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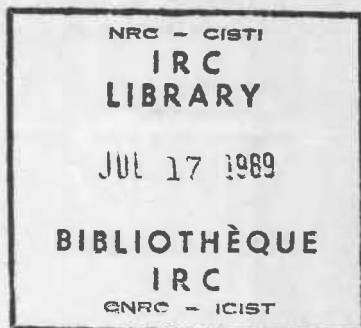
The Flame Retardance Mechanism of the Sb_2O_3 -Halogen System: Gaseous Species Detected by Mass Spectrometry

by Xifang Hu, J.B. Stewart, F.R.S. Clark and Y. Tsuchiya

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Résumé

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Les espèces gazeuses présentes au-dessus d'échantillons de polystyrène contenant du Sb_2O_3 et certaines paraffines chlorées, du tétrachlorobisphénol A et du tétrabromobisphénol A ont été déterminées au moyen de la spectrométrie de masse par ionisation chimique sous pression atmosphérique lors d'une exposition à la chaleur radiante en présence d'air. On a constaté que le $SbOCl_3$, le $SbCl_3(OH)$, le $SbCl_4$ et le $SbCl_3(OH)_2$ étaient présents en plus grande quantité que le $SbCl_3$, l'espèce à laquelle est normalement attribuée l'action ignifugeante des systèmes Sb-halogène.

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The Flame Retardance Mechanism of the Sb_2O_3 -Halogen System: Gaseous Species Detected by Mass Spectrometry

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SYNOPSIS

The gaseous species present above samples of polystyrene containing Sb_2O_3 and selected chlorinated paraffins, tetrachlorobisphenol A and tetrabromobisphenol A were determined by atmospheric pressure chemical ionization mass spectrometry during exposure to radiant heat in the presence of air. SbOCl_3 , $\text{SbCl}_3(\text{OH})$, SbCl_4 , and $\text{SbCl}_3(\text{OH})_2$ were found to be present in greater amounts than SbCl_3 , the species normally identified with the fire retardant activity of Sb-halogen systems. Mass spectral analyses were performed on the vapour above SbCl_3 in air at atmospheric pressure and room temperature, to identify these species produced from the reaction between Sb_2O_3 and the chlorine source.

INTRODUCTION

Antimony trioxide in conjunction with a halogenated organic compound constitutes one of the most commonly used flame retardant systems for polymeric materials [1,2]. Because of its effectiveness and commercial importance, the antimony-halogen system has been studied extensively [1,3,4]. During the last decade several studies of the synergistic effect of Sb_2O_3 in the presence of halogen have been published; most [5-9] identify the active species and determine the phase in which the flame retardant action takes place.

Although there is only limited agreement about the antimony species present and their roles in fire retardance, each study indicates the presence of SbCl_3 . Significantly, none of these studies were carried out under oxidative (real fire) conditions.

The aim of this work was to evaluate the action of the Sb_2O_3 -halogen system in a more realistic fire situation, by monitoring the gaseous species produced from fire-retarded polystyrene (FRPS) in an oxidative atmosphere (air). Several species not previously reported in such systems, i.e., SbOCl_2 , SbOCl_3 , SbCl_3 , $\text{SbCl}_3(\text{OH})$, $\text{SbCl}_3(\text{OH})_2$, $\text{SbBr}_3(\text{OH})$, $\text{SbBr}_3(\text{OH})_2$, SbCl_4 have been identified in the gas phase. A modified mechanism for fire retardant action of the Sb_2O_3 -halogen system has been suggested that accounts for these species.

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EXPERIMENTAL

Materials

FRPS samples were made from polystyrene (PS) pellets (Aldrich Chemical Co. Ltd.), antimony trioxide (Fisher Scientific Co.) and halogenated organic fire retardants, all used as received without further purification. Three halogenated fire retardants were used in the study: Cereclor 70 (CP70, solid chlorinated paraffin, ICI), tetrachlorobisphenol A (TCBPA, Polyscience Inc.) and tetrabromobisphenol A (TBBPA, Polyscience Inc.).

