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Note

Influence of sodium chloride on volatile products formed by pyrolysis of cellulose: Identification of hydroxybenzenes and 1-hydroxy-2-propanone as major products

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There have been many previous studies of the volatile products that are formed by the pyrolysis of cellulose. Several workers have used gas–liquid chromatography–mass spectrometry (g.l.c.–m.s.), and many volatile products, containing 1–6 carbon atoms, have been found (see, *e.g.*, refs. 1–3). More recently, curie-point pyrolysis has been integrated with low voltage m.s. in order to analyze the immediate, volatile, pyrolysis products[4,5].

Previous studies of the effects of inorganic salts on cellulose pyrolysis have mostly been focused on those salts known to function as fire retardants. Occasionally, alkali-metal halides have been included, but the objectives of these studies have been centered around flame retardation[6,7], or the general effects of additives on char formation, and the volatile products were not rigorously studied.

We have recently found that the products of pyrolysis of the (1→3)-β-D-glucan curdlan are dramatically influenced by the presence of sodium chloride in the polysaccharide, the salt favoring reactions leading to the formation of metasaccharinolactones[8], and we now describe the effect of sodium chloride on the pyrolysis products of cellulose.

Cellulose samples were pyrolyzed *in vacuo*, and the products were isolated as three distinct fractions: a black, solid residue remaining in the pyrolysis furnace (char), a viscous liquid that condensed in a cold-water condenser (tar), and a non-viscous liquid that condensed in a liquid-nitrogen trap. Inorganic compounds added to cellulose prior to pyrolysis have previously been shown to catalyze char-forming reactions[9], resulting in increased yields of char and decreased yields of tar. This effect is also observed in Table I, where the addition of sodium chloride great-

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TABLE I

YIELDS OF THE MAJOR PRODUCTS FROM VACUUM PYROLYSIS OF CELLULOSE CONTAINING SODIUM CHLORIDE

	Sodium chloride content (%)			
	10	*10*	*10*	*0*
	Pyrolysis temperature (degrees)			
	290	*315*	*340*	*350*
	Pyrolysis time (h)			
	3	*2*	*1*	*1*
Products	*Percent (based on cellulose)*			
Char	34	29	26	9
Tar	8	12	18	66
Liquid-nitrogen condensate	54	51	53	24
1,2-Dihydroxybenzene	0.2	0.2	0.2	n.d.
1,4-Dihydroxybenzene	0.1	0.1	0.1	n.d.
1,2,3-Trihydroxybenzene	0.4	0.4	0.3	n.d.
1,2,4-Trihydroxybenzene	0.5	0.6	0.4	n.d.
Levoglucosan	0.2	0.3	0.4	36
1-Hydroxy-2-propanone	2.8	4.5	5.0	<0.005

ly increased the yields of char and of liquid-nitrogen condensate, whereas the yield of tar was greatly lessened.

The tar fractions of sodium chloride-treated samples were obtained in a yield of ~15%, and, when examined by g.l.c. of the per(trimethylsilyl) (Me_3Si) ethers, gave complex chromatograms in which two peaks predominated. By comparison of their mass spectra and g.l.c.-retention times with those of authentic compounds, these were shown to be 1,2,4- and 1,2,3-trihydroxybenzene. Also present in smaller amounts were 1,2- and 1,4-dihydroxybenzene, and 1,6-anhydro-β-D-glucopyranose (levoglucose). The absolute yields, determined by use of an internal standard, are shown in Table I. Traces of saccharinolactones were also detected.

It was not possible to detect either 1,3,5-tri- or 1,3-di-hydroxybenzene in the products, but this does not eliminate the possibility that they were formed in the pyrolysis, as they may be more reactive, and hence less likely to survive, than the other hydroxybenzenes.

One of the most dramatic effects of sodium chloride is suppression of theformation of levoglucosan, from a yield of 36 to <1%. This effect had previously been demonstrated with a wide range of other salts[6,7]. No significant trend in the yields of the hydroxybenzenes was found on varying the temperature of pyrolysis from 290 to 340°.

