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IDENTIFICATION BY GAS–LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY OF LOW-MOLECULAR-WEIGHT PRODUCTS FROM THE AQUEOUS ALKALINE DEGRADATION OF CELLULOSE*

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ABSTRACT

Low-molecular-weight products from the degradation of pure cellulose in 0.3–0.65M sodium carbonate or hydrogencarbonate at 300° have been identified by g.l.c.–m.s. Both the aqueous residual phase and the floating-oil product phase were examined, and contained essentially the same compounds, which were further characterized by the trifluoroacetyl derivatives. They consisted primarily of unsaturated aliphatic and alicyclic hydrocarbons, aldehydes, ketones, alcohols, and furans. Specifically identified were cyclopentanone, cyclohexanone, phenol, cresols, 2-ethylcyclopentanone, 2- or 3-methylcyclopentanone, 2,5-dimethyl-2-cyclopentenone, acrolein, 2,5-dimethyl-2,4-hexadiene, and octene. Probably present were 2,4-dimethylfuran, 2,5-diethylfuran, ethylmethylfuran, 4-octyne, and decyne. The formation of these compounds demonstrates not only the degradation of cellulose but the resynthesis of molecules with carbon-chain lengths greater than 6 atoms.

INTRODUCTION

The production of fuel and chemicals from carbonaceous materials other than coal and oil ("biomass") has been the subject of studies for well over a century. Pyrolytic oils were obtained by Hoppe-Seyler[1] in 1871 and later by other authors[2]. A modification of the pyrolysis process involved the addition of water or alkali, or both, to the biomass, which was converted to oil, gas, charcoal, and water-soluble organic compounds[3-7]. Further variations in which hydrogen or carbon monoxide, or both, are used as reducing gases for the conversion of the biomass and coal into oil have been studied[8,9], with a resurgence of interest within the last 20 years[10-12]. The fundamental chemistry of these processes is still very poorly understood. The mechanism of the pyrolysis process has received most attention, and some of the initial steps in the conversion of cellulose into its pyrolysis products have been eluci-

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dated, notably by Shafizadeh and associates[13–15] and Broido *et al.*[16] among others. The thermochemical digestion process is poorly understood, and the mechanism of conversion of simple products derived from cellulose into higher-molecular-weight oils has been virtually ignored. There are also no current data on the conversion of other biomass components, such as lignin and hemicellulose, in any of these processes. We report the initial results of an on-going study into the fundamental chemical mechanisms involved in the conversion of pure cellulose into an oil through thermochemical digestion in aqueous sodium carbonate or hydrogencarbonate at temperatures in excess of 300°.

EXPERIMENTAL

Generation of oil and aqueous-phase samples. — The experiments reported here were performed with an oil sample and an aqueous-phase sample derived from two of a series of 129 autoclave experiments. The cellulose used throughout was BW-200 grade Solka-Floc (Brown Co., Berlin, NH 03570, U.S.A.) of 95.8% purity and containing water (3.9%), ash (0.3–0.5%), and nitrogen compounds (0.04–0.0034% of N). Sodium carbonate (anhydrous, Fisher Certified ACS Grade) was of 99.0% minimum purity. All water used was distilled, and all solvents were analytical-reagent grade.

For preparation of the oil samples, cellulose (1.7 kg) was mixed with water (5.45 L) and anhydrous sodium carbonate (0.342 kg) in a 7.5-L autoclave, at an initial pH of 12.1. After heating the mixture to 307° over a 2-h period, maintaining it at this temperature for 20 min, and cooling it to room temperature over a 2.5-h period, an oil was recovered, together with char and an aqueous phase containing organic material. The final pH of the product was 7.0. The oil product (floating layer) was manually separated from the aqueous phase with a separatory funnel; the char was carried in the oil. The aqueous phase was not further investigated. The oil and char fraction was exhaustively extracted with acetone in a Soxhlet thimble to yield an acetone-soluble fraction and an insoluble char-residue in 19 and 21% yield, respectively, based on the weight of cellulose. After evaporation of the acetone, the residue was air-dried for one day, giving the "oil", which was analyzed by g.l.c.–m.s.