Samples containing chlorinated compounds, i.e., CP70 and TCBPA, were made by the same procedures as described in a previous paper [10], except that Sb_2O_3 was added. The chlorinated compound and polystyrene were thoroughly mixed in the presence of methylene chloride. Antimony oxide was then added to the viscous mixture. The solvent was removed during storage for 3 hours at 60 C under vacuum. In order to avoid interference from the trace methylene chloride in the mass spectral analysis, TBBPA- Sb_2O_3 -PS samples were mixed at 140 C with a mixer/extruder.

Sample sheets, 0.8 mm thick, were prepared from the samples using a hot press [10] operated at 160 C in air. Antimony trichloride ($SbCl_3$ 99% reagent) was used as received for mass spectral analysis of vapour species of $SbCl_3$ in air.

Instrumentation and Test Procedures

A combustion apparatus composed of a radiative cone, cone-shaped quartz tube (of 40 mm inner diameter at the top and 164 mm inner diameter at the bottom) and a spark igniter [11] was connected to an atmospheric pressure chemical ionization tandem mass spectrometer (APCI/MS/MS), a SCIEX model TAGA 6000 as shown in Figure 1.

Purified and dry (<10 ppm water) air from a cylinder was forced in the combustion apparatus through an annular sinter below the sample position

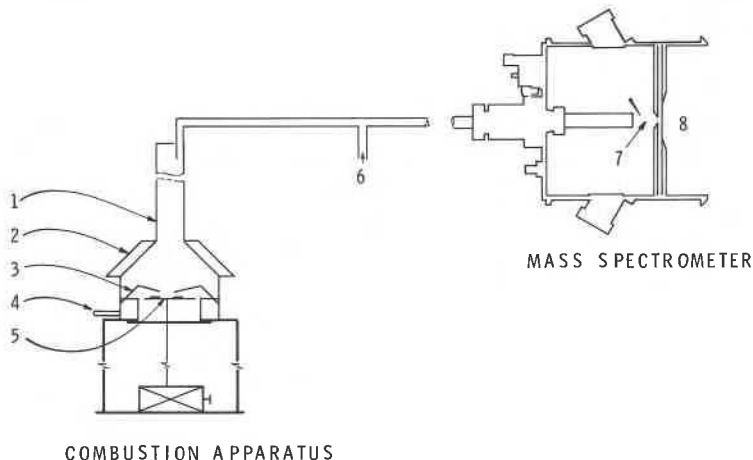


Figure 1 Experimental set-up showing the combustion apparatus and mass spectrometer; (1) cone-shaped quartz tube, (2) electric radiative heater, (3) spark igniter, (4) air inlet, (5) sample holder, (6) make-up air inlet, (7) atmospheric pressure chemical ionization ion source, (8) mass analyzer (10^{-6} torr).

at 9 L/min throughout the combustion and during the mass analysis, allowing examination under conditions close to those expected in many fires. Before testing, the heat flux of the cone heater was measured by a radiometer at the sample position.

Samples were held by two circular stainless steel plates, both 100 mm in diameter and 0.7 mm thick. The upper plate was pierced with a hole 45 mm in diameter, defining the area of the sample exposed to heat. A spark igniter was placed 10 mm centrally above the sample and gave sparks at 1 second intervals for a duration of 1/10 second.

The tandem mass spectrometer used for mass analysis has been described elsewhere [12,13]. Effluent gases from the combustion zone were conducted from near the top of the quartz tube to the spectrometer through a glass capillary (1.8 mm inside diameter, 400 mm long) and a soft corrugated polyethylene pipe (20 mm inside diameter, 400 mm long). The species residence time in the transfer line to the spectrometer was approximately 1 second. In order to obtain a baseline, reference mass spectral data acquisition was started 30 s prior to sample insertion.

