APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 101–111 (1996)

Flame-retardancy and Smoke-suppression Studies on Ferrocene Derivatives in PVC

P. Carty,* J. Grant† and E. Metcalfe‡§

* Department of Chemical and Life Sciences, Univesity of Northumbria, Ellison Place, Newcastle-upon-Tyne NE1 8ST, UK, † Vita Liquid Polymers, Wythenshawe, Manchester M22 4TP, UK, and ‡ School of Chemical and Life Sciences, University of Greenwich, Wellington Street, London SE18 6PF, UK

A range of substituted ferrocenes has been synthesized and studied for flame retardancy and smoke suppression on incorporation into plasticized PVC at 0.1–5.0 phr. Smoke suppression by up to 50% and enhancement of the limiting oxygen index by up to 4 units were observed. The differences in performance could not be correlated with char formation, thermal analysis or chemical structure of the additive. A negative correlation was found between smoke suppression and flame retardancy. The most effective smoke suppressant additive appears to accelerate the rate of dehydrochlorination of PVC while the most effective flame retardant appears to have little effect on the dehydrochlorination process.

Keywords: ferrocenes; flame retardancy; smoke suppression; PVC; dehydrochlorination

INTRODUCTION

Although rigid poly(vinyl chloride) (uPVC) is inherently flame retardant due to its high chlorine content, flexible (pPVC) exhibits increased flammability and also increased smoke production, due to the presence of plasticizers. Widely researched flame retardant additives include phosphorus compounds,[1] antimony(III) oxide[2,3] and a range of oxides, hydroxides and carbonates of molybdenum, scandium, aluminium, magnesium, calcium, zinc and some compounds of iron[4–14].

The most effective smoke-suppressant additives for PVC are generally compounds of the transition metals, including molybdenum and copper[15,17,18], iron,[19,20] tin[16] and zinc.[9] These compounds are believed to modify the degradation mechanism occurring during pyrolysis or burning, by cross-linking to increase char formation. Of these additives perhaps molybdenum trioxide and ferrocene are the most widely studied, although Ongard II, a commercially available magnesium oxide and zinc oxide formulation (Cookson PLC), is used commercially. Ferrocene is thought to act through conversion during combustion to the ferrocenium ion, which may function as a Lewis acid, catalysing dehydrochlorination, cross-linking and char-forming reactions,[12] but it has been suggested that the active smoke suppressant is the decomposition product α-Fe_2O_3 and intermediate iron oxychloride or chlorides[19]. It has also been suggested that ferrocene influences the gas-phase chemistry, e.g. by inhibiting soot nucleation and growth.

While there is some agreement that the addition of ferrocene to PVC has three effects,[11]

(i) reduction of smoke formation,
(ii) enhancement of char formation and
(iii) reduction of volatile aromatics with enhancement of volatiles aliphatics,

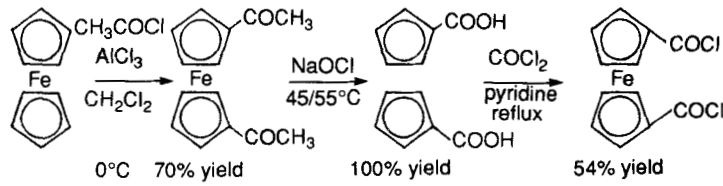
there is still debate about the mechanism of char formation[11,15] and the relative importance of char residue oxidation and cracking by some metal oxides.[22] It has been shown recently that the active smoke–suppressing char–forming intermediate is iron(III) oxychloride.[23] Some recent work has suggested that a cationic Lewis acid cross-linking process is occurring.[24] It has been suggested that high-temperature cationic cracking of the char formed during pyrolysis and burning may hinder the commercial development of Lewis acid-type smoke-suppressing compounds.[25]

A major drawback of ferrocene is its volatility, since considerable amounts are lost due to sublimation at normal processing temperatures. We have previously reported the synthesis of ferrocene derivatives with good thermal stability, reduced volatility and significant flame retardant/smoke suppressant activity[20,29]. In this work we

§ Author to whom correspondence should be addressed.

CCC 0268-2575/96/020101-11

Received 24 February 1995
Accepted 23 May 1995



Scheme 1 Preparation of 1,1′-ferrocenyl dicarboxylic acid chloride

have aimed to identify materials with both flame-retardant and smoke-suppressant activity using ferrocenyl amides and esters formed by condensation reactions between ferrocene monocarboxylic acid, or ferrocene 1,1′-dicarboxylic acid, and halogenated aromatic groups.

EXPERIMENTAL

Ferrocenyl amides

The starting material for the preparation of the ferrocenyl amides was 1,1′-ferrocenyl dicarboxylic acid chloride. This was prepared in substantial quantities using the sequence of reactions beginning with ferrocene, shown in Scheme 1. The ferrocyl amides were then prepared in high yield from acid chlorides by reacting the acid chloride with the appropriate amide in alkaline conditions, eg as in Eqn [1].

