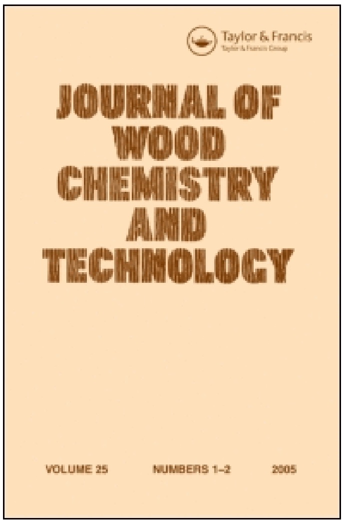

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DEHYDRATION AND OXIDATION OF CELLULOSE HYDROLYSIS PRODUCTS IN ACIDIC SOLUTION[1]

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ABSTRACT

The conversion of cellulose in homogenous solution to hydrolysis, dehydration, and oxidation products was investigated. A reaction sequence involving acetylation and degradation by aqueous acids led to humic acid, hydroxymethylfurfural, and levulinic acid as the isolated end-products. The influence of various reaction parameters upon the yields was studied. In the presence of ferric chloride some furfural was formed in addition to the other products.

INTRODUCTION

Acid catalyzed hydrolysis of cellulose to glucose has received a lot of interest. The heterogenous process is the cornerstone of the saccharification of wood, very likely with renewed technical importance. When carried out with hot acid, consecutive reactions of glucose lead to the formation of 5-hydroxymethylfurfural, levulinic acid, formic acid and humic substances as the main products. The behavior of glucose in these reactions was studied by McKibbins et al. [2]. The potential of levulinic acid as an organic intermediate was emphasized by Leonard [3]. Yields from hexoses were up to 55 % (of theory); conversions from cellulose would be smaller. Also the production of hydroxymethylfurfural is a matter of continued technical interest, e.g. [4]. The mechanism of dehydration reactions of carbohydrates was lastly reviewed by Feather and Harris [5]. In a different context Nickerson [6] studied the behavior of various celluloses in boiling hydrochloric acid, containing oxidizing metal salts. From his findings of a rapid loss of one molecule of carbon dioxide per anhydroglucose unit, the formation of another molecule with five carbon atoms is conceivable. An oxidation-decarboxylation-hydrolysis sequence might give rise to furfural. An oxidative hydrolysis of cellulose to furfural would be of technical interest, because so far the latter can only be obtained from the pentosans of wood, restricting the yield of furfural to about 10 % of this raw material.

In the context of chemical utilization of wood, the formation of levulinic acid as well as furfural from cellulose seemed interesting. Recently, the homogenous hydrolysis of cellulose via an esterification was described [7]. Continuing the reaction between dissolved carbohydrates and aqueous acid leads to products of dehydration. We decided to investigate this homogenous route from cellulose to furan compounds and levulinic acid in some detail. The effect of different experimental conditions, including addition of oxidation agents, was expected to elucidate the reaction route and demonstrate preparative possibilities.

EXPERIMENTAL

Cotton linters (Type 4417/45, bleached, P. Temming AG) was used as cellulose. All chemicals were reagent grade. Dissolution to cellulose acetate hydrogensulfate was achieved as described [7] by agitating the cellulose with acetic acid, acetic anhydride and sulfuric acid at 120 - 140°C. The mole ratio of Ac_2O to a C_6-unit was 3.4 : 1. Standard reaction solutions containing 6 % cellulose and 0.06 % H_2SO_4 were obtained after 3 to 5 min and kept under nitrogen. To the boiling mixture various amounts of aqueous acids were added dropwise, resulting in the concentrations given in the Tables. Heating under reflux or in an autoclave was continued, and samples were withdrawn after 1, 2, and 4 hrs. During this time the initially colorless solutions became dark and a black solid formed. This residue ("humic acid") was isolated by filtration and weighed. The diluted aqueous filtrate was then continuously extracted by dichloromethane (initially chloroform was used). In the CH_2Cl_2-solution, the content of 5-hydroxymethylfurfural (HMF) was determined by ultraviolet spectroscopy using the absorption at 279 nm after calibration. After evaporation to dryness of the dichloromethane solution, a brown oil was left. The weight of this organophilic extract was determined, and its content of levulinic acid (LeA) measured by potentiometric titration. The yields of HMF and LeA were confirmed by comparison of the infrared and (for typical samples) proton resonance spectra of the extracts with spectra of authentic samples and mixtures thereof [8]. In the aqueous solutions left after the extractions, the content of carbohydrates (not decomposed by dehydration to organophilic products) was determined with orcinol-sulfuric acid and calculated as glucose.