SbCl₃ vapour was monitored in argon or air/argon (<5 ppm water) mixtures at ambient temperature using a modification of the apparatus in Figure 1. A T-shaped glass pipe (22 mm inside diameter) holding a small vial of SbCl₃ was connected by a soft corrugated polyethylene pipe (20 mm inside diameter, 400 mm long) to the mass spectrometer. Air or air/argon mixtures forced under the vial at 5L/min, conducted the analyte to the inlet port of the mass spectrometer.

RESULTS AND DISCUSSION

Identification of Gaseous Species from the oxidative pyrolysis of Sb₂O₃-CP70-PS

Polystyrene containing CP70 and Sb₂O₃ (20% Cl by weight and mole ratio of Cl/Sb = 3) was heated under the radiative cone (of total flux 2.11 W/cm² at the sample position) in air and the gas phase was sampled by the APCI MS/MS. Figure 2 shows the mass record of the species evolved after an exposure sufficient to cause intermittent flame flashing but no sustained flame. Several fragments containing chlorine were detected: m/e (mass-charge ratio) = 35 (Cl), 36 (HCl), 68 (HClO₂), 209 (SbOCl₂), 228 (SbCl₃), 244 (SbOCl₃), 245 (SbCl₃(OH)), 262 (SbCl₃(OH)₂), and 263 (SbCl₄). Phenol (m/e = 93), methyl phenol (108) and a cluster of phenol and O₂ (126) were also observed.

Analysis of Vapour Species from SbCl₃

In order to identify those species in Figure 2 produced from the reaction between Sb₂O₃ and the chlorine source, mass spectral analyses were performed of the vapour above SbCl₃ in air at atmospheric pressure and room temperatures. Figure 3 shows the mass spectra of the vapour above SbCl₃ analyzed using the modified apparatus mentioned before. The following species were observed (Figure 3): species at m/e = 35 (Cl), 36 (HCl), 68 (HClO₂), 209 (SbOCl₂), 228 (SbCl₃), 244 (SbOCl₃), 245 (SbCl₃(OH)), 262 (SbCl₃(OH)₂), 263 (SbCl₄).

SbCl₃ would be expected to hydrolyze readily under these conditions to produce SbOCl (m/e = 174), Sb₄O₅Cl₂ or Sb₂O₃, and HCl [3,9]. The presence

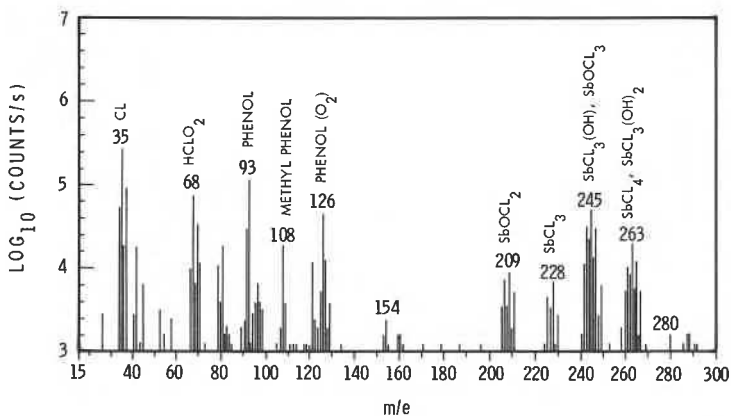


Figure 2 Mass spectrum of species evolved from a polystyrene-CP70-Sb₂O₃ composite (20% Cl, Cl/Sb = 3 (mole)); 2.11 W/cm², in air at atmospheric pressure.

