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REVIEW

Mechanistic aspects of the thermal stabilisation of PVC by organotin compounds

Joseph William Burley
Lankro Chemicals Limited, PO Box 1, Eccles, Manchester M30 0BH, UK

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When subjected to heat and mechanical shear PVC decomposes via the elimination of HCl. This process is controlled most efficiently by the use of organotin stabilisers. This review outlines the basic degradation/stabilisation mechanisms which are involved in these processes. The organotin compounds of most commercial significance receive particular attention. Model compound studies which highlight potential stabilisation mechanisms are discussed but emphasis is placed on in-situ studies which are much more realistic. Finally the phenomenon of synergism is discussed with reference to conventional alkyltin and the more novel estertin compounds.

Keywords: Introduction, mechanisms of PVC decomposition, organotin compounds useful in PVC stabilisation, basic stabilisation mechanisms, model compound studies, in-situ studies, synergism

INTRODUCTION

PVC is the most versatile of today's commercial polymers. A recent survey[1] of US markets suggests that it finds its way into more than 60 end applications produced by a wide variety of processing techniques.

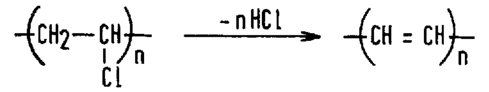
This situation has been reached in spite of its unstable nature. Virgin PVC starts to decompose to eliminate hydrogen chloride, discolour and lose its physical properties in the region of 100°C. Hence the incorporation of stabilisers is required in order to process PVC from the raw polymer into the finished articles. Typically temperatures in the region of 180–200°C are employed and the unstabilised polymer decomposes rapidly in this temperature range. The reasons for the instability of PVC are still a point of great debate. The need to stabilise PVC during processing has not limited its use, however, and it has led to the growth of an industry solely devoted to the stabilisation of this polymer. No single class of compounds can fulfil the broad stabilisation requirements of PVC and a range of primary stabilisers are available. Lead salts, mixed metal soap stabilisers (Ba/Cd, Ca/Zn and more recently Ba/Zn) have their role to play but the most effective class of compounds are the organotin stabilisers. In spite of their relatively high cost (offset to some extent by lower levels of use) these compounds are the preferred stabilisers for many applications due to their excellent properties. These include good heat stability, good light stability, excellent compatibility with PVC (ensuring lack of exudation and plate-out problems) and the ability to impart crystal clarity to the PVC formulation.

Not surprisingly the commercial success of these materials has prompted detailed studies of their mechanistic actions. The reader's attention is drawn to several reviews which have already appeared in this area. The work of Wirth and Andreas[2] presents a good overall view of the preventive and curative actions exhibited by organotin compounds in PVC stabilisation. Most writers in the PVC field appear to favour either the ionic decomposition mechanism[3] or the free radical mechanism.[4] Exponents of the former mode of decomposition relate stabilisation closely with the ability to replace 'active' chlorine atoms within the polymer. A review by the Russian workers Minsker, Kolesov and Zaikov[5] highlights the main structural defects within the polymer which are believed to give rise to the elimination of HCl. The early work of Winkler[4] and Stromberg et al.,[6] and the more recent review by Cooray and Scott,[7] however, serve to highlight the alternative view that the free radical initiated decomposition process is the more important (particularly under dynamic processing conditions). A slightly later review by Brecker[8] supports the now rather out-moded theories of Frye, Horst and Paliobagis[9] with regard to co-ordination between active chlorine atoms within PVC and the central tin atom of the organotin compound. This review, however, does give an excellent description of the organotin stabilisers which are of real commercial significance. Another group of Russian workers, Troitskii et al.,[10] have undertaken the mammoth task of comparing the stabilising activity of 40 different organotin compounds. A comprehensive comparison employing several different experimental techniques was performed. The most recent review in this area appears to be the chapter by Blunden, Cusack and Hill[11] in *The Industrial Uses of Organotin Compounds*. This work covers almost all aspects of stabilisation by organotin compounds, ranging from structural irregularities within the polymer, through mechanisms of action, to general aspects of stabilisation involving toxicology, odour, migration, compatibility and lubrication during processing.

This review attempts to highlight the most significant aspects of PVC stabilisation by organotin compounds and to present a critical view of some of the work already published in this area. The review largely, but not exclusively, covers the period from approximately 1980 onwards.

MECHANISMS OF PVC DECOMPOSITION

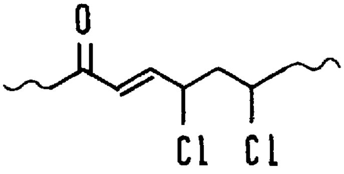
Unquestionably PVC decomposes by the elimination of HCl to give conjugated polyene sequences. These give rise to the characteristic discoloration and the loss of physical properties which is largely associated with cross-linking (Scheme 1). Different groups of workers, however, appear to attach varying degrees of significance to the two main decomposition mechanisms. This is the 'ionic' versus 'free radical' controversy which has now persisted for some time.



$$\left(\mathrm{CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}}\right)_n \xrightarrow{-n\mathrm{HCl}} \left(\mathrm{CH=CH}\right)_n$$

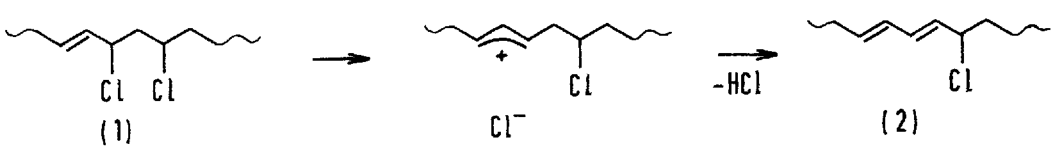
Scheme 1

Essentially the ionic mechanism for dehydrochlorination is based on the presence of unstable entities within the polymer characterised by an active chlorine group. There is even argument as to the nature of the major decomposition centre. The majority of opinion, however, favours the allylic chlorine entity (1) (Scheme 2) The C-Cl bond in this group is susceptible to ionisation and, therefore, to the elimination of HCl. Ionisation of the so-formed allylic species (2) will then be even more facile due to enhanced resonance stabilisation of the resultant positive ion. The review by Minsker et al.[5] suggests that the keto-chloroallylic group (3) may be even more susceptible to dehydrochlorination with the rate constant for this reaction being a factor of 10^2–10^3 greater than the same process with the simple chloroallylic group (1). Hjertberg and Sörvik[12] have, however, concluded that there is little evidence for the existence of (3) in commercially produced PVC. The rate of dehydrochlorination of structure (1) will be enhanced by any species which will facilitate ionisation of the C-Cl bond by accepting the chlorine ion. Razuvaev and co-workers[13] suggest that HCl already eliminated from the degrading polymer acts to catalyse its further dehydrochlorination. In this situation HCl is considered to be an acceptor for Cl^- to give the triple ion HCl_2^- and hence facilitate the elimination of HCl.

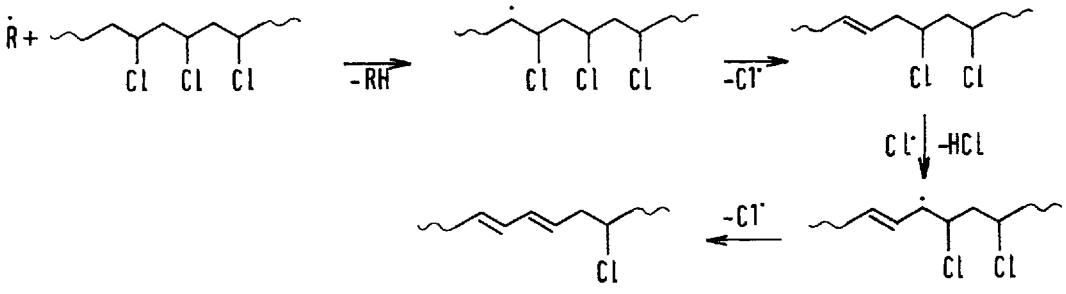


(3)

Hjertberg and Sörvik[12] have comprehensively reviewed the available information related to structural imperfections in PVC and have also



Scheme 2



Scheme 3

summarised the attempts to correlate this data to the proposed degradation mechanisms for PVC. Based on their own work they conclude that there is a stronger correlation of dehydrochlorination rate with secondary chlorine groups rather than with allylic chlorine moieties.

As early as 1959 Winkler[4] proposed the alternative view that the decomposition process is based on free radical rather than ionic reactions. He proposed the radical chain process is initiated by catalyst residues from the polymerisation process (Scheme 3).

More recently the view that thermomechanical scission of polymer chains can produce the initiating radicals has been put forward.[14] Since almost all industrial techniques for the conversion of raw polymer to the finished article include not only heat but also some degree of mechanical shear, then this latter suggestion would appear to be particularly relevant. Even the most avid exponent of this theory, however, accepts that under conditions of static oven heat ageing, the ionic process may still provide a significant route for decomposition.[15] The ionic versus radical decomposition discussion has been reviewed previously by Ayrey, Head and Poller[16] and it is not the object of this review to repeat this exercise. Indeed, it is likely that both decomposition routes operate simultaneously, the processing conditions dictating the predominant mechanism.

