Pyrolysis Products of Untreated and Flame Retardant-Treated α-Cellulose and Levoglucosan

FRANK A. WODLEY,* *Naval Radiological Defense Laboratory, San Francisco, California 94135*

Synopsis

A typical gas chromatogram of the volatile pyrolysis products of untreated α-cellulose contains 39 peaks; however, mass spectral data indicate that at least 59 compounds, with molecular weights less than about 150, are present. A total of 37 compounds have been identified, 13 of which have not been previously reported. Most of the newly identified compounds contain a benzene ring, indicating that these compounds may be products of reactions between initial volatiles. A comparison of the products generated in the temperature range of 330°–440°C indicates that the formation of pyrolysis products is essential independent of temperature. Comparisons of the chromatograms obtained for untreated levoglucosan and cellulose indicate that most of the decomposition of cellulose probably forms levoglucosan which then decomposes to yield the observed pyrolysis products. In addition, the products of flame retardant-treated levoglucosan are essentially the same as those of cellulose with the same retardant treatment. This suggests that the retardants act on the levoglucosan formed in the decomposition of the cellulose rather than on the cellulose directly.

INTRODUCTION

Scope and Objectives

When cellulose burns, volatile products are formed which undergo combustion with the air. Flame retardants suppress the total quantity of volatile products and reduce their flammability. In order to develop more effective flame retardants, it is important to know what reactions occur when cellulose is pyrolyzed and how these reactions are altered by flame retardants. This report describes the identification and comparison of the more volatile pyrolysis products obtained from treated and untreated α-cellulose, i.e., those products with boiling points less than 225°C. The treatments include a basic salt ($KHCO_3$), an acid salt ($NH_4H_2PO_4$), a chemically substituted inorganic (iodine), and a chemically substituted organic (benzhydryl). This information may be helpful in explaining the differences in flammability of the material or may provide clues as to the changes in the decomposition mechanisms which in turn help define the mechanism of decomposition of untreated cellulose. Furthermore, since it is possible that the majority of the pyrolysis products are formed through

* Present address: V. A. Hospital, Palo Alto, California.

the decomposition of levoglucosan, the volatiles of levoglucosan are also identified and compared with those of cellulose to further clarify the degradation mechanism.

Experimental Approach

The more volatile components of pyrolysis products have been studied by several investigators, using only gas chromatography.[1-5,10,11] Schwenker and Beck[2] and later Glassner and Pierce[3] have found that the pyrolysis mixture from untreated cellulose contains at least 34 compounds, 14 of which were . identified. Their investigations indicated that compounds with boiling points to about 200°C were able to pass through the gas chromatograph. Identifications were based primarily on retention times, i.e., comparison of retention times for unknown peaks with those of known compounds; however, they also relied on chemical tests of the effluents. Since the gas chromatograph is essentially a separation tool, its use as an identification tool requires one to compile large amounts of retention time data on possible compounds. Furthermore, identification by retention times becomes almost impossible when several compounds have the same retention time, i.e., the unknown mixture gives a chromatogram which contains unresolved peaks. In order to obtain the maximum amount of information about the identification of effluents, the mass spectrometer has been linked to the gas chromatograph.[6-8]

Recently, this approach was applied to the analysis of pyrolysis products from cellulose.[9] The use of the gas chromatograph–mass spectrometer combination instrument for the analysis of unknown organic mixtures has the following advantages: (1) No previous knowledge about the composition of the sample is necessary. (2) Any GC peak can be shown to contain either a single compound or mixture simply by scanning different portions of the peak; if the peak is a mixture, it is possible to "resolve" the peak into individual components simply by analyzing the mass spectral data. (3) Times for separation and analysis of mixtures are much shorter than for any other technique. (4) Small samples are readily separated and analyzed. (5) Contamination and losses of sample are eliminated. (6) Retention times of knowns may be determined even if a known is contaminated; (this is done by taking spectra of all the GC peaks that appear when the contaminated known is injected and then selecting the peak that has the exact spectra of the known). (7) It may be possible to quantitatively analyze unresolved peaks.

EXPERIMENTAL

Generation and Collection of Pyrolysis Products

α-Cellulose sheets were treated with $KHCO_3$ and $NH_4H_2PO_4$ by soaking in a 2% solution and drying at 25°C to a constant weight (the samples retained 2% by weight of the salts when dried). Three other treatments

were prepared by Lipska[16] and include 4% iodination, 6% benzhydrylation, and 4% iodination–6% benzhydrylation.

A simple method has been developed to generate and collect pyrolysis products. Cellulose sheets ($\sim$3-in. $\times$ 4-in. $\times$ 0.015-in.) are formed into tubes about $^3/_8$ in. inside diameter. The tubes are ignited by a Bunsen burner at the top and are burned in the air, since it was decided that the products should be formed as close to the actual temperatures found in fires as possible. The inside diameter of the tube is critical here, since it has to be such that flames cannot propagate down the cylinder. When the lower end of the tube is placed in a cooled test tube, a considerable amount of the products that are formed inside the tube from the pyrolysis of the cellulose flow downward and condense. Although some pyrolysis products are flowing upward and are being combusted, the combustion products do not flow downward and are therefore not collected. After the condensate is collected, the tube is centrifuged and a small sample (10 μl) is drawn into a syringe and injected into the GC. Obviously this technique will not effectively transfer the fixed gases or more volatile compounds; however, these compounds have been studied in detail already. It should be stressed that the products collected in the above manner are the initial volatiles, i.e., they have not undergone combustion with the air.

