Investigation of the Action of Flame Retardants in Cellulose. I. Investigation of the Flame Retardant Action of 2,2'-Oxybis(5,5-Dimethyl-1,3,2-Dioxaphosphorinane-2,2'-Disulfide) in Cellulose*

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Synopsis

Pyrolysis experiments were performed in high vacuum and under reduced air pressure (100 Pa). The volatile products of pure cellulose and cellulose containing various amounts of flame retardant 2,2'-oxybis (5,5-dimethyl-1,3,2-dioxaphosphorinane-2,2'-disulfide), i.e., Sandoflam 5060 of Sandoz AG, were studied by means of gas chromatography in combination with mass spectroscopy. The volatile products were characterized with infrared spectroscopy. The studies revealed that the incorporation of the flame retardant enhanced the water release and shifted the onset of this reaction to lower temperatures. On the basis of these findings an explanation for the mechanism of flame retardancy in generated cellulose fibers modified with this particular flame retardant is attempted. From experiments with different residual air pressure the influence of oxygen on the primary processes of the pyrolytic degradation of cellulose is being discussed.

INTRODUCTION

Flame retardants for regenerated cellulose fibers are of particular importance since these fibers are widely used in clothing textiles, upholstery fabrics, etc. According to these applications, state regulations in various countries[1] call for meeting certain standards of flame retardancy. The fiber and textile industry seriously aims to meet the set goals. In accordance with this situation, the mechanism of the thermal degradation of cellulose and its decomposition products have been carefully investigated[2,3]. Several active flame retardants for cellulose substrates are known[4].

In previous studies it has been suggested that some of these flame retardants intervene by repressing the formation of levoglucosan[4], which is regarded to be an important intermediate in the formation of easy flammable products[2]. It is generally agreed that some acids do achieve this by acting as dehydration agents. However, not all known flame retardants for cellulose have been found to act in this way[5].

Among a series of organic pyrophosphate compounds, those carrying thionophosphoryl group were found to be not only very active flame retardants but also very stable against alkaline hydrolysis.[6] This made them

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*Dedicated to Prof. Dr. Herman Mark on the occasion of his ninetieth birthday.

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especially suited for the manufacture of flame retardant regenerated cellulose fibers and films using viscose technology. Sandoz AG of Basel/Switzerland marketed some years ago 2,2'-oxybis-(5,5-dimethyl-1,3,2,-dioxaphosphorinane-2,2'-disulfide) as a viscose additive under the trade-name Sandoflam 5060. The chemical composition of this compound is the following:

In a study of the flame retardancy action of this compound using Curie-point pyrolysis[7] chemists of Sandoz AG found that the presence of this additive in cellulose substrates prevents the formation of levoglucosan and favors the forming of levoglucosanone,[8] which derives from the former through dehydration.

In this study the formation of volatile products, such as water, carbon dioxide, or carbon monoxide were not recorded. It was therefore the aim of the investigations reported here to study especially the dehydration reaction going on during cellulose pyrolysis.

EXPERIMENTAL

Materials

High-wet-modulus viscose fibers without and with different amounts of Sandoflam 5060 flame reatardant (6.4, 11.1, 16.3, and 22.0% by weight) were obtained from Lenzing AG (Austria). The flame-retardant compound had been incorporated through addition of a well-stabilized suspension of the extremely fine ground material to the viscose spinning dope prior to the extrusion through the spinnerets. In the following all data concerning the amount of flame retardant present in the cellulose fibers will be given in wt%.

Procedures

Isothermal Pyrolysis. The pyrolysis experiments were performed in a thermal volatilization analysis (TVA) apparatus.[9] Details of the layout used by us were given in a recently published paper.[10]

Three grams of the fiber sample were placed in the pyrolysis vessel, evacuated at 30°C to a certain reduced pressure and subsequently heated as rapid as possible (within 5–10 min) to the desired test temperature. This temperature was then kept for 1 h. The particular settings (temperature and pressure) applied in each experiment during the course of the test procedure described above are given in Tables I and II.

The volatile liquid products which evolved during the pyrolysis process were collected in a trap cooled with liquid nitrogen and transferred into small storage vessels for further analysis. To obtain quantitative results

the amounts of the volatile products, the charred residue, and the tar fraction with limited volatility (i.e., the "cold ring fraction") were determined gravimetrically.