In this analytical evaluation volatile products were neglected. To include the determination of furfural, a series of reactions containing $FeCl_3$ in the dehydration stage, resembling Nickerson's conditions and with continuous distillation, was carried out (Table 6) and analyzed as follows: water, acetic acid, hydrochloric acid, and gaseous reaction products distilled during the reaction and were collected in a trap, while a water/acetic acid mixture was dropwise added to keep the composition of the solvent roughly constant. Also a stream of nitrogen or oxygen was led through the mixture. The distillate was analyzed for acids by potentiometry and for furfural by high pressure liquid chromatography (Li-chromosorb 5RP18 column in a SP 2000 of Spectra Physics).

RESULTS AND DISCUSSION

Figure 1 indicates the overall reaction paths in the presence of aqueous hydrochloric acid and ferric chloride. The nature of the intermediates leading to HMF has been discussed several times,

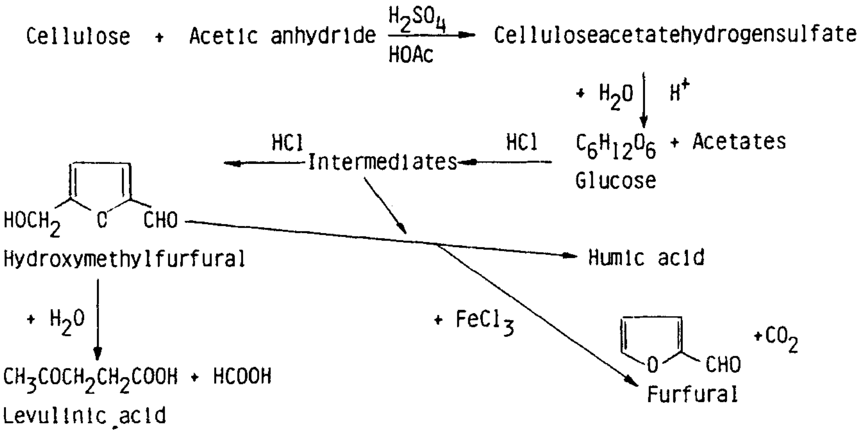

FIGURE 1. Reaction paths leading to dehydration and oxidation products.

e.g.[5]. A compound with an uv-absorption at 230 nm was detected but never isolated. The same absorption was found in our products after short reaction times. The organophilic extracts consisted almost exclusively of HMF and LeA. Only at low conversions additional compounds containing acetate ester groups were also present in considerable amounts. The course of the reaction for a longer period - reflected in the yields of the three fractions: residual sugar, nonvolatile extracts and insoluble residue - is given in Fig. 2 in semilogarithmic plots. The carbohydrate consumption followed first order kinetics up to 4 hours. No induction period was observed. Extract and residue yields follow a more complex course, typical for competing and consecutive reactions. In later stages much of the carbohydrate is eventually converted to volatile products, and the residue formation becomes more pronounced. The yield of the extract can apparently not be improved by longer reaction times alone. In order to find suitable conditions for the preferential formation of levulinic acid and furfural, some reaction parameters were systematically varied. The results are given in the Tables.