Samples of levoglucosan, including untreated, $KHCO_3$-treated, and $NH_4H_2PO_4$-treated samples, were heated in air in a distilling flask. The volatiles were collected in a cooled test tube and handled like those of cellulose described above. In order to determine whether there were differences in the generation and collection of pyrolysis products, samples of untreated α-cellulose were run in the following ways: (1) cellulose cylinders were burned as described above, the products being formed at about 400°C; (2) samples were heated in air in a distilling flask; and (3) samples were isothermally pyrolyzed at about 330°C in a nitrogen-fluidized sand bath.[14]

Mass Spectrometer–Gas Chromatograph

The gas chromatograph–mass spectrometer combination instrument, which is used exclusively for the identification of the more volatile compounds, was described earlier.[9] Since that time, the following improvements have been made to increase the sensitivity of the instrument:

1. The fine-pore-size (4–5.5 microns) effusion chamber of the separator was replaced by one having ultrafine porosity (0.5–1.4 microns). This required more of the organics to go to the mass spectrometer and less to the fore pump, thus increasing the efficiency of the transfer.

2. The exit constriction was replaced by precision-bore capillary (Wilmad Glass Co., New Jersey) with an inside diameter of 0.0762 cm (0.003-in.) and a length of about 3 cm. The precision-bore capillary facilitates both the determination of the optimum constriction size and the replacement of the constriction.

3. The inlet constriction was replaced by a variable leak valve (Granville Phillips Series 203) so that the amount of effluent entering the separator could be optimized. This also allows the mass spectrometer to be isolated from the gas chromatograph.

4. The sensitivity of the mass spectrometer itself was increased by cleaning the multiplier.

It has been noted that the above improvements increased the sensitivity of the combination instrument markedly. The replacement of the separator alone increased the transfer efficiency by a factor of 10.

The pyrolysis products from the treated and untreated samples are injected, as a 10-μl aliquot, onto the analytical column (10% Carbowax 20M on 80/100 mesh Chromosorb) of the Beckman IV gas chromatograph. With a helium flow rate of 60 ml/min, the column is ballistically temperature programmed from 90°C to 220°C, while the detector block is maintained at 225°C, the injection port at 240°C, and separator assembly at about 100°C. A thermoconductivity detector is used to record a chromatogram, with total ion current (mass spectrometer output) serving as a secondary record. Sample holdup between the detector and the ion source of the mass spectrometer is small; therefore, spectra are taken as soon as a peak appears in the chromatogram. In order to get the maximum amount of sample into the mass spectrometer and obtain a representative mass spectrum, the leak valve is opened so that all the GC effluent goes to the separator. Since "the valve-open condition" allows the background to continually increase (MS getter-ion pump is inefficient in pumping He), the valve is opened usually only for those GC peaks that were to be identified, although it is possible to have it open for the entire run.

Mass spectral identifications are made by comparing unknown spectra (after subtracting background) with reference tables of mass spectra.[12,13] When a likely compound is found, its retention time is determined, and if it agrees with that of the unknown, the identification is considered positive. If the retention time is obviously not the same as that of the unknown, other possible compounds are found and investigated.

RESULTS AND DISCUSSION

Identification of Volatile Pyrolysis Products

As previously noted, care has been taken to ensure that the initial volatiles that are formed by the pyrolysis of cellulose are collected before they undergo combustion. We have observed, however, that at least part of this condensate will decompose to a char before it evaporates, and this has been substantiated by a char buildup in the injection port of the gas chromatograph. This means that at least some of the compounds passing through the gas chromatograph and being analyzed are not initial volatiles but actually their decomposition products. In fact, it appears that those volatiles that do decompose can only be analyzed by methods which do not
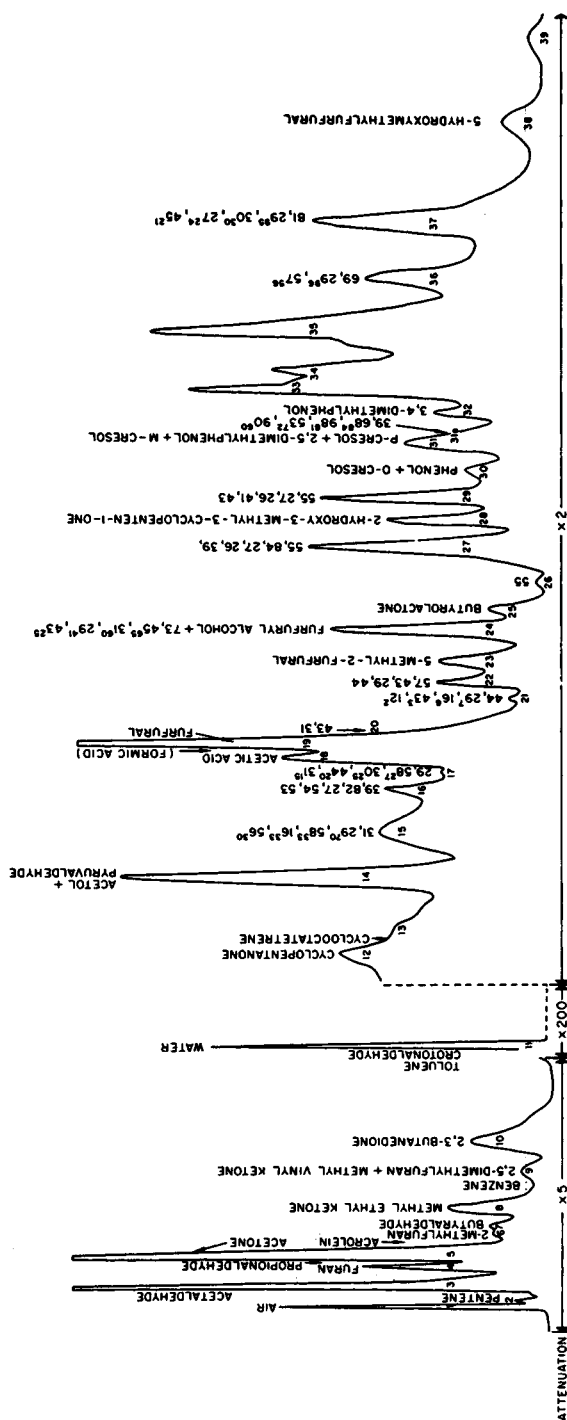
Fig. 1. Gas chromatogram of volatile products from the pyrolysis of α-cellulose.

