A review of the role of iron containing compounds in char forming/smoke suppressing reactions during the thermal decomposition of semi-rigid poly(vinyl chloride) formulations

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The mechanism of how iron compounds affect char forming reactions during the thermal degradation of semi-rigid poly(vinyl chloride) (PVC) containing dioctylphthalate (DOP) plasticizer is discussed. Work from earlier studies with PVC both in rigid and semi-rigid systems is reviewed and chemical reactions involving iron species acting in char forming/smoke suppressing reactions are suggested. The involvement of reactive intermediates derived from a range of inorganic and organometallic iron compounds in the overall reaction pathway are proposed. The key role of plasticizer degradation and hydrogen chloride formation is highlighted as being important in the formation of smoke during the thermal decomposition of PVC formulations.

(Keywords: poly(vinyl chloride); smoke suppression; char formation; iron compounds; reaction mechanism; DOP plasticizer)

INTRODUCTION

Poly(vinyl chloride) (PVC) continues to be manufactured and used in large quantities[1,2]. Because of its high chlorine content PVC is inherently fire resistant[3] and this property has, in the main, allowed PVC to be used in a wide range of commercial and domestic 'plastic' materials. Applications of PVC vary from its use as a covering insulation for electrical and communications cables to domestic uses in guttering, window frames, doors, house sidings, etc. However, for applications where flexible or semi-rigid PVC is required, certain organic plasticizers such as dioctylphthalate (DOP) [di(2-ethylhexyl)phthalate] are incorporated at varying levels. A plasticizer such as DOP has dramatic effects on both the flammability and smoke production when PVC decomposes thermally. Rigid PVC (i.e. PVC polymer formulated without plasticizer) has a limiting oxygen index (LOI)[4] of about 49 and when a plaque of rigid PVC is evaluated for smoke production in the flaming mode using an NBS Smoke Chamber according to the standard[4] ASTM DE-2863-77 it has a maximum smoke density, $D_{\max}$ (corr. 7 g), value of 320. When DOP is incorporated in the polymer formulation at 30 parts per hundred (of PVC polymer) the LOI falls to 28 and smoke production rises to $D_{\max} = 450$ for the same sample size. This represents a 46% increase in flammability (as determined by LOI) and smoke production increases by $\sim$29%. However, the addition of small but significant amounts of mainly metal oxides will restore the fire resistance. To significantly reduce smoke however, is more problematical.

Most of the combustion and thermal studies on PVC have been carried out on rigid PVC formulations, i.e. unplasticized formulations where plasticizer has no role in the chemistry of decomposition. Plasticized PVC has however been much less thoroughly studied and since plasticizers may be used in appreciable amounts (up to 80% in totally flexible PVC wire and cable formulations) it is important to consider the role which plasticizers such as DOP play in flammability and smoke producing reactions. Much work on PVC has been done and reported. Many of these investigations have been aimed at gaining an understanding of the mechanism of how PVC decomposes thermally and the effect which additives have on the chemistry of the decomposition. Some excellent work has been done by Kroenke and Lattimer in the rigid PVC system[5–11]. Work also by Marks *et al.*[12],

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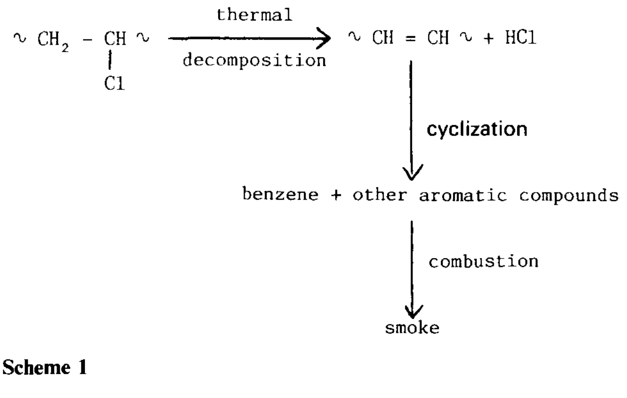
Starnes *et al.*[13–15], O'Mara[16], Michell and Shah[17], Ballistreri *et al.*[18], Burley[19], Iida and Goto[20,21], Lawson[22,23], Cullis and Hirschler[24–27], Brauman[28–31], Descamps and Delfosse[32], Michel and Guyot[33–36], as well as Carty *et al.*[37–42], to name but a few authors, has been published in the chemistry and polymer literature. Literally hundreds of patents on PVC have been published in the last 20 years or so. It is not the purpose of this paper to review all this research but the essential details about the chemistry of PVC decomposition, and its stabilization, are now fairly well understood and are pertinent to this discussion. This paper attempts to explain how iron compounds chemically interact with thermally decomposing PVC.

