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Mechanism of Smoke Reduction by Ferrocene in PVC Combustion

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ABSTRACT

This paper reports on results obtained on molded sheets of rigid PVC containing up to 1.5% of ferrocene by weight of polymer. Thermogravimetric and flash pyrolysis in combination with gas chromatographic analysis showed that the introduction of such small quantities of ferrocene considerably increases the amount of low molecular weight volatile materials and simultaneously decreases the amount of benzene generated by the decomposition of the samples. Smoke opacification data revealed that ferrocene plays a noticeable role as a smoke suppressant only at temperatures higher than 500°C and unexpectedly strongly enhances the amount of smoke generated at 400°C. A linear correlation has been found between the amount of benzene evolved from the degradation and the amount of smoke generated by the combustion of the samples at temperature higher than 500°C. Experimental evidence shows that in the presence of HCl generated by the degradation of PVC in air, ferrocene molecules readily oxidize to α-ferric oxide. It is believed that the ferrocene molecule is not itself the active species in the mechanism

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of benzene and smoke suppression, but rather its decomposition products. Finally, other results obtained on numerous salt-containing PVC samples revealed that both benzene and smoke were significantly reduced in the presence of salts and support the idea that the benzene-smoke correlation found in the case of ferrocene additive could largely be generated.

INTRODUCTION

Because of the versatility of PVCand its use in many industrial applications, there is a concern about flamability and smoke evolution from burning PVC. Rigid PVC is inherently flame retardant, so no additional additives are required to improve flame retardancy; however, it generates more smoke and toxic materials on burning than many other polymers and is, therefore, considered less safe from the point of view of fire hazard [1].

Many smoke suppressant additives for rigid PVC have been developed during the last few years on a purely empirical basis. Some of these additives have proved to be rather effective [2].

A few years ago, it was shown [3] that a low concentration of ferrocene-based derivatives both improve flame resistance and suppress visible smoke in rigid PVC. These ferrocene derivatives are now widely used in industrial PVC compounds, because they are rather simple to use, produce significant reduction in the smoke generation during combustion, and have minimum impact on products properties.

However, the mechanistical basis for the activity of these additives still remains unknown.

The general purpose of our present work is to attempt to clarify this mechanistic basis for ferrocene derivatives action on a more fundamental point of view, in the hope that the difficult problem of smoke formation and smoke suppression in burning PVC will be more efficiently controlled in the future.

The background ideas of our investigations lie in the following simple considerations.

It has been believed for a long time that the origin of black smoke from burning organic materials is bound to the formation of polyacetylenic and polycyclic aromatic molecules; yet, the opinion generally differs as to the relative importance of both types of products [4]. However, it is well known that the pyrolysis products of rigid PVC samples are mixtures of essentially benzene-containing volatiles [5].

A first objective is to try to correlate benzene evolution with

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smoke evolution from burning PVC samples, and to see how ferrocene derivatives affect the pyrolysis gas and level of smoke production during combustion.

Preliminary results have already been published elsewhere [6]; this paper expands on the experimental evidence and gives more helpful discussion. Since completion of this work, a paper by Lawson has appeared [7], in which the role of ferrocene as a smoke-retardant additive for vinyl polymers is discussed. Lawson further suggests that in halogenated polymers, the oxidation of ferrocene to ferricenium is an important feature, in that ferricenium is a Lewis acid capable of catalyzing both dehydrochlorination and crosslinking processes.

EXPERIMENTAL

Materials and Sample Preparation

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The experiments were carried out generally on translucent molded PVC sheets with an apparently even dispersion of ferrocene, kindly supplied by B. A. T. Tarare (France). Six such sheets with 1.0 mm thickness and ferrocene contents ranging from 0.0 to 1.5% were used in thermal degradation and smoke opacification investigations.

Weight-average molecular weight $\overline{M}_w$ and molecular weight distribution $(\overline{M}_w/\overline{M}_n)$ of the polymer molecules estimated by GPC in THF at room temperature were respectively 3×10^4 and 1.8. The ratio of the optical densities in the IR at 635 (crystalline, syndiotactic) and 695 cm^{-1} (amorphous, isotactic and syndiotactic) D_{635}/D_{695} was about 1.5. The polymer samples also contained 2% Paraloid KA 20 N (processing agent), 2% Stannofix 843 (stabilization agent), and 2% Loxiol G16 (lubrication agent).

Other experiments were carried out on PVC films containing 1.5% by weight of various inorganic salts. These films were prepared by codissolution of polymer and salts in freshly distilled THF, slow evaporation of the solvent at room temperature, and vacuum drying at 40°C for 24 hr. The residual amount of THF was about 4% by weight in any case.

Ferrocene and inorganic salts were obtained commercially and used without any further purification.

Ferricenium chloride was easily prepared by the action of ferric chloride on ferrocene [8], according to the redox reaction (1).

$$FeCp_2 + FeCl_3 \rightleftharpoons FeCp_2Cl + FeCl_2 \qquad (1)$$

A 1-g portion of ferrocene (5.4×10^{-3} mole) was poured into a solution of 2.0 g of ferric chloride (6.0×10^{-3} mole) in 100 ml 6 N HCl. Ferrocene dissolved readily, and the solution became dark-blue as evidence of ferricenium formation. The ferrous cations were reoxidized into ferric cations by a minimum aqueous peroxide (20 vol), and the ferric cations were then extracted twice with 50 ml of hexane. Ferricenium chloride was recovered by slow evaporation of water; yield was about 80%. Chemical tests on the ferricenium chloride solution in water so obtained could detect only traces of ferrous and ferric cations, while UV spectrophotometry showed a strong absorption band centered at 610 nm [9].

