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The products of the zinc chloride-promoted decomposition of cellulose in aqueous phenol at 350°C

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ABSTRACT

When cellulose was degraded at 350°C for 1 h in aqueous phenol with zinc chloride as catalyst, 10% of the carbon atoms were found in monosaccharide products, 4% in neutral aromatic derivatives (80% xanthene), 34% in the methyl groups of methylated phenols, 14% in the non-aromatic moieties of bis(hydroxyphenyl)methanes and *C*-methylated derivatives thereof, and 22% in the char. Carbon-containing gasses were also produced, and some of the cellulose carbon atoms appeared in the aromatic rings of the neutral and phenolic products. These observations suggest that formaldehyde was a key intermediate. In pure phenol as the solvent, 10% of the carbon of cellulose was converted into the methylene carbon of xanthene.

INTRODUCTION

The finite nature of the world's fossil-fuel resources has led to a resurgence of interest in renewable biomass as a source of energy (including liquid fuels), and considerable attention has been paid to the liquefaction of biomass and to the thermal degradation of cellulose, its main component[1–8].

In a novel approach to the liquefaction of cellulose, Miller and Fellows[9] pointed out that there would be a probable advantage in avoiding non-specific, heterogeneous processes during the degradation of cellulose material, and therefore selected conditions which would favour solvolytic, acid-catalysed depolymerisation to discrete products of low molecular weight. An initial study was undertaken of the decomposition of the polysaccharide and of woods at 350°C in aqueous phenol and in the presence of the Lewis acid zinc chloride, that is, conditions under which cellulose is known to dissolve. They reported that xanthene (**1**) comprised ~ 80% of the neutral products formed whether cellulose, hardwood, or softwood was

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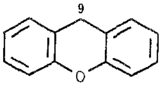
used, and, also, that phenol appeared to be produced from the complex feedstocks. Because of the latter observation, which is consistent with the known occurrence of aromatic substances, including phenols, amongst the thermal-degradation products of carbohydrates, including cellulose[3,5,10–13], a more extensive study has been carried out. Whilst it seemed apparent that the methylene group of the xanthene would have been derived from the carbohydrate source, it was uncertain as to whether the benzenoid moieties originated either partly or exclusively from the solvent. Clearly, the assessment of the economic merit of any related process would depend on the resolution of this point.



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In this paper, conditions suitable for degradation of cellulose are described, the products of reaction are investigated, and a pathway for transfer of carbon from cellulose to methyl and methylene carbons of the aromatic products is considered. The following paper[14] details the means by which the xanthene is produced.

RESULTS AND DISCUSSION

The initial experiments explored the effects of variation of time, temperature, and the molar proportion of phenol in the solvent. The products of liquefaction were fractionated and analysed to give the results in Table I; the gases were detected by mass spectrometry, but were not assayed.

Selection of 350°C for 1 h as the standard conditions represented a compromise of many factors, several of which were assessed individually. Thus, at temperatures between 25 and 400°C for 1 h, the yields of the intermediates glucose, phenyl glucosides, and 1,6-anhydroglucose each reached a maximum (7, 3.5, and 1.5%, respectively, of the cellulose) near 300°C (Fig. 1), which is consistent with the observation[15] that the endotherm of the zinc chloride-catalysed decomposition of cellulose has a maximum value at 310°C. Likewise, the yields of bis(hydroxyphenyl)methanes and their *C*-methyl derivatives rose rapidly from 10% at 250°C to a maximum of ~ 60% at 350°C and then fell rapidly, and the yields of phenols and their *C*-methylated derivatives increased from 50% at 250°C to 85% at 350°C and stayed at that level. The yield of xanthene rose to 18% at 350°C and then remained constant, whereas the total yield of the neutral products continued to increase with increase of temperature up to 400°C.

The yield of xanthene formed at 350°C rose to a maximum of 18% in 1 h and this time of reaction was selected as the standard. The concentration of catalyst used [0.4 M; molar proportion $ZnCl_2$: cellulose (calculated as anhydroglucose) = 1 : 3] gave close to maximum yields of both the carbohydrate products and xanthene.