The products were all solids, produced in 50–70% yields, which were easily recrystallized from ethanol, and are described in Fig. 1. They all gave good elemental analyses and melting points (AA, 212 °C; DCA, 205–207 °C; TCA, 284–286 °C; PBA, 237–241 °C) and the main structural features were confirmed by IR and UV spectroscopy. Full experimental details have been published elsewhere.[27]

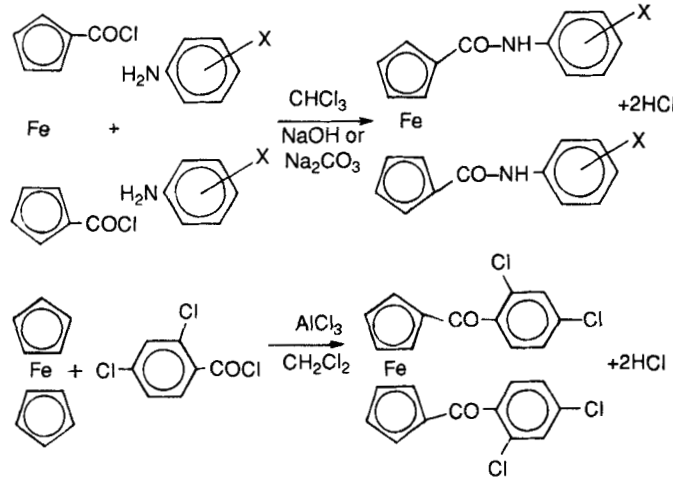
Benzoyl Ferrocenes

There are several methods available for carrying out Friedel–Crafts acylation reactions with ferrocene. In this work the method described in Ref. 29 was used. In order to synthesize substantial quantities of the compound 1,1′-bis(2,4 dichlorobenzoyl) ferrocene(1,1′-DCBF), the method shown in Eqn [2] was used.

The compound was prepared in poor yield (~30%) as red crystals (m.p. 122–124 °C) and was purified by column chromatography using neutral alumina eluting with a mixture of 60:40 petroleum ether (b.p. 40–60 °C)/diethyl ether. Purity was checked by TLC. Satisfactory analyses for C,H, Fe and Cl were recorded. (Calc. %, C = 56.0, H = 2.6; Found %, C = 54.3, H = 2.5).

Chlorendic anhydride (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid anhydride)ferrocene derivative (FCA)[29]

Reaction of anhydrous aluminium chloride with ferrocene and freshly prepared chlorendic anhy-



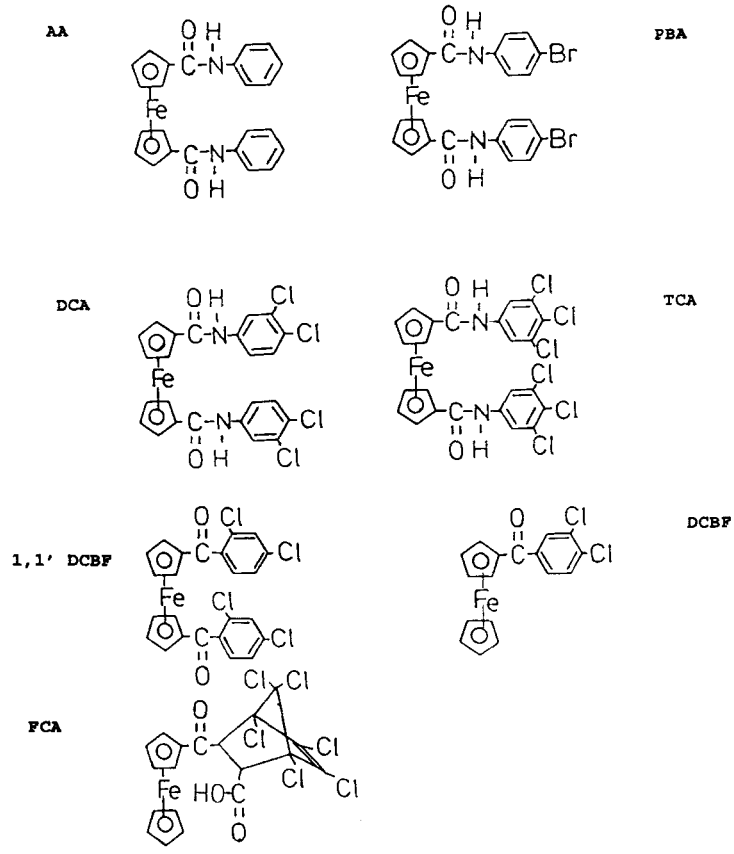


Figure 1 Derivatives chosen for flammability testing.

dride in dry dichloromethane gave the monosubstituted product in modest yield (eqn. [3]).

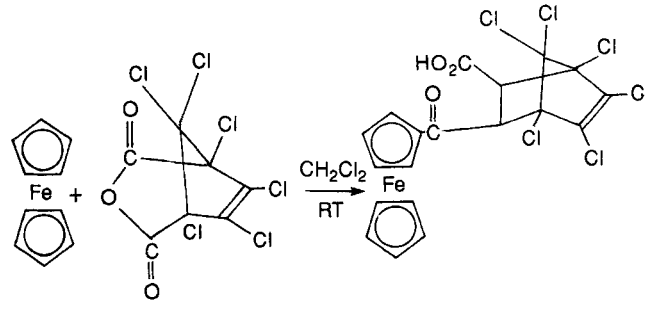
Recrystallization from benzene/petroleum ether (50:50) gave dark red, air stable crystals. Satisfactory microanalysis, IR, UV/visible and NMR spectroscopy were obtained from the compound. Its structure was confirmed by

(1) reduction with lithium aluminium hydride to the alcohol in dry ethanol, and

(2) reaction with diazomethane in dry ethanol to give the methyl ester in high yield.