Phenol and cresols have been identified among the products from the pyrolysis of "cellulose sheets" at atmospheric pressure, and polyhydroxybenzenes have been generated from D-glucose in acidic[10] and basic[11] solutions. All of the diand tri-hydroxybenzenes mentioned in Table I have also been detected in cellulose-cigarette smoke[12]. However, the present work constitutes the first report of polyhydroxybenzenes as major components of the tar resulting from the pyrolysis of cellulose. Evidently, the presence of sodium chloride facilitates the reactions leading to such products, but the mechanism of the formation is not yet clear. The recombination of such free-radical, initial pyrolysis products as acetyl (CH_3CO) could be envisaged as leading to hydroxybenzenes, especially trihydroxybenzenes, but such a mechanism would be unlikely to yield 1,2,3-trihydroxybenzene as a major product, and there is no reason to presume the catalysis of such reactions by sodium chloride. Another possible mechanism is the dehydration and cyclization of six-carbon fragments derived from D-glucosyl units (*e.g.*, $C_6H_{10}O_5 - 2\ H_2O \rightarrow C_6H_6O_3$). Presently, sufficient data is not available to elucidate the mechanism involved.

TABLE II

RELATIVE YIELDS OF MAJOR COMPONENTS OF THE LIQUID CONDENSATE FROM THE VACUUM PYROLYSIS[a] OF CELLULOSE CONTAINING 10% OF SODIUM CHLORIDE

	Pyrolysis temperature (degrees)		
	290	*315*	*340*
	Pyrolysis time (h)		
Products[a]	*3*	*2*	*1*
1-Hydroxy-2-propanone	**1.0**	**1.0**	**1.0**
Acetic acid	0.2	0.2	0.2
2-Furaldehyde	0.2	0.2	0.2
2-Acetylfuran	0.1	0.1	0.005
4-Hydroxybutanolactone	0.2	0.2	0.2

[a]G.l.c. peak-areas relative to 1-hydroxy-2-propanone

TABLE III

RELATIVE YIELDS OF MAJOR COMPONENTS OF THE LIQUID-NITROGEN CONDENSATE FROM VACUUM PYROLYSIS[a] OF CELLULOSE

Products	*Peak area*[b]
Levoglucosenone	**1.0**
2-Furaldehyde	0.3
1,4:3,6-Dianhydro-D-glucose	0.2
5-(Hydroxymethyl)-2-furaldehyde	0.1

[a]Pyrolysis temperature, 340°; pyrolysis time, 1.0 h. [b]In g.l.c. relative to that of levoglucosenone as unity

This discovery of benzene compounds derived from cellulose may be related to the processes of char formation, as charring of cellulose produces a large amount of aromaticity that is enhanced in the presence of sodium chloride[13]. It may also be related to the processes that yield aromatic structures in humic substances derived from lignocellulosic materials. Hence, these results suggest that some of the aromatic components of humic substances may be derived from cellulose, rather than from lignin.

Apart from water, the major component of the liquid-nitrogen condensate from the pyrolysis of cellulose containing sodium chloride was 1-hydroxy-2-propanone (see Table II). This was not a major product in the absence of sodium chloride (see Table III), and its formation appears to be catalyzed by the salt. A previous report[14] also noted that the pyrolysis of cellulose in the presence of potassium nitrate yields 1-hydroxy-2-propanone as the major, volatile product, although in that study no hydroxybenzenes were detected. The mechanism of formation of the 1-hydroxy-2-propanone is as yet unknown.

EXPERIMENTAL

Substrates. — Acid-washed cellulose was prepared by stirring CF-11 cellulose powder (Whatman Laboratory Products; 20 g) in 0.1M sulfuric acid (800 mL) for 3 h at room temperature. The sample was then rinsed with distilled water, and extracted with water for 8 h in a Soxhlet extractor, to remove all traces of acid. Sodium chloride–cellulose mixtures were prepared by adding an aqueous solution of sodium chloride to dry CF-11 cellulose powder, and then removing the water *in vacuo* at 50° with vigorous agitation, giving a final content of 10 g of NaCl per 100 g of cellulose.

Pyrolysis conditions. — Vacuum pyrolyses were conducted on a 0.5-g scale under a flow of nitrogen at 200 Pa (1.5 torr) as described previously[15]. In some pyrolyses, a liquid-nitrogen trap was added, downstream of the furnace, to condense the more-volatile compounds.