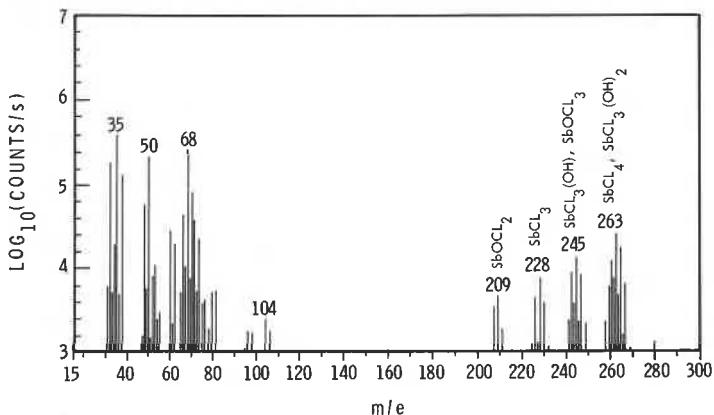
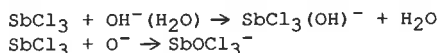


Figure 3 Mass spectra of the vapour species above SbCl₃ at atmospheric pressure and ambient temperature.

of HCl in relatively large amounts in the present work (*m/e* 35, 36, 37) is thus consistent with the hydrolysis of SbCl₃. However, no evidence was found in the present work for the presence of SbOCl, in agreement with observations by Lum [6] on the laser-vaporized species of SbOCl.

Ion-molecule clustering is known to occur in the APCI system [14]. SbCl₃ may thus react with ions such as O⁻, O⁻(H₂O) or OH⁻(H₂O), which are present in the negative mode in the APCI source, to produce antimony oxychlorides:



The radical anion of *m/e* = 68, attributed to HClO₂⁻, may be a cluster of HCl (a hydrolytic product of SbCl₃) and O₂.

The major species resulting from the interaction of Sb_2O_3 and CP70 (Figure 2) are similar to those from $SbCl_3$ (Figure 3), except that in the former case intensities of $SbCl_3(OH)$ ($m/e = 245$) and $SbOCl_3$ ($m/e = 244$) appear higher and $SbCl_3$ ($m/e = 228$) lower. This similarity suggests that the major species of the action of Sb_2O_3 with a chlorine source is $SbCl_3$ under these experimental conditions.

Two narrow-scan-range mass spectra have been taken for the vapour phase above $SbCl_3$; assignments for the molecular ions of $SbOCl_3$ and $SbCl_3(OH)$, $SbCl_3(OH)_2$ and $SbCl_4$ have been made on the basis of calculations of masses for the possible combinations of the isotopes of Sb (^{121}Sb , 57.25%; ^{123}Sb , 42.75%) and Cl (^{35}Cl , 75.53%; ^{37}Cl , 24.47%) [15]. Table 2 shows the comparison of the calculated and experimental results. All the predicted masses were observed.

Table 1 Vapour Phase Masses of $SbCl_3$ - Calculated Probabilities and Analyzed Relative Intensities

Molecular Weight, calculated from the possible combinations of Sb and Cl isotopes				Relative Mass Ratio (%)				
				Calc.		Experimental		
$SbCl_3$	$SbOCl_3$	$SbCl_3(OH)$	$SbCl_3(OH)_2$	$^{35}Cl_3$	$SbCl_3$	$SbOCl_3$	$SbCl_3(OH)$	$SbCl_3(OH)_2$
226	242	243	260	50.71		57.47	62.11	52.78
228	244	245	262	100.00		100.00	100.00	100.00
230	246	247	264	62.25		59.30	58.19	74.80
232	248	249	266	17.72		15.38	14.77	25.12
234	250	251	268	1.71				
$SbCl_4$				$^{35}Cl_4$	$SbCl_4$			
				43.55	52.07			
				100.00	100.00			
				83.87	75.11			
				33.34	26.42			
				6.39	5.00			
				0.48				

It is clear that the relative (referring to the most intense ion in the group) intensities tested for each compound agree well with the calculated probabilities for $SbOCl_3$, $SbCl_3(OH)$, $SbCl_4$ and $SbCl_3(OH)_2$. The intensities of mass clusters of $SbCl_2(OH)$, $SbOCl_2$ and $SbCl_3$ from Figure 3 are in agreement with calculated data. It is therefore concluded that $SbCl_2(OH)$, $SbOCl_2$, $SbCl_3$, $SbCl_3(OH)$, $SbCl_3(OH)_2$ and $SbCl_4$ were present in the vapour phase of $SbCl_3$, as well as in the gas phase of the oxidative pyrolysis of a Sb_2O_3 -CP70 system under atmospheric pressure.