The aqueous product from another experiment was analyzed for low-molecular-weight, soluble products. Cellulose (5.7 kg) was mixed with water (17.7 L) and sodium carbonate (0.56 kg) at an initial pH of 11.9. After being heated to 304° in 3.5 h in a 38-L autoclave, maintained at this temperature for 1 h, and cooled to room temperature over a 2.5-h period, the reaction product had a pH of 6.4. The aqueous and oil phases were separated as described earlier (yield of oil, 29%; of char, 23%). A 50-mL portion of the aqueous phase was extracted with diethyl ether (50 mL). The extract was dried (sodium sulfate), filtered, and evaporated to give the "aqueous extract" (0.20 g; yield 1.3%, based on cellulose).

Sample analysis. — The sample components were analyzed by g.l.c.–m.s. Direct g.l.c. of the oil was unsuccessful, whereas direct g.l.c. of the aqueous extract gave a good separation. Of the three treatments examined (boron trifluoride–methanol, followed by methylation, silylation, or trifluoroacetylation), the last named gave the best separation of components. However, the trifluoroacetate derivative obtained was somewhat labile; after one week at 20°, a rearrangement of the peaks in the chromatogram was observed. G.l.c. was performed with a Perkin–Elmer Model 900 chromatograph, equipped with a 1.5-m × 0.5-cm stainless-steel SCOT column filled with LB 550 X and operated at an initial temp. of 70°, raised to 130° at 4°/min, and held at 130° for 30 min. Combined g.l.c.–m.s. was performed with a Hewlett–Packard model 5980 mass spectrometer equipped with the same column and under the same conditions as described.

RESULTS AND DISCUSSION

The compounds were identified by g.l.c.–m.s. and specific tests at three levels of probability: highly probable (H), probable (P), and tentative (T) (see Table I). Observed mass spectra were compared to the Eight-peak Index of Mass Spectra[17], as frequently multiple spectra are reported for a single compound, with considerable differences between these spectra. The identification was difficult on this basis alone, and additional tests were performed. In total, structures were assigned to 23 of the volatile components of the cellulose thermochemical degradation products (see Table I). Only the lower-molecular-weight compounds (up to cresols) were identified, as compounds having higher retention times in g.l.c. were generally more impure because of column bleeding and peak overlap. All of the compounds reported constitute less than 10% of the total "oil" or "extract" material. None of the compounds were present in more than 1% overall concentration in the "oil" or "extract".

The thermochemical liquefaction of pure cellulose described in this report is part of a larger program to assess the potential of biomass as a source of chemical feedstocks and fuel oil. Most previous work has been performed on such substrates as sugar cane[18], peat[19], sewage sludge[20], and similar ill-defined substances. By use of a pure, well-defined substrate, it may be possible to determine the pathway of condensation of the degradation products of cellulose to form oils and water-soluble organic compounds. Cellulose decomposition in alkali has been widely studied because of its importance in paper-pulp manufacture. Initially, the reaction is one of "peeling", from the end of the cellulose chain[21], of D-glucose units that are degraded to D-glucometasaccharinic acid *via* the intermediate 3-deoxy-D-glucosulose[22,23]. Isomerization to the enediol, followed by dehydration and ring formation, leads to the additional production of furan derivatives, including 5-hydroxymethyl-2-furaldehyde[22], whereas fragmentation of D-glucose through reverse aldol reaction leads to pyruvaldehyde, D-lactic acid, and D-glyceraldehyde as additional intermediate products[24]. By contrast, the pyrolytic reaction of cellulose involves the formation of 1,6-anhydro-β-D-glucopyranose[25], and subsequently of 1,6-anhydro-3,4-dideoxy-β-D-glucopyranosen-2-ulose, 1,6-anhydro-β-D-glucofuranose, 3-deoxy-D-*erythro*-hexosulose[26], and other products[13,27–29].

Of these other products, only acrolein has been observed both in pyrolysis

TABLE I

COMPOUNDS IN PRODUCTS OF THE THERMOCHEMICAL REACTION OF CELLULOSE AND STANDARDS IDENTIFIED BY G.L.C.–M.S.

