **114**, 1191 (1905); Liebigs Ann. Chem. **351**, 38 (1906).
- [3] N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.* **15**, 1167 and 1255 (1923).
- [4] C. Kullgren and H. Tyden, *Ing. Vetenskaps Akad. Handl.* **94**, 3 (1929).
- [5] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.* **6**, 123 (1934); **9**, 318 (1937).
- [6] G. M. Kline and S. F. Acree, *BS J. Research* **8**, 35 (1932)RP398.

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