A profile of the major vapour species of $SbCl_3$ evolved over time was obtained in argon, air/argon (1:25), air/argon (1:1). In pure argon (99.99%) the intensity of $SbCl_3$ is, as expected, higher than other oxygen- or hydroxyl-containing antimony chlorinated compounds. However, by increasing the air to argon ratio, the intensity of $SbCl_3$ dropped relative to that of the other species. The results agree with the proposed mechanism of the production of these species.

Effect of Different Halides

Three kinds of halogenated compounds, CP70, TCBPA and TBBPA, were used to compare the action of different halides in combination with Sb_2O_3 . Mass spectra for polystyrene containing three fire retardants (20% halides by weight, halogen/Sb(mole) = 3), exposed to radiation ($3 W/cm^2$) in air are shown in Figure 4. The mass spectra just before ignition (at $3.1 W/cm^2$) for the CP70- Sb_2O_3 combination are quite similar to those in Figure 2 (which were produced from samples heated at $2.1 W/cm^2$). Analysis of the distribution of intensities in the high mass clusters provides strong evidence of the presence of $SbCl_2(OH)$ (208), $SbOCl_2$ (209), $SbCl_3$ (227), $SbOCl_3$ (244), $SbCl_3(OH)$ (245), $SbCl_3(OH)_2$ (262) and $SbCl_4$ (263).

Oxidative pyrolysis of PS containing TCBPA and Sb_2O_3 yielded a gaseous mixture that differed from PS containing CP70 and Sb_2O_3 . The intensities of the masses were in general weaker for TCBPA/ Sb_2O_3 , but two groups of peaks at $m/e = 245$ and 263 suggest the presence of $SbOCl_3$ (244), $SbCl_3(OH)$ (245), $SbCl_3(OH)_2$ (262) and $SbCl_4$ (263) as before. Given the similarity in product distribution between the two chlorine-based fire retardants, it is likely a common intermediate, probably HCl , is involved. The formation of HCl from chlorinated paraffins should be more facile than from chlorinated phenols, and if subsequent reaction with Sb_2O_3 to produce the active fire retardant is not rate limiting, chlorinated paraffins should be more