Apparatus and Analytical Methods

Thermogravimetric analysis (TGA), in combination with gas chromatography (GC) was used to determine quantitatively the volatiles evolved during thermal degradation of rigid PVC samples. The apparatus has already been described elsewhere [10]. Experiments were carried out on 200-mg samples under nitrogen flow (1.8 liter/hr) and a furnace heating rate of 1 or 2°C/min. Separation of the volatiles was achieved isothermally by using a 3-ft column packed with Porapack Q. Low molecular weight products were analyzed at an oven temperature 160°C and gas carrier pressure of 2.0 kg/cm^2. Benzene evolution from the same samples, was investigated in subsequent experiments by using an oven temperature of 200°C and a gas carrier pressure of 2.2 kg/cm^2. The time interval between two successive automatic chromatographic analysis was 4.0 min.

Flash pyrolysis chromatography was realized by means of a Girdel flash pyrolyzer connected to an IGC 15 Intersmat gas chromatograph. Ferrocene-containing samples were dissolved in THF and 5 μl of solution (3%) was used in each experiment. Pyrolysis time was 40 sec.

The Limiting Oxygen Index (LOI) measurements were performed with a Stanton Redcroft Apparatus on 1.0 × 6.5 × 150 mm strips held vertically and lighted at the top with a butane burner. In another series of experiments, the test specimen were carefully wrapped in stainless steel gauze before being ignited and the charred residues weighed after complete burning of the sample.

For smoke density measurements, the samples (200 mg molded sheets) were placed in quartz containers in a horizontal static furnace (80 cm long, 4 cm diameter) with low temperature gradient (Heraeus). The containers were rapidly introduced to the middle of the furnace by using a magnetic device. The smoke evolution from burning samples

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was followed by optical measurement of the obscuration of a light beam across a measured path between a light source and a photocell receiver. The apparatus was designed by us, with reference to the DIN 53436 and DIN 53437 normalization project [11]. A Stanton Redcroft light emitter and a photocell receiver equipped with removable optical filters were firmly fixed at the extremities of a cylindrical stainless steel tube 20 cm long and 4 cm in inner diameter. Besides the main tubular inlet and outlet for smoke circulation, two extra air inlets (flow rate 15 liter/hr) located at both ends of the cylindrical tube were provided to prevent any soot redeposition on the light emitter and photocell receiver window, which would alter the light transmission. The smoke density chamber was connected to the furnace through a 2-liter flask to ensure good homogeneity of smoke. The attenuation of the light beam was analyzed by the Stanton Redcroft module, recorded as percentage obscuration A versus time by a graphical recorder and subsequently transformed into optical density D by the well-known formula (2):

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$$D = \log [100/(100 - A)] \tag{2}$$

The amount of smoke F was calculated according to

$$F = (S/U)p \text{ (dec} \times \text{min/g)} \tag{3}$$

where S/U is the area of the surface under the opacification curve versus time (dec × min) and p is the weight of the polymer sample (g).

The opacification rates V were obtained by Eq. (4):

$$V = D_{max}/pT_{max} \text{ (dec/min} \times \text{g)} \tag{4}$$

where D_{max} is the maximum optical density (dec) and T_{max} is the time interval to observe the maximum optical density (min).

The experiments were carried out under air flow of 300 liter/hr at temperatures ranging from 300 to 700°C. The air flow on polymer weight ratios were held constant throughout the whole temperature range to allow more significant comparison of experimental results [11].

Other experiments on salt-containing films were carried out at 600°C under the same conditions. Each measurement was repeated three times (and up to six times at 400° C). The accuracy of measurements was within 10%.

The thermal stability of ferrocene molecules in the presence of HCl was tested in a quartz tube equipped with a gas inlet at the bottom and placed in a vertical Heraeus furnace. The height and inner diameter of the quartz tube were 80 and 8 cm, respectively. Experiments were made at 200 and 500° C under HCl and HCl/air (1/1) mixtures. A 1-g portion of ferrocene was used in each experiment, and a gas flow rate of 50 liter/hr was arbitrarily chosen.

RESULTS

TGA - GC Experiments

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Figure 1 shows the TGA traces in N_2 for two molded sheets containing 0.0 and 1.5% of ferrocene. From the first part of the curves (up to 400° C), it can be seen that the introduction of 1.5% ferrocene enhances the rate of dehydrochlorination and reduces the temperature of 50% loss of the initial weight by about 20° C. Moreover, the onset of initial weight loss measured at the leveling off is slightly reduced. In the second parts of the curves (temperature higher than 400° C) the difference becomes vanishingly small as the temperature rises and the curves are roughly superimposable within experimental error at the highest temperatures. Similar TGA traces have been obtained under air flow and will not be discussed here.

Our TGA results are in good agreement with those recently reported by Lawson [7], although not in complete agreement as far as the high temperature parts of the curves are concerned, probably because our heating rate is ten times slower.

The rates of benzene and low molecular weight volatiles production as a function of temperature and ferrocene content of the samples are illustrated in Figs. 2 and 3. From Fig. 2, it can be seen that the maximum rate is observed around 320° C for benzene and around 460° C for the four major volatiles. The relative amounts of the low molecular weight products are nearly independent of the ferrocene content of the samples, but the total amounts of these low molecular weight products increase considerably with increasing ferrocene content, while the amount of benzene simultaneously decreases. These results and others concerning the weight loss after the first step (below 400° C) and the temperature of maximum rate for benzene production are gathered in Table 1.