TABLE I
Identification of Volatile Pyrolysis Products

GC peak	Unknown: Identification or mass spectrum	Unknown: R_t^a	Known: R_t^a	Known: bp, °C	Known: MW	Means of identification: R_t^a	Means of identification: MS	References
1	Fixed gases	-4.5	—			N.I.	T	new
2	Pentene	-2.7	-2.9	36	70	P	P	1–5, 9–11
3	Acetaldehyde	-0.8	-1.1	21	44	P	P	1, 3, 5, 9, 10
4	Furan	-0.1	-0.2	32	68	P	P	1–5, 9, 10
4'	Propionaldehyde	-0.0	-0.0	49	58	P	P	1–5, 9–11
5	Acetone	0.6	0.6	56	58	P	P	1–5, 9–11
5'	Acrolein	2.3	1.9	53	56	P	P	1–5, 10, 11
6	2-Methylfuran	3.0	2.7	62	82	P	P	9, 10
7	Butyraldehyde	4.8	4.4	76	72	P	trace	5, 7, 8, 10, 11
8	Methyl ethyl ketone	6.7	6.4	79	72	P	P	1, 7, 8, 11
8'	Benzene	8.2	—	80	78	N.I.	P	new
9	2,5-Dimethylfuran	8.3	7.6	94	96	P	P	new
9'	Methyl vinyl ketone	11.3	11.4	80	70	P	P	5
10	2,3-Butanedione	20.5	20.2	88	86	P	P	1, 5, 9
11'	Toluene	20.5	20.5	110	92	P	P	new
11'	Crotonaldehyde	23.0	23.8	104	70	P	P	5
11	Water	6.1	5.8	100	18	P	P	1–5, 9–10
12	Cyclopentanone	7.6	4.8	130	84	P	P	new
13'	Cyclooctatetraene	12.6	12.3	143	—	T	T	new
14	Acetol	12.6	12.6	146	74	P	P	9
14'	Pyruvaldehyde	17.4	7.5	72	72	T	P	11
15	$31, 29^{70}, 58^{33}, 16^{33}, 56^{30}$	19.2	—	—	—	—	—	—
16	$39, 82, 27, 54, 53$	—	—	—	—	—	—	—

No.	Compound	R_t	R_t					Ref.
17	29, 58^{27}, 30^{25}, 44^{30}, 31^{15}	19.5	—	—	—	—	—	—
18	Acetic acid	21.1	20.0	118	60	P	P	1-3, 9
19	Furfural	23.3	22.6	162	96	P	P	1-3, 9, 11
19'	Formic acid	23.3	—	101	46	not present		—
20	43, 31	—	—	—	—	—	—	—
21	44, 29^{7}, 16^{5}, 43, 12	25.6	—	—	—	—	—	—
22	57, 43, 29, 44	28.5	—	—	—	—	—	—
23	5-Methyl-2-furfural	30.4	29.8	187	110	P	P	1, 9
24	Furfuryl alcohol	33.1	31.8	171	98	P	P	9
24'	73, 45^{55}, 31^{60}, 29^{41}, 43	33.1	—	—	—	—	—	—
25	Butyrolactone	35.4	34.6	206	86	P	P	9
26	55	36.5	—	—	—	—	—	—
27	55, 84, 27, 26, 39	39.2	—	—	—	—	—	—
28	2-Hydroxy-3-methyl-3-cyclopenten-1-one	41.5	42.9	—	—	P	P	new
29	55, 27, 126, 41, 43	43.8	—	—	—	—	—	—
30	Phenol	45.8	44.9	182	94	P	P	new
30'	o-Cresol	45.8	44.5	191	108	P	P	new
31	p-Cresol	48.9	48.2	202	108	P	P	new
31'	m-Cresol	48.9	52.2	203	108	T	P	new
31a	2,5-Dimethylphenol	48.9	48.3	211	122	P	P	new
32	39, 68^{84}, 98^{81}, 53^{72}	—	—	—	—	—	—	—
36	3,4-Dimethylphenol	52	51.5	225	122	P	P	new
37	69, 29^{96}, 57^{56}	—	—	—	—	—	—	—
38	81, 29^{95}, 30^{90}, 27^{74}, 45^{21}; 5-Hydroxymethylfurfural	—	75.4	110	126	T	N.I.	2

ᵃ R_t = Retention time: time between appearance of unknown peak and reference peak. Units are arbitrary. All R_t of compounds occurring before water with reference to acetone; R_t of others versus water. Units are arbitrary.