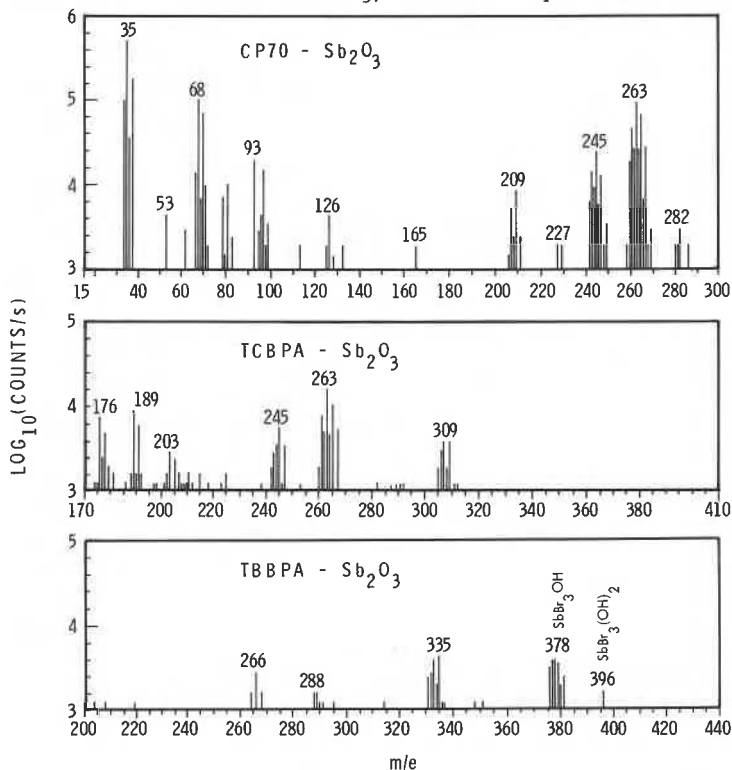


Figure 4 Mass spectra of gaseous species above samples of polystyrene containing halogen fire retardants exposed in air to radiant heat (about $3 W/cm^2$)

effective fire retardants when combined with Sb_2O_3 . Consistent with this hypothesis, the limiting oxygen index (LOI) is higher and the time to ignition is longer for polystyrene treated with CP70/ Sb_2O_3 (Table 3). Other explanations of the LOI performance, including viscosity effects, are also possible.

Table 2
Comparison of Ignition Time and LOI of Different Halogen-Containing Composites

Sample	Ignition by Radiation Cone		LOI
	Heat Flux (W/cm^2)	Time (s)	
PS/CP70/ Sb_2O_3	3.13	60	28.2 (22.0 without Sb_2O_3)
PS/TCBPA/ Sb_2O_3	3.02	31	27.0 (24.3 without Sb_2O_3)
PS/TBBPA/ Sb_2O_3	3.02	No Sustained Flame	30.0 (27.2 without Sb_2O_3)

Shown at the bottom of Figure 4 is the mass spectrum obtained from the gas above a sample of PS/TBBPA/ Sb_2O_3 . The presence of $SbBr_3(OH)$, $SbOBr_3$ and $SbBr_3(OH)_2$ in the volatile products was deduced from the natural abundance of the isotopes involved and the relative intensities of masses in the high mass clusters at $m/e = 378$, 379 and 396, respectively. It seems that the interaction between bromine source and Sb_2O_3 proceeds in a manner similar to the chlorine-containing systems. This finding may be compared with the work of J. Simon [8], who reported that neither Sb_xBr_y nor $SbOBr_x$ compounds were detected.

The Influence of Heat Flux on the Oxidative Pyrolysis of Polystyrene Containing Sb_2O_3 -CP70

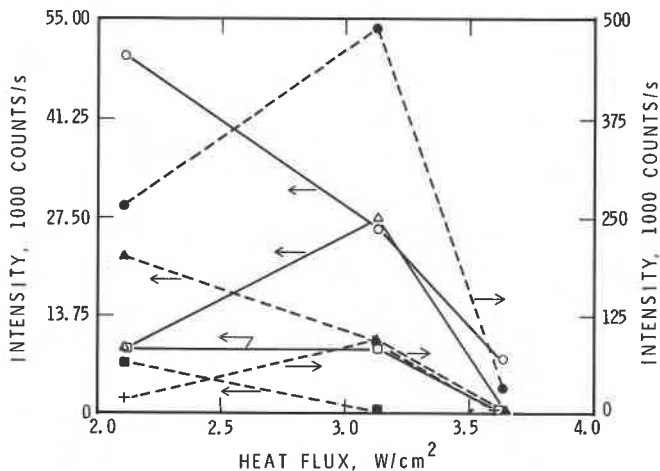


Figure 5 Dependence of intensities of key species in gas phase above polystyrene-CP70- Sb_2O_3 (20% CP, $Sb/Cl = 3$ (mole)) just before ignition as function of radiant heat flux; ○ = $SbCl_3OH$, △ = $SbCl_3(OH)_2$, □ = $SbOCl_2$, ▲ = $SbOCl_3$, ■ = $SbCl_3$, + = $SbCl_4$, ● = ^{35}Cl .

Figure 5 and Table 3 show the comparison of volatile products evolved from PS/CP70/Sb₂O₃ (20% Cl, Cl/Sb = 3) just before ignition, at three different heat fluxes (2.11, 3.13, 3.64 W/cm²).

