

Flame-Retardant Action of Chlorine Compounds and Antimony Trioxide on Cellulose Fabric

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Synopsis

Chemical research on the flame-retardant action of halogen compounds and antimony trioxide on cellulose fabric was carried out by thermogravimetry, infrared spectrum analysis, and x-ray diffraction analysis. The following results and conclusion were drawn: (1) Independently of the type of chlorine atoms introduced, that is, whether chlorine atoms are chemically bonded with cellulose chains or not, the introduction of chlorine atoms alone has little flame-retardant effect, while combination of chlorine atoms with antimony trioxide is more effective. (2) Addition of only antimony trioxide to samples obtained from the dechlorination of chloroexocellulose is as effective as the combination of chlorine compounds and antimony trioxide, in spite of a trace of chlorine in the DCDC samples. (3) Introduction of chlorine compounds yielded the formation of carbonyl and double bond groups in the cellulose chains. The formation of the latter groups was accelerated by the combination of antimony trioxide; that of the former groups was inhibited. Most of the introduced chlorine atoms were missing in the condensed phase even at 300 °C while a large portion of the initially added antimony trioxide remained in the condensed phase at least up to 400°C. One mode of flame-retardant action of the combination of chlorine compounds and antimony trioxide was assumed to be the catalytic effect on the dehydration of cellulose to yield a thermostable polyene structure in the cellulose chains.

INTRODUCTION

This paper describes a mode of flame-retardant action of chlorine compounds, antimony trioxide, and a combination of these components on cellulose. Halogen compounds as well as phosphorus compounds have flame-retardant properties.¹⁻³ Their power increases by their combination with antimony trioxide.⁴⁻⁷ Certain halogen compounds, e.g., chlorinated paraffin, decabromodiphenyl oxide, etc., are used commercially.^{8,9} Much attention has been paid to research for more effectual halogen compounds as flame retardants. These compounds are believed to operate as radical scavengers in the flame zone.^{11,12} Recently, Brauman¹³ had some doubt about this conventional concept and investigated the influence of flame retardants on the decomposition of polymers. Combinations of chlorinated wax and polystyrene, polypropylene, and polyester were used as flame retardant and polymer, respectively. This flame retardant inhibited physically oxidative polymer decomposition by forming a surface barrier that limited oxygen access.

We have taken a new look at the flame-retardant action of chlorine compounds and antimony trioxide.

EXPERIMENTAL

Materials

Chlorodeoxycellulose (CDC) was prepared according to the literature.¹⁴⁻¹⁶ Ground filter paper (20 mesh, Toyo Roshi Ltd., Code No. 2) was swollen in dry N,N-dimethylformamide at room temperature and then treated with thionyl chloride in N,N-dimethylformamide at room temperature or 75°C. The product was poured into ice water, treated with sodium carbonate solution (pH 9.5-10) to remove formate groups, washed with water until chloride ions were undetected in the filtrate, and then dried under reduced pressure. Reaction conditions are summarized in Table I together with chlorine contents. The infrared spectrum of the product showed absorption at 750 cm⁻¹ (C—Cl).

Chlorinated paraffin-containing cellulose (PC) was used. Cellulose powder (80 mesh) was dipped with tetrahydrofuran solution of chlorinated paraffin that contained 70 wt. % chlorine and dried under reduced pressure.

Dechlorinated samples (DCDC) of chlorodeoxycellulose were also used. DCDC samples were prepared by heating CDC (6.5 and 15.7 wt. % chlorine) under vacuum (10⁻³ torr) at 180°C. The chlorine contents in the resulting products were less than 0.9 wt. %.

Three samples were mixed with antimony trioxide using an agate mortar and pestle. The mixing molar ratio of antimony to chlorine atoms was about 1:3. The samples used in this study are shown in Table II.

Flammability Test.

A modified limiting oxygen tester was used to determine the flame-retardant properties for powder-like cellulose samples. Ground samples (80 mesh, 90 mg) were packed into Pyrex glass tubes (4.6 mm i.d. × 80 mm), and cylindrical testing specimens were pushed out from the tubes. The specimens were placed in a stream of nitrogen and oxygen mixture (flow rate 4.0 ± 0.1 cm/sec, which is consistent with that employed in the standard ASTM oxygen index method ASTM D2863-70) and ignited by touching them on top with a butane flame. The limiting concentration of oxygen in the gas mixture to burn a 10-mm length was determined. This test procedure was repeated at least five times and the average value was obtained. The deviation of the values was less than 5%.