ORGANOTIN COMPOUNDS USEFUL IN PVC STABILISATION

The organotin compounds which have found most use as PVC stabilisers are almost entirely based on mono- and dialkyltin derivatives of the general structures $RSnY_3$ and R_2SnY_2. R is an alkyl radical and is either Me, Bu, Oct or $CH_2CH_2CO_2Bu$; Y is a radical based on a carboxylic acid, a maleate half ester, a mercaptan or a mercaptoester. With regard to compounds of commercial significance this area has been reviewed fairly recently.[8] A number of points are, however, worth emphasising here. One of the first organotin stabilisers to find commercial application was dibutyltin dilaurate. This compound, however, finds little, if any, use in PVC today. The dibutyltin bis(alkyl maleate half-esters) exhibit particularly good light stability in rigid, clear PVC and, hence, are useful in the production of sheet for outdoor applications. By far the most widely used class of tin stabilisers are the mixed mono/di alkyltin mercaptoesters: $(RSn(SCH_2CO_2R')_3/R_2Sn(SCH_2CO_2R')_2$ $(R'=$ alkyl)). These find application in the production of PVC bottles, sheet and films of many types. Iso-octylthioglycollate (USA) and 2-ethylhexylthioglycollate (Western Europe) derivatives are by far the most common but more recently longer chain analogues of the mixed octyltin derivatives have been patented and commercialised.[17] Mixtures of mono- and dialkyltin compounds are employed due to their synergistic action, since this combination results in superior heat stability in comparison to either of the pure compounds.

In the USA improvements in both machine and formulation technology related to the extrusion of white pipe has led to the development of organotin stabilisers based on long chain carboxylic acid derivatives of mercaptoethanol. These stabilisers are high monoalkyltin containing mixtures based on either methyl or butyltin compounds and give the excellent early colour control which is of prime importance.

Dibutyltin bis lauryl mercaptide is the only unsubstituted mercaptide derivative of any commercial significance. Its use is limited to the injection moulding area where the superior lubrication properties of this compound in comparison to other thiotin stabilisers are exploited.

Organotin sulphides are sometimes employed to improve the heat stability of other thiotin stabilisers. The action of these compounds is again synergistic but in many cases high cost, due to the high tin content, precludes their use. This is not so, however, in formulated stabilisers where the tin content is kept to a minimum (approximately 5%) and here the organotin sulphides present a cost effective method of introducing tin.

Dialkyltin maleates and cyclic dibutyltin derivatives based on mercaptoacetic and mercaptopropionic acids exhibit reasonable heat stability but are rarely used because of their extremely poor processing characteristics. These compounds actually appear to impart an anti-lubricating effect to the PVC formulation.

BASIC STABILISATION MECHANISMS

Whilst controversy still exists concerning the exact nature of the labile chlorine structure responsible for the initiation of dehydrochlorination, and with regard to the exact mechanism of this process, there appears to be a far more unified view of the reactions which are responsible for stabilisation. These have recently been catalogued by Owen[18] in line with conclusions drawn by other authors.[2,7,14,19] These processes are listed and discussed briefly here. Later sections of this article will focus on the model compound studies and the in situ studies of the stabilised degrading polymer which have provided the evidence in support of these mechanisms.

Hydrogen chloride scavenging

It now seems that the majority of evidence supports the theory that the dehydrochlorination of PVC is catalysed by HCl.[13,20–22] Again the mechanism of this catalysis is not absolutely clear but from a use point of view, the ability of organotin compounds to react efficiently with HCl will provide some degree of stabilisation. The limited stabilising capacity of dibutyltin dilaurate is undoubtedly attributable to its ability to neutralise HCl. With the more efficient stabilisers such as dialkyltin bis(iso-octylthioglycollates) ($R_2Sn(IOTG)_2$), HCl scavenging probably plays a minor role. These compounds delay the onset of dehydrochlorination for a much longer period than the neutralisation of HCl eliminated by the unimolecular elimination of HCl would suggest.[23]

Reaction with labile chlorine

Elimination of labile chlorine atoms in the PVC backbone by exchange processes with the Y groups in either $RSnY_3$ or R_2SnY_2 will give rise to more stable structures which will delay the onset of dehydrochlorination. With this mode of stabilisation the effect is temporary, since ultimately these groups are converted back to their original structures by reaction with HCl.[5] Hence there is ultimately no change in the number of these labile groups during the degradation of PVC in the presence of organotin stabilisers.[23]

Destruction of polyenes

Dehydrochlorination of PVC gives rise to relatively small numbers of long polyene chains with the result that blackening occurs with the loss of $<0.1\%$ of the contained HCl. Efficient stabilisers, therefore, will have the capacity to interrupt the developing conjugation by some mechanism whereby the stabiliser itself, or a group generated from the stabiliser, will add to the unsaturated system.[2,24]

Radical scavenging

The free radical chain mechanism for PVC is believed to be propagated by $Cl^{\bullet}$ radicals.[4] Compounds which have the capacity to consume these or other radicals in the kinetic chain will therefore contribute to the overall stabilisation process.

Destruction of hydroperoxides

It is now well established that hydroperoxides which are produced in the oxidative degradation of PVC have a detrimental effect on the stability[7] since they can decompose by radical processes to give rise to other radical species which further contribute to the degradation process. Destruction of hydroperoxides has, therefore, been identified as a further process whereby stabilisation of PVC can be effected.

The role of organotin chlorides

The majority of organotin stabilisers which are in use today are converted, ultimately, to their corresponding organotin chlorides ($RSnCl_3$ or R_2SnCl_2). In view of the Lewis acid nature of these materials (particularly $RSnCl_3$) they will exhibit a prodegradant effect. Processes which delay the formation of, or reagents which destroy or chelate the organotin chlorides will therefore exhibit a secondary stabilising effect.

MODEL COMPOUND STUDIES

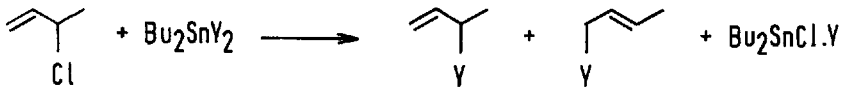
In a commercial environment the qualitative assessment of the relative efficiencies of a range of potential stabilisers is fairly simple. A range of performance tests—oven heat stability, press stability, dynamic mill stability and Brabender plastograph degradation provide sufficient comprehensive data to enable the development of products suited to specific processes or applications. Hence, in many cases, organotin stabiliser development has progressed by an empirical approach with relatively little understanding of their modes of action.

On the other hand the academic world has sought to correlate the stabilising action of organotin stabilisers with their ability to react with certain labile chlorine-containing compounds in the belief that these low molecular weight materials are true models for the sites within the PVC at which degradation is believed to be initiated.

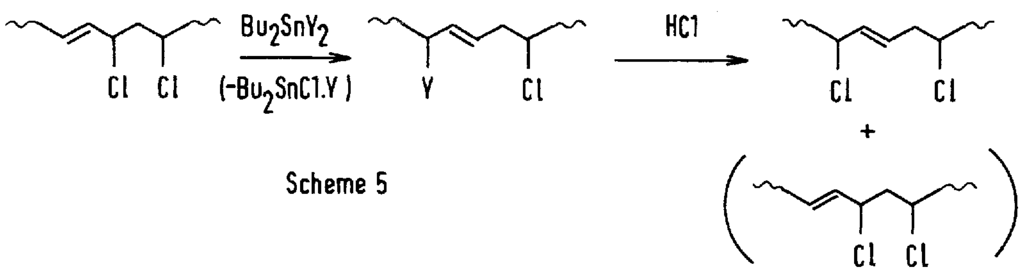
In line with the suggestions made by Baum[25] and Drusedow,[3] Klemchuk[26] also concluded that the allylic chlorine moiety in PVC is the most likely source of dehydrochlorination. These conclusions were reached from relative rate studies on 4-chloro-2-pentene and 2-chloro-2-methyl butane with several organotin stabilisers. Ayrey[27,28] has perpetuated this approach with studies of $Bu_2Sn(IOTG)_2$ and $Bu_2Sn(O_2CC_{11}H_{23})_2$ in combination with 3-chloro-1-butene. Unlike the work of Klemchuk, the choice of 3-chloro-1-butene as model compound allowed the observation of isomerisation upon reaction with the organotin compound (Scheme 4). Ayrey and co-workers conclude that isomerisation of the allylic group within the PVC backbone would give rise to a stabilising effect even though subsequent elimination of the Y group might still occur. This is debatable since re-isomerisation of the initially isomerised group would be catalysed by HCl. (or Bu_2SnCl_2) and the beneficial effect would be negated (Scheme 5). In any case the isomerised group would remain susceptible to radical chain degradation (Scheme 3).

The review by Ayrey et al.[16] gives a summary of the low molecular weight chlorocarbons which had been employed as model compounds up to approximately 1974.