Preparation of flexible PVC

The additives (0.1–5.0 phr) were mixed with 100 phr PVC resin (BP grade S110/10), dioctyl phthalate plasticizer (30 phr), tribasic lead sulphate stabilizer (5 phr) and calcium stearate



[3]

lubricant (1 phr). This mixture was compounded on a steel two-roll mill heated to 160 °C until a homogeneous mix was obtained and a hide of required thickness (1 mm) obtained. (phr = parts per 100 w.r.t. the PVC contents of the formulation).

Smoke density measurement with the NBS smoke density chamber (ASTM E 662–79)

The flaming mode only was used in this work.[21]

Limiting oxygen index (LOI) measurement (ASTM D 2863–77, BS 2782 Part 1, Method 14 1b; Nord Test Method NT Fire 013)

A Stanton–Redcroft flammability apparatus was used for the LOI measurements. The LOI values obtained were analysed statistically by the Dixon method.[21]

Thermal analysis

Thermogravimetric analysis was performed in a Stanton–Redcroft TG 750/770 thermobalance in flowing air or dinitrogen (25 ml min^{-1}) at a heating rate of 10 °Cmin^{-1}. Samples were cut to size with a leather punch to give sample weights of 5–9 mg. Differential thermal analysis was carried out on samples of *ca.* 5 mg using a Stanton–Redcroft DTA 673–4 instrument under flowing nitrogen (10 ml min^{-1}) at 10 °Cmin^{-1}. Quartz holders were used with alumina (Al_2O_3) as the reference material. A Perkin-Elmer DSC2 differential scanning calorimeter was also used to study samples of 3.0–6.2 mg from 150 to 400 °C at a heating rate of 10 °Cmin^{-1} in a static nitrogen atmosphere.

Char analysis

Samples of polymer (0.5 g) containing the additives were pyrolysed in nitrogen or air for

Table 1 Summary of results for limiting oxygen index (LOI), NBS smoke density chamber test, char formation and iron loss from the char

Additive	(phr)	Δ(LOI)	Δ(NBS) (%) +	Char (%)	Iron lost (%)
Blank[a]		0	0	10.9	—
AA	0.24	1.4	18	15.8	37
AA	3	1.8	39	18.6	38
AA	5	3.1	31	17.6	34
DCA	1	3.4	19	16.8	40
DCA	3		19	17.6	26
DCA	5	4.1	23	18.3	37
TCA	1	1.4	32	17.0	42
TCA	3	2.1	30	18.1	21
TCA	5	1.9	16	17.2	33
PBA	1	3.1	13	16.7	—
PBA	3	3.1	37	17.0	26
PBA	5	2.4	20	16.8	41
Ferrocene	1	2.8	28	15.8	
DCBF	1	1.2	48	16.8	
1,1′-DCBF	1	1.4	30	15.0	
1,1′-DCBF	4	1.1	43	17.0	
FCA	1	1.6	23	15.5	
FCA	4	1.9	32	18.4	
Fe_2O_3	0.2	0.8	37	17.1	
Fe_2O_3	0.4	0.1	39	19.8	
Fe_2O_3	0.6	0.9	37	18.6	
Fe_2O_3	0.8	0.9	45	21.3	
Ongard II	0.1	1.5	18		
Ongard II	1	1.3	37		
Ongard II	5	1.6	49		

[a] Blank: LOI 28.4
NBS 450
Char 10.9%

10 min at 600 °C and the char weight noted. In some cases the residues were digested in aqua regia and analysed for iron using atomic absorption spectrometry.

Dehydrochlorination kinetics

Samples (20 mg) were placed on a small platinum boat attached to a short piece of nichrome wire and introduced into a furnace at 200–300 °C (+3 °C stability) inside a 19 mm (i.d.) quartz tube. The decomposition products were carried by a stream of oxygen-free nitrogen at 100 ml min^{-1} into a fritted bubbler containing distilled water, and the pH was continuously monitored, enabling the rate of HCl evolution to be determined. The short tubing between the furnace and the bubbler was maintained at 150 °C to minimize adsorption losses.

RESULTS AND DISCUSSION

Smoke and flammability testing

The limiting oxygen index and NBS smoke density chamber data are summarized in Table 1, together with the results of the char test and the iron analysis of the char residues. For ease of interpretation, the results are expressed as Δ(LOI) the increase in LOI with respect to the polymer formulation free of additives polymer and Δ(NBS) the percentage decrease in smoke formation i.e. 100 [D_{MC} (blank)−D_{MC} (blank)] where D_{MC} is the maximum smoke density corrected for a 7.5 g sample). The following observations may be made.

(1) All samples exhibit both flame retardancy, smoke suppression and char promotion.
(2) In the samples analysed, some 60–75% of the iron remains in the char. The remaining