Determination of Water Release by On-Line Mass Spectroscopy. Contrary to the isothermal pyrolysis experiments, where the total amount of water released at a distinct temperature during a period of 1 h. was measured, in nonisothermal heat exposure experiments the amount of water instantly released in the course of programed heating (10°C/min; from 40 to 440°C) has been monitored. For this purpose the pyrolysis equipment of the TVA-apparatus was attached directly to the mass spectrometer rather than to the sample collecting trap, as in the case of the isothermal pyrolysis experiments described before.

The mass spectrometer was adjusted to monitor just the $m/e = 18$ peak during each run. The particular ion current of this ion is proportional to the rate of water release during the pyrolytic degradation. Integration of the traces obtained yields the overall amount of water released during the heat treatment.

In the evaluation, the curves were reduced to equal sample weight. Since a calibration on a quantitative scale was not possible with the particular equipment, the amounts of water released during these tests are given in arbitrary, relative units.

Analysis of the Liquid Products with Gas Chromatography and Mass Spectroscopy (GC/MS). The liquid products were separated by means of a Hewlett-Packard Gas Chromatograph Model 5830 on a OV-17 column at 150°C (carrier gas: helium, 30 L/min). The compounds were identified with a Balzers QmG 511 mass spectrometer, coupled to the gas chromatograph by means of a jet separator. The pressure in the mass spectrometer was 10^{-4} Pa.

The amounts of liquid organic compounds could be estimated from the peak areas of the signals generated from the FID detector of the gas chromatograph. In the case of acetic acid and acetone, the response factors were measured to obtain the absolute quantities of these compounds among the liquid products. The amount of water in the liquid fraction, however, could not be measured with the FID detector because of the lack of sensitivity to water. The determination of the water content was achieved using the mass spectrometer as detector. The mass spectrometer was adjusted to monitor continuously the $m/e = 18$ value (M^+ peak of water), and this particular ion current was recorded during each GC/MS run. From the peak areas the amount of water in the liquid sample was determined. As in the case of the organic compounds, the system has been calibrated by the injection of known amounts of water.

Investigation of the Char and Residues of Low Volatility by Infrared Spectroscopy (IR). IR spectra were recorded by means of a Perkin-Elmer IR Spectrometer Model 283. For quantitative analysis 10 mg of residue were mixed with 3 g of KBr and homogenized carefully. For each spectra 150 mg of the mixture were compacted to a pellet. Using this procedure, the intensity of the OH vibration at 3450 cm^{-1} could be compared without any additional calculations. Analoguous experiments were performed with the original fiber samples.

RESULTS

Yields of Char, Tar, and Volatiles during isothermal pyrolysis of samples with varying amounts of flame retardant. After isothermal pyrolysis, the amount of dry char and of volatile liquids were determined gravimetrically. From the data obtained the amount of tar and other volatiles (gases,[11] CO, and CO_2) were calculated.

The results of the one hour pyrolysis at 260°C for samples with different contents of flame retardant are given in Table I. It can be seen from the data that with increasing amount of flame retardant present in the cellulose substrate the total weight loss, the amount of liquid volatile products, and the amount of tar (cold ring fraction) increases continuously. The results, furthermore, indicate that the pyrolytic decomposition of the cellulose starts in the presence of flame retardant earlier and more vigorous.

For three selected samples wit 0, 6.4, and 22% flame retardant, similar experiments were performed at seven different temperatures (up to 440°C). The results obtained in these pyrolysis experiments are listed in Table II. It should be noted that in these experiments the pressure (residual air) was kept 100-fold higher than under the conditions of the experiments reported in Table I. In comparing the data obtained in this second series of experiments (cf. Table II) at 260°C with those reported in Table I, it can be seen that the distribution of the different fractions obtained in the pyrolysis of the samples containing no flame retardant is quite similar. This indicates that the different amounts of residual air do not influence the weight loss and the formation of decomposition products of the pure cellulose significantly.

The sample containing 6.4% flame retardant, however, loses much more weight during pyrolysis that higher pressure of residual air (1000 Pa) than at lower pressure (10 Pa). Also the formation of pyrolysis products is remarkably enhanced.

The sample with 22% flame retardants yields an only slightly increased weight loss and a relatively similar distribution of decomposition products in both low pressure (Table I) and high pressure (Table II) experiments. The weight loss data of both samples containing 6.4 and 22% flame retardant, respectively, are at the higher pressure experiments essentially the

TABLE I
Isothermal Pyrolysis (260°C) of Cellulose in Presence
of Varying Amounts of the Flame Retardant[a]

Sample Sandoflam (wt %)	Total weight loss (wt %)	Liquid products (wt %)	Char (wt %)	Cold ring b and other volatiles (wt %)
0	12.57	11.66	87.43	0.9
6.4	26.66	16.33	73.33	10.33
11.1	32.66	20.66	67.33	12.0
16.3	35.66	22.66	64.33	13.0
22.0	50.33	25.66	49.66	24.55

[a] In high vacuum (10 Pa); time of pyrolysis 1 h.