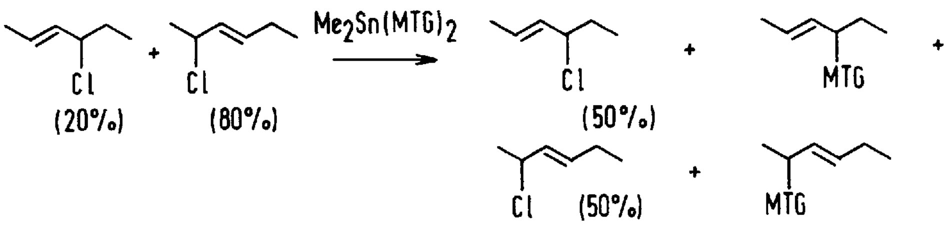
One of the most comprehensive studies of the reaction between an allylic chlorine model compound and a model organotin stabiliser is the work by Michel, Guyot and Nolle.[29] These workers studied the reaction between an isomeric mixture of 4-chlorohex-2-ene and 2-chlorohex-3-ene (referred to as CHE) and dimethyltin bis(methylthioglycollate) ($Me_2Sn(MTG)_2$) by ^1H NMR spectroscopy. To some extent the observations parallel the work of Ayrey et al. with regard to the formation of an isomeric product mixture and isomerisation of the CHE to the thermodynamic equilibrium concentration of the CHE isomers (Scheme 6).



Scheme 4 (Y=$SCH_2CO_2i\text{-}C_8H_{17}$, $O_2C.C_{11}H_{23}$)

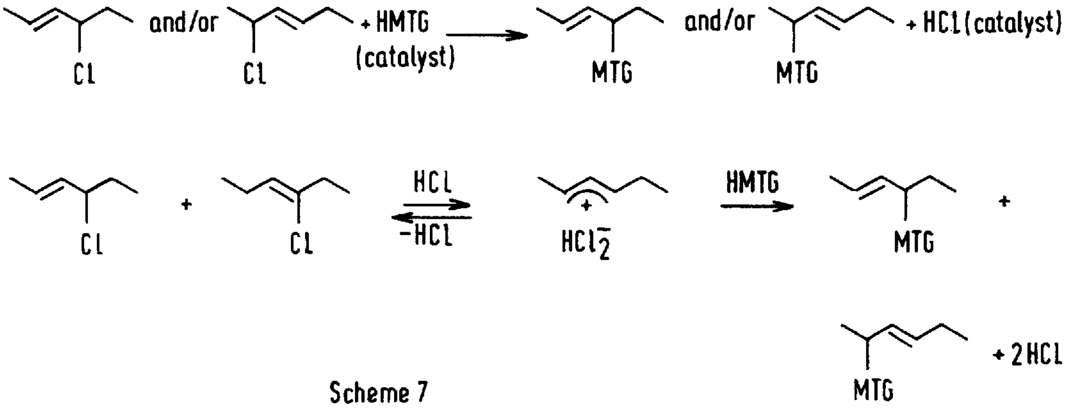


Scheme 5



Scheme 6

(MTG=-SCH2CO2Me)

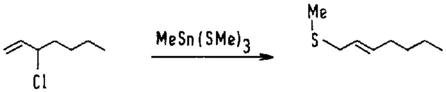


Scheme 7

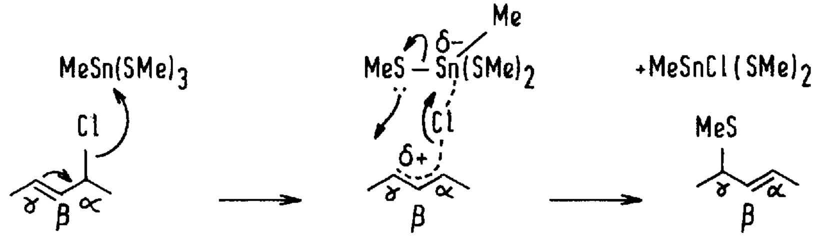
This reaction proceeded at a reasonable rate at ≧100°C and was catalysed by HCl. $Me_2SnCl(MTG)$ reacted with CHE at a faster rate but gave the same product mixture. HMTG reacted fastest of all with CHE and again the reaction was catalysed by HCl. The last observation led the authors to propose that CHE reacts with $Me_2Sn(MTG)_2$ principally by an ionic mechanism in which HMTG is first cleaved from the parent stabiliser by HCl. Subsequently this adds to the allylic carbonium ion formed by the catalysed ionisation of the CHE (Scheme 7).

A more recent study by Katz and Starnes[30] suggests that monoalkyltin tris thiolates react with allylic chlorides almost exclusively by a quasiconcerted mechanism which gives the allylic rearranged sulphides. These conclusions were based on ^{13}C NMR studies of the reactions of $MeSn(SMe)_3$ with chloroheptenes and chlorodecene (Schemes 8 and 9).

The reaction of Scheme 8 is far more stereospecific than that observed for similar reactions of dialkyltin bis(thioglycollate esters)[26-29] and dialkyltin bis carboxylates.[27] Mechanistically the formation of an intermediate ion pair is indicated (Scheme 9). It is hardly surprising that the mechanisms of these reactions are dissimilar since



Scheme 8

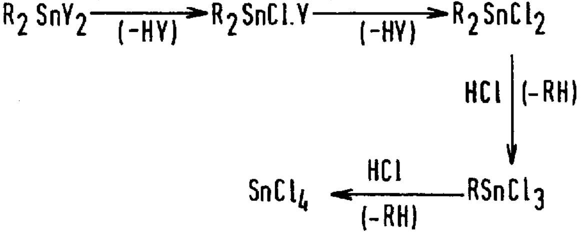


Scheme 9

there are many differences between these two studies, e.g. solvent, temperature, degree of alkylation in the organotin and use of a simple thiol versus a thioglycollate ester. A simple demonstration of this last factor is that $Bu_2Sn(IOTG)_2$ is a far more efficient stabiliser than $Bu_2Sn(SC_{12}H_{25})_2$. The absence of a concerted mechanism with the dialkyltin thioglycollate esters is almost certainly due to the lower electronegativity of the central tin atom and the fact that ester coordination (for example in $Bu_2Sn(IOTG)_2$)[31] may sterically prevent the formation of the appropriate transition state. There is obviously scope here to clarify these aspects with similar model compound work on $R_2Sn(SR')_2$ and $RSn(SCH_2CO_2R'')_3$ ($R, R', R'' =$ alkyl).

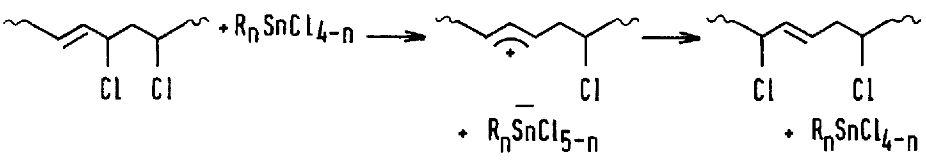
A relevant observation here comes from the work of van den Heuvel and co-workers.[67] They performed XRF and high resolution NMR studies of the stabilisation of a commercial grade of PVC by $Oct_2Sn(2EHTG)_2$. This in situ study suggests that during heat ageing at 180°C destruction of the allylic chlorine moieties by reaction with organotin stabiliser is a rather inefficient process. Only 25–30% of these active dehydrochlorination sites were consumed during the degradation process. Thus it was also concluded that by far the majority (~70%) of the organotin compound was consumed in stabilisation processes other than reaction with allylic chlorines.

Some workers have attempted to correlate stabiliser activity simply with HCl cleavage of the Y groups in R_2SnY_2. An early attempt at this by Rockett and co-workers[32] utilised aqueous HCl under unspecified conditions. The observations made by these workers would appear to be hardly relevant to the reactions undergone by organotin stabilisers at between 180 and 200°C in a polymer matrix. These workers did, however, observe that organotin mercaptides underwent facile cleavage to organotin chlorides and mercaptans, and that the corresponding carbothiolic derivatives gave carbothiolic acids. A later attempt by Ayrey and his associates[33] used gaseous HCl under more realistic conditions. Alkyltin stabilisers such as $Bu_2Sn(IOTG)_2$ gave Bu_2SnCl_2 and HIOTG as expected, but a variety of functionally substituted akyltin compounds underwent C-Sn cleavage to $RSnCl_3$ and $SnCl_4$ (Scheme 10). Both of these are recognised prodegradants for PVC (especially $SnCl_4$). These observations correlated quite well with the abilities of various compounds to stabilise plasticised PVC at 195°C. One aspect of this study, however, gives cause for concern. In many cases the yields of $R_2Sn(IOTG)_2$ obtained in the preparative experiments were low (~70–80%) and in the case of $R = CH_2CH_2CO_2Et$ the yield was 44%. This is particularly surprising since this class of compound (with $R = CH_2CH_2CO_2Bu$) can be produced by economically viable processes and have achieved a degree of commercial success. This would also tend to suggest that the C-Sn cleavage demonstrated in model studies on these compounds either does not occur or has little significance under actual processing conditions. It has subsequently been demonstrated that the addition of $Cl_2Sn(CH_2CH_2CO_2Bu)_2$ to PVC has no prodegradant effect in comparison to virgin PVC or the addition of Oct_2SnCl_2.[15]



Scheme 10

The role played by organotin chlorides in the stabilisation or degradation of PVC has prompted a number of studies utilising model compounds. Wirth and co-workers observed that the ocyltin chlorides OCT_nSnCl_{4-n} ($n = 1-3$) reduced the rate of dehydrochlorination in relation to the number of alkyl groups in the organotin compound. These workers proposed that the stabilising effect is associated with isomerisation of allylic chlorine moieties in the PVC backbone (Scheme 11 and Fig. 1).