Ferrocene induces a noticeable decrease in the temperature for

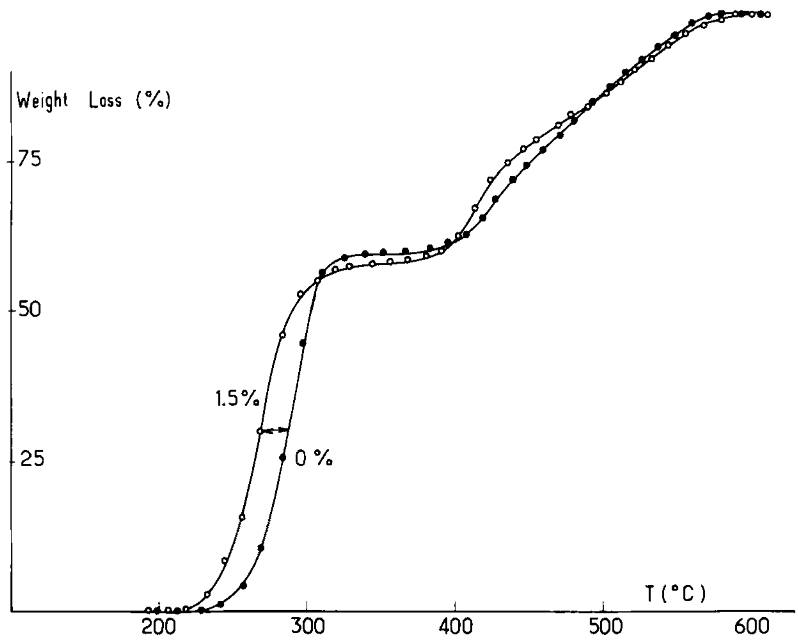

FIG. 1. TGA traces (2°C/min under nitrogen) for sheets of rigid PVC (150 mg) containing (●) 0 and (○) 1.5% of ferrocene.

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maximum rate for benzene evolution. This is to be connected with the catalytic action on dehydrochlorination process reported above, and further supports the idea [12] that benzene cyclization from growing polyenic sequences instantaneously follows dehydrochlorination. We note here that, contrary to what is found for benzene evolution, the temperature for maximum rate for low molecular weight volatiles is unaffected by the ferrocene content of the sample under investigation.

On the other hand, the weight percentage of initial weight loss decreases from 60 to 57% as a function of ferrocene content. This may be only partially explained by the parallel reduction of the benzene quantities from 2.5 to 1.0%. As the residual discrepancy definitely lies outside experimental errors, it may be supposed that the dehydrochlorination becomes less complete in the presence of ferrocene.

From Table 1, it further appears that most of the changes are achieved for 0.5% ferrocene content. The experimental data for initial

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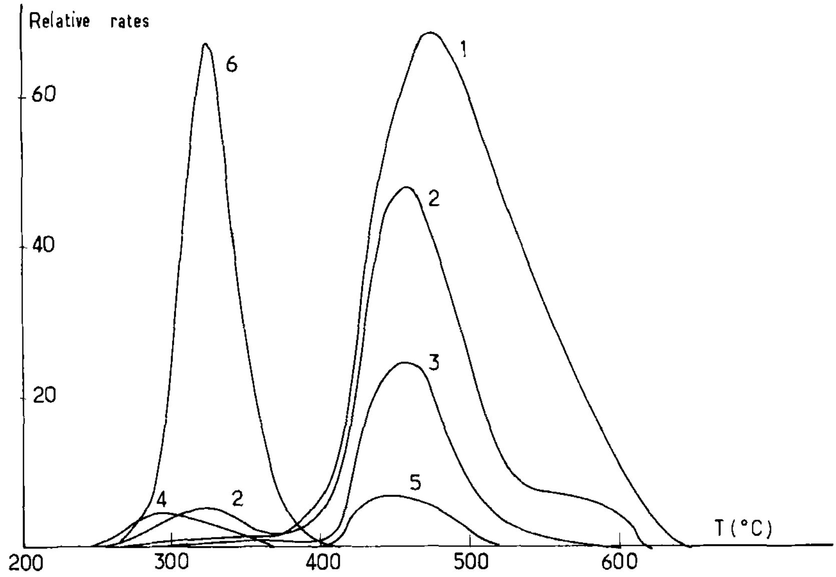

FIG. 2. Relative rates (arbitrary units) of evolution of benzene and the volatiles as a function of temperature (heating rate 2°C/min under nitrogen, 1.8 liter/hr) for a sample of rigid PVC (150 mg) containing 0.8% of ferrocene: (1) methane; (2) ethylene; (3) propylene; (4) propane; (5) mixture of butene isomers; (6) benzene.

weight loss and amount of benzene are almost identical under N_2 or air flow, but the amounts of volatiles are much higher under N_2 flow. Similar results have already been published by Wooley [5]. The difference between the temperatures for maximum rate for benzene generation under N_2 and air flow is mainly due to the difference in the heating rates for the two series of experiments (1 and 2°C/min, respectively).