TABLE II
Isothermal Pyrolysis of Celluloses with Various Amounts
of Sandoflam at Different Temperatures[a]

Sandoflam (wt %)	Pyrolysis temperature (°C)	Total weight loss (wt %)	Liquid products (wt %)	Char (wt %)	Cold ring fraction and other volatiles (wt %)
0	150	10	5	90	5
0	200	12	3.66	88	8.33
0	260	12	11.6	88	(0.33)
0	300	22.6	17.3	77.3	(5.3)
0	350	64	30.3	36	33.6
0	400	73.6	32.3	26.3	41.3
0	440	84	36	16	48
6.4	150	8.66	2	91.3	6.6
6.4	200	10	3	90	7
6.4	260	55.66	30.33	44	25.33
6.4	300	65	34.66	35	30.333
6.4	350	71	33.66	29	37.33
6.4	400	73	(21.33)	27	(51.66)
6.4	440	75.33	37	24.66	38.33
22	150	8	1.6	92	6.3
22	200	10.66	2.66	89	8
22	260	54	26.3	46	27.6
22	300	66.6	28.6	33	38
22	350	71.6	33	28.3	38.6
22	400	73.3	32	26.6	41.3
22	440	72	34.6	25	40.3

[a] Pressure 1000 Pa; time of pyrolysis 1 h.

same. This suggests that with respect to the weight loss behavior a saturation in the flame-retardant action occurs in the region of a flame-retardant content of approximately 20%, independent of the residual air pressure. In this connection, it is notable that in the range between 6 and 22% flame-retardant content the cellulose fibers become self-extinguishing when the ignition source is being removed.

Infrared Studies on the Charred Residue and on the Cold Ring Fraction (Tar of Lower Volatility) Obtained in the Pyrolysis Experiments. The charred residues remaining in the pyrolysis experiments at various temperatures were investigated by infrared spectroscopy. The spectral results were compared with those obtained on the corresponding untreated fiber samples. Attention was directed to the OH vibrations. Because of the similar procedure in the preparation of the samples for the IR spectroscopic investigations, the intensities of the respective absorption bands could be compared on a quantitative scale.

The evaluation of the results of these infrared studies on a numerical scale is given in Table III for the maximum absorption in the OH region measured at 3450 cm^{-1}, the ratio of the peak heights at maximum absorption in the OH and CH region at 3450 and 2900 cm^{-1}, and the area ratios of absorption in the OH and CH region between 3050 and 3650 cm^{-1} and 2750 and 3000 cm^{-1}, respectively.

TABLE III
Quantitative Infrared Studies of Charred and Tared (Cold Ring Fraction) Samples, Obtained on Heating Cellulose Samples with and without Flameretardent Additive at Various Temperatures in Vacuum[a]

Sample	Treatment temperature (°C)	% absorption at 3450 cm⁻¹	Decrease in absorption	Peak height of absorption At 3450 cm⁻¹	At 2900 cm⁻¹	Decrease in OH absorption (peak height)	Peak ratio 3450/2900	Absorption area (mm²) 3050–3650 cm⁻¹ (OH region)	2750–3000 cm⁻¹ (CH region)	Decrease in OH Absorption (peak area)	Absorption ratio (OH/CH)·(1/3.3)
Pure cellulose	—	87	1.00	9.15	3.25	1.00	2.82	4263	434	1.00	2.98
Char	260	46	0.53	5.35	1.45	0.58	(3.69)	2274	151	0.53	(4.56)
	400	12	0.14	1.68	0.95	0.18	1.77	640	115	0.15	1.69
Tar	400	37	0.43	4.85	2.20	0.53	2.20	1532	209	0.36	2.22
Cellulose + 22% Sandoflam 5060	—	65	1.00	8.55	3.15	1.00	2.71	3423	430	1.00	2.41
Char	260	41	0.63	4.00	1.60	0.47	2.50	1488	214	0.43	2.10
	400	35	0.54	2.80	1.30	0.33	2.15	1052	160	0.31	1.99
Tar	400	20	0.31	2.15	1.60	0.25	1.34	987	163	0.29	1.83

[a] Transmission data at 3450 cm⁻¹ associated with the OH-Vibration mode.