TABLE I

Products of liquefaction of cellulose in aqueous phenol containing zinc chloride

Component [a]	Cellulose used (%)	Conversion of cellulose carbon (%)
Levoglucosenone	1.0	1.3 [d]
3,6-Anhydroglucose [b]	0.4	0.4 [d]
α,β-Glucose	4.2	3.8 [d]
1,4:3,6-Dianhydroglucose	0.3	0.3 [d]
1,6-Anhydroglucose	1.4	1.4 [d]
α,β-Cellobiose	0.8	0.8 [d]
Phenyl α,β-glucopyranoside	2.4	1.5 [d]
o-Cresol	15.1	8.6 [e]
p-Cresol	18.9	
2,4-Dimethylphenol	12.9	
2,5-Dimethylphenol	3.2	14.2 [e]
2,6-Dimethylphenol	15.6	
2,4,5-Trimethylphenol	3.3	
2,3,6-Trimethylphenol	2.7	10.2 [e]
2,4,6-Trimethylphenol	5.7	
2,3,4-Trimethylphenol	5.3	
Tetramethylphenol	2.3	1.7 [e]
Pentamethylphenols	trace	
Bis(2-hydroxyphenyl)methane	trace	
Bis(4-hydroxyphenyl)methane	11.0	3.4 [e]
2-Hydroxyphenyl(4-hydroxyphenyl)methane	13.9	5
Methyl-bis(hydroxyphenyl)methanes	22.4	5.7 [e]
Dimethyl-bis(hydroxyphenyl)methanes	13.8	5.0 [e]
Diphenyl ether	0.7	
Dibenzofuran	0.5	
2-Methyldibenzofuran	0.2	0.1 [e]
4-Methyldibenzofuran	0.3	
Xanthene	18.1	2.7 [e]
Methylxanthenes	1.6	0.4 [e]
Xanthone	1.4	0.2 [e]
Dimethylxanthenes	0.2	0.1 [e]
Trimethylxanthenes	0.1	0.1 [e]
CO_2, CO	[c]	[c]
Char	13.3	22.4 [f]
Aromatic rings (see following paper)		4.5
		88.8%

[a] Phenol produced was not detectable. [b] Tentative identification. [c] Not assayed. [d] Calculated on the basis of conversion of cellulose carbon into product carbon. [e] Calculated on the basis of conversion of cellulose carbon into methyl and methylene group carbon. [f] Calculated on the basis of conversion of cellulose carbon into char carbon.

Preliminary studies of the effect of the water content of the solvent (Fig. 2) showed that higher proportions of phenol resulted in higher yields of monosaccharide derivatives and xanthene, and reduced char.

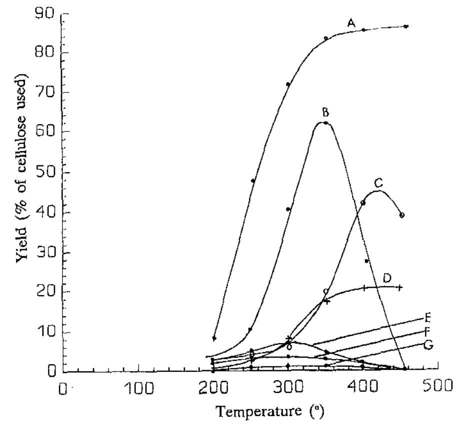


Fig. 1. Weight percentages of compounds formed by heating a mixture of cellulose (100 mg), water (100 mg), phenol (300 mg), and zinc chloride (25 mg) for 1 h at different temperatures: A, methylphenols; B, bis(hydroxyphenylmethanes); C, total neutral compounds; D, xanthene; E, glucose, F, phenyl glucopyranoside; G, 1,6-anhydro-β-glucopyranose.

Under the standard conditions (350°C, 1 h), ~10% of the cellulose was converted into carbohydrate derivatives of low molecular weight (see Table I). The glucose, cellobiose, and phenyl glucosides resulted from solvolysis reactions, and the 1,6- and 3,6-anhydroglucose, 1,4:3,6-dianhydroglucose, and levoglucosenone (1,6-anhydro-3,4-dideoxy-D-*glycero*-hex-3-enopyranos-2-ulose) are known pyrolysis products of cellulose and of the compounds of solvolytic degradation[16–19]. There are complex links within these sets of compounds, and probably between them, since, for example, 1,6-anhydro-D-glucose could have been a thermolysis product

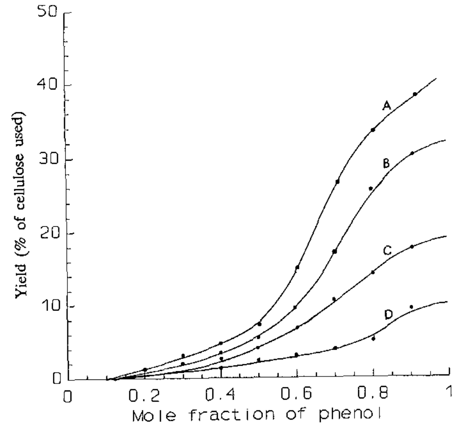
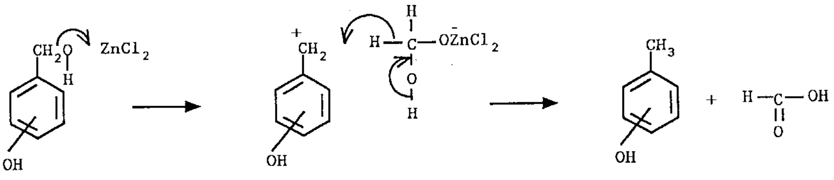