Scheme 11

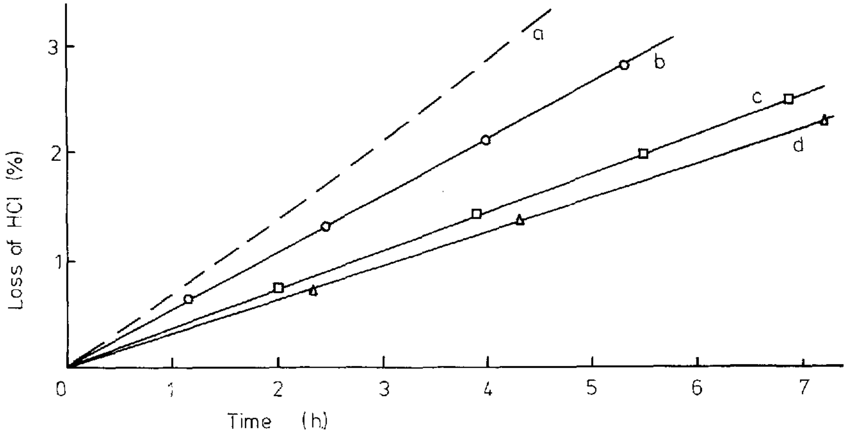


Figure 1 Thermal dehydrochlorination curves of PVC at 175°C in presence of octyltin chlorides (5 mmol 100 g^{-1} PVC): (a) no stabiliser; (b) $OctSnCl_3$; (c) Oct_2SnCl_2; (d) Oct_3SnCl.

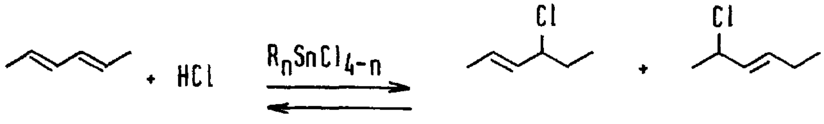
(Reproduced by kind permission of the Society of Plastics Engineers.)

In an attempt to prove this hypothesis they have studied the isomerisation of 3-chloro-2-butene by a number of organotin chlorides (R_nSnCl_{4-n}, R = Me, Bu, Oct; $n = 1$–3). Monoalkyltin trichlorides and the lower alkyltin chlorides were found to be the most efficient. This order of catalytic activity did not, however, correlate with the order of stabilisation and it is extremely unlikely, therefore, that the stabilisation exhibited by Oct_3SnCl and Oct_2SnCl_2 can be associated with the isomerisation of allylic groups within PVC.

Extensive studies of the organotin chloride catalysed dehydrochlorination of CHE to hexa-2,4-diene have been performed by Van Hoang, Michel and Guyot.[35] Using Bu_nSnCl_{4-n} ($n = 1$–3) they studied both dehydrochlorination and hexadiene formation in 1,2-dichloroethane solution in sealed glass ampoules. They observed the fastest rates of dehydrochlorination and hexadiene formation with $BuSnCl_3$ which is in line with the relative Lewis acidities of these organotin compounds. Later[37] the same group extended their studies to involve phenyltin chlorides and β-carbobutoxyethyltin chlorides ($(\beta CBE)_nSnCl_{4-n}$ ($n = 1, 2$). These so-called estertin chlorides were found to decrease the rates of CHE decomposition relative to their corresponding butyltin analogues in 1,4-dichlorobutane at 80°C. This effect was attributed to the reduced Lewis acid strength of the estertin compounds as a result of ester co-ordination.[37,38] This may be the case for $(\beta CBE)_2SnCl_2$ since Burley et al.[39] have demonstrated that the Lewis acidity of these compounds is markedly lower than the simple dialkyltin dichlorides. However, the Lewis acidity of compounds such as $Cl_3SnCH_2CH_2CO_2R$ (R = Me, Pr, Bu, etc.) with regard to formation of 1:1 complexes is apparently unperturbed in comparison to $BuSnCl_3$ and it is less likely, therefore, that this effect can explain the reduced dehydrochlorination rate.

Finally, Van Hoang and associates have examined the effect of organotin chlorides upon the addition of HCl to hexadiene.[40] Catalysis of this reaction again followed the order of the Lewis acidities $RSnCl_3 \gg R_2SnCl_2 > R_3SnCl$. In fact this group have merely approached the same equilibrium situation from both sides since they have worked in a closed system (Scheme 12). Model system studies suggest that organotin chlorides may have some stabilising effect. More realistically, however, $BuSnCl_3$ has been shown to exhibit a prodegradant effect and Bu_2SnCl_2 a neutral effect when added to virgin PVC.[41]

Studies of the addition of organotin chlorides



Scheme 12

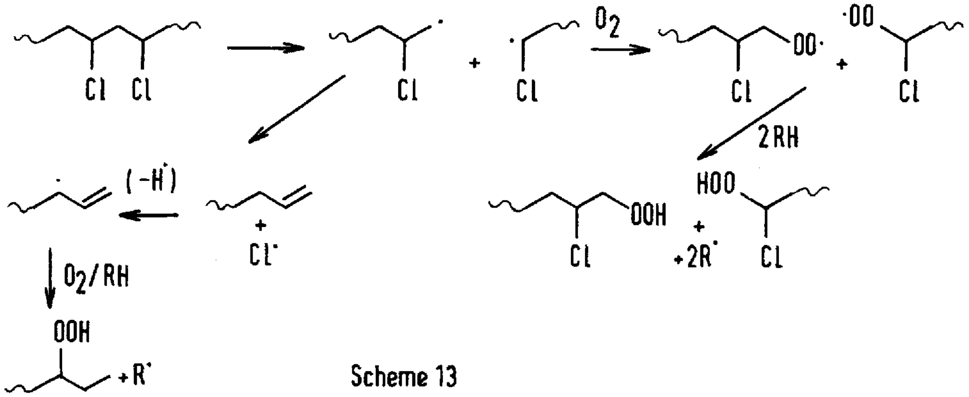
alone to PVC, or to model compounds are more relevant to the degradation of PVC at the end of the stabilisation process than to the stabilisation process itself. The concentration of these compounds in PVC will be very small until the end of the stabiliser's useful life (i.e. all Y groups have been cleaved from the tin compound).

The PVC solution studies conducted by Ayrey and co-workers provide a useful link between model compound work and the most realistic in situ studies to be described later. Their work with radioactively labelled Y groups in R_2SnY_2 (Y = SBu, 2EHTG, $O_2CC_{11}H_{23}$, and $O_2CCH{=}CH.CO_2Me$(MMM)) provides supportive evidence for the early work of Frye, Horst and Paliobagis[9] with regard to incorporation of these groups into the PVC backbone. With $Bu_2Sn(SBu)_2$[42] an autocatalytic rate curve was observed and explained in terms of an initial reaction between the stabiliser and active Cl groups in the polymer, followed by a faster reaction of liberated thiol with polyene sequences. The opposite effect was observed with $Bu_2Sn(2EHTG)_2$[23] (fast initial rate followed by a slower reaction) and the same mechanism was proposed. Perhaps these observations are consistent with the poor early colour performance characteristics of $Bu_2Sn(SC_{12}H_{25})_2$ in comparison to $Bu_2Sn(2EHTG)_2$. Two particularly interesting factors emerge from this study: (1) the addition of thiols to degraded PVC discharged, to a large extent, the colour that had been generated—providing irrefutable evidence that thiols add to conjugated polyene sequences; and (2) degraded PVC accumulated radioactivity at the same rate as virgin PVC upon reaction with Bu_2SnY_2 (Y = SBu, IOTG)—this suggests that the concentration of degradation initiation sites does not change during the early stages of the PVC degradation process.

UV spectroscopic studies and the radiochemical tracer studies also confirmed that the MMM ligands from $Bu_2Sn(MMM)_2$ are also incorporated into degrading PVC. Due to the very long degradation times (typically 10–20 hours) encountered in this anaerobic solution work and the instability of $Bu_2Sn(MMM)_2$ under these conditions the relevance of this section of the work to a realistic stabilisation situation (degradation times of 1–2 hours) is questionable.

The free radical degradation processes appear to have received far less attention than possible ionic mechanisms in model system studies. Ayrey and co-workers[19] have, however, reported a brief study of the interaction of Bu_2SnY_2 (Y = OCOR and SR′) with photochemically generated $Cl^\bullet$. In both cases Bu_2SnCl_2 is formed. With Y = SR′, $R'S^\bullet$ and R′SSR′ are formed which would appear to represent an efficient scavenging process. With Y = OCOR, however, $RCO_2^\bullet$ (and RCO_2H) are formed with the generation of other radicals. Conceivably, therefore, $Bu_2Sn(SR')_2$ may be more efficient at interrupting radical chain processes than $Bu_2Sn(OCOR)_2$. A much more recent review of Michell[65] proposes that $Cl^\bullet$ scavenging is the prime role of both thio- and non-thiotin stabilisers as well as for metal soap and lead stabilisers. He appears to present little direct evidence for his proposal (called 'true stabilisation'), an aspect of the review which also drew published criticism from the Referee.[65]

Cooray and Scott have focussed their attention on the role of hydroperoxides in PVC degradation. These species are generated during the thermomechanical degradation of PVC under oxidative conditions and hence these studies are relevant to many commercial processing techniques. The calendering of film or sheet will be particularly prone to this mode of degradation whilst the extrusion of pipe and profile or the injection moulding of various fittings will be less susceptible to this mechanism (Scheme 13).



