Investigation of the Mechanistic Basis for Ferrocene Activity During the Combustion of Vinyl Polymers

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Synopsis

The influence of ferrocene on the flammability and smoke generation behavior and thermal characteristics of poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA) was examined in order to understand the basis of ferrocene's activity as a flame-retardant and smoke-suppressant additive. Ferrocene increased char formation in PVC by 20–60% while increasing the limiting oxygen index (*O.I.*) by 15–19%. Little char was found either with or without ferrocene in PVA, which had little improvement in *O.I.* Visible smoke was significantly decreased by ferrocene in PVA and in PVC of low to moderate molecular weight, but was unchanged in high molecular weight PVC. *O.I.* of PVC appeared to vary with molecular weight of the polymer. Thermogravimetric analyses and thermal degradation experiments showed that ferrocene promotes early weight loss and crosslinking in PVC. This effect is coincidental with the formation of ferricenium cation, which was identified by its visible spectrum and which may be a possible catalyst. Smoke inhibition of PVA by ferrocene occurs predominantly through gas-phase processes, while in PVC evidence and analogy for activity in both the gas phase and condensed phase are found.

INTRODUCTION

A variety of additives function as flame retardants in poly(vinyl chloride) (PVC) plastics.[1] Whereas many of these additives simultaneously increase visible smoke density during burning, a low concentration of dicyclopentadienyl iron, ferrocene (I),
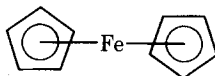
I

or a ferrocene-based additive both improves flame resistance and suppresses visible smoke in rigid PVC.[2]

The combination of smoke and flame retardation from ferrocene is of great interest in view of increased concern over polymer smoke generation characteristics. Ferrocene has been known for some time as a smoke-suppressant additive for fuels.[3] However, the flame processes through which this smoke suppression is achieved are thought to be contradictory to the inhibition of flame propagation.[4] The use of ferrocene as a UV-sensitive crosslinker in PVC has also been studied.[5] In that case, it was concluded that ferrocene was incorporated into the polymer structure, to function as a dehydrochlorination catalyst upon UV curing.

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In the work reported here, the influence of ferrocene on the flammability and smoke properties and thermal behavior of PVC and poly(vinyl alcohol) was studied in order to establish the basis of ferrocene's smoke- and flame-retardant behavior.

EXPERIMENTAL

Materials and Sample Preparation

The polymers examined included commercial, suspension-polymerized PVC resins (Firestone Plastics Co., Pottstown, Pa.), with inherent viscosities of 0.52, 0.97, and 1.32, determined as 0.2% solution in cyclohexanone, 30°C. Gel permeation chromatography at room temperature in THF using Waters Associates Model 200 GPC (Styragel, elution rate 1 ml/min) showed $\bar{M}_w/\bar{M}_n$ for the three resins of $4.06 \times 10^4/1.37 \times 10^4 = 2.96$, $11.03 \times 10^4/4.26 \times 10^4 = 2.59$, and $16.51 \times 10^4/6.73 \times 10^4 = 2.45$, respectively. For processing, the resins were combined with 3.75% by weight of a stabilizer, dibutyltin bis(mercaptolaurate), 2% by weight calcium stearate as an internal lubricant, and desired levels of ferrocene on a plastics mill at 163°C. Sheets of desired thickness for flammability or smoke evaluations were then obtained by pressing at 170°C and 4.9 MPa for 5 min. A poly(vinyl alcohol) resin, du Pont 71-30-G, was also studied. This was mixed with ferrocene by evaporating a solution of ferrocene/methylene chloride from the powder. Translucent, molded sheets with apparently even dispersion of ferrocene were prepared by pressing the powder at 110°C and 36.6 MPa for 25 min. Ferrocene was obtained commercially and purified by repeated vacuum sublimation to give material of mp 175–176°C.

For purification, the PVC resins were dissolved in a large volume of THF and precipitated by slow addition of the solution to isopropyl alcohol. This was generally repeated, and the isolated polymers were dried by vacuum filtration, then heated at 50°C/1.33 kPa for a day. o-Dichlorobenzene was purified by vacuum distillation from calcium chloride onto activated type 4A molecular sieves to remove excess moisture.