Compounds[a]	*Yield (% × 100)*	*Identification*[b]	R_T *(min)*[b]	*Mol. wt.*	*Major* m/e *values (% of base peak)*
Cyclopentanone (H)	10; 6; 7	A; 1; 2	2.0	84	84(41), 56(30), 55(100), 42(15), and 41(26)
Cyclopentanone (Std.)				84	84(38), 56(28), 55(100), 42(14), and 41(32)
Phenol (H)	20; 10	A; 1(F)	17.5	94	94(100), 66(27), 65(25), and 55(11)
			(2.9F)	(190F)	190(100), 88(28), 83(30), 76(40), 69(70), 65(73), 44(62), and 39(24)
Phenol (Std.)				94	95(7), 94(100), 66(19), 65(17), 55(6), 47(5), 40(8), and 39(13)
2,4-Dimethylfuran (P)	50; 20	A,2	4.9	96	96(84), 95(10), 68(16), 67(100), 65(8), 53(38), 41(15), and 39(15)
2,4-Dimethylfuran (Std.)				96	96(100), 95(43), 81(19), 68(11), 67(65), 65(13), 53(32), and 39(38)
Cyclohexanone (H)	10	A	3.9	98	98(37), 81(24), 70(26), 69(33), 55(100), 42(60), 41(29), and 39(18)
Cyclohexanone (Std.)				98	98(44), 81[c], 70(23), 69(31), 55(100), 42(54), 41(36), and 39(21)
3-Heptene	20	A	2.7	98	83(58), 81(21), 69(80), 57(58), 55(59), 46(21), 43(100), and 41(64)
Heptene isomer (T)	9	1	3.4	98	
Heptene (Std.)				98	98(28), 69(56), 56(66), 55(48), 41(100), and 39(32)
2-Methylcyclopentanone (H)	30; 8; 6	A; 1; 2	2.5	98	98(58), 83(19), 70(32), 69(53), 56(28), 55(76), 42(100), and 41(40)
2-Methylcyclopentanone (Std.)				98	98(54), 83[c], 70(20), 69(30), 56[c], 55(38), 42(100), and 41(43)
4-Methyl-3-penten-2-one (H)	6	2	1.8	98	98(53), 84(16), 83(100), 56(12), 55(72), 53(17), 43(35), and 39(19)
4-Methyl-3-penten-2-one (Std.)				98	98(59), 84[c], 83(100), 56[c], 55(87), 53(13), 43(51), and 39(23)
2,5-Dimethyltetrahydrofuran (H)	10	A	8.3	100	100(11), 85(65), 57(20), 56(100), 43(32), 41(37), and 39(7)
2,5-Dimethyltetrahydrofuran (Std.)				100	100(8), 85(86), 57(14), 56(100), 43(54), 41(74), and 39(10)
2-Hydroxy-2-methyltetrahydro-	30	1(F)	4.4(F)	102	71(100), 69(42)[d], 44(35), 43(43), 42(15), 41(26), and 40(17)
furan (T)	20	2(F)	4.4(F)	102	71(100), 69(31)[d], 44(12), 43(36), 42(12), 41(21), and 40(5)
2-Hydroxy-2-methyltetrahydrofuran (Std.)				102	71(100), 69[c], 44(8), 43(51), 42(11), 41(25), and 40[c]
p-Cresol (H)	3	1(F)	4.2(F)	108 (204F)	204(64), 107(100), 91(37), 90(40), 77(37), 69(31)[d], and 41(20)
p-Cresol (Std.)				108	108(100), 107(99), 79(23), 77(28), 53(17), 51(22), and 39(18)
m- or *p*-Cresol (H)	10	A	20.3	108	108(100), 107(89), 79(37), 77(28), 44(24), 41(17), and 39(22)
o-Cresol (H)	9	A	18.5	108	108(100), 107(88), 90(27), 89(18), 79(39), 77(29), and 51(18)
o-Cresol (Std.)				108	108(100), 107(75), 90(23), 79(32), 77(32), 51(26), and 39(26)
4-Octyne (T)	30	2	7.5	110	110(70), 109(19), 95(28), 81(18), 68(18), 67(100), and 41(17)
4-Octyne (Std.)				110	110(97), 95(34), 81(87), 68(53), 67(100), 52(33), and 41(40)
Octene and Octyne (T)	10	A	5.5	110 112	112(35), 95(32), 83(100), 67(63), 56(59), 55(80), and 41(50)