Fig. 2. Yields (%) of compounds formed by heating cellulose (1 g) with zinc chloride (0.25 g) in aqueous phenol (3 mL), as a function of the proportion of phenol, at 350°C for 30 min: A, xanthene; B, glucose; C, phenyl glucopyranosides; D, 1,6-anhydro-β-glucopyranose.

that could yield glucose and phenyl glucoside by acid-catalysed solvolysis, of which the latter reaction could be reversible[17]. Under the conditions used, D-glucose, phenyl D-glucopyranoside, and 1,6-anhydro-D-glucose were each degraded, to give many of the observed products, including xanthene. Thus, it is proposed that, at a temperature above that required for the thermal depolymerization of cellulose, the polysaccharide is degraded to glucose, phenyl glucoside, and levoglucosan, which can interconvert and be degraded.

The composition of the phenolic fraction indicated that considerable *C*-alkylating reactivity was developed during the degradation, and the hydroxymethyl groups bonded to the phenol rings suggested that formaldehyde was the most probable alkylating agent, which functioned by co-ordination with the Lewis acid. Indeed, hydroxybenzyl alcohols may be prepared by condensation of phenol with formaldehyde even without a catalyst[20], but the process is catalysed by acids and by divalent metal cations[20]. Under the standard conditions, paraformaldehyde reacted with aqueous phenol in the presence of zinc chloride to produce the *C*-methylphenols and the bis(hydroxyphenyl)methanes noted in Table I, that is, the products of cellulose liquefaction. Reduction of benzyl alcohols to toluene analogues by formaldehyde in acid conditions is a disproportionation reaction akin to an acid-catalysed "crossed Cannizzaro" process (**2** → **3** → **4**).

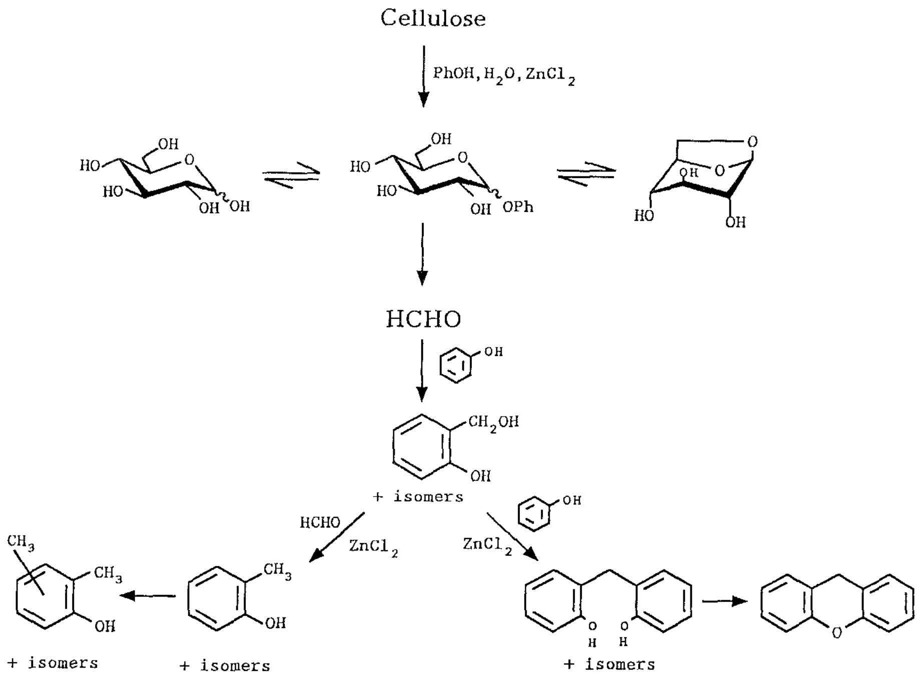


2 3 4

Xanthene was also produced in the paraformaldehyde experiment, and also in a similar experiment using *o*-hydroxybenzyl alcohol which, in addition, gave 2-hydroxyphenyl(4-hydroxyphenyl)methane, which indicated that the bis(hydroxyphenyl)methanes produced from cellulose were formed by the *ortho*- and *para*-substitution of phenol by the hydroxybenzyl carbonium ion, the xanthene being derived by dehydration of the bis(2-hydroxyphenyl) isomer.