From the maximum absorption at 3450 cm^{-1} it can be concluded that the highest amount of hydroxyl groups is present in the untreated non-modified cellulose samples. The presence of the flame retardant agent reduces clearly the relative amount of hydroxyl groups in the flame retardant modified cellulose samples by approximately one quarter, in good relation to the 22% addition. The samples being exposed to 260°C over a longer period clearly show the loss of hydroxyl functions in the course of the pyrolysis.

For the pyrolysis treatments at 400°C both charred material and the corresponding tar (cold ring fraction) were investigated for their infrared absorption behavior. It is interesting to note that the amount of hydroxyl groups is in the case of the pyrolytic treatment of pure cellulose less in the charred material than in the corresponding tar. In contrast to this, in the pyrolysis of cellulose in the presence of flame retardant agent the tar contains apparently less hydroxyls than the charred pyrolysis residue.

The evaluation for peak height and absorption area in the OH and CH region allows the same conclusions. The loss of hydroxyl functions in the pyrolysis treatments is far more regular and less drastic in presence of the flame retardant agent than in the case of pure cellulose. Furthermore, there is an indication by the high OH/CH ratios observed on the charred residue remaining in the 260°C pyrolysis of pure cellulose that initially this treatment results apparently in a highly water adsorptive residual product.

Besides these studies also other regions of wavelengths have been monitored. A minor band at 1630 cm^{-1} shifted to 1600 cm^{-1}. Such a phenomenon was already reproted in the literature[12] in the course of investigations on another flame retardant/cellulose system. This finding was attributed to conjugate double bonds. Moreover, in the degraded materials a new band appeared at 1690–1700 cm^{-1} indicating the formation of aldehyde or keto groups.

Investigation of the Composition of the Volatile Liquid Products Realeased during Isothermal Pyrolysis. The lower molecular weight liquid products of the thermal degradation were identified by means of the GC/MS technique as water, acetone, acetic acid, acetaldehyde, and methylpropylketone. This is in agreement with the results presented already previously in the literature.[2]

The release of water is highly suggested also from the IR-studies presented in the foregoing paragraph. In fact, it turned out that water is the major constituent of the liquid products of the pyrolytic degradation amounting in general to more than 90%. The amounts of water, acetone, and acetic acid released at different temperatures from pure cellulose and from samples with different flame retardant content are shown in Figure 1.

As can be seen from Figure 1(a), the amount of water released in the isothermal pyrolysis experiments is at temperatures beyond 200°C in all cases much higher for the samples containing flame-retardant agent. Furthermore, these samples start to eject larger amounts of water at lower temperatures (220–250°C) in comparison to pure cellulose (above 300°C). There is an indication that the cellulose sample with the flame-retardant content of 22% is somewhat more active in releasing water in the pyrolytic treatment than the cellulose sample containing only 6.4% flame retardant.
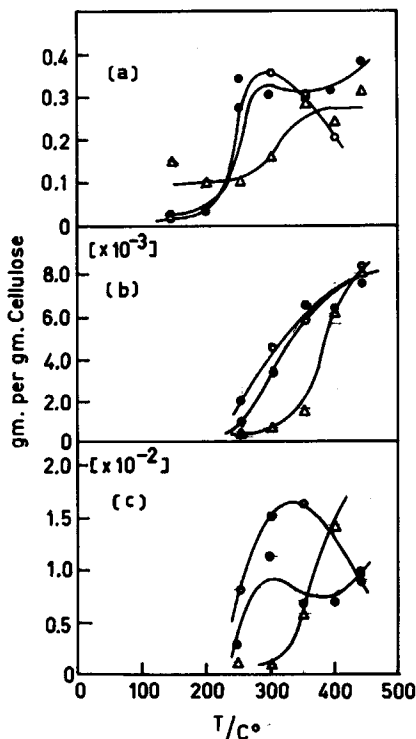
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Fig. 1. Yields of volatile liquid products cellulose vs. temperature of pyrolysis: (△) pure cellulose: (○) cellulose with 6.4% flame retardant, (●) cellulose with 22% flame retardant; (a) water; (b) acetone; (c) acetic acid.

In general, the amounts of acetone [Fig. 1(b)] and acetic acid [Fig. 1(c)] formed at different temperatures of pyrolysis show a similar pattern as discussed for the water release. This indicates that also these organic degradation products may be formed from reaction steps with similar activation energies as those responsible for the water ejection. Also their formation starts to occur in presence of the flame-retardant agent at lower temperatures than in its absence. The overall quantities of these substances formed during the pyrolytic treatments, however, are very low when compared with the amounts of water released from the samples.