PVC DECOMPOSITION

Virgin PVC decomposes at temperatures between 150°C and 230°C with the evolution of hydrogen chloride and discoloration. Large amounts of smoke are also produced (*Scheme 1*). This reaction has been studied by several groups of workers over the years. PVC is normally processed in the 150–200°C temperature range and the conjugated polyene sequences which may develop in non-stabilized PVC polymer during processing give rise to intense yellow-brown colours as the PVC decomposes. Loss of hydrogen chloride leaves, as a residue, a conjugated polyene which can undergo further reactions to yield a vast array of hydrocarbon products. As these dehydrochlorination and decomposition reactions proceed, useful properties, such as electrical resistance and mechanical strength deteriorate, and in addition, the hydrogen chloride liberated will attack and corrode metal parts of the machinery used to process PVC commercially[43]. The production of dioxins from burning PVC in domestic rubbish has been described[44] and the toxicity of PVC smoke has been discussed[45]. The corrosion of electrical components in telecommunications equipment, computers and other office equipment by hydrogen chloride in fires is also a cause for concern[46]. These undesirable effects of hydrogen chloride can be significantly reduced by adding stabilizers to the PVC prior to processing. Compounds of lead, barium and tin can often be used in conjunction with secondary organic stabilizers.

Additives to reduce the flammability and the smoke producing properties of PVC both in rigid and semi-rigid/fully flexible PVC formulations have also been studied. The great majority of this work has however been done with rigid PVC formulations. The major metal based additives used to reduce the flammability of PVC are antimony and tin while the most important commercial smoke suppressants are zinc and molybdenum compounds. Some work with iron based smoke suppressants has been reported by several workers, notably Lawson[22], Kroenke and Lattimer[5], Hirschler[26], Brauman[31], Iida and Goto[20,21], Guyot *et al.*[34], Uegaki and Nakagawa[46] and Carty *et al.*[37–39,42]. Because of their colour however, iron based compounds have had little commercial success even though the effectiveness of some iron and organo-iron compounds is exceptional[41].



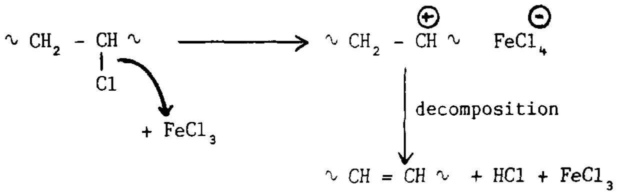
Scheme 1

PVC/IRON INTERACTIONS AND CHAR FORMATION

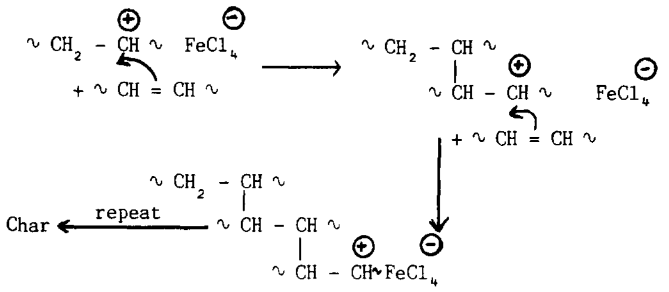
Using mainly thermal methods of analysis, Brauman[31] investigated the effect of iron(III) pyromellitate, zinc pyromellitate and molybdenum trioxide on the thermal decomposition of rigid PVC. She found that iron compounds catalyse early dehydrochlorination in rigid PVC and iron pyromellitate was especially active in forming char. She also clearly established that iron compounds change the nature of the volatile products formed during pyrolysis. The iron compound she studied in rigid PVC greatly increased the amount of aliphatic volatiles formed and decreased in the same way the amounts of pure aromatics formed when measured against a control formulation containing no additive. Several other workers have confirmed this observation and it has also been unequivocally established[10] that the organic volatiles released are produced from non-crosslinked regions in the decomposing PVC. Benzene is a known precursor of smoke, and a reduction in the amount of benzene formed during PVC decomposition inevitably leads to the formation of less smoke (however, see ref. 34). The ability of iron compounds to suppress smoke production in rigid PVC has been rationalized in terms of the Lewis acid properties of iron(III) chloride in relation to its catalytic function by invoking the fact that iron promotes an ionic decomposition mechanism. There is little convincing evidence in the literature on how the iron compounds produce char and evidence is also scarce on the process of how iron compounds act in the semi-rigid PVC system. Starnes and Edelson[14] have hypothesized on how related molybdenum compounds act, and Marks *et al.*[12] have discussed possible reaction mechanisms for some commercial tin additives in the rigid PVC system.