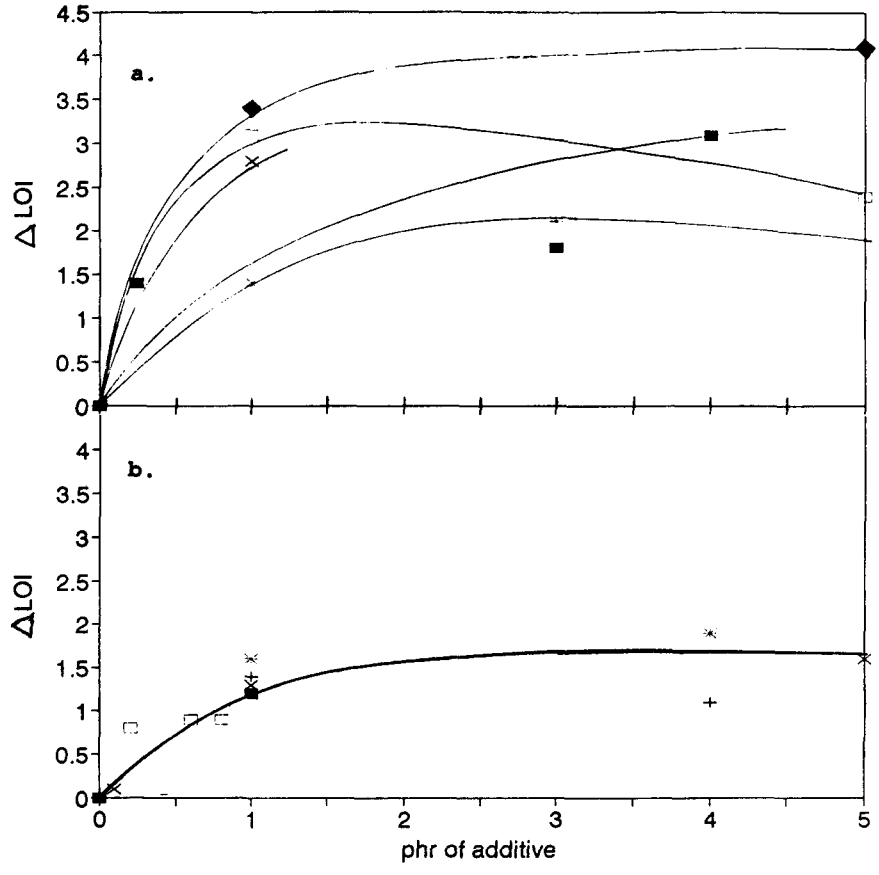


Figure 2 Increase in LOI function of additive content. (a) ■, AA; ◆, DCA; *, TCA; □, PBA; ×, ferrocene. (b) ■, DCBF; +, 1,1′-DCBF; *, FCA; □, Fe_2O_3; ×, Ongard II..

25–40% is lost as volatile or particulate material.

(3) Increasing additive concentrations above 2 phr does not lead to further significant enhancement of either flame retardancy or smoke suppression. In most instances the optimum formulation occurs at around 1 phr additive (Figs 2 and 3).

(4) Although all the formulations exhibited enhanced char production, no correlation exists between char yield and either smoke suppression, as might be expected, or flame retardancy. Thus identical char weights are found for the 1 phr DCA and DCBF (see Table 1) formulations although the latter is about two and a half times more effective as a smoke suppressant. This indicates that char formation may not be the only mechanism of smoke suppression.

(5) The better smoke suppressants, e.g. DCFB and Fe_2O_3, are poor flame retardants while PBA and DCA which exhibit the best flame retardancy, have limited smoke suppressant ability. This negative relationship was examined by plotting Δ(NBS) vs Δ(LOI) for 1 phr formulations, using extrapolated or interpolated values for Fe_2O_3 and AA, in Fig. 4. A clear negative correlation is demonstrated (r^2 = 0.653) and a regression line determined:

$$\Delta(\text{NBS}) = 50(\pm 7) - 10.0(\pm 2.8)(\text{LOI})$$

A reasonable explanation of this relationship is that the smoke suppression mechanism is due to the suppression of the evolution of smoke precursor aromatic molecules with a consequent increase in the evolution of more flammable aliphatic molecules[11]. There is, however, a residual net flame retardancy in all cases, consistent with a combination of solid phase (char formation) and vapour-phase mechanisms

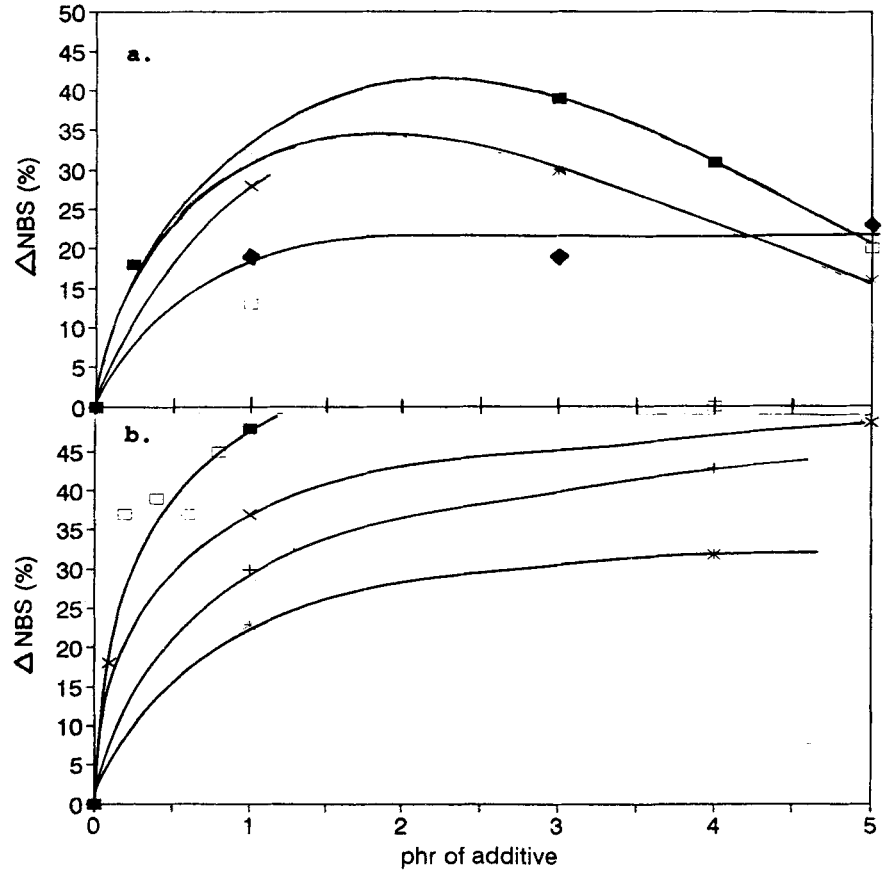


Figure 3 Decrease in smoke production as a function of additive content. Symbols as in Fig. 2(a) and (b), respectively.