G.l.c. analyses. — All such analyses were made on packed nickel columns (3 m × 2.2 mm o.d.), using nitrogen as the carrier gas, flame-ionization detection, and digital integration. Three column packings and conditions were used: (*A*) 3% of SE-30 on Gas-Chrom Q (100–120 mesh), programmed from 80 to 240° at 3°/min, with an initial, 2-min hold-period; (*B*) 3% of OV-225 and 2.5% of HI-EFF-9BP on Gas-Chrom Q (80–100 mesh), used isothermally at 205°; and (*C*) 5% of carbowax 20M-TPA on Gas-Chrom Q (80–100 mesh), programmed from 60 to 140° at 4°/min, and then from 140 to 240° at 10°/min.

Volatile materials that condensed immediately outside the furnace (namely, tar) were derivatized for g.l.c. analysis in 2 ways. An aliquot was per(trimethylsilyl)ated with Tri-sil reagent (Pierce Chemical Co.), and the products analyzed on column *A*, with methyl eicosanoate (arachidate) as the internal standard. A second aliquot was acetylated with 1-methylimidazole–acetic anhydride[16], and analyzed on column *B*. Quantification of polyhydroxybenzenes was conducted by using the trimethylsilyl ethers on column *A*, rather than with acetates on column *B*, as the latter analysis suffered more interference from other tar constituents. In addition, small variations in the extraction procedure after acetylation were found to have a strong effect on the acetoxybenzene content, making this technique less suitable for quantitative analysis.

Volatile compounds collected in the liquid-nitrogen trap were warmed to room temperature, and diluted to 4 mL with acetone. This solution was then analyzed directly by g.l.c. on column *C*, and the content of 1-hydroxy-2-propanone was determined by using ethyl 3-methoxybenzoate as the internal standard. The yields of other constituents are expressed as the integrated peak-areas, relative to that of 1-hydroxy-2-propanone.

Identification of hydroxybenzenes from the pyrolysis of CF-11 cellulose–NaCl — A sample of CF-11 cellulose–NaCl was pyrolyzed, and the acetylated tar was analyzed by g.l.c. (column *B*). A peak having the same retention time as 2,3,4-tri-*O*-acetyl-1,6-anhydro-*β*-D-gluco-D-furanose was observed, and later identified by mass spectrometry and g.l.c. retention-time as 1,2,4-triacetoxybenzene. Analysis of the same tar by g.l.c. (column *A*) after per(trimethylsilyl)ation gave a chromatogram having four peaks, with retention times identical to those of the per(trimethylsilyl) ethers of 1,2- and 1,4-dihydroxybenzene (4.5, 5.9 min) and 1,2,3- and 1,2,4-trihydroxybenzene (8.0, 8.9 min). In addition, the mass spectra of these four peaks were identical to those of the per(trimethylsilyl) ethers of the authentic polyhydroxybenzenes.

Identification of products trapped by liquid nitrogen. — (*a*) *From cellulose–NaCl.* Pyrolysis of cellulose–NaCl provided one major product (other than water) in the volatile compounds trapped with liquid nitrogen, as shown by g.l.c. (column *C*) without derivatization. By g.l.c.–m.s., this product was found to be 1-hydroxy-2-propanone, and its retention time (7.7 min) coincided with that of a freshly distilled, authentic sample. Subsequently, smaller amounts of acetic acid (11.2), 2-furaldehyde (11.9), 2-acetylfuran (13.0), and 4-hydroxybutanolactone (16.2 min) were also identified by comparison of their mass spectra and g.l.c. retention-times with those of authentic samples. Five smaller, unidentified peaks were eluted at 9.1, 17.2, 19.5, 19.9, and 25.0 min.

(*b*) *From acid-washed cellulose.* Four major components were observed, by g.l.c. (column *C*), in the volatile compounds resulting from the pyrolysis of acid-washed cellulose, and trapped with liquid nitrogen. By comparison of their mass spectra and retention times with those of reference compounds, these were found to be 2-furaldehyde (12.0), levoglucosenone (24.2), 1,4:3,6-dianhydro-*α*-D-glucopyranose (28.8), and 5-(hydroxymethyl)-2-furaldehyde (29.7 min).

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