Kroenke[5] showed that α-Fe_2O_3, present in rigid PVC at 5 phr, increased char formation by ~43%. Brauman[29] also established that several iron based compounds at the 5 phr level also in rigid PVC increased char formation by between 40% and 44%. Carty and Docherty[38] found that a range of inorganic and organometallic iron containing compounds increased char formation by between 52% and 98% in a semi-rigid PVC formulation containing 30 phr DOP. Although some work has been published on char formation[47], few authors have attempted to clarify the chemistry involved in these char forming reactions in the semi-rigid PVC system.

Iron(III) chloride is an excellent Lewis acid catalyst[48] and it is probably one of the best acceptors of chlorine atoms among the range of Lewis acid catalysts studied. During thermal decomposition of PVC formulations containing iron compounds, it has been suggested that iron(III) chloride is formed *in situ* from a reaction between the iron additive and hydrogen chloride formed from the dehydrochlorinating PVC[34].



Scheme 2



Scheme 3

Anhydrous iron(III) chloride is reasonably stable (see later) and being molecular is fairly mobile in the mainly organic semi-rigid PVC formulation.

It is also proposed here that iron compounds are active participants as smoke suppressants in PVC formulations. *Scheme 2* shows the dependence on the high Lewis acid activity of iron(III) chloride. When PVC containing active iron compounds is heated, small amounts of iron(III) chloride are formed in the decomposing polymer. This iron(III) chloride reacts with the PVC by accepting a chlorine atom from the polymer forming an ion pair (*Scheme 2*).

The primary carbonium ion formed, being relatively unstable decomposes into alkene, hydrogen chloride and iron(III) chloride. The iron(III) chloride formed then reacts again as shown in *Scheme 2*. Then a reaction not unlike cationic polymerization occurs when an intact portion of a PVC chain activated by iron(III) chloride reacts with a partially degraded part of a PVC chain. This is the beginning of the formation of carbonaceous char which is formed by a series of crosslinking reactions essentially catalysed by iron(III) chloride (*Scheme 3*).

Hence the rate of dehydrochlorination in PVC will be accelerated at least in the early stages of decomposition but once iron(III) chloride is formed in catalytic amounts crosslinking reactions replace dehydrochlorination reactions. Brauman[31] found that in the case of iron pyromellitate, after an initial increased rate of decomposition, the weight loss slowed down to such an extent that a rigid PVC formulation containing no iron decomposed faster. We would like to suggest that small amounts of iron(III) chloride formed *in situ* produce carbonium ions which react with unsaturated groupings in the PVC to build up char and subsequently reduce smoke formation. Also, the hydrogen chloride released during these reactions acts as a flame retardant. Hydrogen chloride is a well documented flame poison[49] and its production *in situ* is probably the major reason why rigid PVC has such a high LOI value. Some of this iron(III) chloride formed will, by disproportionation, be reduced to iron(III) chloride. This was found to occur in rigid PVC containing iron compounds some time ago by Iida and Goto[20]:

$$2FeCl_3 \rightarrow FeCl_2 + Cl_2$$

Some of the iron(III) chloride ($\Delta H_f^\circ = -342.22$ kJ mol^{-1}) being less thermally stable than iron(III) chloride ($\Delta H_f^\circ = -400.32$ kJ mol^{-1}) will in turn generate more iron(III) chloride[50] and iron(III) oxide ($\Delta H_f^\circ = -821.3$ kJ mol^{-1}) especially on the surface of the burning polymer where oxygen is readily available[51]:

$$6FeCl_2 + \tfrac{3}{2}O_2 \rightarrow Fe_2O_3 + 4FeCl_3$$

This freshly formed iron(III) chloride will react with PVC as before. This reaction then repeats through the mass of the polymer (see *Scheme 2*) so that polymer carbon is converted into carbonaceous char thus dramatically reducing the amount of carbon which would otherwise be available for the formation of smoke via the dehydrochlorination/cyclization pathway (see *Scheme 1*).

Several workers have identified various iron containing species in PVC formulations containing iron compounds using various techniques. Iron metal, iron(III) chloride and iron(III) oxide have been identified as being present in chars from rigid PVC[5]. The formation of red Fe_2O_3 in PVC has been observed by Michel[35] and he has some evidence that iron(III) oxide formed *in situ* from iron(II) chloride will reduce smoke in PVC systems by oxidizing carbonaceous char to oxides of carbon.