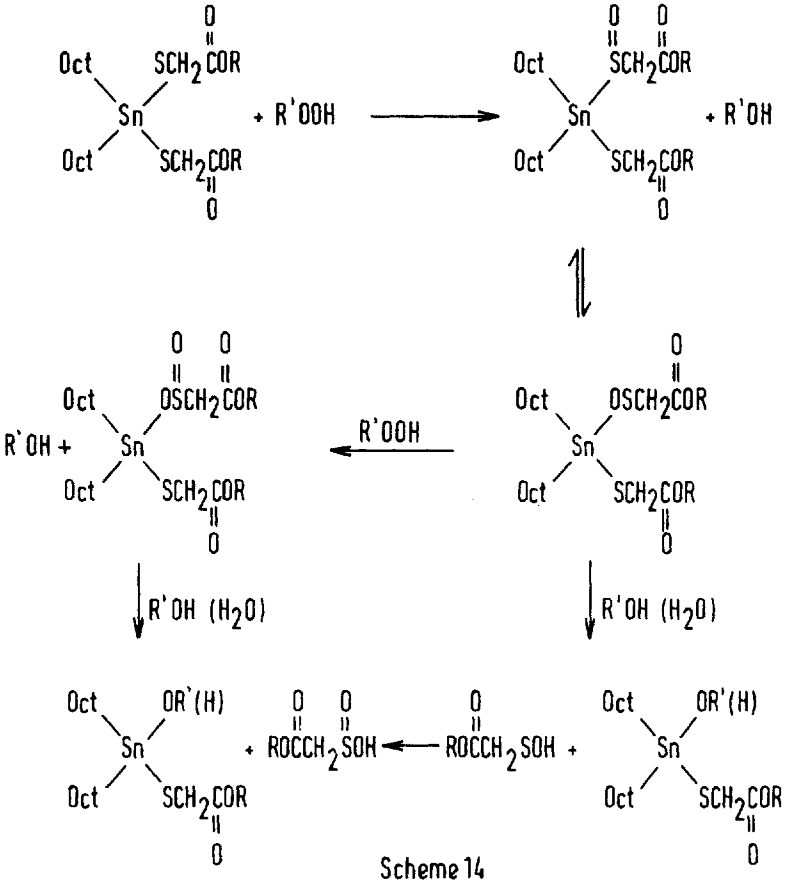
Scheme 13

Thiotin stabilisers are efficient decomposers of hydroperoxides.[43] Model system studies with cumene hydroperoxide (CHP) and t-butyl hydroperoxide (TBHP) demonstrated that the mechanisms are complex and proceed by a combination of radical and ionic schemes. In the early stages hydroperoxides are converted principally to alcohols and oxidation occurs at S within the mercaptoester giving rise to sulphoxide and sulphonate esters. Subsequently a pro-oxidant stage, analogous to that observed for antioxidant thiols, is observed with the formation of alkoxide radicals. Ultimately dialkyltin sulphate is formed along with sulphur oxides. It is unlikely that the latter stages of this scheme are relevant to PVC processing since HCl cleavage will compete with oxidative reactions in this situation. The early stages of this scheme are presented here (Scheme 14).

A similar study[22] with CHP and gaseous HCl highlighted the effect of HCl concentration upon the decomposition mechanism of hydroperoxides. At high [CHP]/[HCl] ratios CHP was decomposed completely by an ionic process. Alternatively, at low [CHP]/[HCl] ratios CHP was decomposed by a radical process which initiated pro-oxidation in cumene. The addition of dibutyltin maleate (DBTM) neutralised HCl thereby eliminating the pro-oxidant effect whereas $Bu_2Sn(IOTG)_2$ not only neutralised HCl but also exhibited a marked antioxidant effect. These observations raise the possibility that the prodegradant effect of HCl in PVC degradation may arise by the pro-oxidative decomposition of hydroperoxide species.

IN SITU STUDIES

A significant contribution in recent years to our understanding of organotin stabilised PVC degradation has been made by Scott's group. Early work by Scott, Tahan and Vyvoda[44,45] demonstrated that when subjected to shear stresses in the presence of oxygen PVC, like many other



Scheme 14

polymers, undergoes degradation by a mechano-chemically initiated free radical process (Scheme 13). This results initially in the formation of mono-unsaturation, the elimination of HCl and the generation of peroxides. In an unstabilised situation the radical reactions auto accelerate with the build-up of polyene sequences (Scheme 3) and the accumulation of other species (Fig. 2).

Organotin stabilisers such as DBTM and $Oct_2Sn(IOTG)_2$ have a marked effect upon the concentrations of unsaturation and peroxides during processing.[46] DBTM has the ability to control these species at a relatively low and even level (Fig. 3). On the other hand, $Oct_2Sn(IOTG)_2$ has the ability to eliminate them completely after initial maxima in their concentrations have been

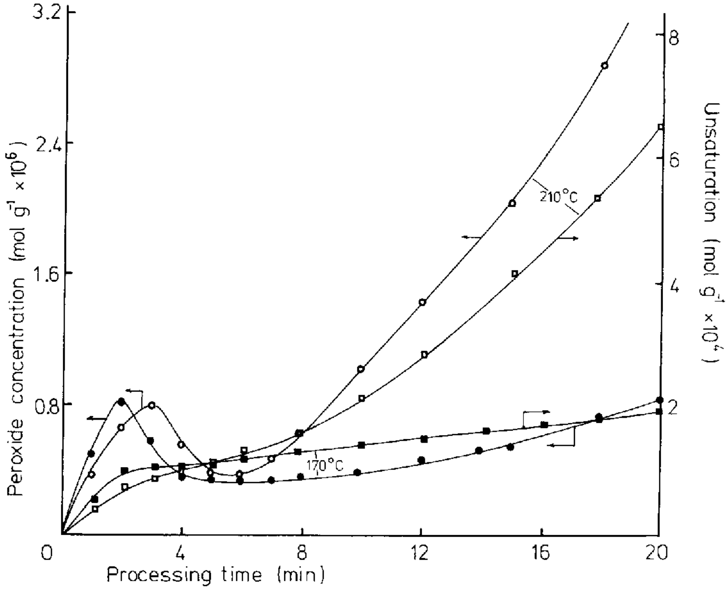


Figure 2 The development of unsaturation and peroxides in unstabilised PVC during processing at 170°C and 210°C. (Reproduced by kind permission of Elsevier Applied Science Publishers Limited.)

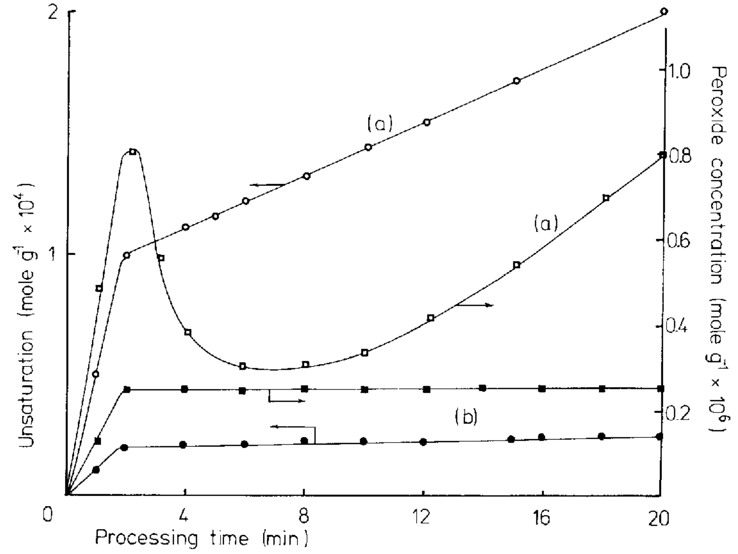


Figure 3 Formation of unsaturation and peroxides during the processing of PVC at 170°C in the presence and absence of DBTM: (a) no additives; (b) DBTM (11.6×10^{-3} mole $100 g^{-1}$)+lubricants.
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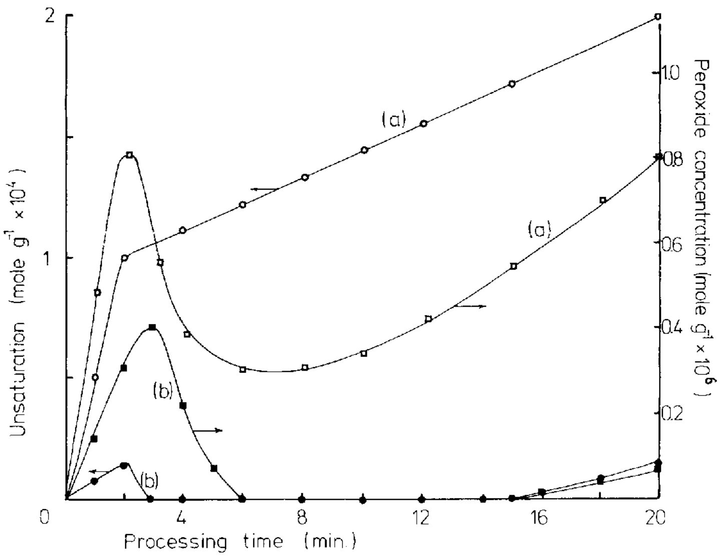