Analytical and Test Methods

Limiting oxygen index (O.I.) measurements were made with a General Electric Oxygen Indexer on $2.5 \times 6.4 \times 152$ mm strips held vertically and lighted with a propane torch at the top. The oxygen index is defined as follows:

$$O.I. = 100 \times \frac{[O_2]_{vol}}{[O_2]_{vol} + [N_2]_{vol}}$$

in a mixture of oxygen and nitrogen at the minimum point of sustained combustion.[6a] Smoke density measurements were made with an Aminco-NBS smoke density chamber. This consists of a closed, 0.5-m^3 box containing heater and pilot flame sources, specimen support, light source, and a photomultiplier/microphotometer to measure attenuation of light. The smoke in-

tensity is measured as specific optical density, the maximum corresponding to

$$D_{mc} = 132 \log \frac{T_c}{T_m}.$$

where T_m is the % transmittance at maximum smoke intensity and T_c is % transmittance upon exhausting the chamber after combustion. Specimens to be burned are cut to 76 × 76 mm square, of varying thickness, dried at 50°C/ 1.33 kPa, and then preconditioned to constant weight at 50% relative humidity. Further details of this test are described elsewhere.[6b]

Char percentages were found by igniting 2.5 × 6.4 × 20 mm chips of the molded resins on wire gauze with a bunsen burner, then determining the residual weights left when ignition could no longer be achieved after exposure to the burner for 30 sec.

Thermogravimetric analyses were performed using a du Pont Model 950 thermal analyzer, and visible spectroscopy measurements were made with a Beckman DK-2A spectrophotometer using conventional procedures.

RESULTS AND DISCUSSION

Flammability and Smoke Properties of PVC

The three PVC resins of this study were first compounded with 0.4% ferrocene and tested by *O.I.* flammability and NBS smoke density methods. The results of these tests, shown in Table I, demonstrate the pronounced flame-retarding effect of ferrocene, which produced a 15–19% increase in *O.I.* over untreated specimens. Two additional features were obvious: First the *O.I.* of the three PVC specimens increased with the polymer molecular weights, with the effect of ferrocene superimposed on the molecular weight effect (Fig. 1). This relationship was opposite that found for nylon, in which *O.I.* varied inversely with polymer viscosity.[7] The contrast would not appear surprising in view of the tendency of PVC to both soften and char under the conditions of the *O.I.* test. Presumably, the charred portion of the polymer can form a wick for molten polymer, much like a candle, increasing the availability of the
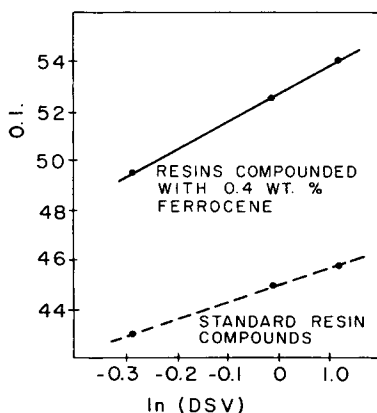

Fig. 1. Relationship between viscosity and oxygen index for PVC resins.

TABLE I
Effect of Ferrocene on Oxygen Index, NBS Smoke Density, and Char
of PVC Compounds

Composition	NBS, flaming, 0.76 mm specimen				Char, wt-%
	O.I.	D_{mc}[a]	$t.9D_m$[b]	tD_{16}[c]	
Resin A ($\bar{M}_w = 4.06 \times 10^4$)	42.9	410	2.8	0.5	9.8
Resin A, plus 0.4% $C_{10}H_{10}Fe$	49.5	310	2.5	0.5	15.6
Resin B ($\bar{M}_w = 1.10 \times 10^5$)	44.9	417	2.8	0.4	12.9
Resin B, plus 0.4% $C_{10}H_{10}Fe$	52.5	300	2.4	0.6	15.7
Resin C ($\bar{M}_w = 1.65 \times 10^5$)	45.5	343	2.2	0.4	11.1
Resin C, plus 0.4% $C_{10}H_{10}Fe$	54.0	356	2.2	0.5	16.9