The data obtained by the modified limiting oxygen tester (*loi*) were plotted to determine the relationship with these obtained by the standard ASTM oxygen index tester (*LOI*) (Fig. 1). The least mean-squares method indicated good correlation between their values:

TABLE I
Conditions of Chlorodeoxycellulose

Sample	Reaction conditions					Chlorine content, wt. %
	Cellulose, g	SOCl ₂ , ml	DMF, ml	Reaction temperature, °C	Reaction time, hr	
CDC-6	20	98	677	room temp.	5.5	5.91
CDC-7	20	98	677		11	6.48
CDC-8	5	31	212		7.2	7.70
CDC-14	5	30	212	75	4	14.2
CDC-16	3	20	317	75	4	15.7

$$(loi) = 1.13(LOI) - 1.80 \quad (1)$$

correlation coefficient = 1

This modified oxygen index tester used for powder-like samples is applicable to determine flame-retardant properties. All the values obtained by the modified oxygen index tester were corrected by eq. (1).

Thermogravimetry

Samples (50 mg) were weighed in quartz pans provided with a Shinku-Riko thermogravimetric analyzer DGC-3. The pans were placed on top of an Alumel-Chromel thermocouple and heated in air at a programmed rate of 4°C/min.

Infrared Spectra

Infrared spectra of the products were recorded as KBr discs using a Nihon-Bunko spectrometer IRA-1.

TABLE II
LOI Values for Modified Celluloses

Sample	Chlorine content, wt. %	Antimony trioxide content, wt. %	Cl/Sb molar ratio	LOI, %
CDC-6	5.91			17.5
CDC-7	6.48			19.3
CDC-8	7.70			20.2
CDC-14	14.2			21.1
CDC-6-Sb	5.46	7.57	2.97	24.6
CDC-7-Sb	5.95	8.17	2.99	25.5
CDC-8-Sb	7.00	9.13	3.15	26.4
CDC-14-Sb	11.9	16.4	2.97	32.6
PC-5	5.05			16.6
PC-7	7.03			16.6
PC-10	9.86			17.5
PC-20	20.0			18.4
PC-5-Sb	4.72	6.49	2.99	19.3
PC-7-Sb	6.41	8.86	2.97	22.0
PC-10-Sb	8.70	11.7	3.03	24.6
PC-20-Sb	15.7	21.5	3.01	35.2
DCDC-7	0.9			18.9
DCDC-16	0.03			20.6
DCDC-7-Sb	0.83	8.11	0.12	23.7
DCDC-16-Sb	0.025	17.6	0.03	32.6
Cellulose				17.5
Cellulose-Sb		7.65		20.2
Cellulose-Sb		15.8		22.0

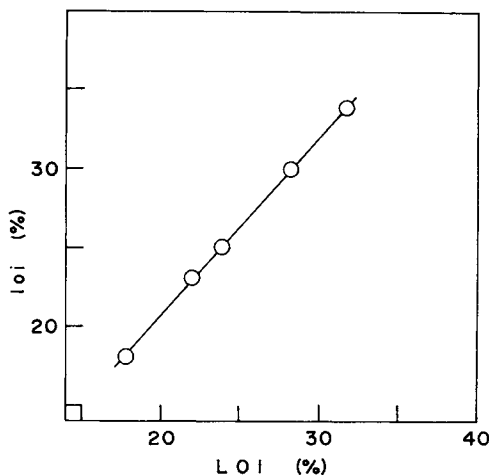


Fig. 1. Correlation of modified limiting oxygen tester and the standard oxygen method (ASTM D2863-70).

X-Ray Diffraction

X-Ray diffraction patterns were obtained with nickel-filtered $\text{CuK}\alpha$ radiation at 30 kV and 10 mA using a Rigaku-Denki Geigerflex D-6C. The intensity was measured with a Geiger counter.

Chlorine and Antimony Analyses

Chlorine contents in the samples were determined by a potentiometric titration method. Samples (10 mg) were burned in a Shoniger combustion flask. The resulting hydrogen chloride was absorbed in water, and the solution was titrated with silver nitrate solution using a Metrohm Herisau automatic titrator E436E.