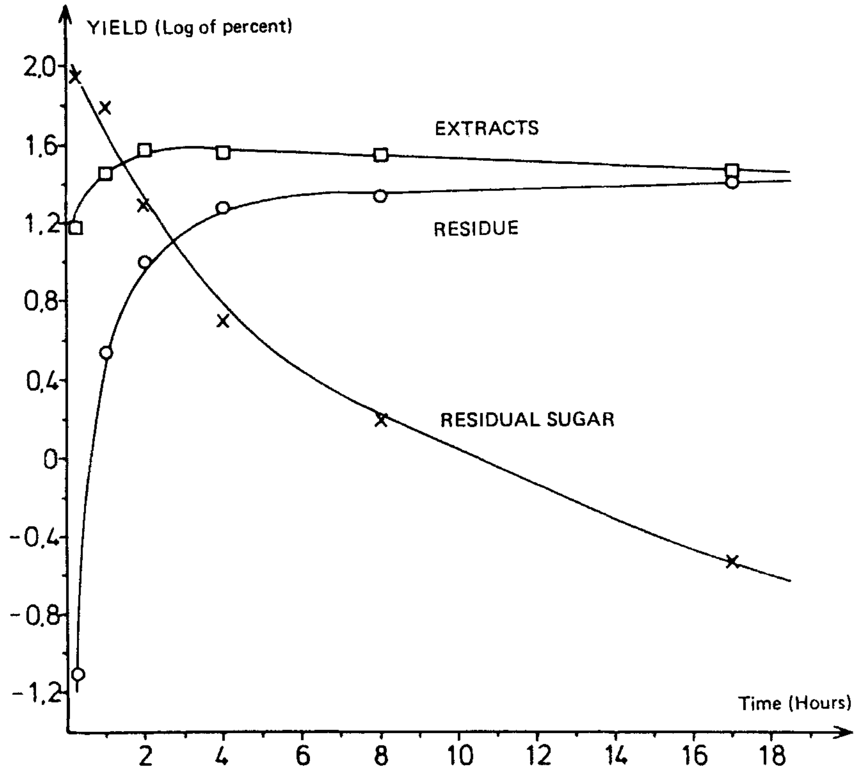

FIGURE 2. Products of dehydration in acetic acid solution containing 4.3% cellulose, 5.7% HCl, 25% H_2O, 0.074 mol/l $FeCl_3$ at 105° C.

Table 1 indicates the product spectrum as a function of the acid present. HCl and H_2SO_4 increase the conversion of the watersoluble "residual sugar" to the organo-soluble "extract" plus residue, probably in a greater than linear manner. The formation of HMF goes through a maximum when the reaction conditions become more severe. Levulinic acid and the "hümic acid" residue are formed in steadily increasing but limited amounts. At higher conversions the sum of the isolated products decreases considerably. Sulfuric acid is

TABLE 1

Products from Acidic Decomposition of Celluloseesters [1]

No	Acid	%	Note	Residual sugar [2]	Residue	Extract	HMF [3]	LeA [3]	Selectivity towards HMF	Selectivity towards LeA
1	HCl	0.37	4)	88.0	0	13.4	6.1	2.0	0.51	0.17
2	HCl	0.90	4)	75.3	0.2	15.3	8.5	4.7	0.34	0.19
3	HCl	2.0	4)	33.8	8.2	34.4	12.9	29.1	0.19	0.44
4	HCl	5.7	4)	11.1	22.6	37.1	5.8	39.9	0.07	0.45
5	HCl	12.6	4)	5.5	23.5	42.3	7.6	42.0	0.08	0.44
6	HBr	2.0	4)	28.8	18.0	31.9	9.6	34.5	0.13	0.48
7	H_2SO_4	2.0	4)	87.1	0.4	20.9	3.3	3.1	0.26	0.24
8	H_2SO_4	0.05	5)	95	0	20.0	6.0	1.5	high	0.30
9	H_2SO_4	0.30	5)	86.6	0	24.2	8.3	4.8	0.60	0.36
10	H_2SO_4	0.90	5)	29.9	3.4	46.0	6.8	35.2	0.10	0.50
11	HCl	0.37	5)	3.8	13.4	34.1	6.9	34.6	0.07	0.36
12	HBr	0.81	5)	17.1	7.3	58.3	14.9	45.2	0.18	0.54

1) Solution contained 25 % H_2O and 4.3 % cellulose; balance acetic acid. The figures are weight percents.
2) Calculated as glucose; % of theoretical yield.
3) HMF (hydroxymethylfurfural) and LeA (levulinic acid); % of theoretical yield.
4) After 4 hrs at 105°C.
5) After 1 hr at 150°C.

a far less efficient catalyst for the dehydration than hydrochloric acid. Hydrobromic acid acts to a similar extent as HCl does. If conversion is defined as consumption of carbohydrate (residual sugar) and selectivity as yield of HMF or LeA divided by conversion,the figures in the last 2 columns of the Table are obtained. The following trends can be derived: selectivities towards HMF decrease with acid concentration. This means the reaction order in acid for the formation of HMF is lower than for its decomposition. The opposite is true for LeA: selectivities increase with conversions caused by higher acid concentrations. Comparisons of different acids for similar conversions (entries 3, 6, and 10) show that the selectivities towards HMF decrease from HCl to HBr to H_2SO_4, whereas for LeA the order is $HCl < HBr < H_2SO_4$. Consequently, a low concentration of HCl is favorable for the preparation of HMF and a high concentration H_2SO_4 favors LeA slightly. The effects of varying the concentration of water in the solvent can be seen from the results of Table 2. In a solvent with only 9.5 % water, intermediates containing acetyl groups accumulate. They are distributed between water and dichloromethane and give rise to high values of "residual sugar" and extract. The formation of residues and de-acetylated products is faster in a solvent with 25 % H_2O,but decreases when the water content is further increased. The selectivities show that there is no obvious trend for the dependence of HMF on the water content. On the other hand,LeA is formed more selectively in solvents rich in water. Higher water contents than 50 % cause the intermediate cellulose ester to precipitate, preventing the desired homogeneous reaction.