[a] D_{mc} = Maximum specific optical density, corrected (limits of experimental error, ± 5%).
[b] Time to 90% of D_m (minutes).
[c] Time to specific optical density = 16 (minutes).

fuel. The higher the melt viscosity, the less likelihood there is for wicking of molten polymer. The O.I. relationship to molecular weight also parallels a trend toward increased thermal stability, as reflected in temperatures of initial weight loss from TGA discussed below. Data supporting such a relationship have been reported elsewhere.[8]

A second feature notable in Table I is that NBS visible smoke intensity under flaming conditions was reduced by about 25% with ferrocene in the two lower molecular weight polymers. This is consistent with previous observations regarding ferrocene.[2] However, in the polymer of highest molecular weight, no change in the smoke intensity within experimental error was observed with ferrocene, despite substantially increased O.I. It thus appeared that O.I. of PVC was molecular weight dependent, while the smoke-inhibitory activity of ferrocene in PVC was molecular weight specific.

The weights of charred residues left after burning the test specimens in air increased by 20–60% in the presence of ferrocene. However, no clear trend in the increase of char could be related either to molecular weights or oxygen index. Char results provided no explanation for the lack of smoke suppressant activity in resin C containing ferrocene. The reduced smoke and more difficult flammability of untreated resin C might be rationalized in light of observations by Chang and Salovey.[9] They have found that the levels of char formation and benzene evolution during PVC thermal degradation depend upon the polymerization temperature, polymer molecular weight, and chain conformation. The last point is important to the extent that the occurrence of crystalline phase syndiotactic trans sequences (TT) TT (TT) disfavors the generation of benzene and favors crosslinking upon thermal dehydrochlorination.[9] For the polymers of the present study, the ratios of optical densities in the infrared at 635 cm^{-1} (crystalline, syndiotactic) and 693 cm^{-1} (amorphous, isotactic, and syndiotactic), D_{635}/D_{693}, were found to be 1.62 for resin A, 1.68 for resin B, and 1.79 for resin C. Although the ratios are very similar, resin C has a conformation which least favors generation of benzene, a pyrolyzate of PVC which might be assumed to contribute to visible smoke. If ferrocene compensates for the effect of tacticity, the smoke results in this series follow at least qualitatively the predicted order of response. The extent to which

TABLE II
DSV Measurements (THF Solution) of Recovered Resins

Resin A	Resin A plus ferrocene	Resin B	Resin B plus ferrocene	Resin C	Resin C plus ferrocene
DSV 0.58	0.55	1.04	1.05	1.38	1.41

conformation is involved in smoke generation may also depend on the rate of heating of the polymer.

The pronounced charring characteristic with ferrocene suggests that ferrocene's predominant function is char promotion.[2] Analyses of the chars showed residual iron resistant to water extraction. However, the iron percentages found (0.16, 0.23, and 0.10% for A, B, and C, respectively) were considerably lower than the 0.66–0.72% expected if all iron had remained in the char. There was no apparent relationship between the amount of iron residue and oxygen index or smoke results.

These systems thus meet criteria for both gas- and solid-phase chemical mechanisms of flame retardancy in that charring is increased, but most of the agent is fugitive from the char.[4] This suggests another possible rationale for lack of smoke inhibition in the high molecular weight polymer: hindered diffusion of ferrocene from the polymer due to high melt viscosity, during a stage of combustion critical to smoke inhibition. The influence of melt viscosity on oxygen index has already been implicated.

The questions of how ferrocene enhances charring, whether condensed-phase or gas-phase processes dominate in smoke inhibition, and what additional roles ferrocene serves are not resolved. Moreover, the lack of smoke suppressant activity by ferrocene in resin C, in spite of increased char and oxygen index, is not readily explained. Further examination of the resins was made to develop information relevant to these questions.

Chemical Evidence

The molded specimens were first examined to establish whether ferrocene had significant activity under conditions of processing. Samples of the processed resins were purified by precipitation from THF solution in methanol. A single repetition of this procedure removed ferrocene and other compounding ingredients. The dilute solution viscosities (DSV) of the recovered resins, showed in Table II, indicated no significant alteration of polymer molecular weight during milling or pressing in the presence of ferrocene, and no evidence for involvement of ferrocene at this stage.