Antimony contents were determined by a colorimetric method. Samples were decomposed with a mixture of concentrated sulfonic acid and perchloric acid. The resulting solution was treated with L-ascorbic acid as a color-producing reagent and the absorbance at 425 nm was measured.¹⁷

RESULTS AND DISCUSSION

Flammability Test

Results of the oxygen index test (Table II) show the following: (1) Independently of the type of chlorine atoms introduced, that is, whether chlorine atoms are chemically bonded with cellulose chains or not, the introduction of chlorine atoms alone has little flame-retardant effect. (2) The introduction of antimony trioxide alone is also ineffectual. (3) The combination of chlorine atoms and antimony trioxide produces effectual flame-retardant properties. (4) The addition of only antimony trioxide to DCDC samples is as effective as the combination of chlorine atoms and antimony trioxide, in spite of a trace of chlorine in the DCDC samples.

Many investigators¹⁰⁻¹² have reported that volatile antimony trichloride, produced by the interaction of antimony trioxide and chlorine-containing

compounds, may operate as a flame inhibitor in the flame zone. This assumption could not explain all our experimental observations, particularly the last observation that the addition of antimony trioxide alone to DCDC samples was effectual. The last observation suggests that a certain interaction between antimony trioxide and residual products from CDC samples would play an important role in flame-retardant properties. Therefore, thermal reactions of CDC samples with antimony trioxide were examined.

Thermal Degradation of Chlorine-Containing Cellulose with Antimony Trioxide

Thermogravimetric curves for CDC and PC samples with or without antimony trioxide are shown in Figures 2 and 3. The introduction of chlorine atoms into cellulose chains initiated a weight loss at low temperatures. A similar acceleration of weight loss was observed in the case of the introduction of antimony trioxide, but the accelerating power was less than that of chlorine atoms. While the combination of CDC samples with antimony trioxide produced a rapid weight loss in the low-temperature regions, it resulted in the formation of a large amount of residual products. Similar thermogravimetric changes were observed in the

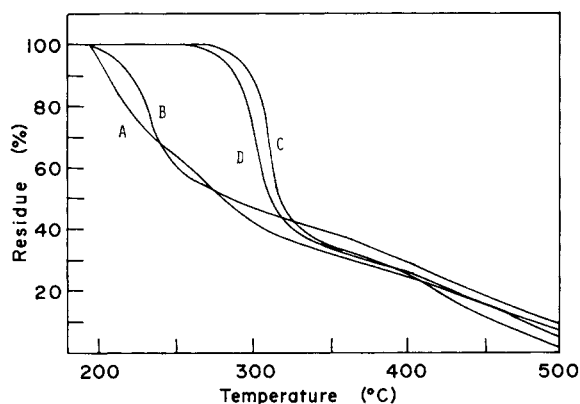


Fig. 2. Thermogravimetric curves for CDC and CDC-Sb samples: (a) CDC-14; (b) CDC-14-Sb; (c) cellulose; (d) cellulose-Sb.

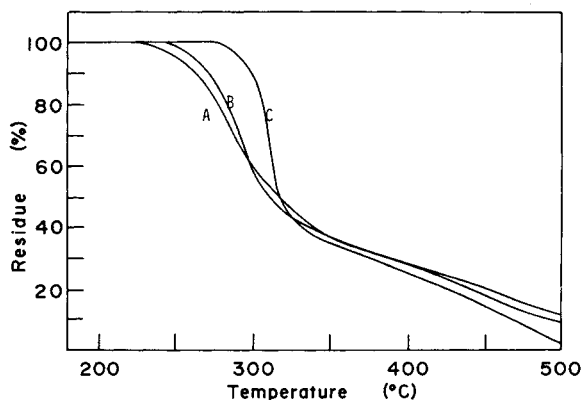


Fig. 3. Thermogravimetric curves for PC and PC-Sb samples: (a) PC-20; (b) PC-20-Sb; (c) cellulose.

case of PC samples (Fig. 3). In spite of only a trace chlorine content in the DCDC sample, this sample also showed similar changes; the DCDC sample experienced a weight loss at low temperature and the addition of antimony trioxide produced a rapid weight loss (Fig. 4). The accelerating power of antimony trioxide was larger toward the DCDC sample than toward the CDC sample. These thermogravimetric results indicate that regardless of chlorine content, antimony trioxide influences thermal degradation, particularly at an early stage of the thermal degradation.

The antimony content in the residual products after heating in air at adequate temperatures was determined (Table III). Results indicate that a large portion (above 90%) of the initially added antimony atoms remains in the condensed phase up to 400°C, which corresponds the temperature of the fabric surface on combustion. The composition of the remaining antimony compounds in the residual products was mostly antimony trioxide from the measurement of x-ray diffraction pattern. No x-ray diffraction pattern of antimony trichloride or antimony oxychloride was observed.