In another series of experiments with varying ferrocene content, higher molecular weight derivatives were condensed by a cold ring system placed at the upper side of the thermogravimetric device and then recovered by dissolution in chloroform. The total amount of the so-condensed derivatives was almost the same (3.5 ± 0.2% of the initial polymer weight), independent of the ferrocene content of the sample. IR spectroscopy of their films were identical and allowed the identification of unsaturated and aromatic structures. Liquid

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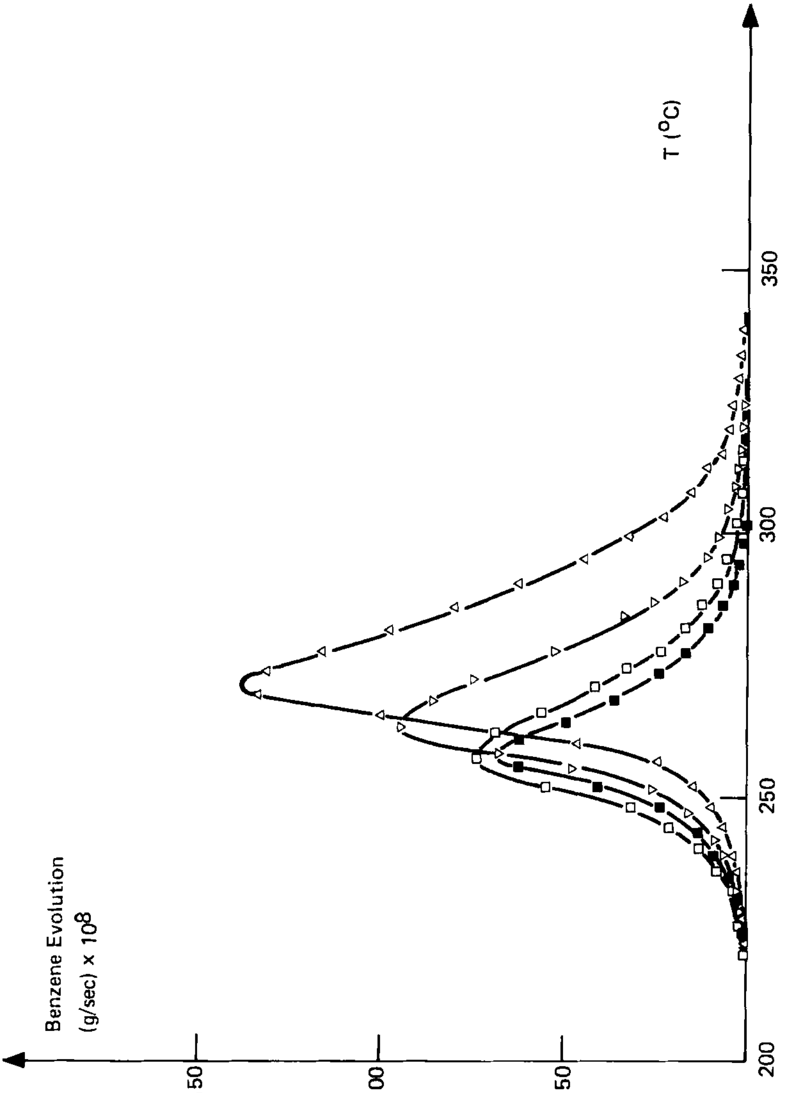

FIG. 3. Rate of benzene evolution as a function of temperature for several ferrocene-containing PVC samples (heating rate 1°C/min under nitrogen flow, 1.8 liter/hr): (◁) 0.0%; (▷) 0.1%; (□) 0.2%; (■) 0.8%.

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TABLE 1. TGA-GC Results for Initial Weight Loss, Amounts of Benzene and Volatiles and Temperature for Maximum Rate of Benzene Generation (T_{max}) as a Function of Ferrocene Content of the Sample[a]

Ferrocene (%) by weight)	First weight loss (% by weight)		Amounts of benzene (% by weight)		Volatiles (arbitrary units)		T_{max} (C_6H_6) (°C)	
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
0.0	60.0	60.0	2.35	2.45	80	33	269	329
0.1	58.8	59.2	1.50	1.35	95	37	264	324
0.2	58.3	58.3	1.20	1.10	97	34	259	316
0.4	57.0	57.2	1.08	0.78	119	46	258	317
0.8	56.7	56.5	0.92	0.73	142	55	256	319
1.5	56.4	56.8	0.71	0.56	138	61	259	317

[a] Heating rate in N_2, 1°C/min; in air 2°C/min.

chromatography in THF at room temperature revealed the existence of four distinct products on a wide molecular weight distribution background with an average molecular weight of 200 (Fig. 4). The four products are virtually the same, independent of the ferrocene content of the sample but, as suggested by the right sides of the curves, it seems that the introduction of ferrocene gives higher proportions of higher molecular weight products.

Flash Pyrolysis

Some results concerning benzene evolution are illustrated in Fig. 5. Again, the amounts of generated benzene regularly decrease down to a limiting value as ferrocene content rises (curve a). However, the absolute quantities are about half those reported in thermogravimetric section (Table 1). This apparent discrepancy can be explained by the great difference in the heating rates used in both experimental techniques (3 to 4 power to ten). In fact, it has been already shown [13] that the amount of benzene generated depends on molecular characteristics of the macromolecules and very likely is influenced by experimental heating rate for degradation.

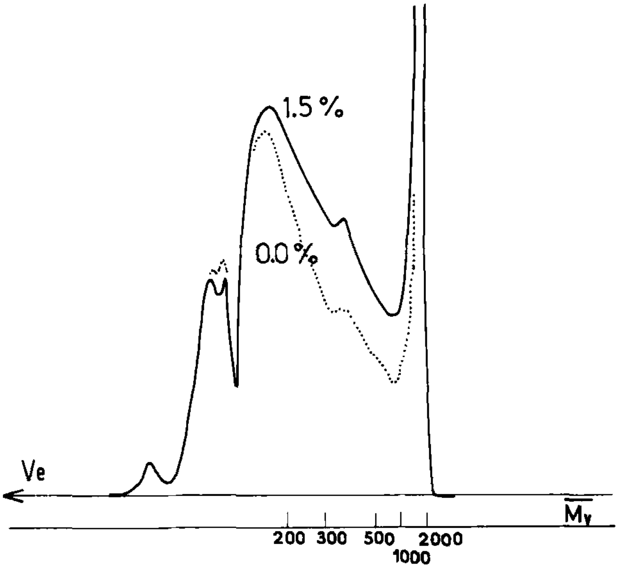

FIG. 4. Liquid chromatograms (refractometric index traces) of the cold-ring condensates in TGA experiments: (• • •) samples without ferrocene; (—) sample with 1.5% ferrocene.