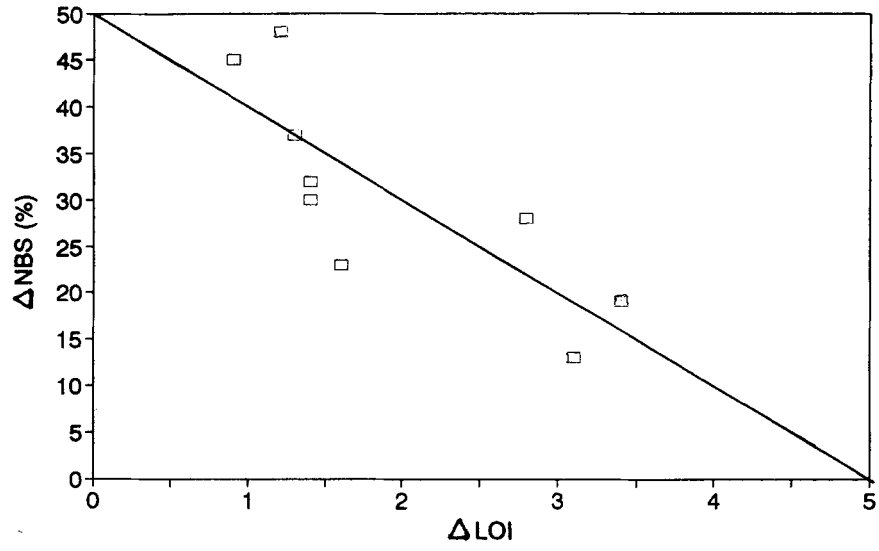


Figure 4 Smoke Reduction vs increase in LOI for 1 phr formulations.

for inhibition of combustion and suppression of smoke by the ferrocene and other compounds on PVC and PVC blends.[23]

Thermal analysis

The thermal stability of the ferrocene derivatives was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC); the results for experiments carried out under dinitrogen are shown in Table 2 and typical DSC results are shown in Fig. 5. The amide derivatives show generally similar behaviour with melting points between 200 and 300 °C, the first major weight loss between 300 and 600 °C, and significant amount of char with residual weights at 600 °C of 32% (AA), 43% (DCA), 42% (TCA) and 62% (PBA). The dichlorobenzoyl compounds both exhibit lower melting points (< 200 °C) but while 1,1′–DCBF is stable to around 400 °C, DCBF decomposes at a relatively low temperature of 200–300 °C, which may be related to its effectiveness as a smoke suppressant. Ferrocene shows the characteristic sublimation behaviour expected, while FCA appears to give some sublimation losses, but no melting behaviour.

Table 2 TGA and DSC data for Ferrocene Derivatives[a, b]

Additive	T_i (°C)	$T_{50\%}$ (°C)	T_p (°C)	T_{mp} (°C)	Comments
AA	300–400	360	215	212	Exotherm 347 °C
DCA	300–400	450	203	205	Exotherm 338 °C
TCA	300–400	440	298	284–286	Complex exotherm 337 °C
PBA	300–400	770	242	237–257	Sharp exotherms 257, 315 °C Sharp endotherm 262 °C 28% weight loss at 400 °C
Ferrocene	100–200	145	—	—	Sublimes
DCBF	200–300	254	159	142–146	Endotherm 217 °C Exotherms 208, 350 °C
1,1′-DCBF	400–500	490	185	172–176	Exotherm at 287 °C
FCA	*ca* 350	440	—	—	Some sublimation Broad exotherm 253 °C

[a] All experiments were conducted under a nitrogen atmosphere.

[b] Abbreviations: T_i, temperature range over which first major weight loss is obtained; $T_{50\%}$, temperature at which 50% weight loss occurs; T_p, peak temperature for melting endotherm; T_{mp}, melting point.