Figure 4 Formation of unsaturation and peroxides during the processing of PVC at 170°C in the presence and absence of $Oct_2Sn(IOTG)_2$: (a) no additives; (b) $Oct_2Sn(IOTG)_2$ (11.6×10^{-3} mole 100g^{-1}) + lubricants.
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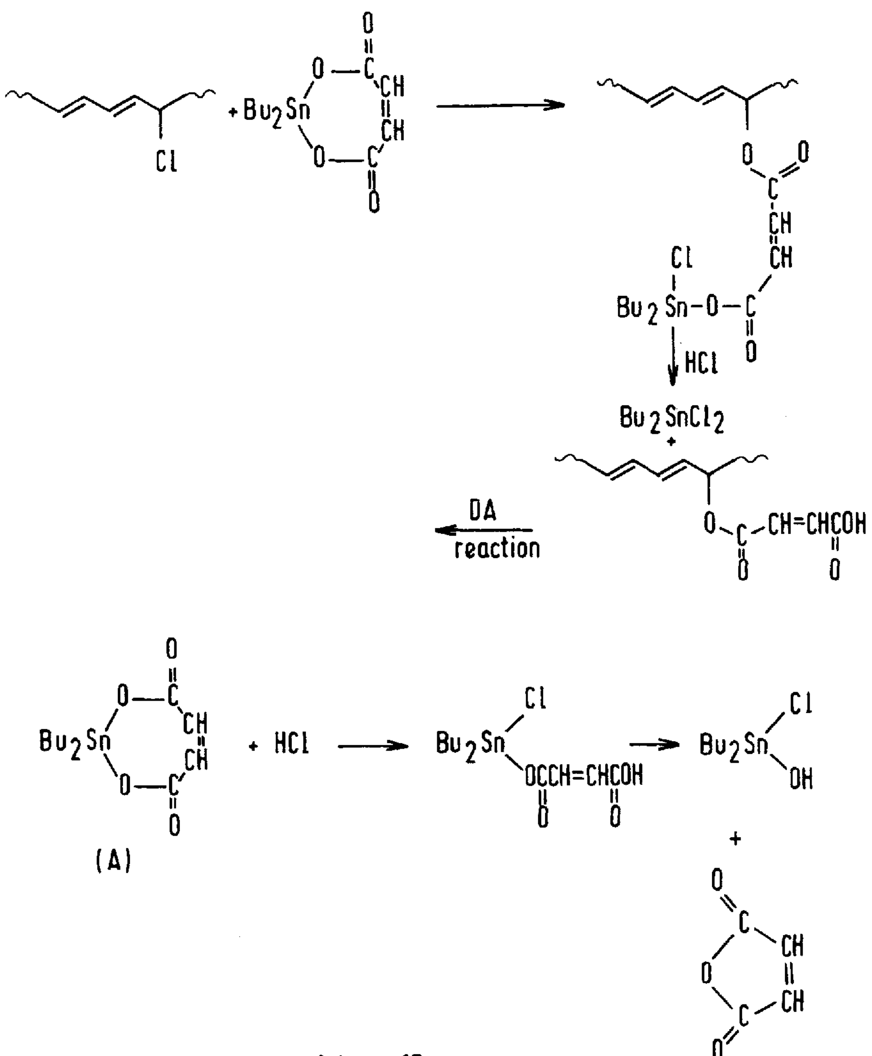
generated (Figure 4). Mechanistically, these observations can be rationalised by the fact that DBTM is incapable of reacting with mono-unsaturation but is capable, by virtue of the Diels–Alder (DA) reaction, of destroying the developing polyene sequences.

A more detailed spectroscopic study of the in situ stabilisation by DBTM has been conducted by Scott and co-workers.[24] This indicates that the initial reaction involves allylic chlorine displacement followed by a DA reaction with a maleic acid residue already bound to the polymer. Maleic anhydride itself is generated during the latter stages of this stabilisation process (Scheme 15).

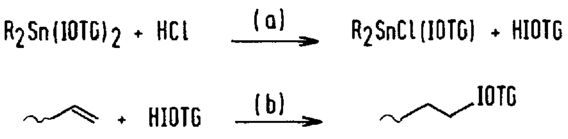
$Oct_2Sn(IOTG)_2$ has the ability to destroy the initially formed mono-unsaturation by virtue of the liberated thiol (HIOTG) addition to the isolated double bond (Scheme 16).

Cooray and Scott[7] sought to confirm this by reacting radio labelled thiol with partially degraded PVC. By monitoring both non-conjugated and conjugated unsaturation as a function of retained thiol they concluded that there is a strong correlation between mono-ene concentration and retained thiol. The alternative conclusion that liberated thiols have little effect upon conjugated unsaturation contradicts conclusions drawn by other workers[2,23,47] and does not appear valid since their experimental technique would not differentiate between long conjugated systems and essentially the same sequence interrupted by a single added thiol (Scheme 17).

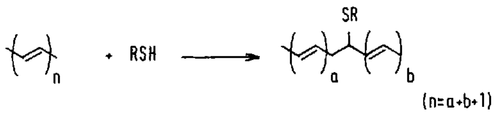
A more extensive direct study of $Oct_2Sn(2EHTG)_2$ has also been performed.[15] This work also compared the efficiency of the simple dialkyltin thioglycollate ester with $(\beta CBE)_2Sn(2EHTG)_2$ by a number of processing techniques. In general terms the estertin stabiliser was more efficient at destroying the initial unsaturation and was converted faster to its half chloride (Scheme 16(a)) reflecting the superior early colour control exhibited by this stabiliser. However, $Oct_2Sn(2EHTG)_2$ was more efficient at hydroperoxide decomposition and controlling peroxide formation. Such observations may explain the more rapid ultimate dehydrochlorination rate with the estertin stabiliser. One aspect of this study is worth deeper consideration. Ideally, the initial product generated from stabilisers of the type $R_2Sn(SCH_2CO_2R')_2$ will be $R_2SnCl(SCH_2CO_2R')$ (by reaction with either HCl or polymer bound active Cl). These reactions are readily monitored by IR spectroscopy by virtue of the characteristic carbonyl region spectra of these organotin compounds.[31] Even the early stages of the simple oven heat stability tests (particularly $R = \beta$CBE) exhibit distinct curvature in the conversion/time profiles (Fig. 5). In contrast to this, Rabinovitch and co-workers[66]



Scheme 15



Scheme 16



Scheme 17

have reported a linear relationship between stabiliser conversion ($Bu_2Sn(IOTG)_2$) and oven ageing time (see Fig. 6). These workers also employed the same infrared technique, reported by Cooray, to monitor the reaction. Differences in sample preparation (solvent cast films in the work of Cooray, extruded strips in the work of Rabinovitch) and differences in subsequent heat treatment (190° versus 163°C respectively) may explain the markedly different observations.

Cooray's data suggest that another organotin compound is involved in the stabilisation process. Of particular relevance here is believed to be the report by Bellenger et al.[48] of the formation of dibutyltin thioglycollate (Bu_2SnTG) (detected by the presence of a strong carboxylate absorption at 1550 cm^{-1} in the IR spectra of thermally treated films) during thermal stabilisation by $Bu_2Sn(IOTG)_2$. These workers proposed that Bu_2SnTG is generated by an ill-defined thermal process (Scheme 18(a)). However, in view of the fact that the same cyclic compound can be generated at room temperature upon storage or during manufacture,[8] a hydrolytic mechanism is an alternative possibility (Scheme 18(b)).

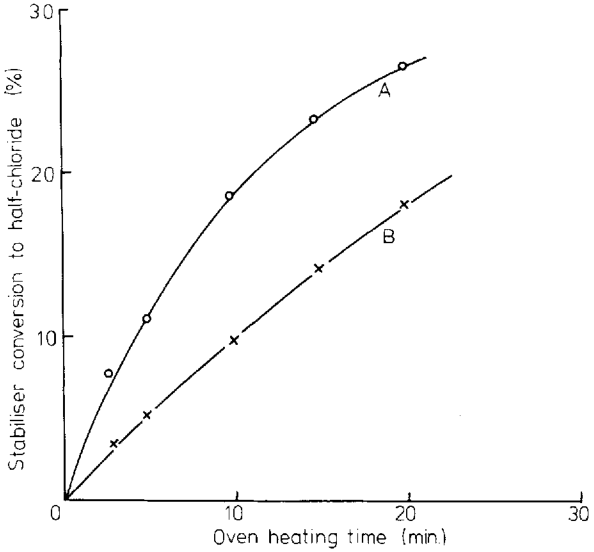


Figure 5 Stabiliser conversion to half-chloride, during oven heating at 190°C: (A) Estertin stabiliser ($(\beta CBE)_2Sn(2EHTG)_2$); (B) Octyltin stabiliser ($Oct_2Sn(2EHTG)_2$).

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Bellenger reports that Bu_2SnTG is very reactive in PVC (reaction with HCl?) and is not normally observed. Cooray and Scott[46] have also observed Oct_2SnTG (a band at 1550 cm^{-1} erroneously attributed to Sn-S) in the spectra of PVC films containing $Oct_2Sn(IOTG)_2$ and comment that it is fairly rapidly destroyed upon UV exposure. There is, therefore, sufficient evidence to suggest that R_2SnTG may be involved in the stabilisation process when $R_2Sn(IOTG)_2$ are employed. The extent to which it is generated will be dependent upon processing techniques and conditions.