On the same figure, plots of the amounts of benzene versus flash pyrolysis temperature are reported for one PVC sample without ferrocene (curve b) and another PVC sample containing 0.1% of ferrocene (curve c). In both cases, the amounts of benzene increase rapidly with temperature; on the other hand, evidence is found for the existence of a critical lower temperature for benzene evolution. Another interesting feature lies in the fact that the introduction of 0.1% ferrocene causes an increase in the critical temperature from 375°C (0% ferrocene) to 550°C (0.1% ferrocene).

Smoke Density

While at 280°C, only dehydrochlorination of the macromolecules occurs, polymer samples begin to smoke at 300°C. Up to 500°C, samples are consumed without flame (smoldering mode of combustion),

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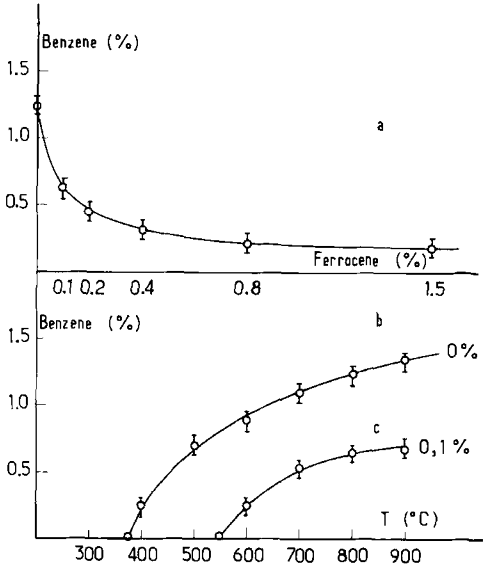

FIG. 5. Flash pyrolysis of PVC containing ferrocene: (a) benzene production (% of the weight loss) as a function of the ferrocene contents at 900° C and as a function of the nominal pyrolysis temperature for samples (b) without ferrocene (c) with 0.5% ferrocene.

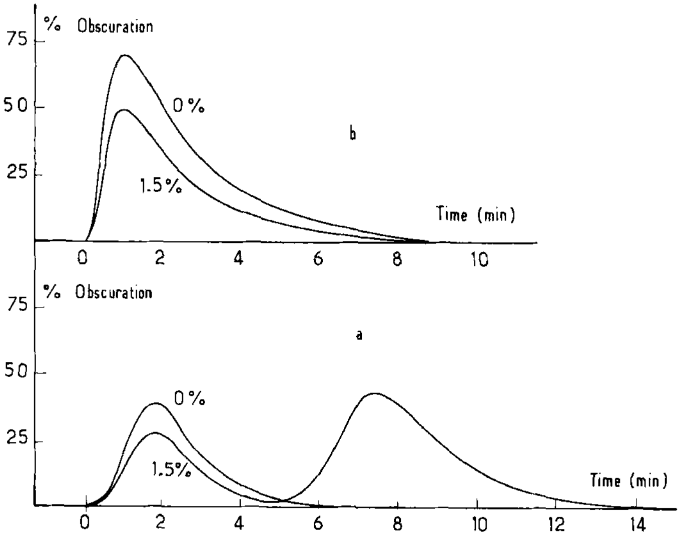

FIG. 6. Obscuration curves as a function of the time for samples without ferrocene or containing 1.5% ferrocene: (a) at 400° C or (b) at 600° C.

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TABLE 2. Smoke Generation at 500, 600, and 700°C[a]

Ferrocene (%)	T = 700°C			T = 600°C			T = 500°C		
	F	V	D_{max}	F	V	D_{max}	F	V	D_{max}
0.0	5.95	16.5	1.45	7.60	9.6	1.45	6.85	5.1	1.25
0.1	4.60	13.5	1.20	5.70	7.0	1.25	6.50	2.7	0.92
0.2	4.45	12.0	1.10	4.75	7.2	1.15	6.40	2.8	0.92
0.4	3.85	11.5	1.05	4.05	6.3	1.00	6.10	2.4	0.85
0.8	3.45	10.5	0.85	4.05	6.5	0.95	5.50	2.1	0.88
1.5	2.75	8.5	0.70	3.65	5.8	0.90	5.55	1.9	0.80
	T_{max} = 0.42 ± 0.05			T_{max} = 0.8 ± 0.1			T_{max} = 1.6 ± 0.2		

[a] Amount of smoke (F) expressed in dec min/g and opacification rates (V) in dec/min g; maximum optical densities (D_{max}) expressed in decades, and mean time intervals to observe the maximum optical densities (T_{max}) are in minutes.

while at 600 and 700°C, they erupt in bright flame (flaming mode of combustion). Smoke evolution curves always exhibit one single sharp opacification maximum, except at 400°C, where two distinct maxima are found for the ferrocene-containing samples. This is illustrated in Fig. 6, where the time variation of smoke density for two PVC samples at the temperatures of 400 and 600°C are shown. The second smoke opacification observed at 400°C is only poorly reproducible.