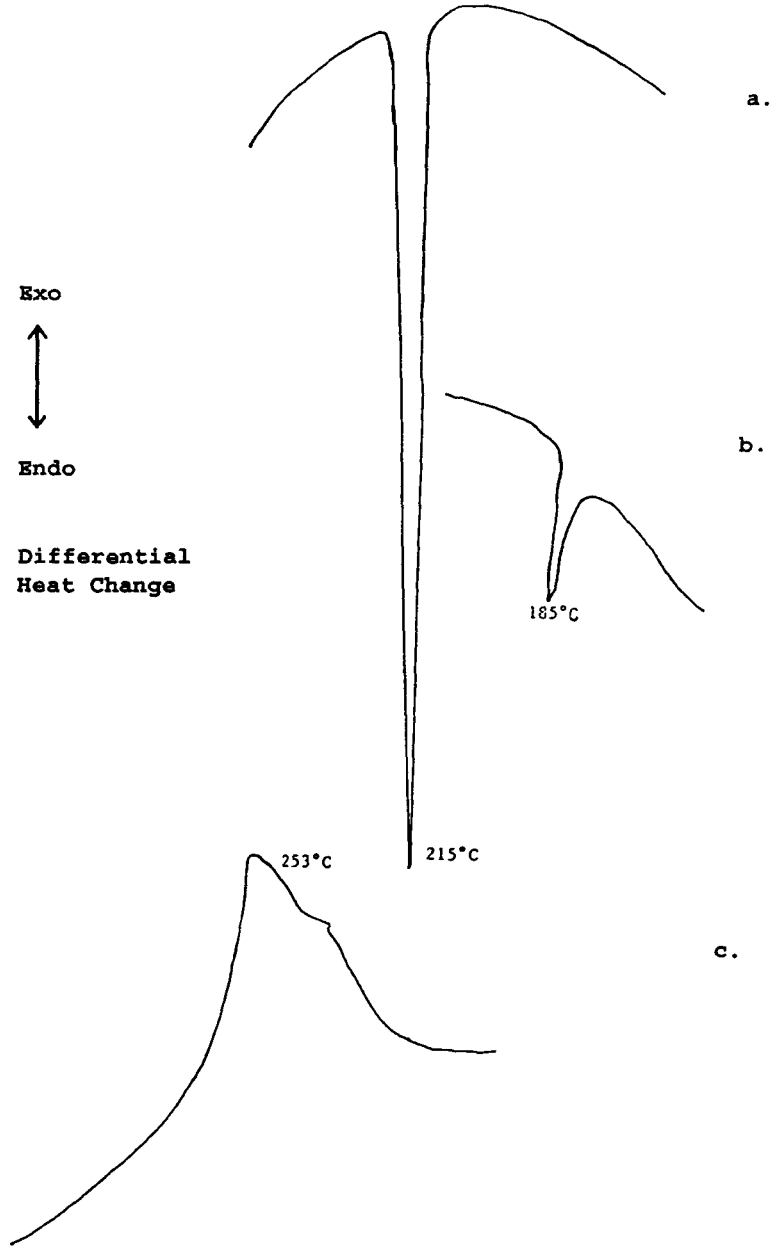


Figure 5 Typical DSC profiles of additives used: (a) AA; (b) 1,1′-DCBF; (c) FCA.

It is interesting to note that the two most effective flame retardants, DCA and PBA, both melt at temperatures similar to the temperature of PVC dehydrochlorination, but do not decompose until much higher temperatures. In the presence of PVC, however, the likelihood must be borne in mind that these derivatives react with the HCl evolved at 200–300 °C; this reaction may be far more rapid in the molten state than in the solid state, and may result in the formation of volatile ferrocene or halogenated vapour active iron flame retardants. Reaction of HCl with the amide derivatives leading to fragmentation would also be expected to be more significant than reaction with the ketones.

Table 3 Summary of TGA results for formulations in air[a]

Additive	(phr)	$T_{1\%}$ (°C)	$T_{50\%}$ (°C)	W_1 (%)	W_2 (%)	W_3 (%)
Blank	—	190	290	32.1	9.5	3.4
AA	0.24	179	277	33.5	19.1	4.1
	3	184	280	36.2	20.0	4.8
	5	192	280	38.0	21.0	5.0
PBA	1	179	280	33.1	17.6	2.9
	4	182	283	33.9	27.1	3.3
	5	186	280	36.0	20.0	5.0
TCA	1	186	284	34.7	17.8	3.4
	3	179	285	34.4	16.0	2.5
	5	172	280	35.7	19.7	3.2
DCA	1	181	284	33.8	7.7	1.9
	3	193	295	32.7	15.0	3.1
	5	179	278	34.0	8.0	3.8
1,1′-DCBF	1	187	286	33.4	16.9	3.4
	4	183	281	36.5	20.0	4.6
DCBF	1	181	278	34.1	17.5	3.7
FCA	1	181	282	33.7	12.7	3.3
	4	181	287	36.2	19.1	3.8
Ferrocene	1	181	279	33.5	16.0	4.0

[a] Abbreviations: $T_{1\%}$, $T_{50\%}$, temperature at which 1 and 50% weight losses occur; W_1, W_2, W_3, weight remaining after stage 1, 2 and 3 decompositions.

Attempts were made to study the performance of the PVC formulations containing the additives by DSC. Generally a complex set of events involving an endotherm and several exotherms between 267 and 327 °C was obtained, but lack of reproducibility, perhaps caused by gas evolution, foaming, or consequent fluctuations in thermal contact, made it difficult to obtain useful information. Differential thermal analysis (DTA) was also found to be

Table 4 Summary of TGA Results for Formulations in Dinitrogen.

Additive	(phr)	$T_{1\%}$ (°C)	$T_{50\%}$ (°C)	W_1 (%)	W_2 (%)
Blank	—	196	302	33.9	16.6
AA	0.24	186	287	35.7	20.0
	3	206	294	38.4	23.5
	5	200	280	39.5	23.9
PBA	1	193	287	36.7	19.7
	4	190	280	35.4	21.5
	5	196	278	37.6	22.4
TCA	1	191	309	36.2	19.4
	3	192	279	36.9	20.6
	5	195	293	37.0	22.4
DCA	1	201	298	36.3	20.2
	3	198	296	36.6	20.5
	5	193	291	38.1	22.9
1,1′-DCBF	1	189	291	36.6	21.0
	4	187	299	35.1	19.2
DCBF	1	194	296	35.1	20.2
FCA	1	204	292	35.7	18.5
	4	194	288	36.8	21.8
Ferrocene	1	182	290	34.5	20.4

[a] Abbreviations: As for Table 3; note that stage 3 is not present in nitrogen.