ᵇ P = Positive identification; T = tentative identification; N.I. = not identified.

require them to be volatilized; such methods might employ TLC for separation and NMR or IR spectroscopy for identification. The following results are still useful, although it may be more difficult to define the mechanism of the decomposition of untreated cellulose from a knowledge of the secondary decomposition products.

Table I is a summary of the results on identification of products from all samples, including treated and untreated α-cellulose and levoglucosan. In the case of untreated α-cellulose (Fig. 1), which produces the largest number of products, 39 distinct GC peaks are observed; however, the MS data indicates that the total number of compounds present is at least 59 because many of the peaks are unresolved. Since the present GC arrangement does not completely resolve all the compounds in the pyrolysis mixture, identifications are more difficult and quantitative interpretations are very limited. It should be noted that where identifications have not been made, mass spectra are given above the peak numbers in Figure 1.

In all, 37 compounds have been identified (including the four fixed gases CO_2, CO, CH_4 and C_2H_6 from the previous report[9]), with five of those being tentative identifications (pentene, 2,5-dimethylfuran, cyclooctatetraene, pyruvaldehyde, and 5-hydroxymethylfurfural). Of the 37 compounds identified 13 have not been previously reported in the literature and include pentene, benzene, 2,5-dimethylfuran, toluene, cyclooctatetraene, cyclopentanone, 2-hydroxy-3-methyl-2-cyclopenten-1-one, phenol, o-cresol, m-cresol, p-cresol, 2,5-dimethylphenol, and 3,4-dimethylphenol.

An additional 20 compounds are still unidentified, and some of their mass spectra are included in Table I. These compounds could not be identified for one of the following reasons: (1) The mass spectrum of the compound could not be determined because the compound was contained in an unresolved GC peak that could not be resolved by reducing the mass spectral data. (2) The mass spectrum of the compound could not be determined since the compound was only a trace or had condensed between the mass spectrometer and the gas chromatograph. (3) The observed mass spectrum did not compare well with any reference spectrum.

Most of the newly identified compounds contain a benzene ring, which indicates that these compounds are not the initial products formed by breaking the cellulose molecule but are probably products from reactions between initial volatiles.

Since the identification of peak 31a (refer to Figs. 3, 4, and 5) turns out to be important (conclusion of comparison section), the existing information about it is presented as follows:

1. Low-resolution mass spectra indicate that the GC peak is probably a mixture, although similar mass spectra are obtained when the peak is scanned. The low-resolution mass spectrum is 39^{100}, 68^{84}, 98^{81}, 53^{72}..., indicating a furan-type structure.

2. High-resolution mass spectra indicate that mass 98 is $C_5H_6O_2$ and probably a parent ion; m/e 96 is $C_5H_4O_2$ and is probably a fragment of some

higher mass number, i.e., it is not a parent.   These data show conclusively
that 31a is a mixture.

3. IR and NMR data are presently being taken and should provide
important clues as to the structure of the compounds present in 31a.

It should be noted that there is very good agreement between this work
and the work of others, especially for the compounds occurring before
water.   In order to make the list of pyrolysis products as complete as
possible, the compounds that have been identified by others comprise
Table II.

TABLE II
Lower Molecular Weight Compounds Identified by Others and Not
Included in Table I

Compound	Mol. wt.	Boiling Point, °C	References
1. Fixed gases			
hydrogen	2	−253	4, 5
methane	16	−162	4, 5
acetylene	26	−84	4, 5
carbon monoxide	28	−190	2, 4, 5
ethylene	28	−104	4, 5
ethane	30	−88	4, 5
carbon dioxide	44	−79	2, 4, 5
2. Formaldehyde	30	−21	2, 3
3. Methanol	32	65	1–3, 5
4. Ethanol	46	79	5
5. Formic acid	46	101	1, 2
6. Glyoxal	58	50	1–3, 11
7. Glycolaldehyde	60	—	11
8. Propionic acid	74	141	1
9. Glyoxylic acid	74	—	11
10. Butyric acid	88	164	1
11. Pyruvic acid	88	165	11
12. 1,3-Dihydroxy-2-propanone	90	—	11
13. Glyceraldehyde	90	—	11
14. Lactic acid	90	122	2
15. Valerolactone	100	207	15
16. Laevalinic acid	116	146	11
17. Maltol	126	sub	15
18. Hydroxypyruvaldehyde	—	—	11
19. Hydroxymethyl-2-furyl ketone	—	—	11
20. Mesoxaldehyde	—	—	11