Complete experimental data concerning smoke quantities and opacification rates are presented in Tables 2 and 3, and some results are further illustrated in Fig. 7. It is clear that, except at 400°C, the introduction of such small amounts of ferrocene as 0.5% by weight of polymer considerably decreases smoke quantities as well as opacification rates from burning PVC samples. At 400°C, however, the decrease in the initial smoke evolution is largely overcompensated by the increase in the second smoke evolution and, as a result, ferrocene containing PVC samples give more smoke when the ferrocene content rises.

Some experimental data as a function of temperature are plotted on

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TABLE 3. Smoke Generation (F) and Charred Residues (CR) at 300 and 400°C[a]

	T = 400°C						T = 300°C			
Ferrocene (%)	F(T)	F(1)	F(2)	V(1)	D_{max} (1)	CR (%)	F	V	D_{max}	CR (%)
0.0	3.25	3.25	0	0.8	0.30	26	1.45	0.18	0.15	38.5
0.1	3.00	2.20	0.8	0.65	0.25	21.5	1.05	0.16	0.12	39.5
0.2	3.50	1.90	1.5	0.61	0.22	20.5	0.95	0.14	0.10	41
0.4	4.50	1.60	2.9	0.55	0.21	16	0.85	0.15	0.10	40.5
0.8	6.80	1.40	4.4	0.49	0.19	10.5	0.95	0.17	0.10	41
1.5	7.40	1.55	5.9	0.46	0.18	9	0.60	0.14	0.08	42
	T_{max} (1) = 2.0 ± 0.3; T_{max} (2) = 7.0 ± 0.5						T_{max} = 3.6 ± 0.4			

[a] At 400°C, total, first, and second smoke generations are indicated by F(T), F(1), and F(2), respectively. Charred residues (CR) are expressed as weight percentages of investigated samples.

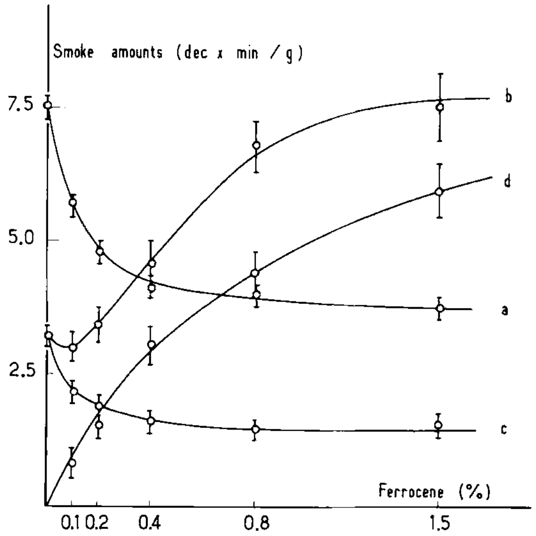

FIG. 7. Amount of smoke as a function of ferrocene content of the samples: (a) smoke generation at 600° C; (b, c, d) total, first, and second smoke generation, respectively, at 400° C.

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a semilogarithmic scale in Fig. 8 as is usually done [11]. From this figure, it can be seen that the introduction of 1.5% ferrocene decreases the temperature of maximum smoke quantity from 600° C (pure PVC) to about 400° C. No such an observation can be reached as far as the opacification rate is concerned. We further note that the results obtained for pure PVC are in fairly good agreement with results already published in the literature [11]; on the other hand, the complex shape of the opacification curves observed at 400° C for the ferrocene containing samples is not clear yet.

LOI and Charred Residues

LOI values and percentages of charred residues observed in LOI experimental conditions are plotted in Fig. 9 as a function of ferrocene content. LOI values increase by 40% when ferrocene content rises to 1.5%. Analogous results have already been published [3, 7]. On the other hand, the weight of charred residues is decreased by

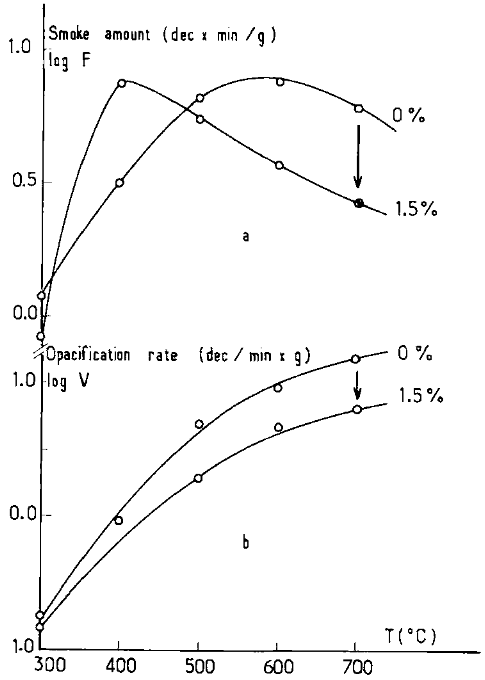

FIG. 8. Plots of (a) amount of smoke and (b) opacification rates as a function of the temperature for PVC samples without ferrocene or containing 1.5% ferrocene (logarithmic scales).

85%. This is rather unexpected and contrary to the previous results of Kracklauer and Sparkes [3], who claimed that predominant function of ferrocene is to promote char formation.

In connection with this, we systematically weighed the charred residues on the PVC samples used in smoke opacification measurements as a function of temperature and ferrocene content. Some results are gathered in Table 3. We must emphasize that we have always found a noticeable decrease in percentage of charred residues as a function of ferrocene content at any temperature above 300° C. Yet at 300° C, a small increase in char residues was observed. At 400° C, the second smoke generation involves a new important decrease in char residues, while at 600° C and 700° C, the char percentages are fairly small. Other experiments carried out under very low air flow (30 liter/hr instead of 300 liter/hr) gave similar results.