Thermogravimetric analysis in air of the compounded resins (Table III and Figs. 2 and 3) demonstrate significant acceleration of the rate of dehydrochlorination and some reduction in temperature for the onset of weight loss in the presence of 'ferrocene. Percentages of intermediate chars were similar, suggesting that dehydrochlorination was complete in all cases. No trend consistent with molecular weight was detected in the additive experiments. Combustion of the final residue was generally observed due to the high temperatures reached in the TGA experiment.

In order to examine the early stages of ferrocene-promoted PVC decompo-

TABLE III
Summarized TGA Results for PVC's of Varying Molecular Weight[a]

| % Weight loss | Temperature at weight loss, °C | | | | | |
| | Resin A | | Resin B | | Resin C | |
	I	II[b]	I	II[b]	I	II[b]
1	270	253	277	270	280	266
2	272	256	280	276	282	274
5	283	267	291	287	293	288
10	295	283	304	300	305	300
20	310	304	312	311	314	309
30	317	314	316	317	317	313
40	327	321	321	327	321	317
50	338	333	330	351	330	327
60	355	359	353	474	355	358
70	469	465	466	510	470	476
80	520	492	525	576	529	536
90	540	515	578	—	575	590
% Residue	ca. 1	0.5	ca. 1	14	0	ca. 1

[a] Air, 80 ml/min, 20°C/min.
[b] Contains 0.4% ferrocene.

sition in more detail, the degradation of resin A was followed at relatively low temperature (176°C) in o-dichlorobenzene solution. In this experiment, flasks containing 300 ml solvent were heated under nitrogen with stirring and charged with 30 g resin A and 30 g resin A plus 1 g ferrocene, respectively. Aliquots taken at 15, 30, 60, 120, and 1440 min were precipitated in isopropyl alcohol, then reprecipitated from THF with isopropyl alcohol. After washing with alcohol, the polymer was dried and analyzed for Cl, Fe, and molecular weight. The results of these analyses are given in Table IV and Figure 4.

The mixture containing ferrocene became dark and intractable after heating for 90 min, while in the absence of ferrocene, polymer $\bar{M}_w$ increased only slightly over 24 hr. GPC determinations of the molecular weights showed that crosslinking was the predominant mode of degradation, and it was greatly accelerated by ferrocene. Dehydrochlorination of neither sample was evident until roughly 60 min of heating, when it became very rapid in the presence of ferrocene, suggesting autocatalysis.

TABLE IV
Chlorine and Iron Analyses of PVC Resins During 176°C Heating in Solution

	0 min	30 min	60 min	120 min	240 min	1440 min
Resin A						
% Cl	56.99	—[a]	57.05	56.25	55.56	55.72
Resin A + 3.3 pbw ferrocene						
% Cl	56.84	56.48	56.15	47.12	—[a]	—[a]
% Fe[b]	0.0004	0.008	0.091[c]	0.36[c]	—[a]	—[a]

[a] Not determined.
[b] Nonextractable iron.
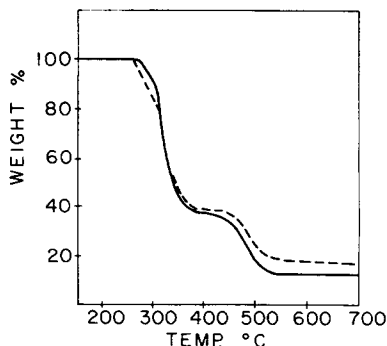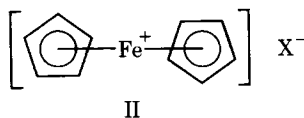[c] Ferricenium ion detected in alcoholic wash of resin (λ_{max} = 610 nm).

Fig. 2. TGA traces for PVC ($\bar{M}_w = 4.06 \times 10^4$) (solid line) and PVC + 0.4% ferrocene (dashed line) in nitrogen (heating rate 25°C/min, gas flow 80–90 ml/min).