Comparison of Generation and Collection Methods

Chromatograms run for the pyrolysis products of α-cellulose, which were
generated and collected using three different methods, are shown in Figure
2.   The two primary differences in the methods are temperature and
atmosphere, i.e., pyrolysis occurs at temperatures between about 330°C
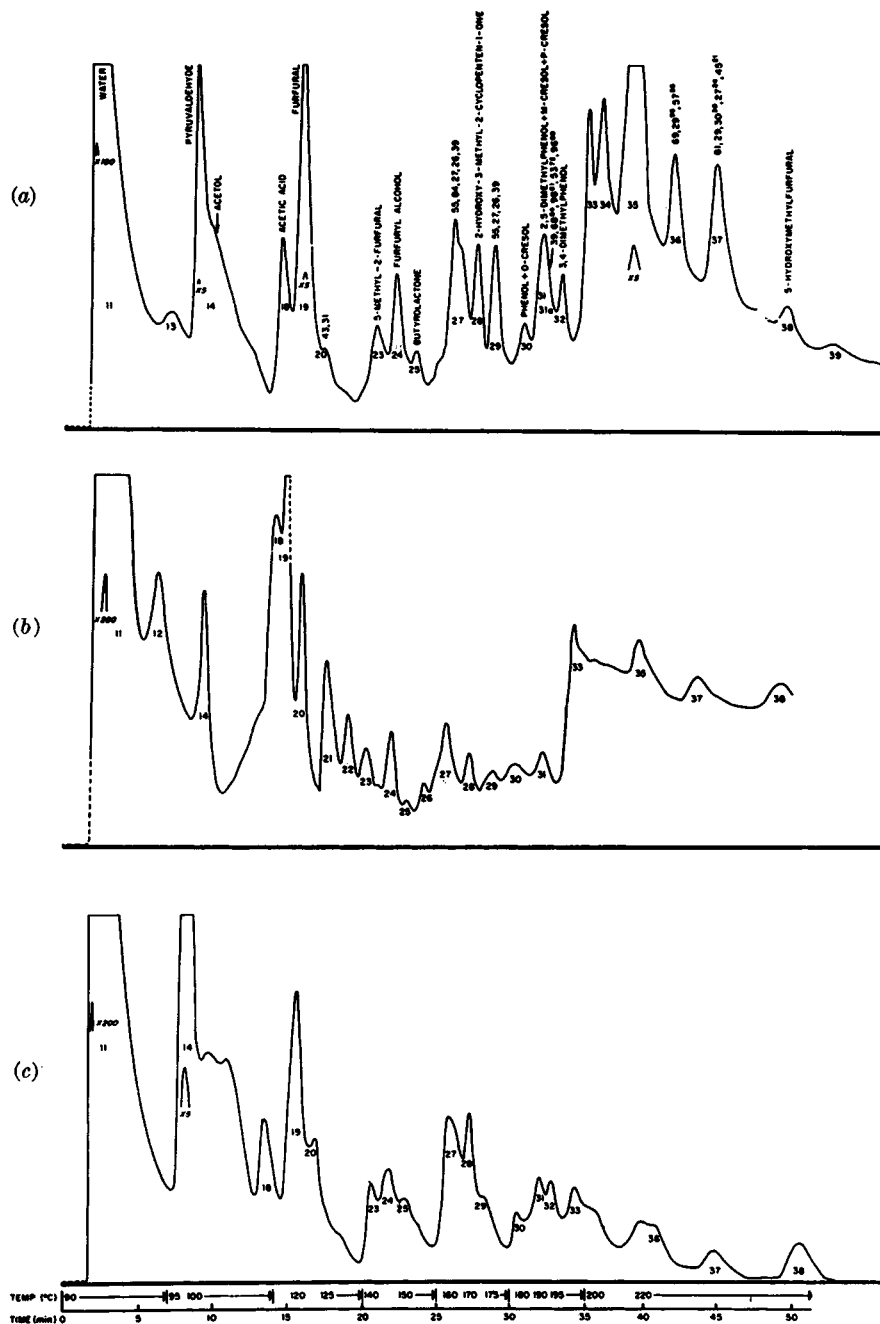and 400°C in atmospheres of air or nitrogen.   Qualitatively, all three

Fig. 2. Gas chromatograms of volatile products of untreated α-cellulose using different generation and collection techniques.   (a) Pyrolysis in air burning card;   (b) isothermal pyrolysis in N₂ at 330°C;   (c) distillation flask pyrolysis in air.

methods yield chromatograms that are very similar; however, the pyrolysis chamber does produce a few more peaks (17, 21, 22, 26) which are absent in the other two methods. These observations indicate that the methods generate pyrolysis products (at least those in the chromatograms) that are very similar; others, such as Schwenker and Beck,[2] have also found that the chromatograms of pyrolysis products generated in different atmospheres (both air and inert) are very similar, suggesting that the mechanism is nonoxidative and mainly thermal in nature. Additionally, Glassner and Pierce[3] have shown that temperature is of little effect above 285°C; this is also in agreement with the above data.

Quantitative differences in the three methods are partly due to differences in collection. The burning tube method appears to be a more efficient method for collection; and this is quite reasonable, since the chance for condensation in the other two methods is higher.

Comparison of Pyrolysis Products from Untreated and Treated α-Cellulose and Levoglucosan

In order to make a comparative study of the pyrolysis products, chromatograms were obtained for the same volume of sample condensate (10 μl). Representative chromatograms are presented in Figures 3 to 5. The burning tube technique was used for treated and untreated cellulose and the distillation flask method, for treated and untreated levoglucosan.