Table 3 The Effect of Heat Flux on the Species Detected

Mass (m/e)	Species	Relative Intensities* at		
		2.11 (W/cm ²)	3.13 (W/cm ²)	3.64 (W/cm ²)
35	³⁵ Cl	267	493	36
36	H ³⁵ Cl	18	38	3
37	³⁷ Cl	90	181	0
45	H ₂ COOH	6	0	298
59	CH ₃ COOH	0	0	76
93	phenol	117	20	23
108	methyl phenol	19	0	59
121	Sb	12	0	6
126	phenol (O ₂)	47	5	11
207	SbOCl ₂	8	6	0
208	SbCl ₂ (OH)	4	0	0
209	SbOCl ₂	9	9	0
211	SbOCl ₂	5	0	0
226	SbCl ₃	5	0	0
228	SbCl ₃	7	0	0
242	SbOCl ₃	12	7	3
243	SbCl ₃ (OH)	32	15	3
244	SbOCl ₃	22	10	0
245	SbCl ₃ (OH)	50	26	7
246	SbOCl ₃	14	6	0
247	SbCl ₃ (OH)	30	13	4
249	SbCl ₃ (OH)	6	4	0
260	SbCl ₃ (OH) ₂	6	19	0
261	SbCl ₄	10	47	3
262	SbCl ₃ (OH) ₂	9	27	0
263	SbCl ₄	21	97	0
264	SbCl ₃ (OH) ₂	6	27	0
265	SbCl ₄	12	69	0
266	SbCl ₃ (OH) ₂	0	7	0
267	SbCl ₄	6	28	0
269	SbCl ₄	0	3	0

*Intensity/1000 counts/sec

Intensity data presented in Figure 5 for each species are those with the highest intensity in each cluster: Cl (35), SbOCl₂ (209), SbCl₃ (228), SbOCl₃ (244), SbCl₃(OH) (245), SbCl₃(OH)₂ (262) and SbCl₄ (263). When the heat flux was increased from 2.11 to 3.64 W/cm², the relative intensities of all species dropped, except those of Cl, SbCl₄ and SbCl₃(OH)₂ which showed maxima at 3.13 W/cm². The relative intensities of ³⁵Cl and SbCl₄ are much higher (for instance, the intensity of ³⁵Cl at 2.11 W/cm² is 5 to 10 times higher) than those of the other species.

It is of particular interest that SbCl₃, the most commonly detected species in many studies [4-8] of the Sb₂O₃-halogen source system, is the least intense among those identified. The formation of oxygenated species from the admixture of SbCl₃ and air has been described in a previous section. In the present experiment the SbCl₃ produced in situ might also abstract the O· or ·OH existing in flames [16] to form species such as SbOCl₃ or SbCl₃(OH) and SbCl₃(OH)₂. The relative intensities of SbCl₃ (228) in the realistic fire conditions (Figures 2 and 4) are lower than that above SbCl₃ (Figure 3), a finding supporting the abstraction.

Pitts [3] in his review of antimony-halogen synergism assumed that SbCl₃ is the effective free radical trap or chain breaker in the gas phase burning process. The discovery, in the present work, of species like

SbOCl_3 and $\text{SbCl}_3(\text{OH})$ which might result from the direct capture of oxonium and hydroxyl radicals in the flame by SbCl_3 , provide direct evidence to support Pitts' hypothesis.

PRODUCT EVOLUTION PROFILE

A typical single ion profile for the main gaseous species produced from the composite of PS/ Sb_2O_3 /CP70 (20% Cl, Cl/Sb = 3), as it ignited at 3.13 W/cm², is shown in Figure 6.