Interestingly, the amount of iron remaining in the resin after reprecipitation increased with time, although the chemical state of the iron was not defined. Upon precipitation of the ferrocene-containing sample at 60 min, a blue coloration was noted and the presence of ferricenium ion (II) was confirmed spectrophotometrically ($\lambda_{max} = 610$ nm in water)[10]:

II

A small concentration of ferric ion was also detectable. Ferrocene heated alone in o-dichlorobenzene for periods up to 24 hr or in a stream of pure HCl for 90 min neither caused gellation nor gave evidence for the formation of ferricenium ion. Ferricenium ion was observed when the ferrocene was heated in a stream of HCl with a trace of air. The generation of ferricenium ion can occur either through one-electron oxidation[11] or sequence (1):

$$\text{I} + \text{HCl} \rightleftharpoons \left[\left(\overset{\text{H}}{\underset{}{\text{Fe}}} \right)^{+} \text{Cl}^{-} \right] \xrightarrow{[O]} \text{II.} \qquad (1)$$
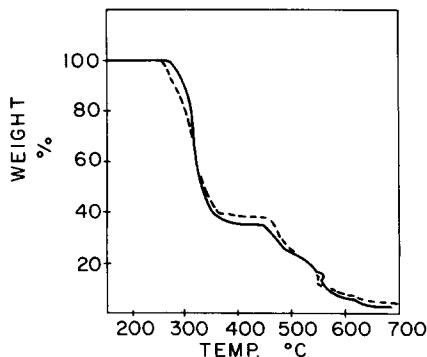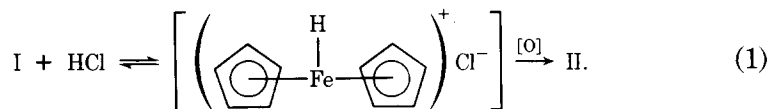

Fig. 3. TGA traces for PVC ($\bar{M}_w = 4.06 \times 10^4$) (solid line) and PVC + 0.4% ferrocene (dashed line) in air (heating rate 25°C/min, gas flow 80–90 ml/min).
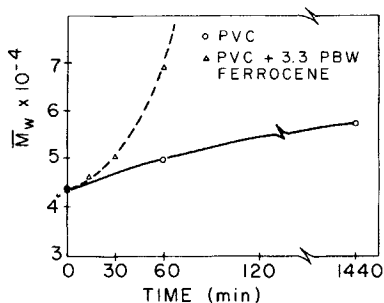
Fig. 4. Effect of ferrocene on PVC molecular weight at 176°C, o-dichlorobenzene solution.

The latter is suggested since the appearance of ferricenium ion coincides with initial stages of dehydrochlorination. Related transformations in polychlorinated substrates upon high energy irradiation have also been reported.[12] The apparent autocatalytic behavior and other observations implicate ferricenium ion as a possible dehydrochlorination and/or crosslinking catalyst in PVC. The parallel involvement of iron oxides or chlorides as catalysts should also be considered, especially under combustion conditions.

Poly(vinyl Alcohol)—Ferrocene Analogy

Poly(vinyl alcohol) (PVA) contains no halogen, and its mechanism of dehydration is not analogous to the dehydrochlorination of PVC. However, the intermediate condensed phase structures obtained in the degradation of the two polymers are believed to be similar.[13] Examination of a PVA resin as a nonhalogenated analogue of the PVC system was undertaken to provide data relative to the possible interaction of ferrocene with intermediate degradation structures. Experiments which paralleled those outlined above were performed.

Comparing the TGA curves of PVA, and PVA plus 1 part by weight ferrocene run in air (Fig. 5), no acceleration by ferrocene of weight loss was detected. Ferrocene appeared to retard weight loss somewhat, although the residue weights at the end of the TGA experiment in air were identical.