It should be stressed that a quantitative analysis is justified only when GC peaks are totally resolved. Even though this is not the case in this work, the peak areas summarized in Table III give some indication of the maximum amounts of compounds present. Note that all chromatograms are recorded at attenuation 2.0, and that all peaks before H_2O are not shown because of nonquantitative transfer technique.

The following are the significant features of the results on treated and untreated α-cellulose:

1. The quantity of water is markedly increased in all treated samples. This increase is the largest for the iodinated and benzhydrylated samples; however, this may be due to the greater extent of their treatment.

2. As previously reported,[9] the products formed from untreated and 2% KHCO₃-treated cellulose are similar; however, peaks 16 (unknown), 25 (butyrolacetone), 30 (phenol, o-cresol), and 33 (unknown) are increased in the treated, while 29 (unknown) and 35 (unknown) are decreased. In the 15% KHCO₃-treated sample, water and peak 14 (pyruvaldehyde, acetol) remain about the same, while the other peaks are decreased in comparison with the 2% KHCO₃-treated sample.

3. The product mixture for NH₄H₂PO₄-treated cellulose contains fewer compounds than does the untreated cellulose. There is a very significant increase in peak 31a (unknown) and somewhat smaller increases in peaks 19 (furfural) and 36 (unknown). Peaks 18 (acetic acid), 23 (5-methyl-2-furfural), and 35 (unknown) remain essentially unchanged.
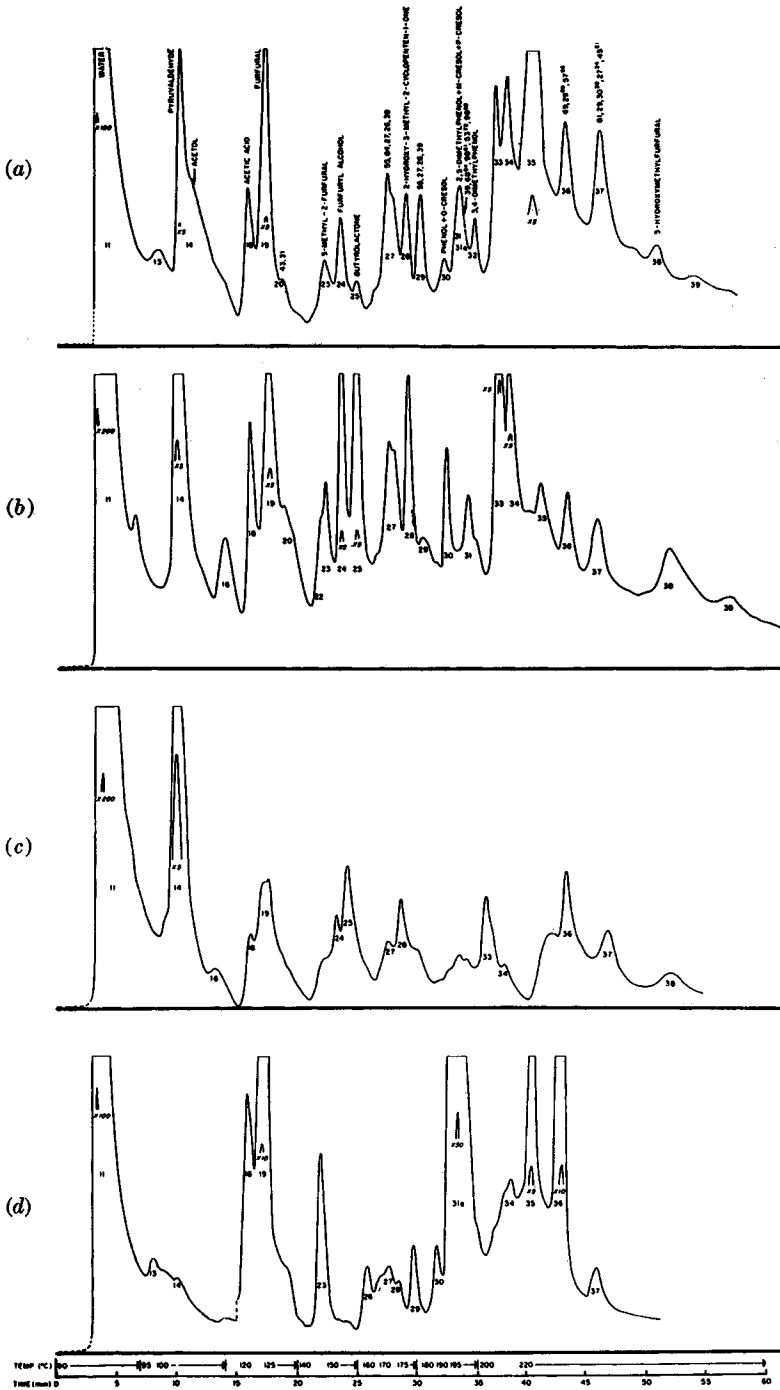
Fig. 3. Gas chromatograms of untreated and salt flame retardant-treated α-cellulose: (a) untreated; (b) 2% KHCO₃; (c) 15% KHCO₃; (d) 2% NH₄H₂PO₄.
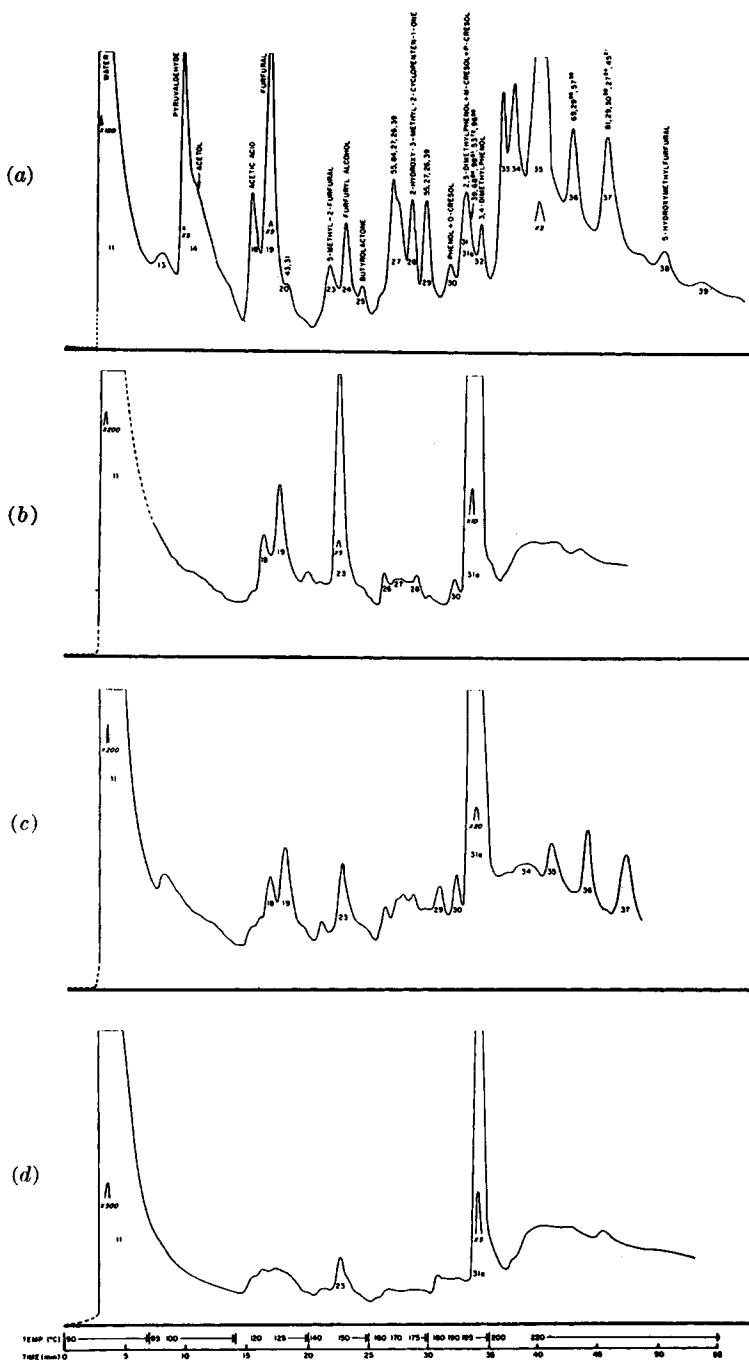
Fig. 4. Gas chromatograms of untreated and chemically substituted flame retardant-treated α-cellulose: (a) untreated; (b) 4 % iodination; (c) 6% benzhydrylation; (d) 4% iodination, 5% benzhydrylation.