The chlorine contents in the residual products were also determined (Fig. 5). Dechlorination from the CDC sample was initiated at about 150°C and accomplished near 300°C. The addition of antimony trioxide retarded dechlorination of the CDC sample; but once dechlorination was initiated, the reaction was rapid and was accomplished at a low temperature of 250°C. This dechlorination indicates interaction between antimony trioxide and the CDC sample. However, it cannot be inferred that the interactions bring about flame-retardant properties

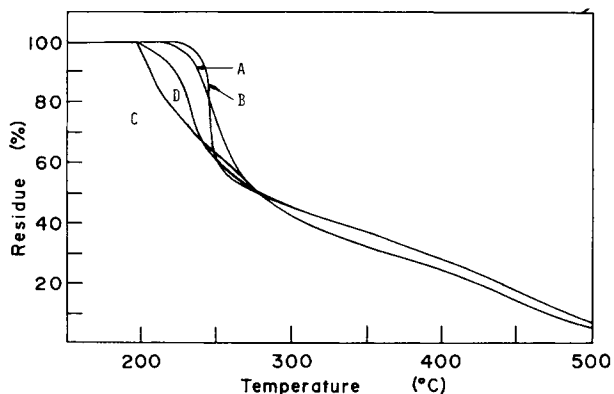


Fig. 4. Thermogravimetric curves for DCDC and DCDC-Sb samples: (a) DCDC-16; (b) DCDC-16-Sb; (c) CDC-14; (d) CDC-14-Sb.

TABLE III
Antimony Content in Residual Products from CDC-7 Sb Sample

Heating temperature, °C	Sb/Sb ₀ ^a
195	100
230	100
320	86.7
410	95.1

^a Sb₀: original Sb content; Sb: Sb content after heating treatment.

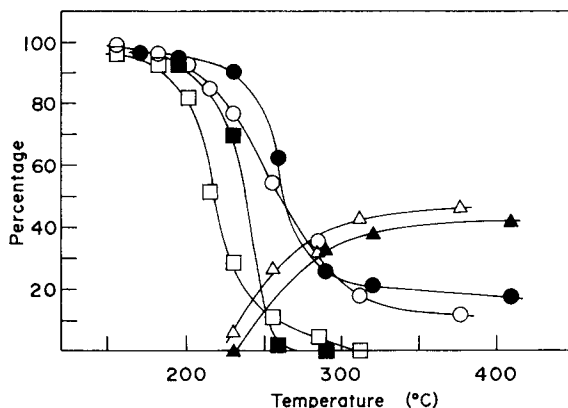


Fig. 5. Degradation products from CDC and CDC-Sb samples. From CDC-14: (O) residual products; (Δ) liquid products; (□) chlorine content in residual products. From CDC-14-Sb: (●) residual products; (▲) liquid products; (■) chlorine content in residual products.

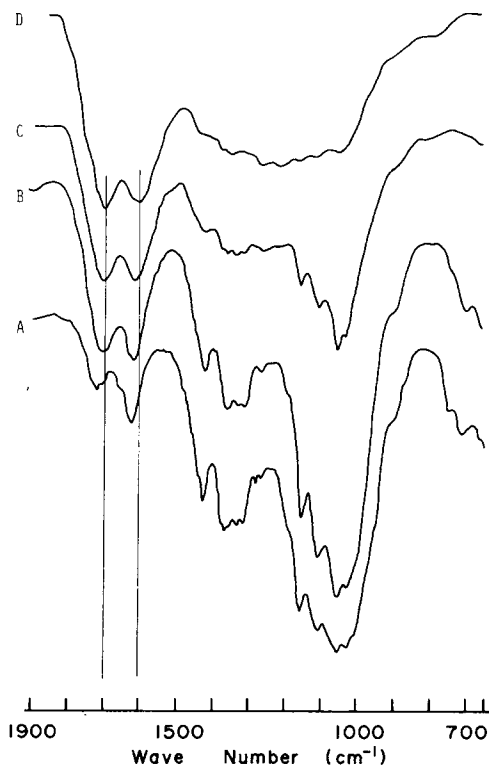


Fig. 6. Infrared spectra of residual products from CDC sample (CDC-8): (a) degraded at 200°C; (b) degraded at 250°C; (c) degraded at 275°C; (d) degraded at 300°C.

for cellulose fabric, since the DCDC sample attains good flame-retardant properties by the addition of antimony trioxide. Other operating mechanisms are proposed in the next section.