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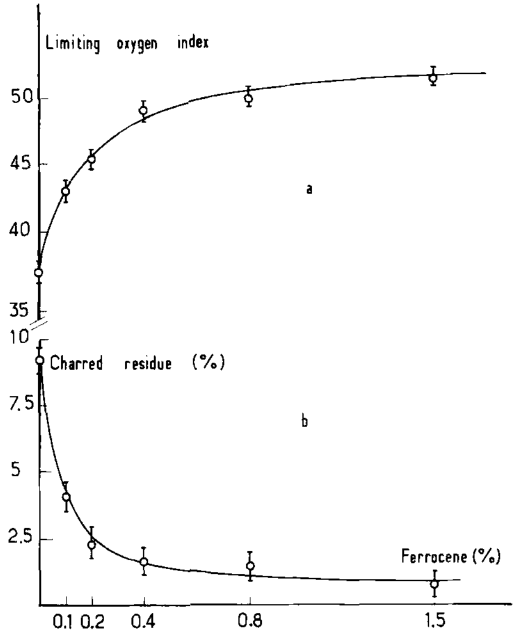

FIG. 9. Plots of (a) limiting oxygen index (LOI) and (b) amount of charred residue (weight percent) as a function of the ferrocene content of PVC samples.

Our experimental data lead us to the conclusion that char promotion by ferrocene should be accepted in a more restrictive way. Experimental conditions for combusion appear to be an important feature in the explanation of the observed discrepancy.

DISCUSSION

Our experimental results show that the introduction of very small amounts of ferrocene strongly modifies the composition of volatile mixtures evolved during thermal degradation and considerably decreases the smoke and the opacification rate during PVC combustion in the temperature range observed in real fires.

As quantities of benzene and smoke generated similarly depend on ferrocene content of the samples, it is to be expected that a linear

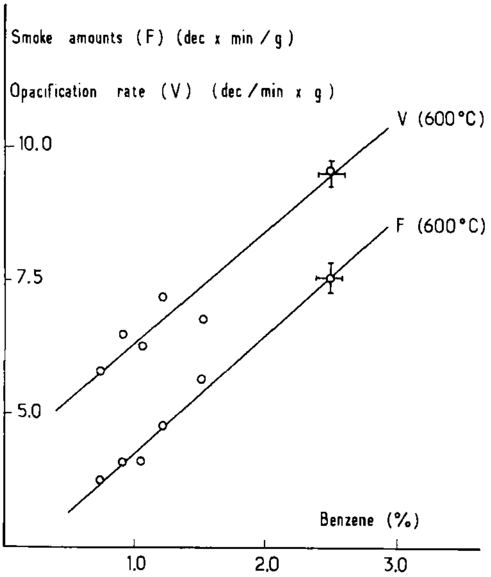

FIG. 10. Plots of amount of smoke (F) and opacification rate (V) at 600° C as a function of the amount of benzene observed in TGA-GC experiments.

correlation could be drawn between them. This is illustrated in Fig. 10, where amount of smoke and opacification rates are plotted versus amount of benzene for the investigated samples (TGA-GC). Similar linear plots could be obtained by use of other pairs of experimental parameters, i.e., amounts of benzene measured by flash pyrolysis and smoke opacification data at any temperature except 400° C.

It seemed important to us to verify if such a benzene-smoke correlation could also be expected for other smoke-suppressant additives. This is shown in Table 4, where experimental data concerning benzene and smoke amounts generated by salt-containing films are gathered together. It is obvious that all the investigated salts simultaneously induce important decreases in amounts of benzene and smoke. Iron derivatives are more efficient as benzene-suppressants, while cupric nitrate [2] appears to be a powerful benzene- and smoke-suppressant additive for PVC.

We now turn to the mechanistic basis for the action of ferrocene as a benzene- and smoke-suppressant additive for PVC.

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TABLE 4. Amounts of Benzene and Smoke Generated from Salt-Containing PVC Films[a]

Salt (1.5% by weight)	Benzene (weight %)	Smoke (conventional units)
-	2.50	5.15
Ferrocene	0.27	2.45
Ferricenium chloride	0.21	2.55
$FeCl_3$	0.25	2.75
$FeCl_2$	0.08	2.50
$ZnCl_2$	1.10	2.50
$SnCl_2$	1.30	2.75
$AlCl_3$	0.60	2.35
$Cu(NO_3)_2$	0.45	2.15

[a] Amount of benzene obtained by TGA apparatus connected to gas chromatographic system, and expressed in percent by weight of investigated samples; amount of smoke obtained at 600°C under 300 liter/hr air flow, expressed in conventional units.

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It has been shown that formation of benzene from heated PVC proceeds through an intramolecular mechanism [14] that could result from thermal activation of π electrons of polyenic sequences formed by thermal dehydrochlorination [15].

Insofar as the above hypothesis is valid, one might think that ferrocene molecules could play a quenching role [16] and cause a physical transfer of the triplet-state energy of the π electrons of the growing polyenic sequences, but the question of the thermal stability of ferrocene molecules in the presence of HCl generated by polymeric degradation immediately arise.

Experiments to test this stability were carried out in our laboratories; they showed that solid ferrocene completely reacts with HCl (gas phase) within a few minutes, even at temperatures as low as 200°C. Mössbauer spectroscopy and chemical tests on the reaction products at 200 and 500°C (under pure HCl flow) revealed the presence of important amounts of ferrous chloride and traces of ferric chlorride (a few percents). Traces of ferricenium chloride (a few parts of 1%) were identified by the light blue coloration of water solutions.