Determination of the Water Release during Heating by On-Line Mass Spectroscopy. Samples of pure cellulose and cellulose with 6.4 and 22% flame retardant content were heated in high vacuum (10^{-4} Pa) with the reaction vessel directly attached to a mass spectrometer. The $m/e = 18$ partial ion current was monitored during these experiments in order to obtain a measure of the water ejection. The data are to some extent influenced due to the formation of other degradation products, such as acetic acid, which also contribute to the observed ion current of $m/e = 18$. However, it has been proved in the preceding paragraph that water is by far the main constituent of the volatile pyrolysis products. The volatile organic compounds formed in the heat treatments are 10^4–10^5 times less than the amount of water released. The results from these experiments are shown in Figure 2(a), 2(b), and 2(c).
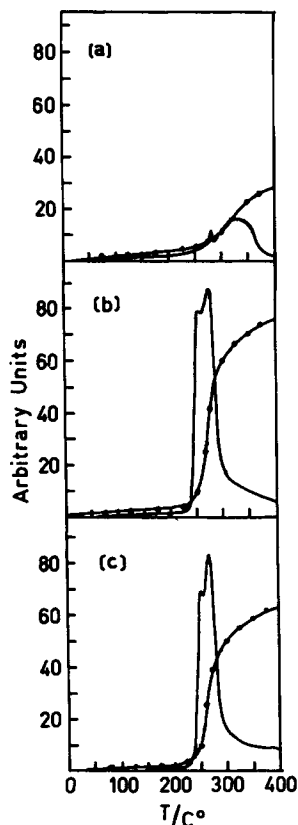
Fig. 2. Water release during heating (10°C/min) in high vacuum determined with the mass spectrometer: (−) rate of water release; (●) integrated curve: (a) pure cellulose; (b) cellulose with 6.4% flame retardant; (c) cellulose with 22% flame retardant.

The observed intensities in arbitrary units are corrected for equal sample weights. The effect of the flame retardant on the amount of water released can be easily seen from the plots. The presence of the flame retardant in the cellulose substrate causes during heat treatment a remarkably enhanced water release in the temperature region of 240°–300°C, whereas in the case of pure cellulose the water release starts somewhat later at 270°C and is less expressed. In the latter case the temperature range over which water is released from the heat-treated pure cellulose covers a much wider range and reaches its optimum only at about 350°C. In all cases the water release seems to be apparently a two-stage process starting with a relatively fast release reaction followed by more gradual water ejection process. The integrated curves, also given in arbitrary units, are indicative for the total amount of water released in the heat treatment experiments.

CONCLUSIONS

In the literature there have been some reports on flame retardant/cellulose systems for which the process of water release goes hand in hand with the flame retardant activity[12,13]. For the addition of Sandoflam 5060

to cellulose as a flame-retardant agent the situation seems to be of a similar type. Our findings suggest that the dehydration reaction has to be considered important for the activity of the flame retardant agent already in the early stages of ignition or burning and at lower temperatures. This is to some extent contrary to statements in other studies claiming that the water release is only effective in the later stages of burning[5].

The release of water from cellulose on heating is accompanied by the loss of hydroxyl functions. The question remains open to discussion whether the more gradual loss of hydroxyl groups observed by us in the pyrolysis of flame-retardant-modified cellulose is caused by the retention of water split off from the cellulose molecules by reaction with the phosphorous-containing flame-retardant agent.

Clearly, an enhanced water release contributes to the effectiveness of any flame retardant in combination with cellulose, since this process is known to be endothermic.[2,3,14,15] In the course of such a reaction the thermal feedback,[16] which is essential for the burning process, is handicaped or in the best case ceased. Furthermore, the water vapor ejected from the sample in an enhanced release reaction hinders the oxygen access to the burning region of the sample.

Finally, the abstraction of water in larger amounts than 1 mol/glucose unit interferes certainly with the formation of levoglucosan,[17] which is regarded as the precursor of flammable pyrolysis products. Thus the flame-retardant action of Sandoflam 5060 in combination with cellulose is due to: (a) the enhanced splitting off water from cellulose under the influence of heat at remarkably lower temperature than in the case of heat exposure of pure cellulose,[18] (b) the endothermic nature of this faster water release hindering the thermal feedback, and (c) the abstraction of apparently more water than 1 mol/glucose unit reduces the formation of levoglucosane which otherwise acts as a precursor for easily flammable pyrolysis products.

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