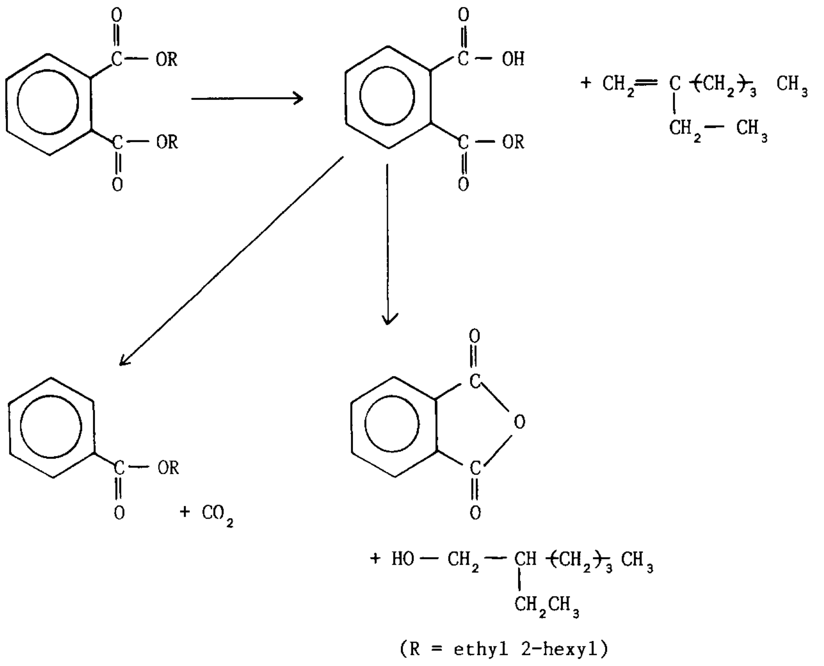
These reactions explain many of the experimental observations. Char formation (crosslinking) is dramatically increased[38,52]. The process is catalytic and Lawson[22] has observed $[(Cp)Fe\text{-}H]^+FeCl_4^-$ species in a related system. Some of the iron additive is converted to iron(III) oxide especially on the surface[17] of the sample and this in turn will reduce smoke by oxidizing carbon char to oxides of carbon. ABS/PVC/iron compound formulations have very high LOI values (often in excess of 35) and produce less smoke[41].

Guyot *et al.*[34] observed that the introduction of a plasticizer such as DOP into PVC causes an increase in flammability and also a large increase in smoke formation.

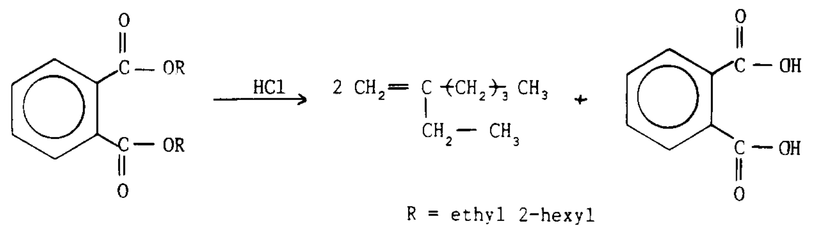
Dickens[53] showed that the three main products of DOP pyrolysis are phthalic anhydride, ethyl hexene and ethyl hexanol. However the amounts of smoke produced by both phthalic anhydride and ethyl hexene are lower than the amounts produced by PVC plasticized with DOP. In the absence of hydrogen chloride five products have been identified; phthalic anhydride, ethyl hexene, ethyl hexanol, ethyl hexyl benzoate and the monoester of phthalic acid (*Scheme 4*).

Hydrogen chloride reacts with DOP to give only two products, phthalic acid and ethyl hexene, the yield of phthalic acid being virtually quantitative (*Scheme 5*).

The important feature of this work is that phthalic acid has been identified as a key component in smoke formation during the burning of plasticized PVC. It was established by Guyot *et al.*[34] that the combustion of phthalic acid produced large quantities of smoke. The hydrogen chloride produced during the decomposition of plasticized PVC has a dramatic effect on smoke production and flammability. As discussed earlier, rigid PVC produces much less smoke than either flexible or semi-rigid PVC. DOP plasticizer, which is present in substantial quantities in semi-rigid and flexible PVC formulations, being an ester is readily decomposed by