TABLE I (*continued*)

Compounds[a]	*Yield* (% × *100*)	*Identification*[b]	R_T (*min*)[b]	*Mol. wt.*	*Major m/e values (% of base peak)*
1-Octene (Std.)				112	70(52), 69(30), 56(64), 55(83), 43(100), 42(63), and 41(78)
2,5-Dimethyl-2,4-hexadiene (P)	8	A	9.3	110	110(71), 95(100), 67(74), 66(20), 42(19), 41(36), and 39(36)
	30	2	8.0	110	110(83), 99(26), 95(100), 67(59), 42(26), 41(33), and 39(26)
2,5-Dimethyl-2,4-hexadiene (Std.)				110	110(56), 95(100), 67(51), 55(35), 53(22), 41(44), and 39(40)
2,5-Dimethyl-2-cyclopentenone (H)	6	A	5.1	110	110(57), 95(71), 82(20), 67(100), 53(22), 41(29), and 39(25)
2,5-Dimethyl-2-cyclopentenone (Std.)				110	110(40), 95(55), 82(27), 67(100), 53(19), 41(35), and 39(40)
Ethylmethylfuran (T)	40	A	7.8	110	96(100), 95(44), 81(43), 67(76), 53(48), 40(20), and 39(23)
5-Ethyl-2-methylfuran (Std.)				110	110(39), 95(100), 67(11), 53(8), 51(8), 43(34), and 39(10)
2-Ethylcyclopentanone (H)	9; 5; 5	A; 1; 2	4.7	112	112(30), 84(100), 83(40), 68(35), 56(65), 55(61), and 41(49)
2-Ethylcyclopentanone (Std.)				112	112(28), 84(100), 83(37), 68(37), 56(75), 55(63), and 41(60)
4-Hydroxy-4-methyl-2-pentanone (T)	20	2F	5.5(F)	116 (212F)	99(7), 95(6), 85(5), 83(5), 69(22)[d], 58(19), 55(8), and 43(100)
4-Hydroxy-4-methyl-2-pentanone (Std.)				116	85[c], 83(1), 69[c], 58(31), 43(100), 42(7), 39(5), and 38(2)
3-Octadienone (T)	20	2	10.6	124	124(100), 96(96), 95(53), 91(69), 79(59), 67(84), and 41(63) (No standard reported)
2,5-Diethylfuran (T)	20	2	11.8	124	124(73), 123(45), 109(100), 95(66), 81(30), 67(46), and 39(26)
2,5-Diethylfuran (Std.)				124	124(30), 109(100), 95(7), 67(7), 53(6), 43(23), and 39(13)
3-Ethyl-2,5-dimethylfuran (alternative, Std.)				124	124(58), 123(14), 109(100), 95(8), 81(6), 43(8), and 39(7)
Methylpropylcyclopentene (T)	40	A	9.5	124	110(69), 109(17), 95(22), 67(100), 54(19), 43(14), and 41(18) (No standard reported)
Decyne (T)	20	2	14.9	138	138(32), 110(67), 96(61), 95(100), 82(31), 67(34), and 53(32)
3-Decyne (Std.)				138	109(67), 95(37), 68(40), 67(100), 55(30), 41(57), and 39(34)
Acrolein hydrate monotrifluoroacetate (T)	30	1F	9.9(F)	170	141(100), 97(12)[d], 69(79)[d], 47(21), 44(32), 43(16), and 40(24) (No standard reported)

[a]Abbreviations: H, highly probable identification; P, identification probable, based on a good agreement with literature m.s. data, or close correlation between the m.s. data of the sample trifluoroacetic ester and those of the underivatized (literature) compound; T, identification tentative, based on poor agreement with reported m.s. data, or lack of a reported standard; Std., standard sample. [b]Sample: A, diethyl ether extract of aqueous phase; F, trifluoroacetate; 1, oil, trifluoroacetate; 2, oil, trifluoroacetate by treatment with trifluoroacetic anhydride. [c]Absent. [d]Indicates a trifluoroacetate fragment peak $CF_3^{+\cdot}$ or $CF_3CO^{+\cdot}$.