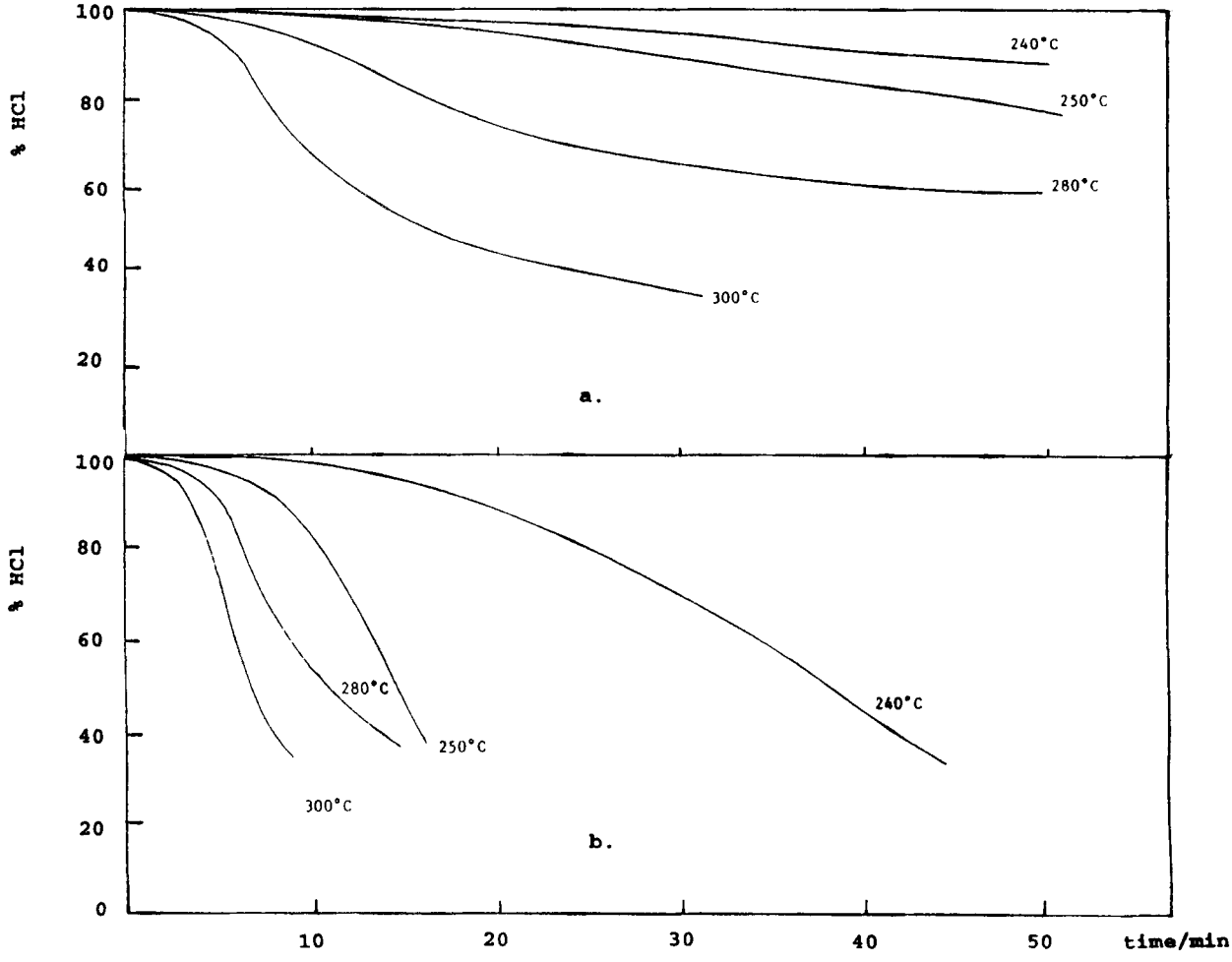


Figure 6 HCl loss during pyrolysis in dinitrogen. [a. Blank Formulation, b. 1 phr DCA]

uninformative since effects due to the additives were not differentiated from the major energy changes associated with the PVC and plasticizer; although some small variations in onset temperature of the PVC endotherms were measured, no significant trends were observed.

TGA studies were carried out on all formulations in both air and nitrogen. These results are summarized in Tables 3 and 4 for the first, second and third weight losses corresponding to HCl and dioctyl phthalate loss, evolution of volatile aromatics, and in air only, char oxidation. The first-stage weight loss (67.9%) for the untreated PVC sample, corresponds closely to the expected values for quantitative evolution of both HCl (42.9%) and dioctyl phthalate (22.1%). Although the onset temperature $T_{1\%}$, defined as the temperature at which a 1% weight loss occurs, for the first weight loss generally shows a slight reduction in the presence of additive, no significant correlation with flame-retardant or smoke-suppressant activity was found.