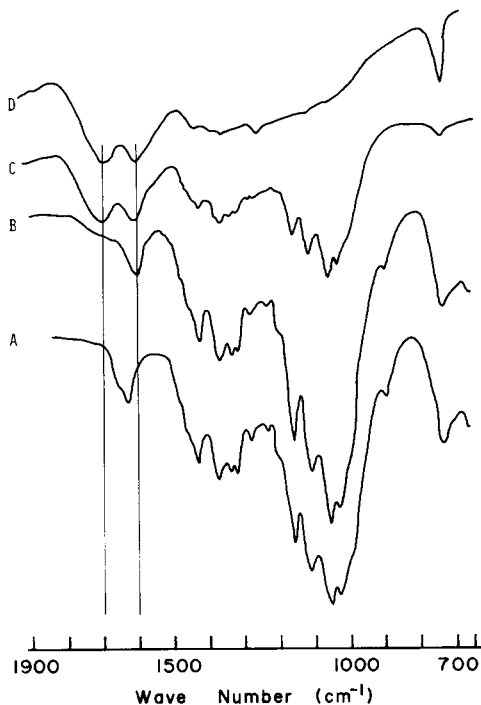


Fig. 7. Infrared spectra of residual products from CDC-Sb sample (CDC-7-Sb): (a) degraded at 200°C; (b) degraded at 250°C; (c) degraded at 275°C; (d) degraded at 300°C.

Thermal Degradation Products

Shafizadeh et al.¹⁸ have reported that the introduction of chlorine atoms into carbohydrates accelerates decomposition to give a large amount of char and to cleave pyranose rings. This acceleration is due to evolution of hydrogen chloride. CDC-8 and CDC-7-Sb samples were pyrolyzed at adequate temperatures for 1 hr; a comparison of the yield of liquid products which are nonvolatile at room temperature and chars is shown in Figure 5. The addition of antimony trioxide to the CDC sample resulted in an increasing amount of char by 10 wt. % and decreasing liquid products. Therefore, the addition of antimony trioxide to CDC samples accelerates charring reactions.

The infrared spectra of these residual products were then measured in Figures 6 and 7. For the CDC-8 sample, new absorption bands appeared at 1720 (C=O) and 1630 cm^{-1} (C=C) at 200°C, where an initial weight loss occurred. At 250°C these two bands shifted to 1700 and 1610 cm^{-1} , respectively. At 275°C each band due to cellulose chains at 1430 (CH), 1370 (CH), 1335 (OH), 1315 (CH_2), 1280 (CH), 1160, 1150, 1050, 1035 cm^{-1} (C—O), etc. became weak; the absorption due to C=O groups became intense. At 300°C the bands due to cellulose chains disappeared; the C=C band at 1610 cm^{-1} shifted to 1600 cm^{-1} . These spectral changes confirmed Shafizadeh's observations. For the CDC-7-Sb sample, alternative spectra were observed: the C=C groups at 1630 cm^{-1} appeared at 200°C, but the C=O groups disappeared. An initial C=O group appeared at 275°C. Moreover, the shift of the band of C=C groups from 1630 to 1600 cm^{-1} occurred at the low temperature of 250°C. These different spectral changes indicate that the introduction of antimony trioxide inhibits the cleavage of pyranose rings and accelerates the formation of conjugated C=C groups in cellulose chains.

It is well known that hydrogen halides operate as catalysts toward dehydration of alcohols.^{19,20} The catalytic power is in the order of $\text{HCl} < \text{HBr} < \text{HI}$. Metal oxides also have catalytic actions on the dehydration.^{19,20} The combination of these reports and our experimental results indicate that a tentative mode of flame-retardant action of the combination of chlorine and antimony trioxide is a catalytic operation on dehydration of cellulose to give large amounts of conjugated double bonds in the cellulose chains. This acceleration results in decreasing the flammable degradation products and brings about flame-retardant properties for cellulose fabrics. This concept could explain why the DCDC sample with antimony trioxide has as much effectual flame-retardant properties as the CDC samples, even though the DCDC sample contains trace amounts of chlorine. The well-known fact that the flame-retardant power of halogen atoms is in the order of $\text{Cl} < \text{Br} < \text{I}$ is understandable from the framework of this concept.

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