Table 3 contains variations in the initial concentration of cellulose. The effect upon the overall conversions is small. The selectivities towards HMF and LeA seem to increase with lowering the cellulose concentration, indicating less competing side reactions (to "residues"). This is expected because the humic acid forming reactions have very likely a higher reaction order in carbohydrate. Remarkable are the high yields and selectivities of LeA in the

TABLE 2

Effect of Water on the Dehydration Reaction [1)]

No	% H_2O in solution	Note	Residual sugar 2)	Residue	Extract	HMF 2)	LeA 2)	Selectivity towards HMF	Selectivity towards LeA
1	9.5	3)	68.7	0.1	48.1	13.7	7.8	0.44	0.25
2	25	3)	49.0	7.9	32.0	23.0	15.1	0.45	0.30
3	50	3)	84.4	0.2	10.6	6.0	5.7	0.38	0.37
4	9.5	4)	48.3	3.5	45.0	11.4	10.4	0.22	0.20
5	25	4)	11.0	22.6	37.1	6.8	39.9	0.08	0.45
6	50	4)	56.9	3.8	24.3	5.8	24.2	0.13	0.56
7	25	5)	3.8	13.4	34.1	6.9	34.6	0.07	0.36
8	50	5)	59.2	2.3	26.8	12.9	19.9	0.32	0.49

1) Solution contained 4.3 % cellulose and HCl as indicated in footnotes.
2) Same as in Table 1
3) With 5.7 % HCl at 105°C after 1 hr.
4) With 5.7 % HCl at 105°C after 4 hrs.

high temperature runs, which demonstrate that the formation of levulinic acid from cellulose is a feasible process.

Some more results from increasing the temperature of the process are presented in Table 4. Higher conversions of carbohydrates lead to more LeA and especially to more residues. Also considerable amounts of volatile products - not only formic acid - must have formed at higher temperatures. Possible among those are carbon dioxide and furfural, whose formation should be promoted by oxidative agents. The results of Table 5 with ferric chloride added to the refluxing solution, similar to Nickerson's experiments, do not indicate that the course of the reaction was changed by $FeCl_3$.

The sum of the non-volatile products deviates considerably from 100 % after long reaction times, an indication that $FeCl_3$ causes gases to form. Experiments with continuous distillation to trap furfural among the volatile products are summarized in Table 6. In the condensates collected every hour, furfural was indeed detected. The yields after 2 and 4 hours, quoted in the

TABLE 3

Effect of Cellulose Concentration on the Dehydration Reaction [1]

No	% Cellulose in solution	Note	Residual sugar [2]	Residue	Extract	HMF [2]	LeA [2]	selectivity towards	
								HMF	LeA
1	2.15	3)	48.6	2.0	38.1	29.7	17.0	0.58	0.33
2	4.3	3)	49.0	7.9	32.0	23.0	15.1	0.45	0.30
3	8.6	3)	68.1	8.0	22.2	13.5	10.2	0.42	0.32
4	2.15	4)	16.7	1.6	56.2	18.2	45.6	0.22	0.55
5	4.3	4)	3.8	13.4	34.1	6.9	34.6	0.07	0.36
6	8.6	4)	12.6	10.9	42.3	17.8	34.6	0.20	0.40
7	2.15	5)	7.3	3.2	43.9	9.7	56.6	0.10	0.61
8	4.3	5)	1.1	15.8	44.2	4.8	50.9	0.05	0.51
9	8.6	5)	4.2	20.7	39.2	7.3	43.9	0.08	0.46

1) Solution contained 25 % H_2O and HCl as indicated in footnotes
2) Same as in Table 1
3) With 5.7 % HCl at 105°C after 1 hr.
4) With 0.37 % HCl at 150°C after 1 hr.
5) With 0.37 % HCl at 150°C after 2 hrs.