Scheme 4



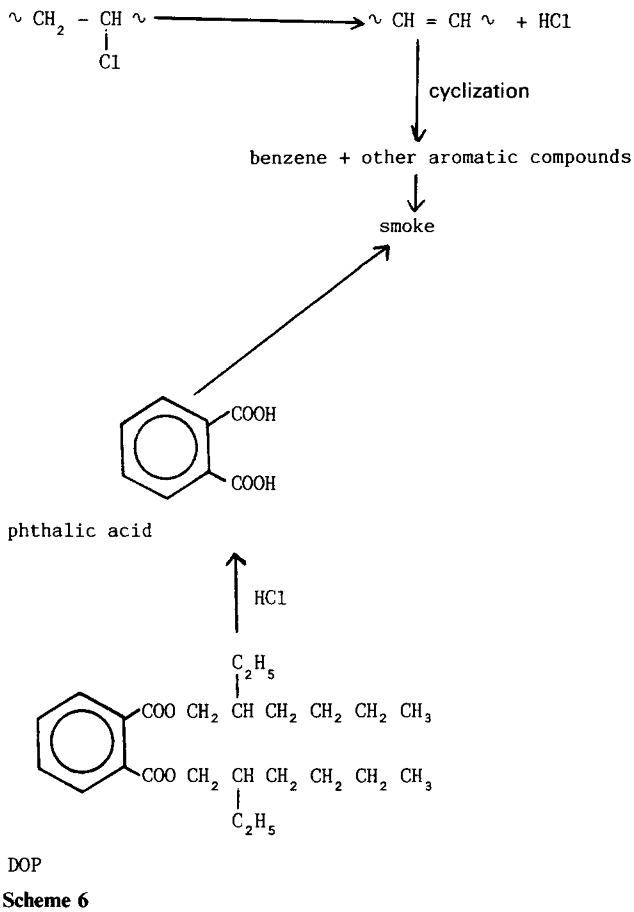
Scheme 5

HCl. Indeed we have identified an inflection point in the thermogravimetric trace which we have attributed to plasticizer degradation in a semi-rigid PVC formulation[37].

In relatively simple systems ester hydrolysis is catalysed by small amounts of acid, however in the essentially non-aqueous complex semi-rigid and flexible PVC systems, where high levels of DOP are available, hydrogen chloride produced from the hot decomposing PVC will react immediately with the ester giving phthalic acid and eventually large quantities of smoke. The hydrogen chloride is thus 'used up' and is therefore not available to act as a radical scavenger in the flame and consequently the LOI of the plasticized PVC is considerably lower than that for rigid PVC (see *Scheme 6*).

Examination of recent ABS/PVC studies provides additional confirmation of the above hypothesis[41]. It has recently been shown that the addition of quite small amounts of iron compounds to an ABS rich (>70%) blend with unplasticized PVC gives very dramatic increases in LOI values with a concomitant reduction in smoke formation. Here there is no DOP to react with the hydrogen chloride nor are there large amounts of phthalic acid produced which would add to the smoke produced from the ABS component of the polymer blend. Carty and White[41] have found that smoke production in ABS/PVC blends is significantly reduced in the presence of iron compounds and we are examining this aspect of the work in more detail.

Brauman[31] observed in the rigid PVC system that virtually all the iron included in the formulation remained



Scheme 6

behind after pyrolysis. Our proposed scheme does not invoke loss of iron from the system, indeed it suggests that the iron is retained in the polymer system undergoing a series of reactions but ending up as Fe_2O_3 and this *in situ* production of iron (III) oxide actually helps to reduce smoke production by its action as a catalyst in which it oxidizes the carbonaceous char formed by the crosslinking action of iron (III) chloride, to oxides of carbon.

CONCLUSIONS

Smoke reduction in PVC both in rigid and semi-rigid formulations and in blends with ABS and possibly other polymers can be effectively achieved by the incorporation of low levels of iron and organo-iron compounds in the polymer system. Some of the early research suggested that this smoke reducing effect is primarily an oxidative one where carbonaceous char is oxidized to oxides of carbon. However, we have found that iron compounds are, in addition, chemically active in these polymer systems. Although the flame retarding effect of some oganometallic iron compounds in PVC and in PVC blends with ABS is difficult to explain at present[41], the very important char forming/smoke suppressant effect of iron compounds is almost certainly a result of crosslinking ionic reactions involving iron (III) chloride acting as a Lewis acid catalyst in the decomposing PVC. Whether or not the activity of these iron compounds is, in addition, a result of the reductive coupling reactions suggested by Kroenke and Lattimer[6] is still open to question, since iron has multiple valencies available. Further work is required to establish unequivocally that iron compounds do behave in this way. The synergistic flame retarding/smoke suppressing effect of some recently prepared aldol compounds derived from monoacetyl ferrocene and some aromatic aldehydes, especially the furoyl derivatives[39], must also be studied in greater detail.

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