Fig. 5. Gas chromatograms of untreated and salt flame retardant-treated levoglucosan: (a) untreated α-cellulose; (b) untreated levoglucosan; (c) KHCO₃ treated levoglucosen; (d) NH₄H₂PO₄ treated levoglucosen.

TABLE III

Semiquantitative Comparison of Pyrolysis Products from Untreated and Flame Retardant-Treated α-Cellulose and Levoglucosan

GC peak number	Untreated α-cellulose	2% KHCO₃	2% NH₄H₂PO₄	4% Iodination	6% Benz.	4% Iodin.– 5% Benz.
11	890	3500	3600	3200	3100	7800
12	—	—	—	—	—	—
13	—	—	—	—	—	—
14	78	90	—	—	—	—
15	—	—	trace	—	—	—
16	—	19	—	—	2	—
17	—	—	—	—	trace	—
18	20	32	17	11	13	—
19	72	71	120	22	23	—
20	trace	trace	trace	2	—	—
21	trace	—	—	—	—	—
22	4	—	—	—	4	—
23	19	28	29	40	18	4
24	18	41	—	—	—	—
25	4.0	57	—	—	—	—
26	trace	—	trace	—	2	—
27	34	49	trace	—	2	—
28	16	35	5	—	—	—
29	14	0.5	—	—	4	—
30	4.1	20	5	—	4	—
31	20	18	—	—	—	—
31a	—	—	980	138	427	51
32	8.2	—	—	—	—	—
33	6.5	44	—	—	—	—
34	13	31	5	—	3	—
35	61	13	47	—	11	—
36	14	12	145	—	12	—
37	26	17	—	—	15	—
38	5.6	25	—	—	—	—

4. The other treatments, including iodination, benzhydrylation, and iodination–benzhydrylation, contain significantly fewer compounds, with about five peaks predominating: 11 (water), 18 (acetic acid), 19 (furfural), 23 (5-methyl-2-furfural), and 31a (unknown).