The flammability and smoke behavior of PVA compositions containing untreated resin, or resin plus ferrocene, were informative (Table V). Whereas ferrocene had no significant effect on the $O.I.$ of PVA, the visible smoke intensity was reduced by 25–30% and the rate of smoke generation was slowed markedly. The percentage decrease in D_{mc} was about the same as that of PVC–ferrocene. However, char residue formation in PVA was low with or

TABLE V
Flammability, Visible Smoke, and Char for Poly(vinyl Alcohol)–Ferrocene Compound

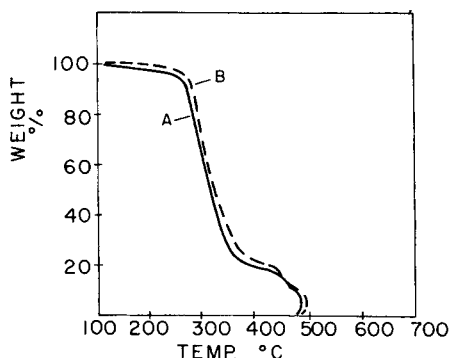| | O.I. | NBS smoke chamber, flaming, 3.18 mm | | |
		D_{mc}	$t.9D_m$, min	tD_{16}, min	Residue, wt-%
Poly(vinyl alcohol)	23.0	509	7.00	1.88	1.2
Poly(vinyl alcohol) + 1 pbw ferrocene	23.5	365	12.87	2.28	2.0

Fig. 5. TGA traces of PVA (A) and PVA + 1 pbw ferrocene (B) in air (25°C/min, air flow 90 ml/min).

without ferrocene. Close observation of the burning, ferrocene-treated PVA specimen revealed no evolution of carbonaceous soot over the first minute of flaming. In contrast, soot was evident from the onset of flaming in untreated PVA. A brown residue of iron oxide was deposited from the combustion gases of ferrocene-containing resin when drawn through a glass fiber filter during the first minute of burning.[14] Extraction of the treated resin with water after heating or partial burning gave no evidence for ferricenium ion or other soluble iron salts.

Presumably, halogen is necessary for the formation of ferricenium salts and their accompanying condensed phase char promotion effects, consistent with sequence (1). Clearly, suppression of smoke by ferrocene in PVA is predominantly the result of vapor phase processes, analogous to its function in energy conversion processes. This function has been related to the ability of metal oxides or hydroxides to catalyze the decomposition of hydrogen or water vapor in the gas phase, leading to the production of hydroxyl radicals which destroy solid carbon.[3,4] As a consequence, it has been suggested that reduction of smoke in this way should be accompanied by increased flame propagation rates and that flame and smoke inhibition may be antagonistic.[4]

CONCLUSIONS

Evidence has been obtained that ferrocene can be active in both the gas phase and condensed phase during the combustion of vinyl polymers. In halogenated polymers, oxidation of ferrocene to ferricenium ion occurs readily. The presence of ferricenium ion is important in that it is a Lewis acid, capable of catalyzing both dehydrochlorination and crosslinking processes. The latter process leads to char formation and improvements in flame resistance. In addition, reduction of mass-burning rate and conversion of otherwise volatile pyrolyzates into char can reduce visible smoke output.[15]

Ferrocene functions predominantly as a gas phase smoke suppressant in poly(vinyl alcohol), having little effect on flammability or char formation. The facts that iron is lost during combustion and that smoke inhibition is not observed in one case where charring and flame retardation are observed suggest the likelihood of similar gas-phase involvement in PVC.

Oxygen index flammability measurements of the three PVC resins studied

revealed a relationship of increased flame resistance with increasing polymer molecular weight. However, the magnitude of this effect was small compared to the effect of additives such as ferrocene.

Failure of ferrocene to alter smoke generation in the highest molecular weight resin, despite pronounced charring, was not explained. Speculation as to the cause of this effect might invoke diffusion of ferrocene into the gas phase hindered by the high-viscosity molten polymer, or an as yet unrecognized dependence of the ferrocene interaction on a property such as polymer tacticity.

The function of ferrocene as both a flame retardant and smoke suppressant in PVC demonstrates that these two objectives are not mutually exclusive in polymers.* The inhibition of both flame propagation and carbon formation may present antagonism when considering only flame processes. However, the complexity of most polymer combustion systems, which involve various condensed-phase and gas-phase processes, offers a variety of points from which to attack the dual problem of smoke inhibition and flame retardation.

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* Since completion of this work, other examples of simultaneous smoke suppression and flame retardation in vinyls have appeared, e.g., A. W. McRowe (to B. F. Goodrich Co.), U.S. Pats. 3,819,577; 3,822,234; 3,862,086, (1974, 1975).