During the liquefaction of cellulose, significant levels of methylated phenols were formed near 200°C and the system then developed alkylating/reducing capacity. The yields of these thermally stable compounds increased up to, but not beyond, a reaction temperature of 350°C. The bis(hydroxyphenyl)methanes reacted above this temperature to give xanthene and the "resols"[21].

The gaseous oxides of carbon, which were not assayed quantitatively, are known to be formed during the thermal degradation of cellulosic material[22,23], 1,6-anhydroglucose[4], and glucose[11,24]. Likewise, char is a major product of cellulose pyrolysis; char may be formed[25] by dehydration of the sugar units to give unsaturated products which polymerise to non-volatile materials that are degraded to



Scheme 1.

carbonaceous residues on prolonged heating. The char produced under the conditions used in the present work contained 75% of carbon and represented 13% of the weight of the original cellulose. However, the formation of char was reduced to only 6% when the reaction was carried out in pure phenol, possibly because char or its precursors were partially soluble in this solvent; also, the yields of glucose, phenyl glucosides, and 1,6-anhydroglucose rose markedly (Fig. 2), which implies that water favours the formation of char. Unexpectedly, in pure phenol, the conversion of cellulose carbon into xanthene was four times as efficient as that under the standard conditions and ~ 10% of the cellulose carbon appeared as the methylene carbon of xanthene.

It is proposed that the degradation of cellulose in aqueous phenol in the presence of zinc chloride proceeds largely as in Scheme 1 by thermolysis and solvolysis of the linkages to give mainly glucose, phenyl glucosides, and 1,6-anhydroglucose, which interconvert and are degraded extensively to products of low molecular weight, of which only carbon dioxide and monoxide were detected. Formaldehyde may be formed either by heterolytic processes or by the homolytic cleavage of contiguous carbohydrate carbon–carbon bonds to give hydroxycarbene followed by rearrangement[26,27], but the mechanism remains to be determined. Formaldehyde is known to be formed during the pyrolysis of carbohydrates[11,28–30] and to be thermally stable, but reactive towards phenol to give the *C*-alkylated products formed from cellulose. There was no evidence for radicals as important intermediates; for example, no biphenyls or diphenyl ethers were formed.

The validity of Scheme 1 was supported by the following percentage conversions of the intermediates and related compounds into xanthene under the standard conditions: cellulose (anhydroglucose), 18.1%; glucose, 16%; phenyl β-D-glucopyranoside, 19%; 1,6-anhydro-D-glucose, 20%; paraformaldehyde, 10%; *o*-hydroxybenzyl alcohol, 54%; *p*-hydroxybenzyl alcohol, 0%; bis(2-hydroxyphenyl)methane, 98%; 2-hydroxyphenyl(4-hydroxyphenyl) methane, 0%.

EXPERIMENTAL

Liquefaction procedures.—In a standard experiment, a mixture of cellulose (100 mg), phenol (300 mg), zinc chloride (25 mg), and water (100 μL) was shaken and heated at 35°C in a thick-walled tube (100 mm, i.d. 4 mm). Dissolved gases were removed by freezing and thawing prior to sealing at 2 mmHg. The tube was then transferred to a pressure vessel (15 × 160 mm), with the tube surrounded with water to compensate for internal pressure generated, and the temperature was increased at 35°C/min. On completion of the experiment, the vessel was allowed to cool for 90 min.

Product fractionation and analysis.—The crude products were decanted into water (20 mL) which was then extracted with hexane (20 mL). The aqueous phase was concentrated, *myo*-inositol was added as the internal standard, and the residue was trifluoroacetylated[31] in CH_2Cl_2 (65 μL) with trifluoroacetic anhydride (30 μL) and pyridine (5 μL) at 20°C for 3 h. The products were analysed on a Pye PU 4500 gas chromatograph with a 25-m BP 1 capillary column and a temperature programme from 50 to 230°C at 6°C/min. Helium was used as the carrier gas.

The hexane phase was washed with 2 M NaOH (20 mL) and water (20 mL), dried ($MgSO_4$), and concentrated to give the neutral products. Neutralisation of the alkaline washings with aq HCl and extraction with CH_2Cl_2 (20 mL) gave the phenolic fraction. Filtration of the original mixtures gave the char which was washed with water and acetone, and dried.

GLC–MS was performed with a Hewlett–Packard HP 59970B mass spectrometer. Compounds were identified on the basis of retention times and comparison of their mass spectra with those of authentic samples or with those available from a data base[32]. Volatile products were examined by MS of the head-space vapours. Dominant peaks had m/z 18 (H_2O), 28 (N_2, CO), and 44 (CO_2); smaller peaks had m/z 16 (CH_4), 30 (C_2H_6, HCHO), and 32 (O_2).

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