Dehydrochlorination kinetics

The rate of HCl loss was monitored for selected formulations, PBA and DCA which yielded optimum flame retardancy, and DCBF, which yielded optimum smoke suppression. The plots of HCl loss vs time as displayed in Fig. 6 for the blank and the formulation containing 1 phr additive. The plots could be resolved into two sections, an induction period followed by a dehydrochlorination which was found to give a reasonable fit to $\frac{3}{2}$-order kinetics as proposed

by Woolley.[28] The activation energy for dehydrochlorination for the blank PVC sample is 90 kJ mol^{-1} and this decreased strongly on addition of PBA (1 phr, 35 kJ mol^{-1}; 5 phr, 60 kJ mol^{-1}), less strongly on addition of DCA (1 phr, 75 kJ mol^{-1}; 5 phr, 72 kJ mol^{-1}) but is hardly affected by DCBF (1 phr, 85 kJ mol^{-1}). The active smoke-suppressant DCBF has little effect on the dehydrochlorination kinetics while the active flame-retardant DCA and PBA both significantly reduce the observed activation energies. The interaction with the polymer degradation process is consistent with the above arguments although the reasons for this are still not clear.

CONCLUSION

While the range of ferrocene derivatives studies in plasticized PVC formulations have all been found to have both smoke-suppressant and flame-retardant activity, a negative correlation is exhibited between flame retardant and smoke suppressant activity. Further investigations based on thermal analysis and dehydrochlorination techniques suggest that the most active flame retardant additives are the chlorinated or brominated aromatic amide derivatives DCA and PBA, which melt at dehydrochlorination temperatures and interact with the polymer degradation mechanism, as shown by increased rates due to a reduction in activation energy for the dehydrochlorination process. It is not clear how the more effective smoke suppressants function, but presumably the most effective material, DCBF, which degrades at low temperatures (< 200 °C) is more readily converted to the oxychloride (or intermediate species), which is known to be a highly effective smoke suppresser.

All the additives promote char formation, but no simple correlations with smoke suppression or flame retardancy can be established. Some of the chars were analysed for iron content and these results suggest that about one-third of the iron is lost in volatilization or in smoke particulates, while the rest remains in the char.

REFERENCES

1. K. Kishmore and M. Joseph, *J. Sci. Ind. Res.* **45**, 257 (1980).
2. A. R. Garcia, *J. Coated Fabric* **11**, 137 (1982).
3. C. F. Cullis and M. M. Hirschler, *The Combustion of Organic Polymers*, Clarendon, Oxford, 1981, p. 261.
4. A. Kuros, K. Miyagama, M. Otsuki, E. Masuda, H. Shirai and F. Shimiuzu, *Text. Res. J.* **55**, 377 (1985).
5. V. A. Uskov, V. M. Lulayan, B. I. Bulgakov, D. Kh. Kulev, R. A. Andnanov and A. A. Berlin, *Plastic Massey* **9**, 53 (1985).
6. E. D. Nelson and J. Kaufman, *Fire Flammability* **13**, 76 (1982).
7. C. F. Cullis, A. Gad and M. M. Hirschler, *Eur. Polym. J.* **20**, 707 (1984).
8. P. Harshad and D. Rudolf, *J. Vinyl Technol* **6**, 25 (1984).
9. W. J. Kroenke, *J. Appl. Polym. Sci.* **26**, 1167 (1981).
10. W. J. Kroenke and R. P. Latimer, *J. Appl. Polym. Sci.* **32**, 4154 (1986).
11. R. P. Lattimer and W. J. Kroenke, *Anal. Pyrol.* 453 (1984).
12. D. F. Lawson, *J. Appl. Polym. Sci.* **20**, 2183 (1976).
13. G. Ortaggi and V. Paolucci, *Acqua. Aria* **1**, 45 (1982).
14. A. Ballistreri, G. Montaudo, C. Puglisi, E. Scamporino and D. Vitalini, *J. Polym. Sci.; Polym. Chem. Ed.* **19**, 1397 (1981).
15. W. H. Starnes and D. Edeson, *Macromolecules* **12**, 97 (1979).
16. P. Cusack, *Flame Retardants '90*, Elsevier Applied Science, London, 1990, p. 176.
17. F. C. Moore, G. A. Weber and T. R. Isigdinos, *Polym. Sci. Technol.* **26**, 215 (1984).
18. G. A. Skinner, and P. J. Hains, *Fire Mater.* **10**, 63 (1986).
19. A. Michel, M. Bert, T. Van Houang, P. Bussier and A. Guyot, *J. Appl. Polym. Sci.* **28**, 1573 (1983).
20. P. Carty and B. N. Adger, *Appl. Organomet. Chem.* **4**, 127 (1990).
21. J. Troitzsch, *International Plastics Flammability Handbook. Principles, Regulations, Testing and Approval*, Hanser, Munich, 2nd edn, 1990, p. 408.
22. M. Bert, A. Michel and A. Guyot, *Fire Res.* **1**, 301 (1978).
23. P. Carty and S. White *Polymer* **36**, 1209 (1995).
24. P. Carty and S. White, *Polymer* **35**, 343 (1994).
25. W. H. Starnes Jr, L. D. Westcott Jr, W. D. Reents Jr, R. E. Cais, G. N. Villacorta, I. N. Plitz and L. J. Anthony, *J. Org. Coat. Appl. Polym. Sci. Proc* **46**, 556 (1982).
26. P. Carty and E. Metcalfe, UK Patent 84 227 787, 1985.
27. J. Grant, Ferrocene-containing Smoke Suppressants and Flame Retardants for Semi-rigid Polyvinyl Chloride, PhD Thesis, University of Northumbria, 1993.
28. W. D. Woolley, *Plast. Polym.* 203 (1972).
29. P. Carty, J. Grant and A. Simpson, *Appl. Organomet. Chem.* **2**, 277 (1988).