An alternative direct approach has been attempted by Allen and co-workers. This group have employed ^{119}Sn Mössbauer spectroscopy to study the fate of organotin stabilisers in degrading PVC. Early work[49,50] on the thermal degradation of PVC stabilised with $R_2Sn(IOTG)_2$ (R = Bu, Oct) and dibutyltin bis (iso-octylmaleate)$_2$ ($Bu_2Sn(IOM)_2$) concluded that at the end of the stabilisation process (black PVC) the stabilisers had only been converted to their respective half-chlorides (Scheme 10(a)). This situation is unlikely in view of the fact that $Oct_2SnCl(IOTG)$ can function as a fairly efficient stabiliser when incorporated into PVC by a conventional hot milling technique (Fig. 7).

An extension of the Mössbauer studies to UV degradation[51] helped to highlight the fact that this technique is rather insensitive and erroneous conclusions are easily drawn. Initially it was

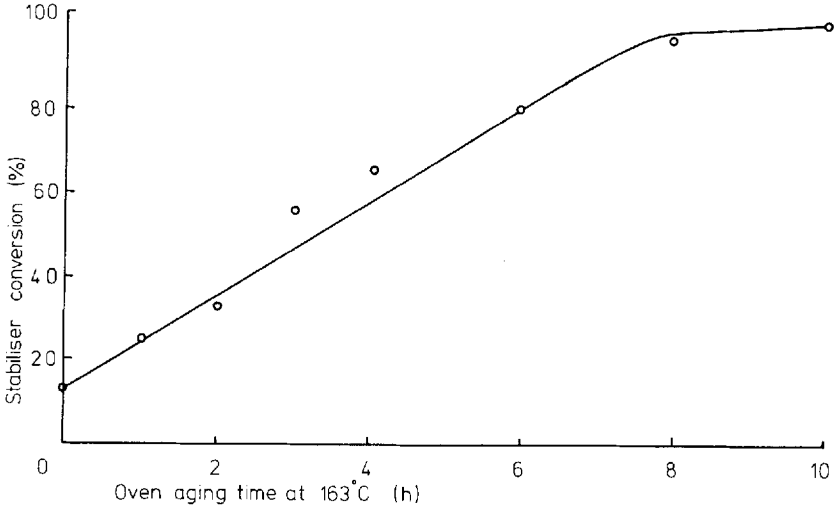
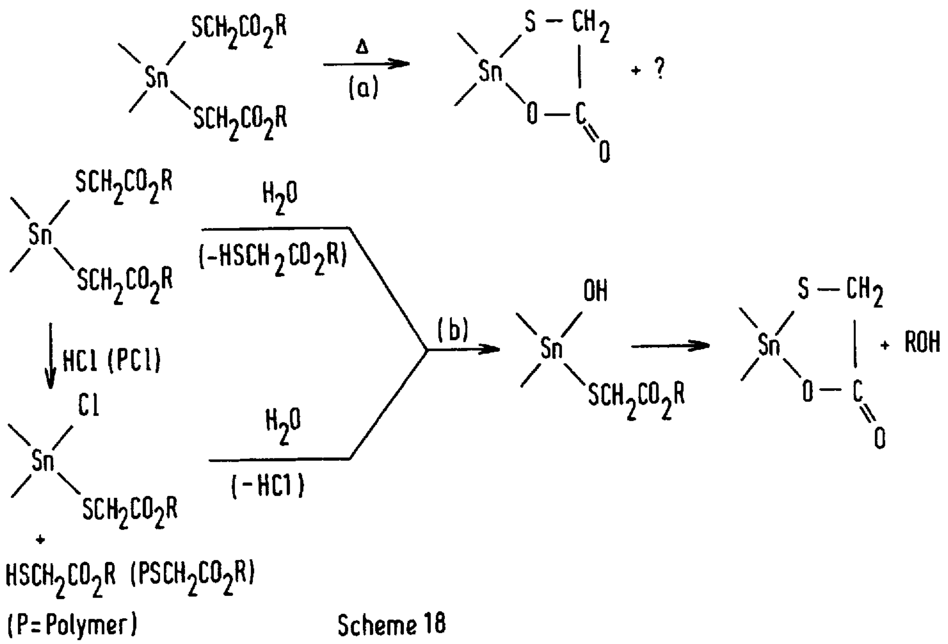


Figure 6 Stabiliser conversion as a function of heat history for PVC with 2 phr. stabiliser ($Bu_2Sn(IOTG)_2$). (Reproduced by kind permission of the Society of Plastics Engineers.)



Scheme 18

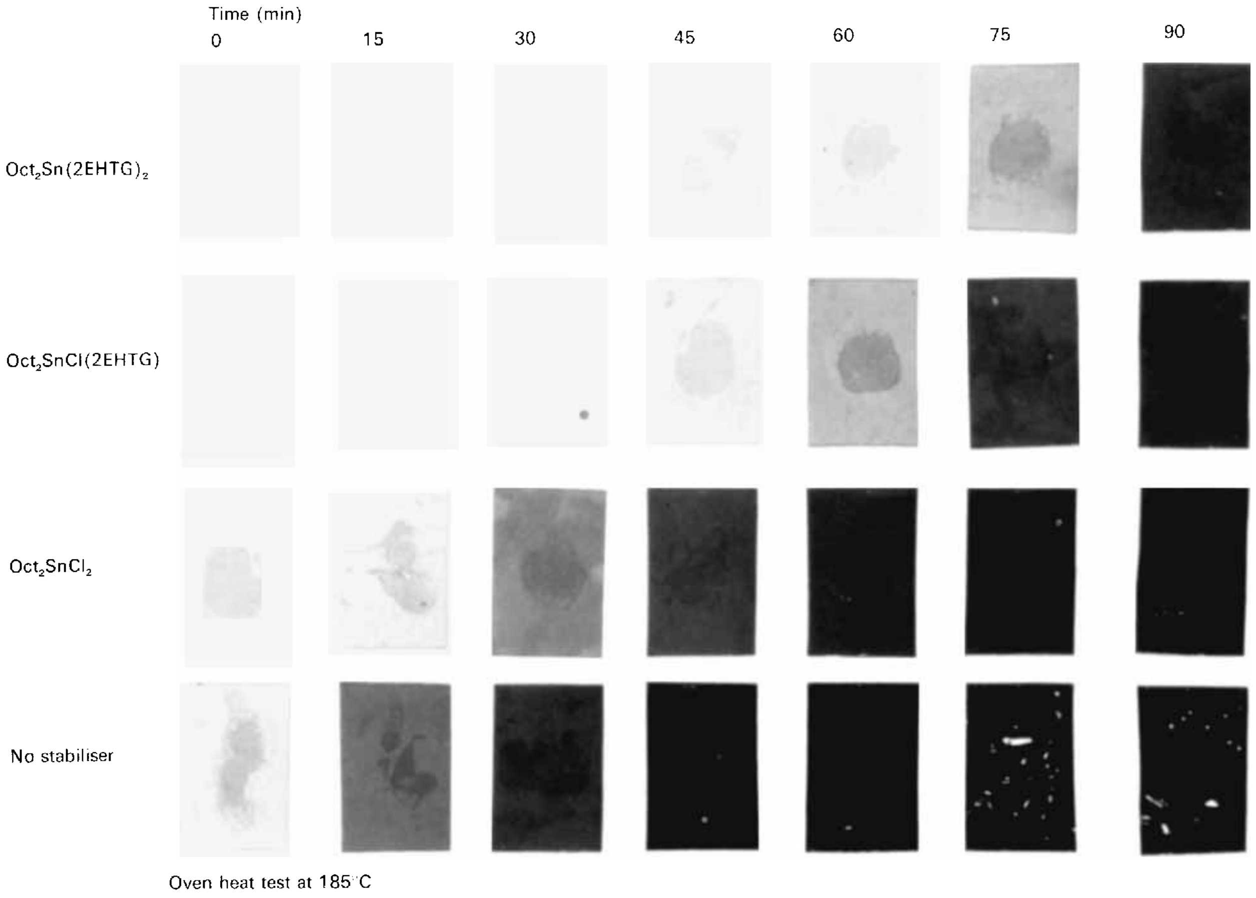


Figure 7 Oven heat test at 185°C for octyl tin compounds.

concluded that the final tin species in the UV degradation of PVC stabilised by $Bu_2Sn(IOTG)_2$ was $SnOCl_2$. Later work demonstrated that $SnCl_4$ is a more likely degradation product.[52] This more detailed study revealed that the Mössbauer parameters (Isomer shift and Quadrupole splitting) of the organotin stabilisers, their half chlorides and Bu_2SnCl_2 were sensitive to the mode of incorporation into PVC (solvent casting or hot milling). The parameters of other tin species such as $SnCl_4$ were also shown to be potentially sensitive to environment within the PVC matrix by virtue of interaction with HCl or Cl atoms within the polymer. These observations suggest that Mössbauer spectroscopy is insufficiently sensitive to draw many conclusions regarding the distribution of tin species which are present during the degradation process.