5. All of the identified compounds contain only C, H, and O. The elements of the retardant (N, P, K, I) do appear in any case, indicating that retardants act predominantly in solid phase.

The results indicating that a flame retardant decreases the number of compounds formed are consistent with the work of Byrne, Gardiner, and Holmes.[11] They noted that furfural was a major pyrolysis product of the pyrolysis of 8% borax/boric acid-treated cotton (typewriter cloth), along with glyoxal, pyruvaldehyde, and 5-hydroxymethylfurfural.

The significant features of the comparison between cellulose and levoglucosan are as follows:

1. Untreated and $KHCO_3$-treated levoglucosan are quite similar. However, they do differ from the cellulosic products: peaks 23 (furfural alcohol), 24 (butyrolacetone), 30 (phenol, o-cresol), 31 (m-cresol, p-cresol, 2,5-dimethylphenol), and 33 (unknown) are absent; peaks 31a (unknown) and 36 (unknown) are increased.

2. $NH_4H_2PO_4$-treated α-cellulose and levoglucosan have essentially the same products.

The above results indicate that the pyrolysis products of cellulose may well be produced from the decomposition of levoglucosan. It appears as if the decomposition of levoglucosan could account for all the pyrolysis products of treated cellulose (except $KHCO_3$).

CONCLUSIONS

1. A typical chromatogram of pyrolysis products for untreated α-cellulose contains about 39 distinct peaks; however, mass-spectral data indicate the presence of at least 59 compounds. Treated α-cellulose pyrolysis products generally contain fewer compounds, although the compounds that are present are the same as those in the untreated samples. Since the initial pyrolysis products undergo decomposition in the injection port of the gas chromatograph, both initial products and subsequent decomposition products are identified. In all, 37 compounds have been identified, including 13 which have not been previously reported. Most of the newly identified compounds contain a benzene ring, indicating that these compounds are probably formed from reactions between initial volatiles.

2. The products generated in the isothermal pyrolysis chamber at 330°C are similar to those generated at the pyrolysis temperature in a fire environment as typified by the burning cylinder. Thus, the research carried out in the isothermal pyrolysis chamber is meaningful as far as fire problems are concerned. In general, a comparison of the pyrolysis products generated under different atmospheres (N_2 and air) in the temperature range of 330°C–400°C indicates that the formation of pyrolysis products is independent of either atmosphere or temperature.

3. Since the products identified contain only C, H, and O, the additional elements introduced into the cellulose by the flame retardants remain in the char. This indicates that the flame retardants that have been used in this work act predominantly in the solid phase.

4. The products of untreated levoglucosan are essentially the same as those of untreated α-cellulose, indicating that most of the decomposition of cellulose probably forms levoglucosan which then decomposes to form the observed pyrolysis products.

5. The products of flame retardant-treated levoglucosan are essentially the same as those of cellulose with the same retardant treatment. This suggests that the retardants act on the levoglucosan formed in the decomposition of cellulose rather than directly on the cellulose itself.

6. Comparison of the pyrolysis products formed for different flame retardants and concentrations indicates that the products depend more on the concentration than on the type of retardant. All of the retardants appear to act on the levoglucosan in the same manner.

References

1. K. Kato, *Agr. Biol. Chem.* (Tokyo), **31**, 657 (1967).

2. R. Schwenker and L. Beck, *J. Polym. Sci.*, **2**, 331 (1963).

3. S. Glassner and A. Pierce, *Anal. Chem.*, **36**, 525 (1965).

4. S. Martin and R. Ramstad, *Anal. Chem.*, **33**, 982 (1961).

5. S. Martin and R. Ramstad, U. S. Navy Radiol. Defence Lab., Rept., USNRDL-TR-810, Jan. 12, 1965.

6. W. McFadden, R. Teranishi, D. Black, and J. Day, *Food Sci.*, **28**, 316 (1962).

7. J. Watson and K. Bieman, *Anal. Chem.*, **37**, 844 (1965).

8. F. Leemans and J. McCloskey, *J. Amer. Oil Chem. Soc.*, **44**, 11 (1967).

9. A. Lipska and F. Wodley, *J. Applied Polym. Sci.*, **13**, 851 (1969).

10. C. Greenwood, J. Knox, and E. Milne, *Chem. Ind.* (London), **46**, 1878 (1961).

11. G. Byrne, D. Gardiner, and F. Holmes, *J. Appl. Chem.*, **16**, 81 (1966).

12. L. E. Kuentzel, *Index of Mass Spectral Data*, ASTM, Philadelphia, 1963.

13. R. S. Gohlke, *Uncertified Mass Spectral Data*, Dow Chemical Co., Midland, Michigan, 1963.

14. A. E. Lipska and W. J. Parker, U. S. Navy Radiol. Defense Lab., Rept., USNRDL-TR-928, Nov. 4, 1965.

15. F. Shafizadeh, in *Advances in Carbohydrate Chemistry*, Vol. 23, W. W. Pigman, Ed., Academic Press, New York, 1968, pp. 419–474.

16. A. E. Lipska and G. E. McCasland, *J. Applied Polym. Sci.*, **15**, 419 (1971).