On the other hand, we have observed that the replacement of the ferrocene content of the samples by the same ferricenium chloride contents enhances the rate of dehydrochlorination process identically and affects the generated benzene and smoke amounts (Table 4). The above experimental data are not in disagreement with Lawson's statement [7] that the presence of ferricenium chloride is important in that it is a Lewis acid able to catalyze both dehydrochlorination and crosslinking processes.

Moreover, it is well known that iron cations are excellent catalysts for crosslinking of PVC [18]. It is thus quite possible that the major action of iron cations generated by degradation of ferrocene involves noticeable decreases of the length and the mobility of the growing polyenic sequences. As a result, benzene formation from these growing sequences would be strongly hindered. The above mechanism could therefore be related to the role of the HCl-$ZnCl_2$ system that has already been extensively investigated in our laboratories [19] and induces oligomerization of hexadiene molecules as well as PVC crosslinking.

In order to get more helpful insight on the crosslinking capability of ferrocene and cations generated by degradation of ferrocene, we made preliminary Brabender experiments on salt-containing PVC at 180°C. They revealed that consistency versus plastograph time for identical amount of ferrocene and ferrous chloride derivatives are strikingly similar. However, introduction of ferric chloride in the same amounts does not seem to induce significant crosslinking but rather causes sudden degradation of polymer chains, as evidenced by a catastrophic decrease in the sample consistency.

Another possible mechanism for iron cation intervention on benzene evolution is through a Friedel-Crafts type of catalytic action. In this case, the benzene molecules would be chemically bound on macromolecular main chains giving indane structures. It has been shown that this kind of reaction is quite possible, even at much lower temperatures [20], but, up to now, no clear evidence for such a mechanism during PVC degradation or combustion has been found in our laboratories (for instance, the presence of indane structures).

However, for thermal treatment of ferrocene at 500°C under HCl/air flow (1/1 mixture), only traces of ferrocene and ferric chloride could be detected on the reaction products, and Mössbauer spectroscopy clearly identified α-Fe_2O_3 ($>$ 90%) and γ-$FeOOH$ ($<$ 10%). The presence of ferricenium chloride was not suspected in this case.

The same results as under HCl/air flow were obtained on charred residues left by combustion of the ferrocene-containing samples at 500°C. The total iron percentages recovered by complete mineralization of the chars left by combustion was only 25% of the theoretical

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value calculated from the ferrocene content of the investigated samples. The remaining 75% is thought to be found in the generated smoke. Similar results have already been reported [2, 7].

Thus, in the presence of HCl and air, oxidation of ferrocene molecules readily occurs up to the final α-Fe_2O_3 state. This largely supports the opinion that, during degradation or combustion in air, the ferrocene molecule itself is not the active species. Rather, it is to be expected that iron cations and ferric oxides are the effective promotors in benzene- and smoke-suppressant action exhibited by ferrocene.

The presence of ferric oxide is important, in that it is a powerful smoke-suppressant for PVC. Furthermore, it has been shown [17] that the introduction of small amounts of ferric oxide induces a strong decrease in aromatic structures and favors the low molecular weight volatiles generated during PVC degradation in air. The action of ferric oxide is thus fairly similar to that observed for ferrocene in this study. With the above complements it is possible to suggest a more complete interpretation of the effect of ferrocene upon the production of smoke. At low temperature (300° C), only the first step of the degradation is observed, which corresponds mostly to the production of HCl and benzene. In the bulk of the PVC sample, a furious dehydrochlorination takes place which probably excludes the diffusion of oxygen in the inner part of the sample. Thus, ferrocene is mostly transformed to ferrous chloride, which causes cross-linking of the polymer and then decreases the amount of benzene produced, with a small amount of ferric chloride which is a catalyst for dehydrochlorination. There is only one smoke production step mainly connected with the reduced benzene production. The charred residue is not very markedly affected by the amount of ferrocene and corresponds quite well to the residue after the first step of the pyrolysis (Table 3 and Fig. 1). At higher temperature the same situation prevails in a first step, but there is also a slow second step of decomposition associated with the production of some aliphatic hydrocarbons and with a rather important weight loss. The combustion of the evolved products might be at the origin of the second smoke wave observed at 400° C. At that temperature slow combustion of the polymer is clearly observed and ferrocene begins to give α-Fe_2O_3, which is a powerful oxidation catalyst. The formation of α-Fe_2O_3 is more rapid as the temperature increases; moreover, the two steps of decomposition are less separated, so that only one smoke wave is observed. The reduction of the total amount of smoke is mainly caused by the catalytic oxidation, which is shown by a large increase of the temperature inside the sample (for instance, the nominal temperature of 600° C rises to 750° C in the presence of 1.5% ferrocene);

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simultaneously the amount of charred residue decreases very much even at 400°C (Table 3).

CONCLUSION

This paper shows that the introduction of very small amounts of ferrocene strongly modifies the composition of volatile mixtures generated during thermal degradation and considerably decreases the conventionally measured amount of smoke and opacification rate during PVC combustion in the temperature range usually observed in real fires. Furthermore, a linear correlation between benzene evolution, smoke formation, and opacification rate has been found in the same temperature range. It is expected that similar correlation could be drawn for other smoke-suppressant additives for PVC.

In the presence of HCl generated by PVC degradation in air, oxidation of ferrocene molecules readily occurs up to the final α-Fe_2O_3 state. Further investigation is needed to ascertain the exact mechanism of ferrocene action as a benzene- and smoke-suppressant. It seems established that the mechanism proceeds through iron cations and ferric oxides generated from the degradation of ferrocene molecules.

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