SYNERGISM

The phenomenon of synergism observed with mixtures of mono- and di-alkyltin stabilisers has been known and exploited commercially for many years. Klimsch and Kuhnert[53] reported that the addition of $BuSn(IOTG)_3$ to $Bu_2Sn(IOTG)_2$ produced a significant improvement in dynamic mill stability and Blunden, Cusack and Hill[11] have recently presented an example of this phenomenon based on static oven heat stability. There are also several patents[54,55] which claim synergism between monoalkyltin compounds and dialkylthiotin stabilisers. The mechanism of this synergism, however, remained obscure for some considerable time. Nass[56] suggested that the process was essentially regenerative although he presented no evidence for his hypothesis. Burley and Hutton,[41] and more recently Brecker,[8] have likened dialkyltin stabilisers to barium or calcium soaps in their characteristic performance (long stability—poor colour control) and mono alkyltin stabilisers to cadmium or zinc soaps (good colour control—short stability). Based on these observations an analogy has been drawn between the synergistic combinations of $R_2SnY_2/RSnY_3$ and Ba/Cd soap (or Ca/Zn soap). In organotin stabilisers this mechanism would involve exchange of Cl and IOTG groups between mono and dialkyltin entities. Several spectroscopic studies[29,31,41,57-59] have demonstrated that facile Cl/mercaptoester exchange equilibria of a number of types do exist (Scheme 19).

Although many equilibria of the type shown in Scheme 19(d) can be written it is envisaged that the overall process giving rise to synergism can be summarised by Scheme 20.

By this mechanism prodegradant $RSnCl_3$ is essentially converted to inert R_2SnCl_2 whilst

$$R_2Sn(SCH_2CO_2R')_2 + R_2SnCl_2 \rightleftharpoons 2R_2SnCl(SCH_2CO_2R') \qquad (a)$$

$$2RSn(SCH_2CO_2R')_3 + RSnCl_3 \rightleftharpoons 3RSnCl(SCH_2CO_2R')_2 \qquad (b)$$

$$Bu_2Sn(OCO\cdot C_{11}H_{23})_2 + Bu_2SnCl_2 \rightleftharpoons 2Bu_2SnCl(OCOC_{11}H_{23}) \qquad (c)$$

$$\begin{array}{ccc} R_2Sn(SCH_2CO_2R')_2 + RSnCl_3 & \rightleftharpoons & R_2SnCl(SCH_2CO_2R') + RSnCl_2(SCH_2CO_2R') \\ & & \updownarrow \qquad\qquad (d) \\ & & R_2SnCl_2 + RSnCl(SCH_2CO_2R')_2 \end{array}$$

Scheme 19

$$RSn(SCH_2CO_2R')_3 + 3HCl(PCl) \longrightarrow RSnCl_3 + 3HSCH_2CO_2R'(PSCH_2CO_2R')$$

$$2RSnCl_3 + 3R_2Sn(SCH_2CO_2R')_2 \longrightarrow 2RSn(SCH_2CO_2R')_3 + 3R_2SnCl_2$$

(P = polymer)

Scheme 20

Table 1 Degradation times of rigid PVC[a] samples stabilised with butyltin derivatives

Compound	Degradation time (min) at 185°C
$Bu_2Sn(IOTG)_2$	90
$Bu_2Sn(IOTG)_2$ with 20%[b] $BuSnCl_3$	100
$BuSnCl_3$	20
No additive	50
$BuSn(IOTG)_3$	80
$BuSn(IOTG)_3$ with 20% Bu_2SnCl_2	80
Bu_2SnCl_2	50

[a] PVC-K value 62.

[b] Mole %.

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$R_2Sn(SCH_2CO_2R')_2$ is converted to the more active $RSn(SCH_2CO_2R')_3$. Further evidence in favour of this mechanism stems from the fact that addition of $BuSnCl_3$ to $Bu_2Sn(IOTG)_2$ gave an improvement in oven heat stability whilst the converse exercise of adding Bu_2SnCl_2 to $BuSn(IOTG)_3$ gave no improvement in performance (see Table 1).[41]

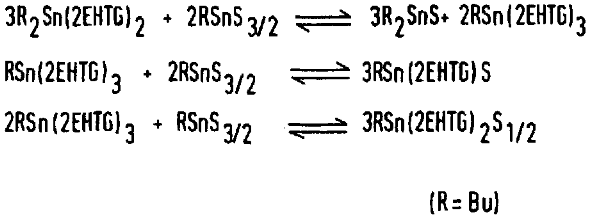
Abeler and Büssing[60] have independently proposed a similar mechanism for synergism based on their own studies and demonstrated sensitivity of the synergistic optimum to lubricant and to the nature of alkyl group attached to Sn (Brecker[8] has also commented on this effect). These observations suggest that lubrication and compatibility phenomena contribute significantly to performance. Model compound studies performed in isolation can take no account of factors such as these.

The positions of equilibria such as 19(a, b, d) are dictated by co-ordination effects within the organotin compounds.[31,41] Where the alkyl group attached to Sn also contains a functional group ($R = CH_2CH_2CO_2Bu$) capable of competing with mercaptoester co-ordination to Sn, then these equilibria can exhibit marked displacement from the case where R = alkyl.[57] Potentially, therefore, this effect may perturb the position of the synergistic optimum. This has been observed.[60]

Unfortunately, the spectroscopic studies performed so far have been limited to relatively low temperatures (20–35°C), the results of which may, or may not, be relevant to PVC processing temperatures (180–200°C). Further work is therefore required in order to extend these initial studies to higher temperatures.

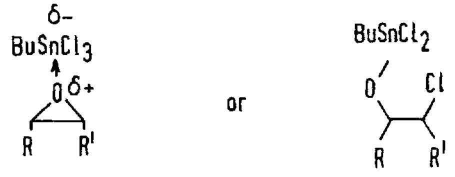
Equilibria such as 19(a, b) normally lie almost exclusively to the right-hand side. This situation could be perturbed under processing conditions (particularly calendering) if the organotin chlorides ($RSnCl_3$, R_2SnCl_2) are volatile. This is another factor which will vary with length of the alkyl chain and could contribute in determining the synergistic optimum.

Synergism has also been claimed between organotin sulphides and organotin mercaptoesters.[55,61,62] A brief proton NMR study[63] of these mixtures indicated that S/mercaptoester exchange occurs here. Mixtures of $R_2Sn(2EHTG)_2$ with $RSnS_{3/2}$ generated not only $RSn(2EHTG)_3$ and $(R_2SnS)_3$ but also smaller equilibrium concentrations of $RSn(2EHTG)_2S_{1/2}$ and $RSn(2EHTG)S$ (Scheme 21).



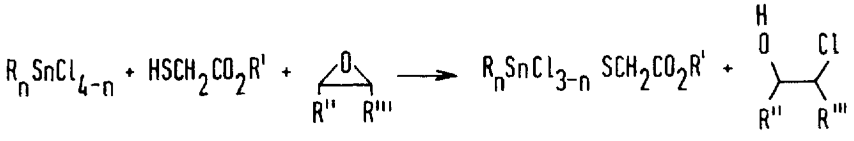
Scheme 21

Finally, Van Hoang and co-workers[64] have extended their model compound work with CHE to study the synergism which exists between organotin stabilisers and epoxy compounds. Their explanation of this phenomenon is related entirely to the interactions between R_nSnCl_{4-n} ($n = 1, 2$) and the epoxy compounds. Namely, the formation of complexes or the generation of β-chloroalkoxides, both of which would be expected to reduce the Lewis acid strength of R_nSnCl_{4-n}.



A possible alternative mechanism for this synergism could be the regeneration of an organotin mercaptoester/chloride (Scheme 22).

The work of Van Hoang and co-workers could be usefully extended to include studies of the intermediate mercaptoester/chlorides.



Scheme 22

(R, R', R'', R''' = alkyl)

CONCLUSION

In the past the replacement of allylic chlorine moieties within PVC by carboxylic or thiolic groups (initially attached to the organotin compounds) was believed to be the most important stabilising reaction. More recent work, however, suggests that replacement of allylic chlorine groups within the PVC plays a relatively small role in the stabilisation process. The studies performed by Scott's group have shown that, particularly under conditions of dynamic shear, the degradation/stabilisation process proceeds by a complex sequence of free radical reactions. It is likely, therefore, that the degradation of unstabilised PVC proceeds by a combination of the ionic and free radical mechanisms.

There is obviously scope for further work in this area. On the model compound side it would be interesting to resolve the mechanistic differences which have been observed for the reactions of dialkyltin bis thioglycollate esters and monoalkyltin tris thiolates with allylic chlorine entities. Also an extension of Michel's work on epoxy/alkyltin synergism to mixed thioglycollate ester/chloride compounds would perhaps be worthwhile.

Mono/di synergism plays a significant role in the formulation of any commercial alkylthiotin stabiliser system. An extension of the work performed on Cl/mercaptoester exchange equilibria to temperatures approaching more realistic processing conditions would, therefore, certainly be informative. The in situ studies performed by Scott's group could also usefully be extended to include mono/di synergism and also to include other processing techniques.

From a commercial point of view it would also be of interest to extend the work of Bellenger et al. on the in situ generation of dialkyltin thioglycollate during stabilisation by dialkyltin bis thioglycollate esters.

One area, discussed only briefly in this review, is that of the loss of volatile organotin chlorides during the processing of PVC. This effect could be particularly important with methyltin stabilisers and may have a marked effect on synergistic optima.

It is believed that such mechanistic studies could help to improve our basic understanding of the stabilisation of PVC by organotin compounds.

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