experiments and in our work under aqueous conditions. Acrolein was found by both Glassner and Pierce[28] and by Heyns and Klier[29]. Heyns and Klier[29] also found 2-methylfuran and 2,5-dimethylfuran as products of the pyrolysis of cellulose at 400 and 450°. Although these were not observed in our work, we did find the closely related 2,4-dimethylfuran and other furan derivatives. Cyclopentanone, cyclohexanone, phenol, and cresols have been reported frequently as products of the pyrolysis of cellulose, and we also found them as thermochemical-liquefaction products. All of the other compounds listed in Table I have not previously been identified among cellulose conversion products.

The similarities between the products of cellulose pyrolysis and those of aqueous thermochemical conversion could be construed as indicating a similarity of mechanisms. This would be misleading, as the mechanism of cellulose pyrolysis is either of the acid-catalyzed (carbonium ion) or of the free radical type[13]. In contrast, the most active ion in thermochemical, alkaline digestion is the hydroxyl ion, which tends to favor carbanion reactions. Thus, the mechanism of the thermochemical, alkaline-digestion reaction would be expected to involve such reactions as the aldol, Claisen, and Dieckmann condensations.

Base-catalyzed cleavage of the D-glucose molecule at C-2–C-3 yields glycolaldehyde, which undergoes a self-condensation to 3,4-dihydroxybutyric acid[24]. This latter product has been shown to be a significant end-product from the alkaline degradation of D-xylose[30]. Further evidence for the formation of low-molecular-weight aldehydes and ketones by base-catalyzed hydrolysis was obtained by Shaw *et al.*[31] who found 2-hydroxybutanones and acetol as products of D-fructose hydrolysis at pH 8.0. In addition, a number of furans were isolated, but no mechanism was suggested for their formation. Thus, formation of low-molecular-weight aldehydes and ketones by cleavage of the D-glucose molecule in a reverse aldol reaction, followed by recondensation of these materials in various ways, appears to be a major pathway for resynthesis of more complex materials from D-glucose. The products identified by g.l.c.–m.s. support this conclusion.

The primary groups of compounds found were furans, ketones, alcohols, phenols, alkenes, and alkynes. Cyclic compounds figure prominently. Much structural similarity and even homology is evident, suggesting a consistency of mechanism in their formation. The isomerism between many of the products (such as cyclohexanone and 2-methylcyclopentanone), the structural similarity (such as cyclohexanone and phenol), and the homology between phenol and cresols suggest common intermediates.

Cyclohexanone has been reported as a product of cellulose pyrolysis[32], from alkaline treatment through the formation of a 1,5-diketone from pyruvic acid, and its subsequent cyclization and dehydration[24]. The formation not only of cyclohexanone, but also of 2-methylcyclopentanone suggests that both compounds arose from a common intermediate, which could be 5-hexenal rather than the 1,5-diketone derived from two molecules of pyruvaldehyde. Formation of 5-hexenal as the intermediate also eliminates the necessity for a hydrogenation following a dehydration step, thus permitting the cyclization to the final products to occur in one step rather than three.

Formation of alkylfurans having more carbon atoms than the D-glucose unit of the starting material confirms the indirect formation of these compounds from degradation products of D-glucose rather than directly from D-glucose itself. The mechanism of their formation is unknown. The apparent formation of straight-chain hydrocarbons is also of interest, as condensations of carbonyl compounds usually lead to branched products. Identification of a range of alkylfurans, carbonyl compounds, aliphatic hydrocarbons, and phenols derived from alkaline degradation of cellulose further extends our knowledge of the reactions of cellulose conversion. A number of previously unidentified products have been characterized by g.l.c.–m.s. These results add further support to the hypothesis that cellulose decomposes to simple materials that are then converted into higher-molecular-weight oils by a series of aldol reactions.

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