It is seen that the sequence of evolution of these ions is: phenol (m/e = 93), Cl (35), $\text{SbCl}_3(\text{OH})$ (245), SbCl_4 (263). The oxidative degradation of PS substrate to phenol occurred first well before ignition. HCl (detected as Cl⁻) was then released from the chlorinated paraffin, which subsequently reacted with Sb_2O_3 (in the solid phase) to produce volatile SbCl_3 . SbCl_3 , the actual flame retardant [4, 16] might react with the free radicals O[·] or [·]OH in the fire and result in the formation of SbOCl_3 or $\text{SbCl}_3(\text{OH})$ etc. The SbCl_4 could subsequently have been formed by reaction of $\text{SbCl}_3(\text{OH})$ with HCl.

Hastie [16] has proposed a mechanism of flame inhibition for Sb_2O_3 -halogenated systems. Based on his proposal and on the species detected in

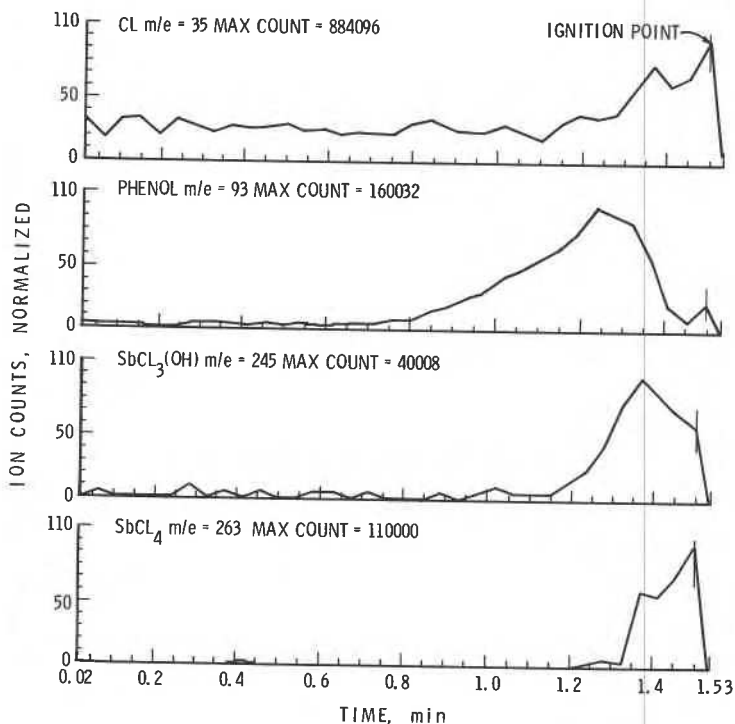
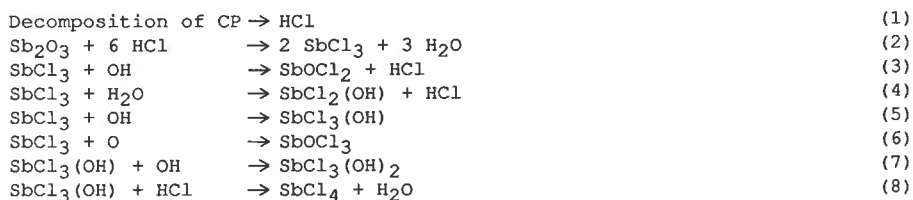


Figure 6 Gaseous species above polystyrene-CP70- Sb_2O_3 (20% Cl, Sb/Cl = 3 (mole)); single ion monitoring of Cl (m/e = 35), $\text{C}_6\text{H}_5\text{OH}$ (m/e = 93), $\text{SbCl}_3(\text{OH})$ (m/e = 245) and SbCl_4 (m/e = 263) as a function of exposure time to 3.13 W/cm radiant flux.

this study, the main reactions involved in the fire retardant effect of the Sb_2O_3 -chlorine system may be summarized as follows.



It is clear that $SbCl_3$ plays a key role in the fire retardant reactions of the Sb_2O_3 -halogen systems. Further work is required to explore the characteristics of the system in real fire combustion and to determine the nature of the synergistic effect of combining Sb and Cl.

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