TABLE 4

Temperature Influence on the Dehydration Reaction 1)

No	Acid	%	Time (hrs)	Temp. (°C)	Residual sugar 2)	Residue	Extract	HMF 2)	LeA 2)	Selectivity towards HMF	Selectivity towards LeA
1	HCl	0.37	4	105	91	0	13.4	6.2	2.0	0.69	0.22
2	HCl	0.37	4	150	1.0	18.3	40.4	2.5	49.3	0.02	0.50
3	H_2SO_4	0.05	1	160	99.5	0	20.0	6.0	1.6	high	high
4	H_2SO_4	0.05	1	175	55.6	1.3	37.0	15.8	8.4	0.36	0.19
5	H_2SO_4	0.05	1	210	4.4	30.2	35.0	14.4	24.9	0.15	0.26

1) Solution contained 4.3 % cellulose and 25 % H_2O
2) Same as in Table 1

TABLE 5

Product Distribution in the Presence of $FeCl_3$ 1)

No	$FeCl_3$ mole/l	Time (hrs)	Residual Sugar 2)	Residue	Extract	Sum of products	HMF 2)
1	0	1	61.5	2.4	25.7	89.6	23.0
2	0.007	1	66.7	2.6	27.0	96.3	20.7
3	0.074	1	63.1	3.7	28.8	95.6	16.7
4	0.37	1	67.0	2.1	28.3	97.4	20.0
5	0	4	15.0	19.0	38.9	72.9	7.5
6	0.074	4	5.6	18.8	35.4	59.8	9.4
7	0.37	4	3.4	8.4	28.4	51.8	4.4

1) Solution contained 4.3 % cellulose, 5.7 % HCl and 25 % H_2O. Temperature 105°C.

2) Same as in Table 1.

corresponding columns, show that ferric chloride promotes an oxidative hydrolysis. Also oxygen and cupric chloride, as an oxidation catalyst in addition to $FeCl_3$, have a slight effect. But even under the most favorable conditions the yield of furfural was only 3 to 4 % of the theory. The yields of the other products after 4 hours are within the expected range. In solutions with more than 50 % H_2O (footnote 4) less organophilic extract is produced analogous to the results of Table 2. Furfural is probably formed independently of this solvent change.

CONCLUSIONS

The dehydration reaction of partially acetylated cellulose in aqueous solution catalyzed by acids proceeds by 1) hydrolysis to hydrophilic carbohydrates with one or more acetate ester groups, followed by 2) conversion to hydroxymethylfurfural, and then to 3) levulinic acid, accompanied by 4) insoluble residues (humic acid). HMF as an intermediate is formed in optimum yields under milder conditions of time and temperature and lower concentrations

TABLE 6

Oxidative Hydrolysis of Cellulose [1]

No	$FeCl_3$ mole/l	$CuCl_2$	Gas	Note	Furfural in 2 hrs [2]	Yields after 4 hrs				
						Fur[2]	HMF[3]	LeA[3]	Total Extr.	Residue
1	0	0	O_2	4)	0.3	0.3	1.5	+	15.6	7.7
2	0.007	0.007	N_2		0.3	0.5	1.4	50.0	39.0	11.7
3	0.007	0.007	O_2		0.6	0.7	1.3	43.6	33.9	6.1
4	0.07	0	O_2	4)	0.9	1.0	1.0	+	10.0	5.6
5	0.19	0	O_2	4)	1.7	2.2	0.6	+	16.0	8.9
6	0.56	0	N_2		1.3	2.6	1.3	34.6	27.2	14.9
7	0.56	0	O_2		2.2	3.7	1.3	34.4	26.7	14.6
8	0.56	0	O_2	4)	3.0	3.3	0.7	+	12.0	15.1
9	1.12	0	O_2	5)	2.3	4.1	0.4	16.3	13.0	22.5

1) Solution contained 4 % cellulose, 9 % HCl and 50 % H_2O.
2) Continuously destilled from reaction mixture; % of theoretical yield.
3) Same as in Table 1.
4) Increasing water content during reaction.
5) Yields obtained after 8 instead of 4 hrs.

of cellulose and acid. HCl is a more efficient and selective catalyst than H_2SO_4 for HMF. The formation of LeA is promoted by higher acid and water concentrations in the medium. H_2SO_4 is more selective than HCl as a catalyst. Increasing the reaction time and temperature favors the competing reaction to the "residue" more than to LeA. Addition of ferric chloride to the dehydration reaction mixture with HCl and continuous distillation leads to some furfural. Yields of 20.... 30 % HMF and of 45.... 55 % LeA, based on theory, from cellulose can be realized, whereas only 3.... 4 % of furfural could be obtained.

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